Supplementary data

Baylis-Hillman Reaction of *N*-Tosyl Aldimines and Aryl Aldehydes with 3-Methylpenta-3,4-dien-2-one

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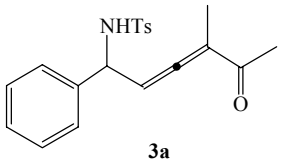
General Remarks. MPs were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; J-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. Satisfactory CHN microanalyses were obtained with a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at medium pressure. The starting materials such as *N*-tosyl aldimines,[1] 3-methylpenta-3,4-dien-2-one,[2] were prepared according to the literatures.

1. Love, B. E.; Raje, P. S.; Williams, T. C. *Synlett* **1994**, 493.
2. (a) Baumgarten, W. E. *Organic Synthesis*, Wiley: New York, **1973**, *5*, 785. (b) Buono, G. *Synthesis* **1981**, 272.

The aza-Baylis-Hillman reaction of *N*-tosyl aldimines with 3-methylpenta-3,4-dien-2-one catalyzed by DMAP. **Typical reaction procedure of *N*-tosyl aldimines with 3-methylpenta-3,4-dien-2-one at room temperature catalyzed by DMAP**.

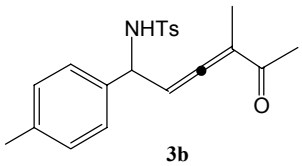
To a Schlenk tube with *N*-(*p*-methylbenzenesulfonyl)benzaldimine (130 mg, 0.5 mmol) and DMAP (6 mg, 0.05 mmol) in DMSO (1 mL) was added 3-methylpenta-3,4-dien-2-one (96 mg, 1 mmol) and the reaction mixture was stirred for 10 min. at room temperature (20 ^{o}C). The reaction mixture was washed with water (10 mL) and extracted with dichloromethane (20 mL). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: EtOAc/petroleum= 1/3) to give adduct **3a** (144 mg, yield 81%) as a white solid.

In all cases, **3** was obtained as a pair of diastereoisomeric mixtures in 1:1 ratio on the basis of ^{1}H NMR spectroscopic data and could not be separated by silica gel column chromatography. ^{13}C NMR spectroscopic data also indicated a pair of diastereoisomeric mixtures in 1:1 ratio.



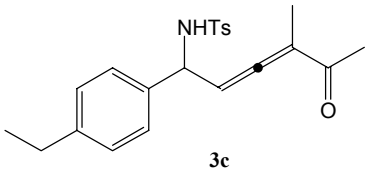
3a

4-Methyl-*N*-(4-methyl-5-oxo-1-phenylhexa-2,3-dienyl)benzenesulfonamide 3a: mp. 91-95 ^{o}C; IR (CH_2Cl_2) ν 3273, 1680 (C=O), 1598, 1330, 1160, 1093 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**3a** and (1S, 3S)-**3a**: 1.65 (3H, d, *J* = 2.4 Hz, CH_3), 2.08 (3H, s, CH_3), 2.39 (3H, s, CH_3), 5.05-5.11 (2H, m, CH, NH), 5.76-5.77 (1H, m, =CH), 7.10-7.15 (2H, m, ArH), 7.19-7.27 (5H, m, ArH), 7.62-7.67 (2H, m, ArH); (1S, 3R)-**3a** and (1R, 3S)-**3a**: 1.72 (3H, d, *J* = 2.4 Hz, CH_3), 2.14 (3H, s, CH_3), 2.40 (3H, s, CH_3), 5.05-5.11 (2H, m, CH, NH), 5.70-5.71 (1H, m, =CH), 7.10-7.15 (2H, m, ArH), 7.19-7.27 (5H, m, ArH), 7.62-7.67 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.92, 13.02, 21.37 (2C), 26.71, 26.76, 56.24, 56.30, 96.83, 96.92, 107.41, 107.65, 126.45, 126.50, 126.88, 126.95, 127.97 (2C), 128.51, 128.59, 129.44, 129.47, 137.31 (2C), 138.94, 139.00, 143.34, 143.40, 198.44, 198.51, 211.72, 211.82; MS (EI) *m/e* 356 (M^++1, 2.51), 355 (M^+, 0.44), 260 (M^+-95, 100), 185 (M^+-170, 23.07), 155 (M^+-200, 51.31), 91 (M^+-264, 68.34); [Found: C, 67.45; H, 6.13; N, 3.83%. $C_{20}H_{21}O_3NS$ requires C, 67.58; H, 5.95; N, 3.94%].



3b

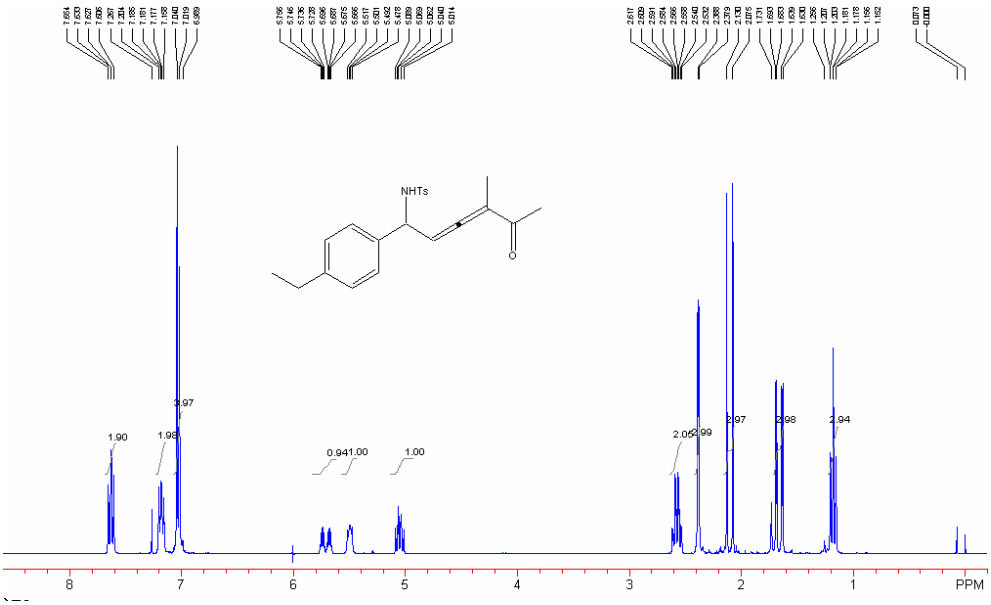
4-Methyl-*N*-(4-methyl-5-oxo-1-*p*-tolylhexa-2,3-dienyl)benzenesulfonamide 3b: mp. 107-110 ^{o}C; IR (CH_2Cl_2) ν 3271, 1952, 1681 (C=O), 1598, 1435, 1331, 1160, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**3b** and (1S, 3S)-**3b**:1.63 (3H, d, *J* = 2.4 Hz, CH_3), 2.07 (3H, s, CH_3), 2.28 (3H, s, CH_3), 2.39 (3H, s, CH_3), 5.00-5.07 (1H, m, CH), 5.52-5.56 (1H, m, NH), 5.72-5.75 (1H, m, =CH), 7.01 (4H, d, *J* = 6.6 Hz, ArH), 7.17-7.22 (2H, m, ArH), 7.62-7.67 (2H, m, ArH); (1S, 3R)-**3b** and (1R, 3S)-**3b** : 1.68 (3H, d, *J* = 2.4 Hz, CH_3), 2.12 (3H, s, CH_3), 2.29 (3H, s, CH_3), 2.40 (3H, s, CH_3), 5.00-5.07 (1H, m, CH), 5.52-5.56 (1H, m, NH), 5.66-5.69 (1H, m, =CH), 7.01 (4H, d, *J* = 6.6 Hz, ArH), 7.17-7.22 (2H, m, ArH), 7.62-7.67 (2H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.93, 13.05, 20.94 (2C), 21.36 (2C), 26.72, 26.78, 56.04, 56.09, 96.89, 97.01, 107.29, 107.54, 126.37, 126.41, 126.89, 126.96, 129.14, 129.22, 129.40, 129.42, 135.98, 136.05, 137.36 (2C), 137.74 (2C), 143.24, 143.31, 198.52, 198.58, 211.68, 211.75; MS (EI) *m/e* 370 (M^++1, 2.29), 274 (M^+-95, 100), 199 (M^+-170, 65.72), 155 (M^+-214, 43.38), 91 (M^+-278, 71.76); [Found: C, 68.15; H, 6.28; N, 3.63%. $C_{21}H_{23}O_3NS$ requires C, 68.27; H, 6.27; N, 3.79%].

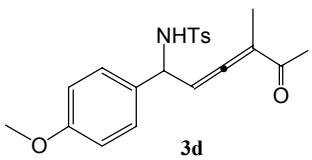


3c

***N*-[1-(4-Ethylphenyl)-4-methyl-5-oxohexa-2,3-dienyl]-4-methylbenzenesulfonamide 3c**: mp. 78-81 ^{o}C; IR (CH_2Cl_2) ν 3271, 1952, 1681 (C=O), 1435, 1330, 1160, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**3c** and (1S, 3S)-**3c**: 1.16 (3H, t, *J* = 7.8 Hz, CH_3), 1.61 (3H, d, *J* = 3.0 Hz, CH_3), 2.06 (3H, s, CH_3), 2.36 (3H, s, CH_3), 2.56 (2H, d, *J* = 7.8 Hz, CH_2), 5.06 (1H, dd, *J* = 14.1, 7.5 Hz, CH), 5.71-5.74 (1H, m, =CH), 6.00-6.02 (1H, m, NH), 6.99-7.03 (4H, m, ArH), 7.13-7.18 (2H, m, ArH), 7.60-7.65 (2H, m, ArH); (1S, 3R)-**3c** and (1R, 3S)-**3c**: 1.16 (3H, t, *J* = 7.8 Hz, CH_3), 1.65 (3H, d, *J* = 3.0 Hz, CH_3), 2.10 (3H, s, CH_3),

2.37 (3H, s, CH_3), 2.56 (2H, d, J = 7.8 Hz, CH_2), 5.06 (1H, dd, J = 14.1, 7.5 Hz, CH), 5.66-5.69 (1H, m, =CH), 6.00-6.02 (1H, m, NH), 6.99-7.03 (4H, m, ArH), 7.13-7.18 (2H, m, ArH), 7.60-7.65 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.92, 13.03, 15.42 (2C), 21.33 (2C), 26.70, 26.75, 28.30 (2C), 56.06, 56.11, 96.88, 96.98, 107.29, 107.53, 126.43, 126.49, 126.87, 126.93, 127.90, 127.98, 129.34, 129.37, 136.14, 136.21, 137.37 (2C), 143.11, 143.19, 144.03, 144.05, 198.53, 198.59, 211.66, 211.72; MS (EI) *m/e* 288 (M^+-95, 100), 272 (M^+-111, 8.59), 155 (M^+-228, 55.17), 91 (M^+-292, 50.20); MS (MALDI) *m/e* 406 (M^+ + Na, 100); HRMS (MALDI) calcd. for $C_{22}H_{26}NO_3S^{+1}$: 384.1628, Found: 384.1640.



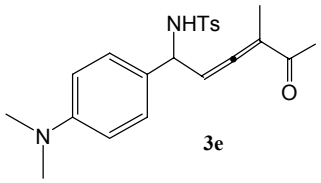


3d

***N*-[1-(4-Methoxyphenyl)-4-methyl-5-oxohexa-2,3-dienyl]-4-methylbenzenesulfonamide**

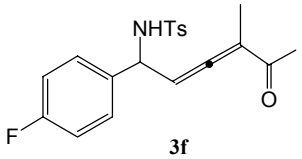
3d: mp. 94-98 ^{o}C; IR (CH_2Cl_2) ν 3272, 1680 (C=O), 1513, 1327, 1160, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**3d** and (1S, 3S)-**3d**:1.62 (3H, d, J = 2.4 Hz, CH_3), 2.06 (3H, s, CH_3), 2.38 (3H, s, CH_3), 2.74 (3H, s, CH_3), 4.99-5.07 (1H, m, CH), 5.71-5.74 (1H, m, =CH), 5.90 (1H, dd, J = 7.5, 1.5 Hz, NH), 6.69-6.74 (2H, m, ArH), 7.02-7.07 (2H, m, ArH), 7.17-7.21 (2H, m, ArH), 7.61-7.66 (2H, m, ArH); (1S, 3R)-**3d** and (1R, 3S)-**3d**: 1.66 (3H, d, J = 2.4 Hz, CH_3), 2.11 (3H, s, CH_3), 2.39 (3H, s, CH_3), 2.74 (3H, s, CH_3), 4.99-5.07 (1H, m, CH), 5.65-5.68 (1H, m, =CH), 5.90 (1H, dd, J = 7.5, 1.5 Hz, NH), 6.69-6.74 (2H, m, ArH),

7.02-7.07 (2H, m, ArH), 7.17-7.21 (2H, m, ArH), 7.61-7.66 (2H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.95, 13.08, 20.94, 21.36, 26.72, 26.79, 55.13 (2C), 55.75, 55.80, 96.96, 97.10, 107.33, 107.57, 113.80, 113.88, 126.89, 126.96, 127.73, 127.79, 129.42, 129.44, 131.07, 131.15, 137.39 (2C), 143.25, 143.32, 159.17 (2C), 198.48, 198.55, 211.66, 211.75; MS (EI) *m/e* 290 (M^+-95, 100), 231 (M^+-154, 6.56), 155 (M^+-230, 38.52), 91 (M^+-294, 53.26); [Found: C, 65.65; H, 6.13; N, 3.51%. $C_{21}H_{23}O_4NS$ requires C, 65.43; H, 6.01; N, 3.63%].



3e

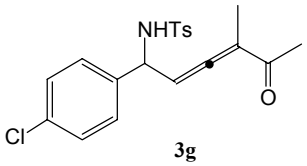
***N*-{1-[4-(Dimethylamino)phenyl]-4-methyl-5-oxohexa-2,3-dienyl}-4-methylbenzenesulfonamide 3e**: mp. 103-106 ^{o}C; IR (CH_2Cl_2) ν 3265, 2924, 1678 (C=O), 1524, 1327, 1160, 1088 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**3e** and (1S, 3S)-**3e**: 1.65 (3H, d, *J* = 2.7 Hz, CH_3), 2.17 (3H, s, CH_3), 2.38 (3H, s, CH_3), 2.89 (6H, s, $2CH_3$), 4.93-4.98 (1H, m, CH), 5.47-5.49 (1H, m, NH), 5.73-5.76 (1H, m, =CH), 6.51-6.56 (2H, m, ArH), 6.94-6.99 (2H, m, ArH), 7.18-7.22 (2H, m, ArH), 7.63-7.67 (2H, m, ArH); (1S, 3R)-**3e** and (1R, 3S)-**3e**: 1.71 (3H, d, *J* = 2.7 Hz, CH_3), 2.10 (3H, s, CH_3), 2.39 (3H, s, CH_3), 2.90 (6H, s, $2CH_3$), 4.96-5.01 (1H, m, CH), 5.49-5.52 (1H, m, NH), 5.67-5.70 (1H, m, =CH), 6.51-6.56 (2H, m, ArH), 6.94-6.99 (2H, m, ArH), 7.18-7.22 (2H, m, ArH), 7.63-7.67 (2H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.03, 13.20, 21.40 (2C), 26.80, 26.90, 40.32 (2C), 55.93, 56.00, 97.15, 97.33, 107.16, 107.45, 112.18, 112.24, 126.39, 126.46, 126.96, 127.03, 127.38, 127.43, 129.42 (2C), 137.50 (2C), 143.08, 143.15, 150.12, 150.14, 198.72, 198.76, 211.65, 211.70; MS (EI) *m/e* 398 (M^+, 5.27), 303 (M^+-95, 77.14), 243 (M^+-155, 15.55), 148 (M^+-250, 100), 91 (M^+-307, 53.80); [Found: C, 66.36; H, 6.67; N, 6.99%. $C_{22}H_{26}O_3N_2S$ requires C, 66.30; H, 6.58; N, 7.03%].



3f

***N*-[1-(4-Fluorophenyl)-4-methyl-5-oxohexa-2,3-dienyl]-4-methylbenzenesulfonamide 3f**:

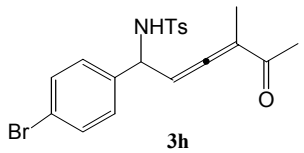
mp. 98-101 ^{o}C; IR (CH_2Cl_2) ν 3270, 1680 (C=O), 1510, 1333, 1159, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**3f** and (1S, 3S)-**3f**: 1.62 (3H, d, *J* = 3.0 Hz, CH_3), 2.06 (3H, s, CH_3), 2.41 (3H, s, CH_3), 5.09 (1H, dd, *J* = 13.8, 7.8 Hz, CH), 5.70-5.73 (1H, m, =CH), 5.89-5.90 (1H, m, NH), 6.86-6.93 (2H, m, ArH), 7.08-7.15 (2H, m, ArH), 7.18-7.28 (2H, m, ArH), 7.60-7.65 (2H, m, ArH); (1S, 3R)-**3f** and (1R, 3S)-**3f**: 1.66 (3H, d, *J* = 3.0 Hz, CH_3), 2.09 (3H, s, CH_3), 2.41 (3H, s, CH_3), 5.09 (1H, dd, *J* = 13.8, 7.8 Hz, CH), 5.65-5.68 (1H, m, =CH), 5.86-5.87 (1H, m, NH), 6.86-6.93 (2H, m, ArH), 7.08-7.15 (2H, m, ArH), 7.18-7.28 (2H, m, ArH), 7.60-7.65 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.89, 12.98, 21.32 (2C), 26.66, 26.70, 55.55, 55.59, 96.63, 96.74, 107.51, 107.70, 115.28 (d, *J* = 21.8 Hz), 115.35 (d, *J* = 20.9 Hz), 126.80, 126.86, 128.27 (d, *J* = 8.6 Hz), 128.32 (d, *J* = 8.3 Hz), 129.43, 129.46, 134.85 (d, *J* = 3.5 Hz), 134.92 (d, *J* = 3.4 Hz), 137.19 (2C), 143.48, 143.53, 162.07 (2C, d, *J* = 245.4 Hz), 198.26, 198.34, 211.66, 211.75; MS (EI) *m/e* 373 (M^+, 0.56), 278 (M^+-95, 90.01), 203 (M^+-170, 25.32), 160 (M^+-213, 39.72), 155 (M^+-218, 76.45), 91 (M^+-282, 100); [Found: C, 64.62; H, 5.35; N, 3.96%. $C_{20}H_{20}O_3NSF$ requires C, 64.33; H, 5.40; N, 3.75%].



3g

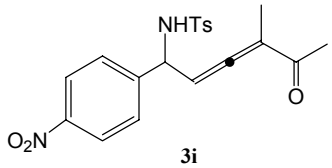
***N*-[1-(4-Chlorophenyl)-4-methyl-5-oxohexa-2,3-dienyl]-4-methylbenzenesulfonamide 3g**: mp. 135-140 ^{o}C; IR (CH_2Cl_2) ν 3270, 1680 (C=O), 1510, 1333, 1159, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**3g** and (1S, 3S)-**3g**: 1.61 (3H, d, *J* = 3.0, CH_3), 2.04 (3H, s, CH_3), 2.39 (3H, s, CH_3), 5.06 (1H, dd, *J* = 14.1, 7.5 Hz, CH), 5.68-5.71 (1H, m, =CH), 6.00 (1H, d, *J* = 7.5 Hz, NH), 7.03-7.08 (2H, m, ArH), 7.13-7.20 (4H, m, ArH), 7.57-7.62 (2H, m, ArH); (1S, 3R)-**3g** and (1R, 3S)-**3g**: 1.64 (3H, d, *J* = 2.4, CH_3), 2.08 (3H, s, CH_3), 2.40 (3H, s, CH_3), 5.06 (1H, dd, *J* = 14.1, 7.5 Hz, CH), 5.62-5.65 (1H, m, =CH), 6.00 (1H, d, *J* = 7.5 Hz, NH), 7.03-7.08 (2H, m, ArH), 7.13-7.20 (4H, m, ArH), 7.57-7.62 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.98, 13.07, 21.40 (2C), 26.76, 26.78, 55.65, 55.68, 96.34, 96.44, 107.68, 107.87, 126.86, 126.91, 127.96, 128.01, 128.62, 128.69, 129.50, 129.54, 133.80 (2C),

137.14 (2C), 137.48, 137.54, 143.64, 143.69, 198.13, 198.21, 211.64, 211.71; MS (EI) *m/e* 390 (M^++1, 1.35), 294 (M^+-95, 72.41), 219 (M^+-170, 17.08), 176 (M^+-213, 25.67), 155 (M^+-234, 83.85), 91 (M^+-198, 100); [Found: C, 61.52; H, 5.12; N, 3.55%. $C_{20}H_{20}O_3NSCl$ requires C, 61.61; H, 5.17; N, 3.59%].



3h

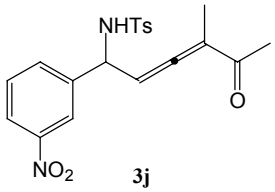
***N*-[1-(4-Bromophenyl)-4-methyl-5-oxohexa-2,3-dienyl]-4-methylbenzenesulfonamide 3h**: mp. 132-136 ^oC; IR (CH_2Cl_2) ν 3268, 1681 (C=O), 1435, 1333, 1160, 1093 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**3h** and (1S, 3S)-**3h**: 1.62 (3H, dd, *J* = 3.0, 1.5 Hz, CH_3), 2.05 (3H, d, *J* = 1.5 Hz, CH_3), 2.41 (3H, s, CH_3), 5.05 (1H, dd, *J* = 14.4, 6.3 Hz, CH), 5.68-5.70 (1H, m, =CH), 5.95-6.01 (1H, m, NH), 6.97-7.02 (2H, m, ArH), 7.17-7.20 (2H, m, ArH), 7.27-7.33 (2H, m, ArH), 7.56-7.62 (2H, m, ArH); (1S, 3R)-**3h** and (1R, 3S)-**3h**: 1.65 (3H, dd, *J* = 3.0, 1.5 Hz, CH_3), 2.08 (3H, d, *J* = 1.5 Hz, CH_3), 2.41 (3H, s, CH_3), 5.05 (1H, dd, *J* = 14.4, 6.3 Hz, CH), 5.62-5.65 (1H, m, =CH), 5.95-6.01 (1H, m, NH), 6.97-7.02 (2H, m, ArH), 7.17-7.20 (2H, m, ArH), 7.27-7.33 (2H, m, ArH), 7.56-7.62 (2H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.97, 13.07, 21.42 (2C), 26.76, 26.78, 55.70, 55.73, 96.23, 96.33, 107.70, 107.88, 121.93 (2C), 126.85, 126.90, 128.28, 128.33, 129.51, 129.54, 131.57, 131.63, 137.10 (2C), 137.96, 138.02, 143.66, 143.70, 198.18, 198.36, 211.62, 211.68; MS (EI) *m/e* 340 (M^+-93, 38.74), 338 (M^+-95, 38.26), 294 (M^+-139, 14.62), 155 (M^+-278, 91.82), 91 (M^+-342, 100); [Found: C, 55.30; H, 4.68; N, 3.04%. $C_{20}H_{20}O_3NSBr$ requires C, 55.30; H, 4.64; N, 3.22%].



3i

4-Methyl *N*-[4-methyl-1-(4-nitrophenyl)-5-oxohexa-2,3-dienyl]benzenesulfonamide 3i: mp. 134-140 ^oC; IR (CH_2Cl_2) ν 3270, 1681 (C=O), 1522, 1347, 1160, 1093 cm^{-1}; ^1H NMR

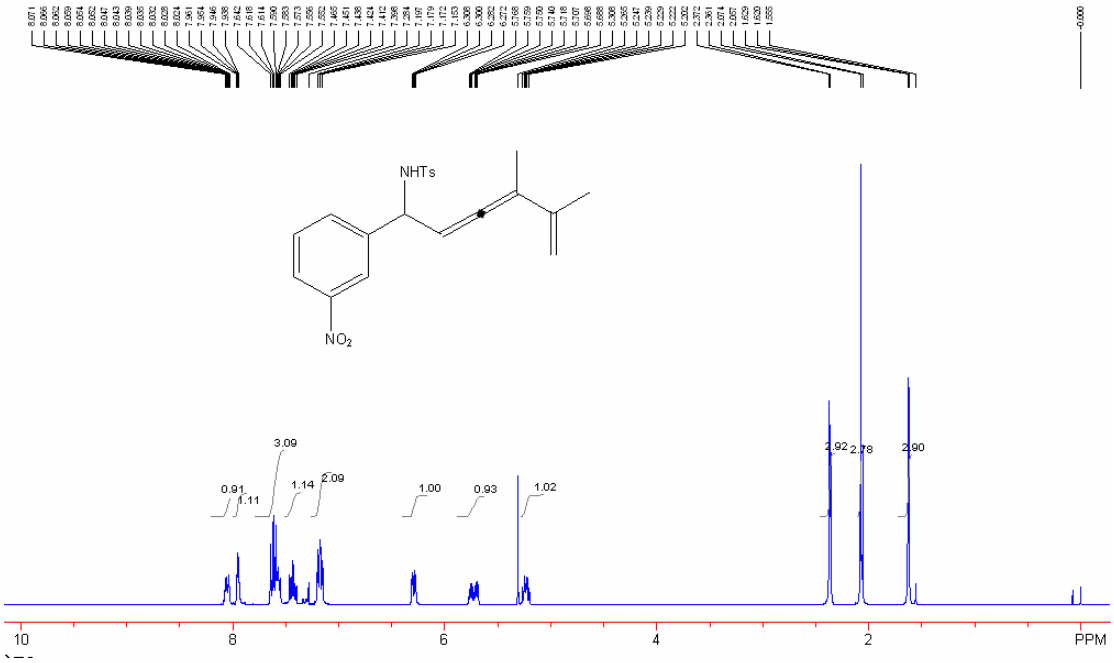
($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**3i** and (1S, 3S)-**3i**: 1.65 (3H, d, *J* = 2.7 Hz, CH_3), 2.09 (3H, s, CH_3), 2.40 (3H, s, CH_3), 5.19-5.23 (1H, m, CH), 5.48-5.20 (1H, m, NH), 5.72-5.73 (1H, m, =CH), 7.20-7.23 (2H, m, ArH), 7.33-7.37 (2H, m, ArH), 7.60-7.65 (2H, m, ArH), 8.07-8.12 (2H, m, ArH); (1S, 3R)-**3i** and (1R, 3S)-**3i**: 1.69 (3H, d, *J* = 2.7 Hz, CH_3), 2.07 (3H, s, CH_3), 2.40 (3H, s, CH_3), 5.19-5.23 (1H, m, CH), 5.48-5.20 (1H, m, NH), 5.66-5.69 (1H, m, =CH), 7.20-7.23 (2H, m, ArH), 7.33-7.37 (2H, m, ArH), 7.60-7.65 (2H, m, ArH), 8.07-8.12 (2H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.12, 13.18, 21.47 (2C), 26.85, 26.87, 55.58 (2C), 95.69, 95.73, 108.31 (2C), 123.80, 123.87, 126.37 (2C), 126.93, 126.96, 127.62, 127.64, 129.71, 129.74, 136.92 (2C), 144.21 (2C), 146.15 (2C), 197.59 (2C), 211.55 (2C); MS (EI) *m/e* 305 (M^+-95, 33.27), 229 (M^+-171, 9.05), 187 (M^+-213, 14.82), 155 (M^+-245, 73.22), 91 (M^+-309, 100); [Found: C, 59.89; H, 5.12; N, 6.90%. $C_{20}H_{20}O_5N_2S$ requires C, 59.99; H, 5.03; N, 7.00%].

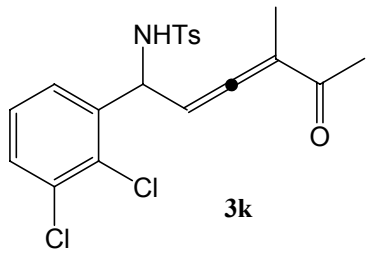


3j

4-Methyl *N*-[4-methyl-1-(3-nitrophenyl)-5-oxohexa-2,3-dienyl]benzenesulfonamide 3j: a pale yellow oil; IR (CH_2Cl_2) ν 3267, 1953, 1681 (C=O), 1531, 1351, 1160, 1092 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**3j** and (1S, 3S)-**3j**: 1.62 (3H, s, CH_3), 2.09 (3H, s, CH_3), 2.36 (3H, s, CH_3), 5.21-5.27 (1H, m, CH), 5.74-5.77 (1H, m, =CH), 6.21 (1H, br s, NH), 7.15-7.20 (2H, m, ArH), 7.40-7.47 (1H, m, ArH), 7.55-7.64 (3H, m, ArH), 7.94-7.95 (1H, m, ArH), 8.03-8.07 (1H, m, ArH); (1S, 3R)-**3j** and (1R, 3S)-**3j**: 1.63 (3H, s, CH_3), 2.08 (3H, s, CH_3), 2.37 (3H, s, CH_3), 5.21-5.27 (1H, m, CH), 5.69-5.72 (1H, m, =CH), 6.21 (1H, br s, NH), 7.15-7.20 (2H, m, ArH), 7.40-7.47 (1H, m, ArH), 7.55-7.64 (3H, m, ArH), 7.94-7.95 (1H, m, ArH), 8.03-8.07 (1H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.00, 13.06, 21.34, 21.35, 26.77, 26.78, 55.51, 55.54, 95.82, 95.85, 108.13, 108.26, 121.67, 121.74, 122.85, 122.86, 126.84, 126.88, 129.60, 129.62, 129.66 (2C), 132.83, 132.88, 136.89, 136.92, 141.05, 141.10, 143.92, 143.99, 148.00 (2C), 197.83, 197.89, 211.75 (2C); MS (EI) *m/e* 400 (M^+, 7.77), 383 (M^+-17, 36.66), 245 (M^+-155, 66.33), 244 (M^+-156, 100), 229 (M^+-171, 34.59), 201 (M^+-199,

26.85), 184 (M^+-216, 24.94); HRMS (EI) calcd. for $C_{20}H_{20}N_2O_5S$: 400.1093, Found: 400.1096.

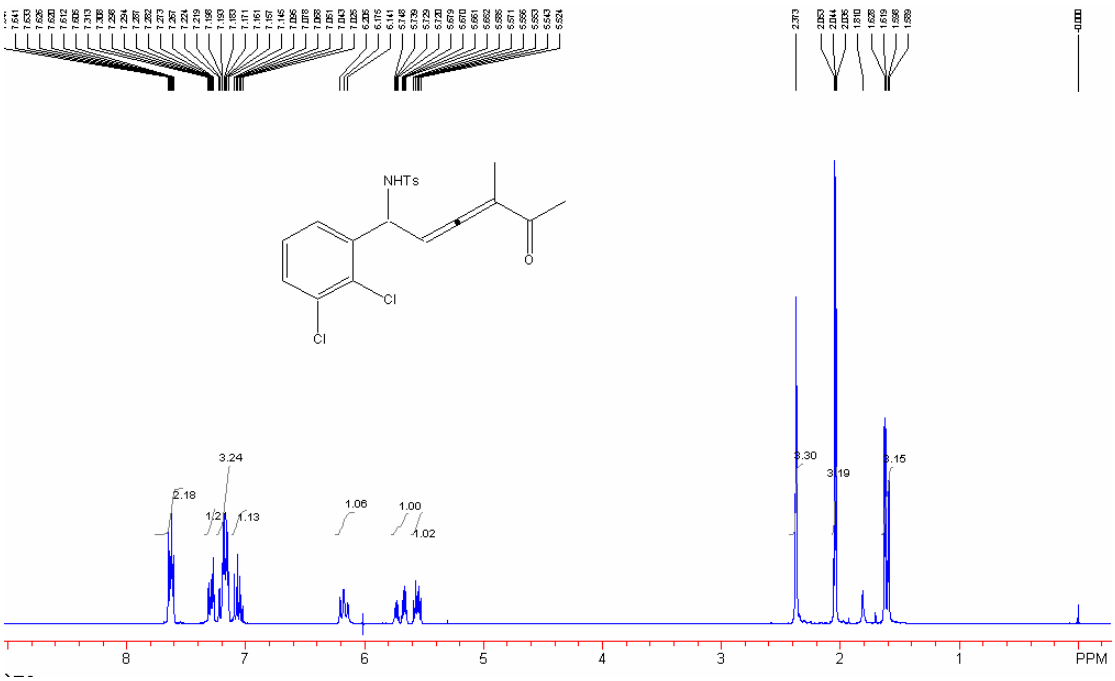


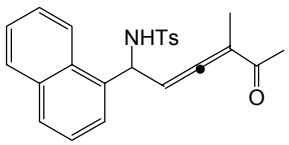


3k

***N*-[1-(2,3-Dichlorophenyl)-4-methyl-5-oxohexa-2,3-dienyl]-4-methylbenzenesulfonamide 3k**: mp. 118-122 °C; IR (CH_2Cl_2) ν 3271, 1683 (C=O), 1435, 1337, 1161, 1092 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**3k** and (1S, 3S)-**3k**: 1.59 (3H, d, *J* = 2.7 Hz, CH_3), 2.04 (3H, s, CH_3), 2.37 (3H, s, CH_3), 5.52-5.59 (1H, m, CH), 5.72-5.74 (1H, m, =CH), 5.97-5.99 (1H, m, NH), 7.07-7.12 (1H, m, ArH), 7.16 (3H, d, *J* = 8.4 Hz, ArH), 7.27-7.31 (1H, m, ArH), 7.63 (2H, d, *J* = 8.4 Hz, ArH); (1S, 3R)-**3k** and (1R, 3S)-**3k**: 1.62 (3H, d, *J* = 2.4 Hz, CH_3), 2.05 (3H, s, CH_3), 2.37 (3H, s, CH_3), 5.52-5.59 (1H, m, CH), 5.65-5.68 (1H, m, =CH), 6.14-6.21 (1H, m, NH), 7.02-7.10 (1H, m, ArH), 7.05-7.22 (3H, m, ArH), 7.27-7.31 (1H, m, ArH), 7.61-7.65 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.74, 12.94, 21.37 (2C), 26.65, 26.75, 55.81 (2C), 95.23, 95.26, 107.98, 108.07, 126.32, 126.35, 126.84 (2C), 127.36, 127.46, 129.40, 129.42, 129.61, 129.63, 130.21, 130.34, 133.10, 133.16, 136.39, 136.44,

138.71, 138.73, 143.73, 143.77, 198.10, 198.14, 211.71, 211.05; MS (EI) *m/e* 424 (M^++1, 1.26), 423 (M^+, 0.84), 330 (M^+-93, 72.94), 328 (M^+-95, 100), 155 (M^+-268, 19.77), 91 (M^+-332, 32.90); HRMS (MALDI) calcd. for $C_{20}H_{20}NO_3SCl_2^{+1}$: 424.0536, Found: 424.0551.





3l

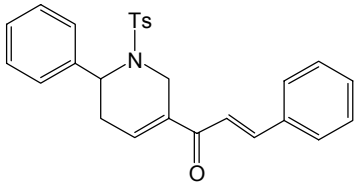
4-Methyl-*N*-[4-methyl-1-(naphthalene-1-yl)-5-oxohexa-2,3-dienyl]benzenesulfonamide

3l: mp. 136-141 ^oC; IR (CH_2Cl_2) ν 3272, 1680 (C=O), 1433, 1337, 1159, 1091 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**3l** and (1S, 3S)-**3l**: 1.52 (3H, d, *J* = 2.7 Hz, CH_3), 1.98 (3H, s, CH_3), 2.33 (3H, s, CH_3), 5.42-5.44 (1H, m, NH), 5.81-5.88 (1H, m, CH), 5.92-5.95 (1H, m, =CH), 7.06-7.11 (2H, m, ArH), 7.29-7.39 (2H, m, ArH), 7.43-7.50 (2H, m, ArH), 7.55-7.62 (2H, m, ArH), 7.70-7.74 (1H, m, ArH), 7.79-7.91 (2H, m, ArH); (1S, 3R)-**3l** and (1R, 3S)-**3l**: 1.57 (3H, d, *J* = 2.7 Hz, CH_3), 1.96 (3H, s, CH_3), 2.34 (3H, s, CH_3), 5.42-5.44 (1H, m, NH), 5.81-5.88 (2H, m, CH, =CH), 7.06-7.11 (2H, m, ArH), 7.29-7.39 (2H, m, ArH), 7.43-7.50 (2H, m, ArH), 7.55-7.62 (2H, m, ArH), 7.70-7.74 (1H, m, ArH), 7.79-7.91 (2H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.52, 12.79, 21.22, 21.24, 26.61, 26.63, 53.10 (2C), 96.68, 96.83, 107.30, 107.44, 122.55, 122.69, 124.37, 124.54, 124.93 (2C), 125.58, 125.60, 126.22, 126.24,

126.68, 126.76, 128.48, 128.53, 128.65, 128.72, 129.13, 129.19, 129.61, 129.74, 133.48, 133.50, 134.35, 134.37, 136.90, 136.97, 143.11, 143.20, 198.41, 198.48, 211.96, 211.99; MS (EI) *m/e* 310 (M^+-95, 100), 191 (M^+-214, 29.63), 155 (M^+-250, 50.60), 91 (M^+-314, 75.73); [Found: C, 70.85; H, 5.71; N, 3.33%. $C_{24}H_{23}O_3NS$ requires C, 71.08; H, 5.72; N, 3.45%].

The aza-Baylis-Hillman reaction of *N*-tosylated aldimines with 3-methylpenta-3,4-dien-2-one catalyzed by PBu_3. Typical reaction procedure of *N*-tosylated aldimines with 3-methylpenta-3,4-dien-2-one at 80 ^oC catalyzed by PBu_3.

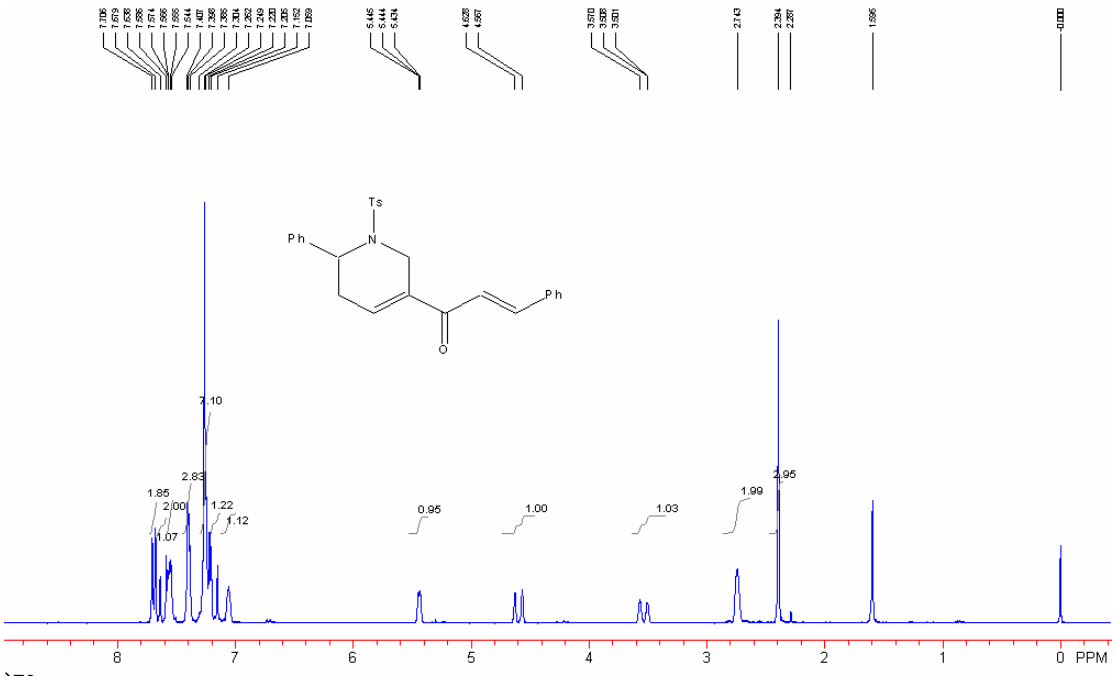
To a Schlenk tube with *N*-(*p*-methylbenzenesulfonyl)benzaldimine (130 mg, 0.5 mmol) in DMSO (1 mL) under argon atmosphere was added 3-methylpenta-3,4-dien-2-one (96 mg, 1 mmol) and PBu_3 (12.5 mg, 0.05 mmol). The reaction mixture was stirred for 30 min. at 80 ^oC. The reaction mixture was washed with water (10 mL) and extracted with dichloromethane (20 mL). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to afford **4a** (eluent: EtOAc/petroleum= 1/3) 72 mg (yield 65%) as a major product and **5a** (eluent: EtOAc/petroleum= 1/2) 52 mg (yield 29%) as a minor product.

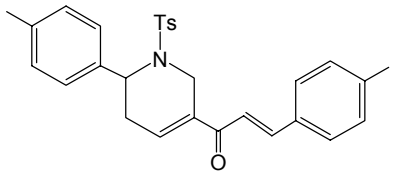


4a

(*E*)-3-Phenyl-1-(6-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)prop-2-en-1-one 4a: mp. 170-174 ^oC; IR (CH_2Cl_2) ν 3030, 1653 (C=O), 1596, 1339, 1154, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.39 (3H, s, CH_3), 2.74-2.75 (2H, m, CH_2), 3.54 (1H, dm, *J* = 18.3 Hz, CH_2), 4.60 (1H, dm, *J* = 18.3 Hz, CH_2), 5.43-5.45 (1H, m, CH), 7.06-7.07 (1H, m, =CH), 7.18 (1H, d, *J* = 15.6 Hz, =CH), 7.22-7.26 (7H, m, ArH), 7.39-7.41 (3H, m, Ar), 7.54-7.57 (2H, m, Ar), 7.61 (1H, d, *J* = 15.6 Hz, =CH), 7.69 (2H, d, *J* = 8.1 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.44, 27.40, 39.36, 52.20, 119.78, 126.96, 127.04, 127.75, 128.22, 128.53, 128.85, 129.58, 130.45, 134.55, 135.90, 136.69, 137.12, 138.15, 143.31, 143.72, 187.78; MS (EI) *m/e*

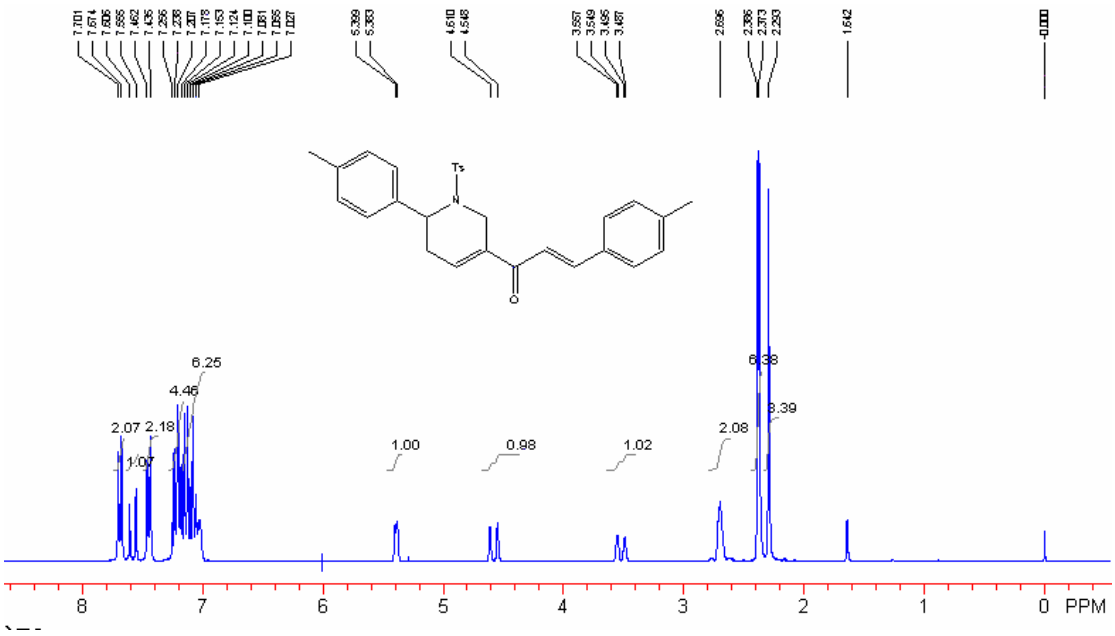
443 (M^+, 28.85), 288 (M^+-155, 37.70), 193 (M^+-250, 100), 131 (M^+-312, 39.37), 91 (M^+-352, 46.69); HRMS (MALDI) calcd. for $C_{27}H_{25}NO_3SNa^{+1}$: 466.1447, Found: 466.1455.

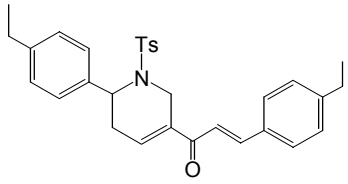




4b

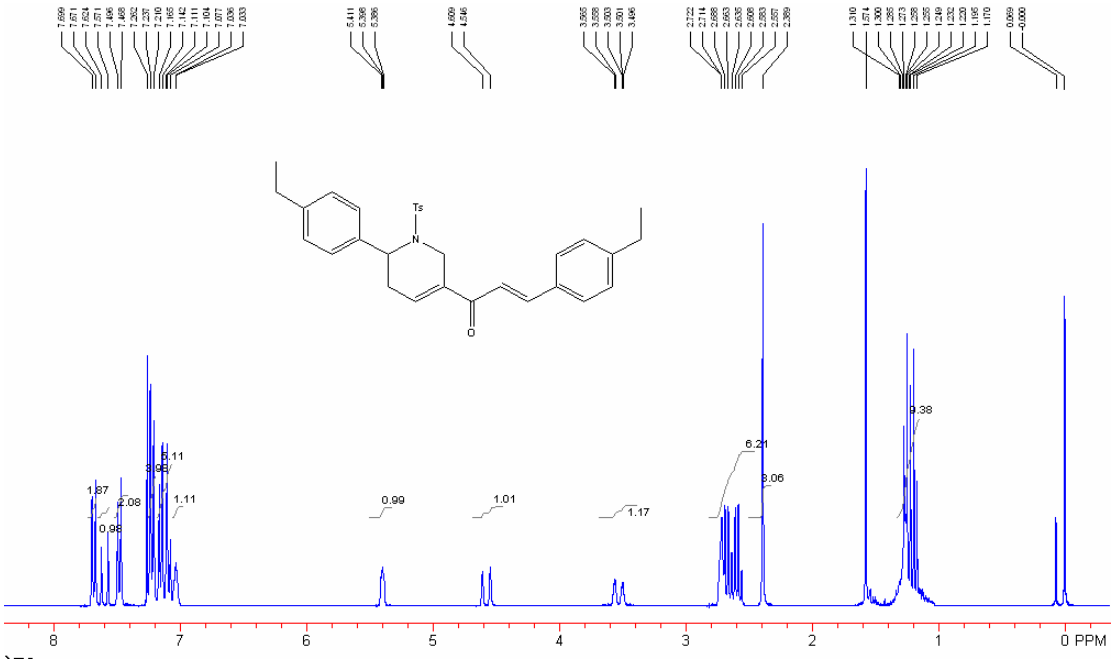
(*E*)-3-*p*-Tosyl-1-(6-*p*-tolyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)prop-2-en-1-one 4b: mp. 155-159 ^oC; IR (CH_2Cl_2) ν 2922, 1653 (C=O), 1595, 1324, 1159, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.29 (3H, s, CH_3), 2.37 (3H, s, CH_3), 2.39 (3H, s, CH_3), 2.70 (2H, m, CH_2), 3.52 (1H, dd, J = 15.6, 2.4 Hz, CH_2), 4.56 (1H, dm, J = 15.6 Hz, CH_2), 5.38-5.40 (1H, m, CH), 7.02 (1H, m, =CH), 7.05-7.26 (9H, m, =CH, ArH), 7.45 (2H, d, J = 8.4 Hz, ArH), 7.58 (1H, d, J = 15.3 Hz, =CH), 7.69 (2H, d, J = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 20.96, 21.48 (2C), 27.48, 39.37, 52.00, 118.87, 127.03, 127.04, 128.28, 129.21, 129.60, 129.63, 131.89, 135.17, 135.65, 136.81, 137.32, 137.52, 141.01, 143.25, 143.82, 187.95; MS (EI) *m/e* 472 (M^++1, 11.66), 471 (M^+, 34.58), 316 (M^+-155, 36.16), 221 (M^+-250, 100), 198 (M^+-273, 26.65), 145 (M^+-326, 35.68), 91 (M^+-380, 37.87); HRMS (MALDI) calcd. for $C_{29}H_{29}NO_3SNa^{+1}$: 494.1760, Found: 494.1782.

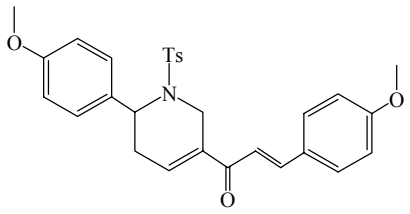




4c

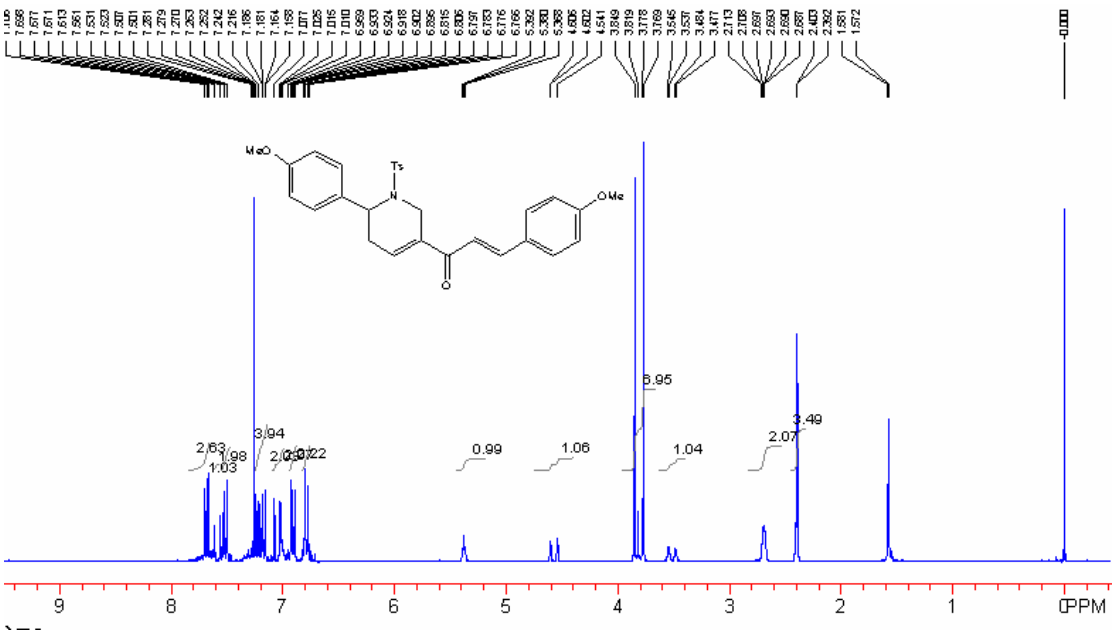
(*E*)-3-(4-Ethylphenyl)-1-[6-(4-ethylphenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]prop-2-en-1-one 4c: a colorless oil; IR (CH_2Cl_2) ν 2965, 1651 (C=O), 1596, 1341, 1160, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.81-0.88 (6H, m, CH_3), 2.38 (3H, s, CH_3), 2.56-2.73 (6H, m, CH_2), 3.56 (1H, dd, *J* = 15.6, 2.4 Hz, CH_2), 4.58 (1H, d, *J* = 15.6 Hz, CH_2), 5.39-5.41 (1H, m, CH), 7.03 (1H, m, =CH), 7.05-7.24 (9H, m, =CH, ArH), 7.48 (2H, d, *J* = 8.4 Hz, ArH), 7.60 (1H, d, *J* = 15.9 Hz, =CH), 7.69 (2H, d, *J* = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 15.29, 15.49, 21.48, 27.63, 28.37, 28.79, 39.42, 52.07, 118.93, 127.08, 127.11, 127.95, 128.03, 128.39, 128.46, 129.57, 132.14, 135.43, 135.67, 136.82, 137.25, 143.22, 143.87, 147.30, 188.00; MS (EI) *m/e* 499 (M^+, 17.32), 344 (M^+-155, 33.11), 249 (M^+-250, 100), 194 (M^+-305, 37.68), 91 (M^+-408, 63.22); HRMS (MALDI) calcd. for $C_{31}H_{33}NO_3SNa^{+1}$: 522.2073, Found: 522.2073.

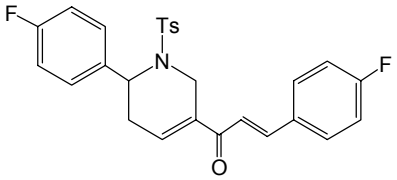




4d

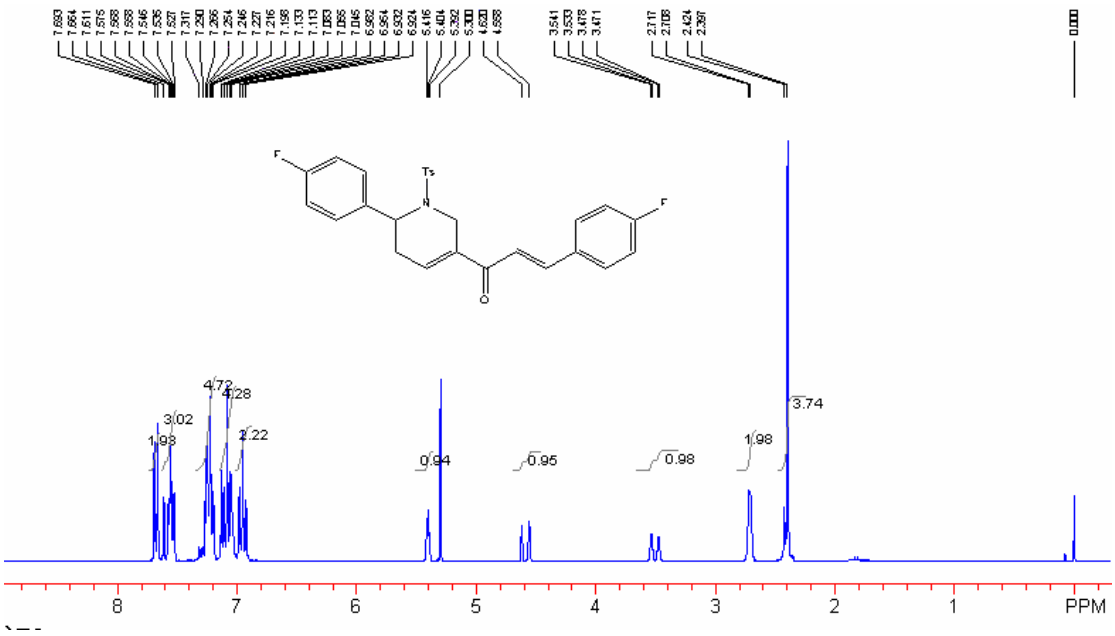
(*E*)-3-(4-Methoxyphenyl)-1-[6-(4-methoxyphenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]prop-2-en-1-one 4d: a colorless oil; IR (CH_2Cl_2) ν 2930, 1651 (C=O), 1590, 1512, 1254, 1159, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.40 (3H, s, CH_3), 2.69-2.70 (2H, m, CH_2), 3.51 (1H, dd, J = 18.3, 2.4 Hz, CH_2), 3.77 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 4.57 (1H, dm, J = 18.3 Hz, CH_2), 5.37-5.39 (1H, m, CH), 6.77-6.82 (2H, m, ArH), 6.89-6.93 (2H, m, ArH), 7.00-7.02 (1H, m, =CH), 7.05 (1H, d, J = 15.6 Hz, =CH), 7.16-7.24 (4H, m, ArH), 7.51-7.53 (2H, m, Ar), 7.59 (1H, d, J = 15.6 Hz, =CH), 7.67-7.71 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.49, 27.64, 39.34, 51.77, 55.26, 55.37, 113.83, 114.33, 117.52, 127.01, 127.03, 127.34, 128.38, 129.59, 130.03, 130.23, 135.26, 136.84, 143.22, 143.60, 159.01, 161.56, 187.86; MS (EI) *m/e* 503 (M^+, 15.93), 348 (M^+-155, 42.34), 253 (M^+-250, 69.93), 214 (M^+-289, 42.19), 161 (M^+-342, 100), 91 (M^+-412, 66.27); HRMS (MALDI) calcd. for $C_{29}H_{29}NO_5SNa^{+1}$: 526.1659, Found: 526.1685.

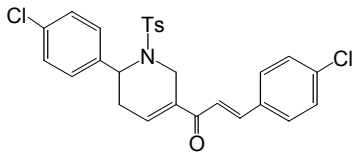




4e

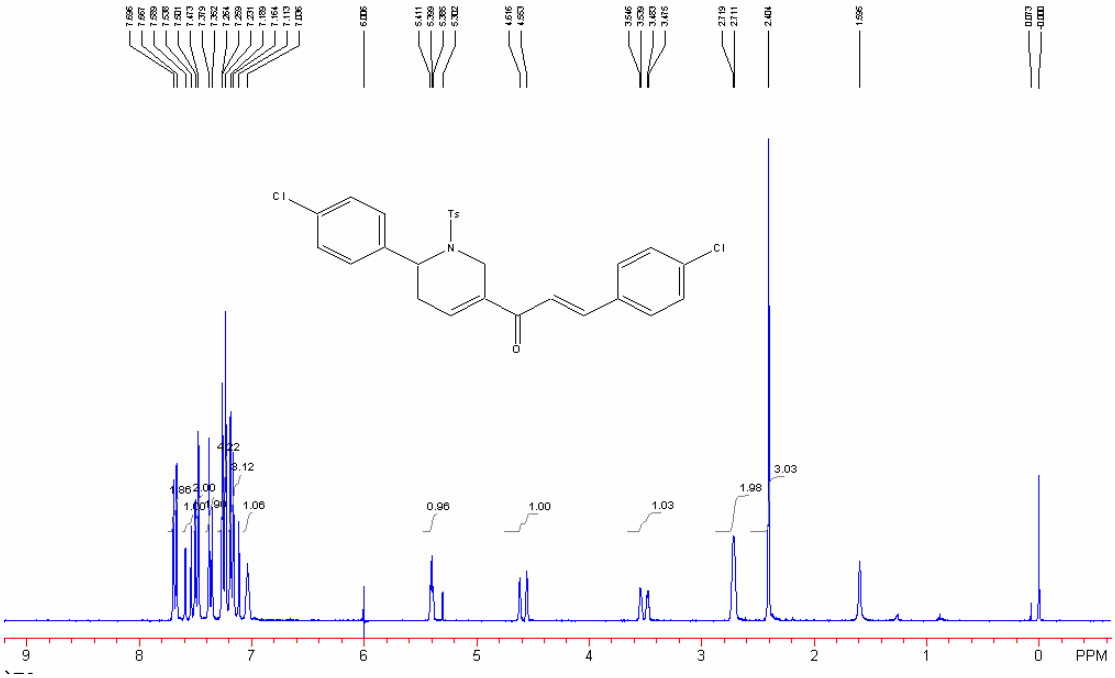
(*E*)-3-(4-Fluorophenyl)-1-[6-(4-fluorophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]pro p-2-en-1-one 4e: mp. 84-88 ^{o}C; IR (CH_2Cl_2) ν 1711, 1654 (C=O), 1509, 1340, 1160, 1096 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.40 (3H, s, CH_3), 2.71-2.72 (2H, m, CH_2), 3.51 (1H, dd, *J* = 18.6, 2.1 Hz, CH_2), 4.59 (1H, dm, *J* = 18.6 Hz, CH_2), 5.39-5.42 (1H, m, CH), 6.92-6.98 (2H, m, ArH), 7.05-7.13 (4H, m, =CH, ArH, =CH), 7.20-7.27 (4H, m, ArH), 7.53-7.61 (3H, m, ArH, =CH), 7.68 (2H, d, *J* = 8.7 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.49, 27.67, 39.30, 51.61, 115.45 (d, *J* = 21.2 Hz), 116.09 (d, *J* = 21.8 Hz), 119.42, 127.02, 128.88 (d, *J* = 8.0 Hz), 129.68, 130.20 (d, *J* = 8.6 Hz), 130.84 (d, *J* = 2.9 Hz), 133.98 (d, *J* = 3.4 Hz), 135.56, 136.82, 137.05, 142.66, 143.50, 162.16 (d, *J* = 245.6 Hz), 163.99 (d, *J* = 250.8 Hz), 187.51; MS (EI) *m/e* 480 (M^++1, 11.12), 479 (M^+, 35.99), 324 (M^+-155, 41.34), 229 (M^+-250, 100), 202 (M^+-277, 30.23), 149 (M^+-330, 52.71), 91 (M^+-388, 44.69); HRMS (MALDI) calcd. for $C_{27}H_{23}NO_3F_2SNa^{+1}$: 502.1259, Found: 502.1281.

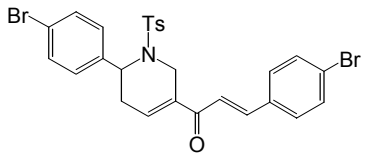




4f

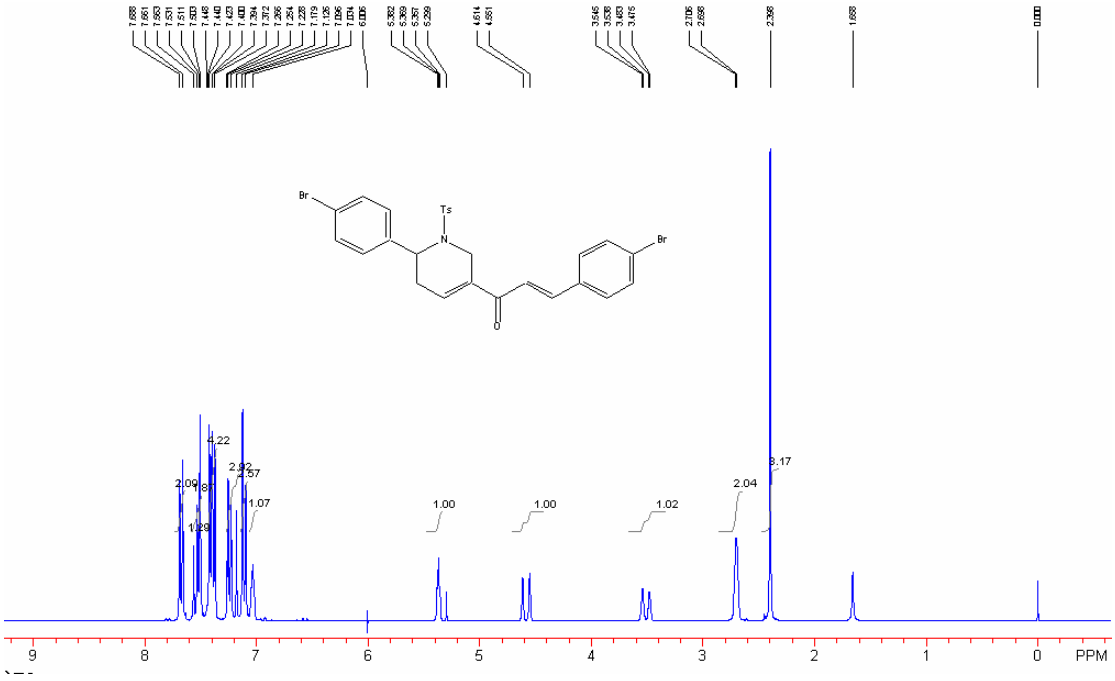
(*E*)-3-(4-Chlorophenyl)-1-[6-(4-chlorophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]prop-2-en-1-one 4f: mp. 163-166 ^{o}C; IR (CH_2Cl_2) ν 2923, 1655 (C=O), 1600, 1567, 1491, 1319, 1159, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.40 (3H, s, CH_3), 2.71-2.72 (2H, m, CH_2), 3.51 (1H, dd, *J* = 18.9, 2.1 Hz, CH_2), 4.58 (1H, dm, *J* = 18.9 Hz, CH_2), 5.39-5.41 (1H, m, CH), 7.03-7.04 (1H, m, =CH), 7.14 (1H, d, *J* = 15.0 Hz, =CH), 7.16-7.19 (2H, m, ArH), 7.23-7.26 (4H, m, ArH), 7.35-7.38 (2H, m, ArH), 7.49 (2H, d, *J* = 8.4 Hz, ArH), 7.56 (1H, d, *J* = 15.0 Hz, =CH), 7.68 (2H, d, *J* = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.47, 27.43, 39.33, 51.64, 120.06, 126.96, 128.48, 128.71, 129.15, 129.41, 129.69, 133.03, 133.67, 135.65, 136.37, 136.66, 136.73, 136.95, 142.46, 143.56, 187.37; MS (EI) *m/e* 513 (M^++2, 23.12), 511 (M^+, 31.86), 358 (M^+-153, 30.14), 356 (M^+-155, 46.88), 263 (M^+-248, 66.26), 261 (M^+-250, 100), 165 (M^+-346, 94.06), 155 (M^+-356, 37.42), 91 (M^+-420, 98.65); HRMS (MALDI) calcd. for $C_{27}H_{23}NO_3Cl_2SNa^{+1}$: 534.0668, Found: 534.0662.

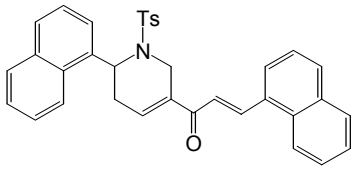




4g

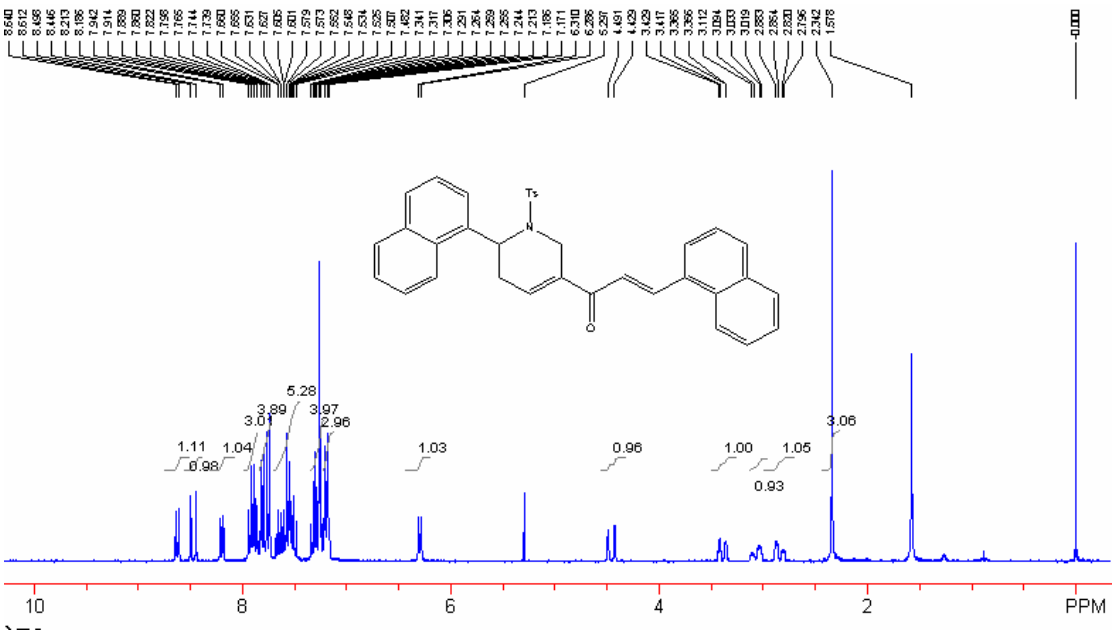
(*E*)-3-(4-Bromophenyl)-1-[6-(4-bromophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]prop-2-en-1-one 4g: mp.168-170 ^{o}C; IR (CH_2Cl_2) ν 3054, 2923, 1655 (C=O), 1600, 1488, 1320, 1159, 1096 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.40 (3H, s, CH_3), 2.70-2.71 (2H, m, CH_2), 3.51 (1H, dd, *J* = 18.6, 2.4 Hz, CH_2), 4.58 (1H, dm, *J* = 18.6 Hz, CH_2), 5.36-5.38 (1H, m, CH), 7.03-7.04 (1H, m, =CH), 7.10-7.13 (2H, m, ArH), 7.20 (1H, d, *J* = 15.0 Hz, =CH), 7.25-7.27 (2H, m, ArH), 7.37-7.42 (4H, m, ArH), 7.50-7.53 (2H, m, ArH), 7.54 (1H, d, *J* = 15.0 Hz, =CH), 7.67 (2H, d, *J* = 8.1 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.51, 27.44, 39.37, 51.69, 120.14, 121.85, 124.79, 126.98, 128.82, 129.62, 129.70, 131.70, 132.14, 133.46, 135.60, 136.78, 136.93, 137.20, 142.56, 143.58, 187.35; MS (EI) *m/e* 603 (M^++5, 1.29), 601 (M^++3, 2.28), 446 (M^+-152, 6.52), 351 (M^+-247, 13.54), 211 (M^+-387, 32.34), 209 (M^+-389, 33.37), 155 (M^+-433, 33.19), 102 (M^+-496, 51.73), 91 (M^+-507, 100); HRMS (MALDI) calcd. for $C_{27}H_{23}NO_3Br_2SNa^{+1}$: 621.9658, Found: 621.9651.

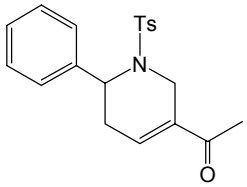




4h

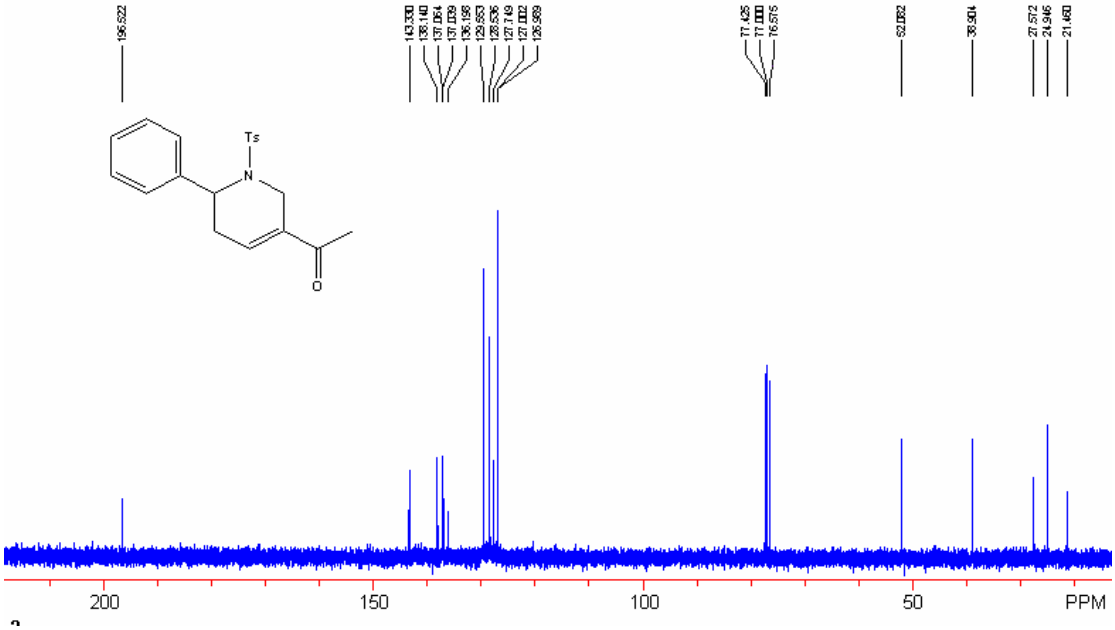
(*E*)-3-(Naphthalene-1-yl)-1-[6-(naphthalen-1-yl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]prop-2-en-1-one 4h: mp. 208-212 ^{o}C; IR (CH_2Cl_2) ν 3051, 1650 (C=O), 1597, 1341, 1158, 1092 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.34 (3H, s, CH_3), 2.80-2.88 (1H, m, CH_2), 3.03-3.11 (1H, m, CH_2), 3.35-3.43 (1H, m, CH_2), 4.46 (1H, dm, J = 18.6 Hz, CH_2), 6.30 (1H, d, J = 7.2 Hz, CH), 7.17-7.34 (6H, m, =CH, ArH, = CH), 7.48-7.66 (5H, m, ArH), 7.74-7.94 (7H, m, ArH), 8.20 (1H, d, J = 8.1 Hz, ArH), 8.47 (1H, d, J = 15.6 Hz, =CH), 8.63 (1H, d, J = 8.1 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.45, 28.04, 39.46, 49.16, 122.58, 123.34, 124.02, 124.14, 124.59, 124.85, 125.35, 126.01, 126.31, 126.85, 126.96, 127.64, 128.71, 128.75, 129.30, 129.53, 130.76, 131.37, 131.63, 132.17, 133.45, 133.67, 134.08, 136.44, 136.85, 136.91, 140.75, 143.67, 187.98; MS (EI) *m/e* 543 (M^+, 6.78), 388 (M^+-155, 11.30), 293 (M^+-250, 7.69), 206 (M^+-337, 24.35), 181 (M^+-362, 82.16), 152 (M^+-391, 100), 91 (M^+-452, 86.59); HRMS (MALDI) calcd. for $C_{35}H_{29}NO_3SNa^{+1}$: 566.1760, Found: 566.1788.

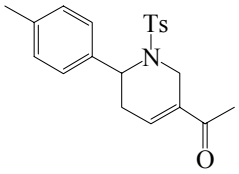




5a

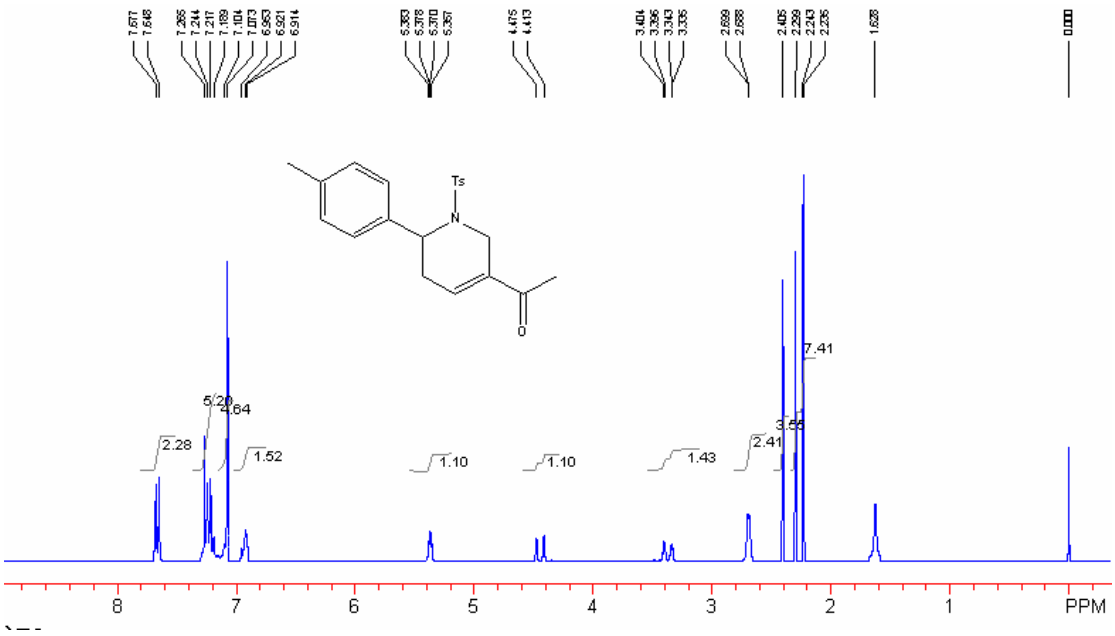
1-(6-Phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)ethanone 5a: IR (CH_2Cl_2) ν 2925, 1667 (C=O), 1598, 1338, 1159, 1097 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.24 (3H, s, CH_3), 2.40 (3H, s, CH_3), 2.70-2.71 (2H, m, CH_2), 3.38 (1H, dm, *J* = 18.6 Hz, CH_2), 4.46 (1H, br d, *J* = 18.6 Hz, CH_2), 5.39-5.41 (1H, m, CH), 6.93-6.94 (1H, m, =CH), 7.18-7.29 (7H, m, ArH), 7.66 (2H, d, *J* = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.46, 24.95, 27.57, 38.90, 52.08, 126.99, 127.00, 127.75, 128.54, 129.55, 136.20, 137.04, 137.06, 138.14, 143.33, 196.52; MS (EI) *m/e* 355 (M^+, 19.99), 200 (M^+-155, 100), 156 (M^+-199, 22.01), 155 (M^+-200, 31.14), 91 (M^+-264, 68.21); HRMS (EI) calcd. for $C_{20}H_{21}NO_3S$: 355.1242, Found: 355.1250.

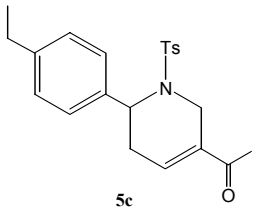




5b

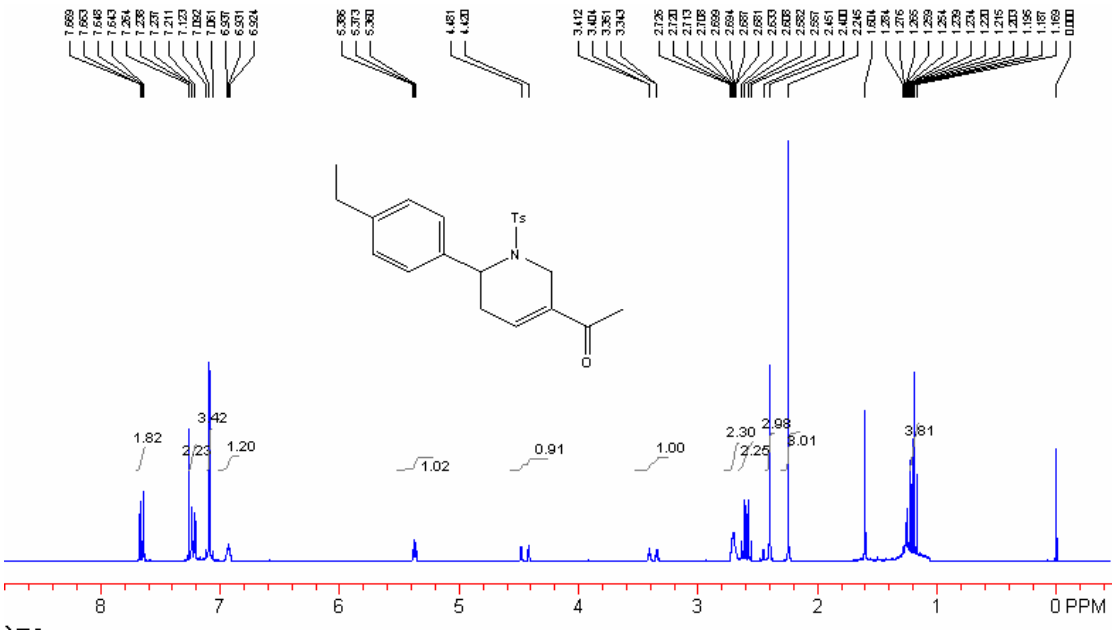
1-(6-*p*-Tolyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)ethanone 5b: IR (CH_2Cl_2) ν 2923, 1699, 1667 (C=O), 1598, 1338, 1160, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.24 (3H, s, CH_3), 2.30 (3H, s, CH_3), 2.41 (3H, s, CH_3), 2.69-2.70 (2H, m, CH_2), 3.37 (1H, dm, J = 18.6 Hz, CH_2), 4.44 (1H, br d, J = 18.6 Hz, CH_2), 5.36-5.38 (1H, m, CH), 6.91-6.92 (1H, m, =CH), 7.07 (4H, s, ArH), 7.23 (2H, d, J = 8.4 Hz, ArH), 7.66 (2H, d, J = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 20.96, 21.49, 24.97, 27.65, 38.85, 51.87, 126.94, 127.06, 128.26, 129.22, 129.57, 135.10, 136.27, 137.16, 137.54, 143.30, 196.56; MS (EI) *m/e* 369 (M^+, 36.26), 214 (M^+-155, 91.46), 184 (M^+-185, 40.87), 155 (M^+-214, 78.23), 91 (M^+-278, 100), 84 (M^+-285, 96.58); HRMS (MALDI) calcd. for $C_{21}H_{23}NO_3SNa^{+1}$: 392.1291, Found: 392.1303.

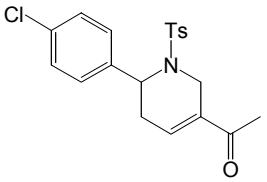




5c

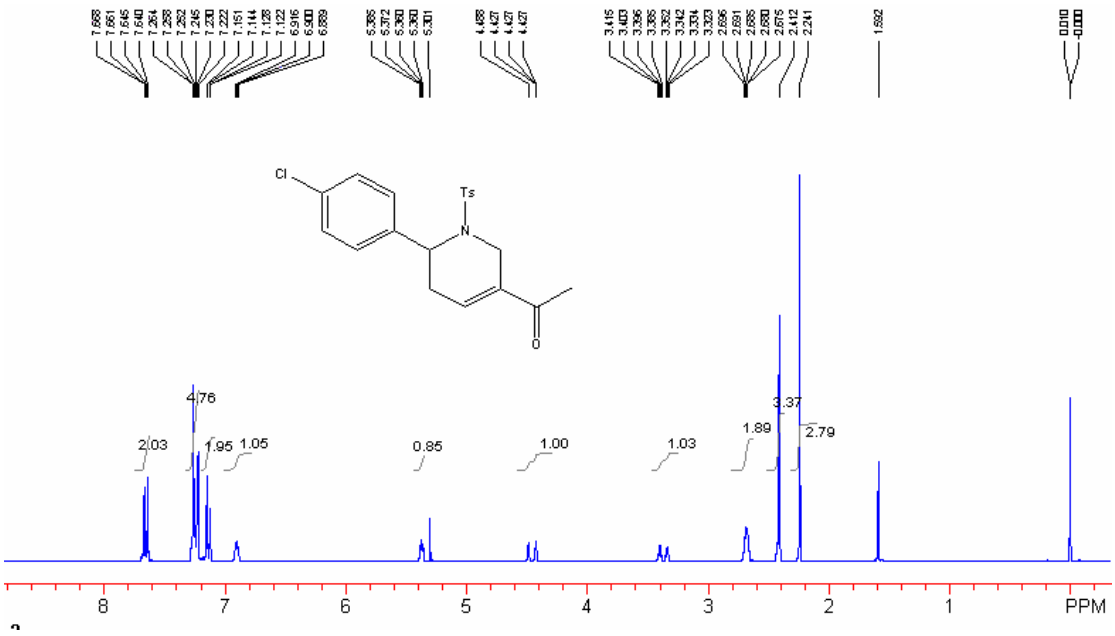
1-[6-(4-Ethylphenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]ethanone 5c: IR (CH_2Cl_2) ν 2927, 1698, 1667 (C=O), 1597, 1337, 1160, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.19 (3H, t, *J* = 7.5 Hz, CH_3), 2.25 (3H, s, CH_3), 2.40 (3H, s, CH_3), 2.60 (2H, q, *J* = 7.5 Hz, CH_2), 2.69-2.71 (2H, m, CH_2), 3.38 (1H, dm, *J* = 18.6 Hz, CH_2), 4.45 (1H, dm, *J* = 18.6 Hz, CH_2), 5.37 (1H, t, *J* = 3.9 Hz, CH), 6.92-6.95 (1H, m, =CH), 7.09 (4H, s, ArH), 7.22 (2H, d, *J* = 8.4 Hz, ArH), 7.66 (2H, d, *J* = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 15.50, 21.48, 24.96, 27.75, 28.35, 38.90, 51.93, 127.02, 127.07, 128.01, 129.53, 135.34, 136.25, 137.14, 137.20, 143.25, 143.88, 196.60; MS (EI) *m/e* 384 (M^++1, 12.68), 228 (M^+-155, 100), 184 (M^+-199, 22.42), 155 (M^+-228, 32.53), 91 (M^+-292, 75.24); HRMS (MALDI) calcd. for $C_{22}H_{25}NO_3SNa^{+1}$: 406.1447, Found: 406.1456.

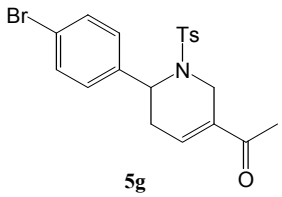




5f

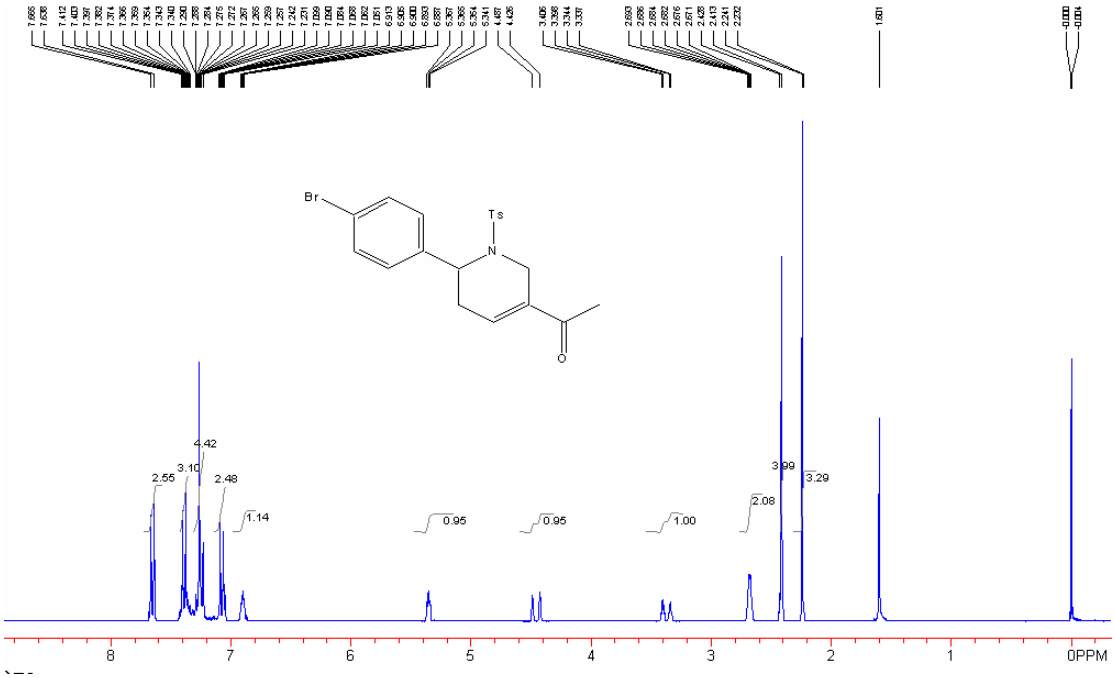
1-[6-(4-Chlorophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]ethanone 5f: IR (CH_2Cl_2) ν 3261, 1708, 1658, 1598, 1509, 1335, 1304, 1160, 1094 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.24 (3H, s, CH_3), 2.43 (3H, s, CH_3), 2.68-2.70 (2H, m, CH_2), 3.37 (1H, dm, J = 18.6 Hz, CH_2), 4.46 (1H, br d, J = 18.6 Hz, CH_2), 5.36-5.39 (1H, m, CH), 6.89-6.91 (1H, m, =CH), 7.13 (2H, d, J = 8.1 Hz, ArH), 7.22-7.26 (4H, m, ArH), 7.65 (2H, d, J = 8.1 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.48, 24.95, 27.52, 38.91, 51.54, 126.99, 128.44, 128.71, 129.66, 133.67, 136.24, 136.57, 136.69, 136.90, 143.56, 196.46; MS (EI) *m/e* 391 (M^++2, 10.55), 389 (M^+, 23.81), 236 (M^+-153, 32.85), 234 (M^+-155, 100), 190 (M^+-199, 16.03), 155 (M^+-234, 31.46), 91 (M^+-298, 60.30); HRMS (MALDI) calcd. for $C_{20}H_{20}NO_3SClNa^{+1}$: 412.0745, Found: 412.0762.





5g

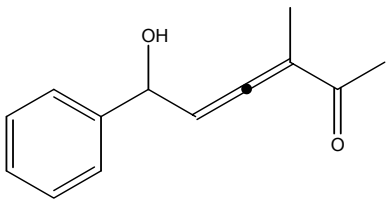
1-[6-(4-Bromophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]ethanone 5g: IR (CH_2Cl_2) ν 3271, 2924, 1713, 1667, 1597, 1488, 1338, 1260, 1160, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.24 (3H, s, CH_3), 2.43 (3H, s, CH_3), 2.67-2.69 (2H, m, CH_2), 3.37 (1H, dm, J = 18.3 Hz, CH_2), 4.46 (1H, br d, J = 18.6 Hz, CH_2), 5.34-5.37 (1H, m, CH), 6.89-6.90 (1H, m, =CH), 7.08 (2H, d, J = 8.4 Hz, ArH), 7.23-7.26 (2H, m, ArH), 7.39 (2H, d, J = 8.4 Hz, ArH), 7.65 (2H, d, J = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.51, 24.98, 27.50, 38.94, 51.61, 126.41, 127.01, 128.79, 129.67, 131.70, 136.28, 136.50, 136.90, 137.24, 143.58, 196.42; MS (EI) *m/e* 435 (M^++2, 31.42), 433 (M^+, 31.00), 280 (M^+-153, 90.55), 278 (M^+-155, 100), 236 (M^+-197, 17.91), 234 (M^+-199, 16.31), 155 (M^+-278, 58.61), 91 (M^+-342, 67.75); HRMS (MALDI) calcd. for $C_{20}H_{20}NO_3SBrNa^{+1}$: 456.0240, Found: 456.0253.



The aza-Baylis-Hillman reactions of aldehydes with 3-methylpenta-3,4-dien-2-one catalyzed by DMAP. **Typical reaction procedure of benzaldehyde with 3-methylpenta-3,4-dien-2-one at 80 ^{o}C catalyzed by DMAP**.

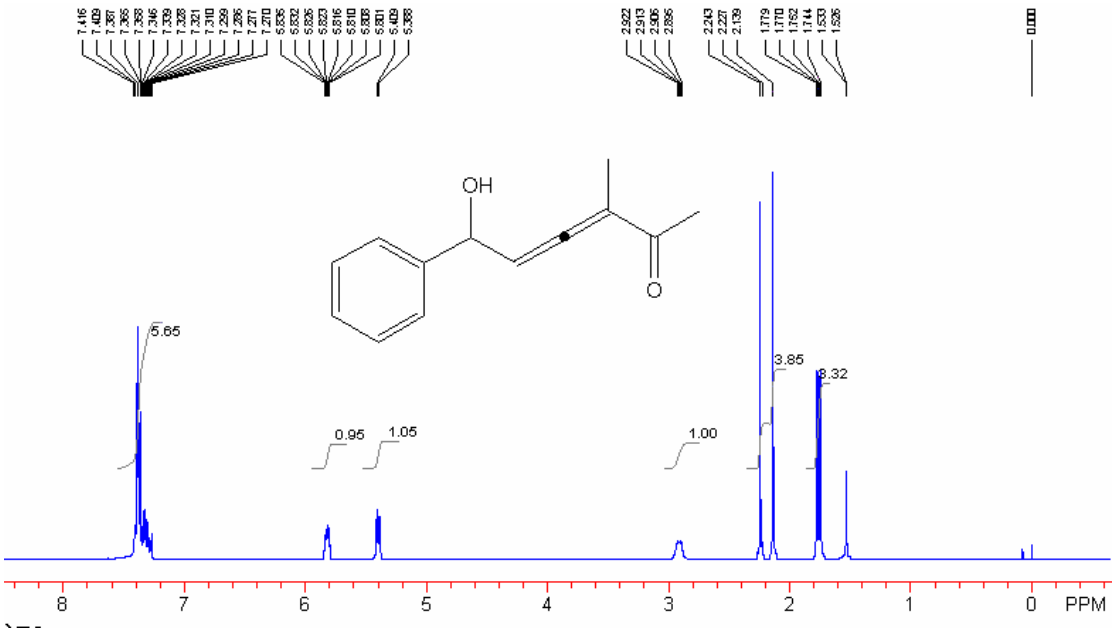
To a Schlenk tube with benzaldehyde (53 mg, 0.5 mmol) and DMAP (6 mg, 0.05 mmol) in DMSO (1 mL) was added 3-methylpenta-3,4-dien-2-one (192 mg, 2 mmol) and the reaction mixture was stirred for 30 min. at 80 ^{o}C. The reaction mixture was washed with water (10 mL) and extracted with dichloromethane (20 mL). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: EtOAc/petroleum= 1/3) to give adduct **6a** (75 mg, yield 61%) as a colorless oil.

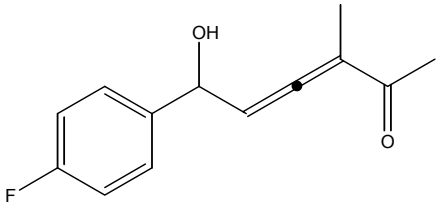
In all cases, **6** was obtained as a pair of diastereoisomeric mixtures in 1:1 ratio on the basis of ^{1}H NMR spectroscopic data and could not be separated by silica gel column chromatography. ^{13}C NMR spectroscopic data also indicated a pair of diastereoisomeric mixtures in 1:1 ratio.



6a

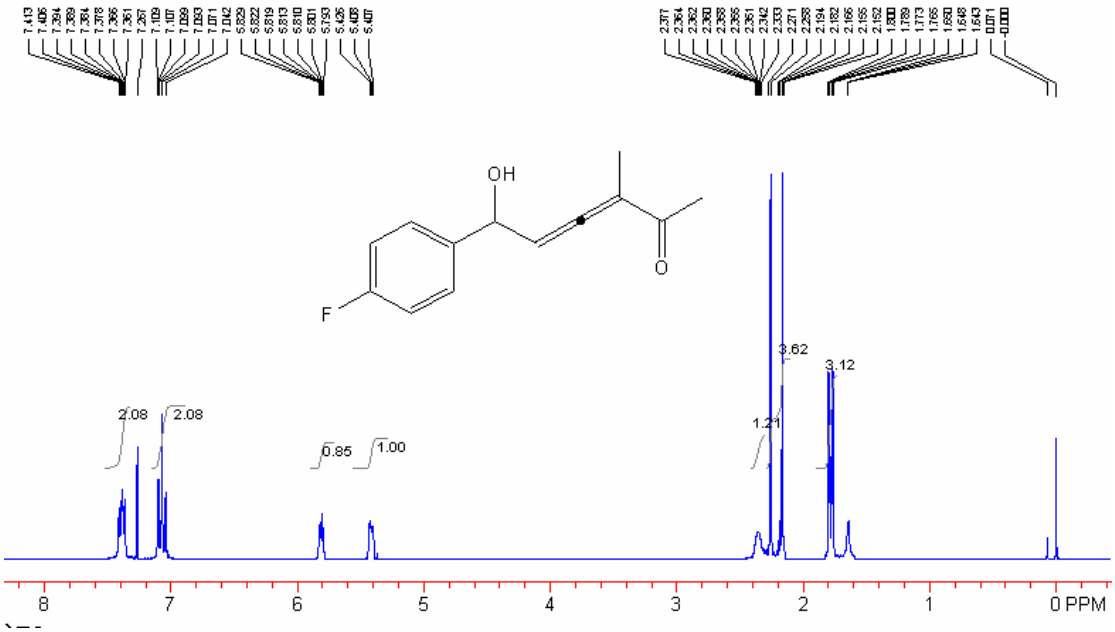
6-Hydroxy-3-methyl-6-phenylhexa-3,4-dien-2-one 6a: a colorless oil; IR (CH_2Cl_2) ν 3410, 2925, 1948, 1674, 1667, 1491, 1356, 1356, 1016 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**6a** and (1S, 3S)-**6a**: 1.75 (3H, d, *J* = 2.7 Hz, CH_3), 2.14 (3H, s, CH_3), 2.91 (1H, br s, OH), 5.40 (1H, d, *J* = 6.3 Hz, CH), 5.80-5.84 (1H, m, =CH), 7.27-7.42 (5H, m, ArH); (1S, 3R)-**6a** and (1R, 3S)-**6a**: 1.77 (3H, d, *J* = 2.7 Hz, CH_3), 2.23 (3H, s, CH_3), 2.91 (1H, br s, OH), 5.40 (1H, d, *J* = 6.3 Hz, CH), 5.80-5.84 (1H, m, =CH), 7.27-7.42 (5H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.19, 13.27, 26.67, 26.76, 71.88, 71.96, 98.84, 98.92, 106.73, 106.90, 125.77, 125.82, 128.07, 128.09, 128.55, 128.58, 142.23, 142.26, 198.90, 198.93, 211.66, 211.72; MS (EI) *m/e* 202 (M^+, 0.43), 185 (M^+-17, 28.27), 141 (M^+-61, 36.52), 107 (M^+-95, 34.98), 96 (M^+-106, 50.80), 79 (M^+-123, 55.33), 43 (M^+-159, 100); HRMS (EI) calcd. for $C_{13}H_{12}O$ (M - H_2O): 184.0888, Found: 184.0899.

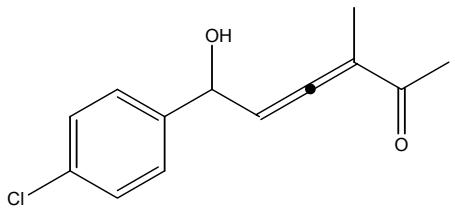




6b

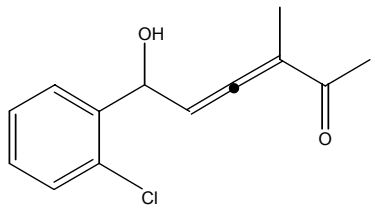
6-(4-Fluorophenyl)-6-hydroxy-3-methylhexa-3,4-dien-2-one 6b: a pale yellow oil; IR (CH_2Cl_2) ν 3424, 1950, 1678, 1603, 1509, 1360, 1157, 1098 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**6b** and (1S, 3S)-**6b**: 1.77 (3H, d, *J* = 2.7 Hz, CH_3), 2.17 (3H, s, CH_3), 2.36 (1H, br s, OH), 5.42 (1H, d, *J* = 6.0 Hz, CH), 5.79-5.83 (1H, m, =CH), 7.04-7.10 (2H, m, ArH), 7.36-7.41 (2H, m, ArH); (1S, 3R)-**6b** and (1R, 3S)-**6b**: 1.80 (3H, d, *J* = 2.7 Hz, CH_3), 2.26 (3H, s, CH_3), 2.36 (1H, br s, OH), 5.42 (1H, d, *J* = 6.0 Hz, CH), 5.79-5.83 (1H, m, =CH), 7.04-7.10 (2H, m, ArH), 7.36-7.41 (2H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.17, 13.23, 26.63, 26.71, 71.15, 71.21, 98.83, 98.91, 106.78, 106.88, 115.35 (d, *J* = 21.2 Hz), 115.38 (d, *J* = 21.8 Hz), 127.52 (d, *J* = 8.6 Hz), 127.57 (d, J = 8.0 Hz), 138.07 (d, *J* = 3.4 Hz), 138.09 (d, *J* = 2.9 Hz), 162.28 (2C, d, *J* = 245.0 Hz), 198.96 (2C), 211.66, 211.71; MS (EI) *m/e* 220 (M^+, 1.95), 159 (M^+-61, 82.68), 125 (M^+-95, 96.11), 96 (M^+-124, 98.49), 84 (M^+-136, 97.60), 43 (M^+-177, 100); HRMS (EI) calcd. for $C_{13}H_{13}O_2F$: 220.0919, Found: 220.0938.





6c

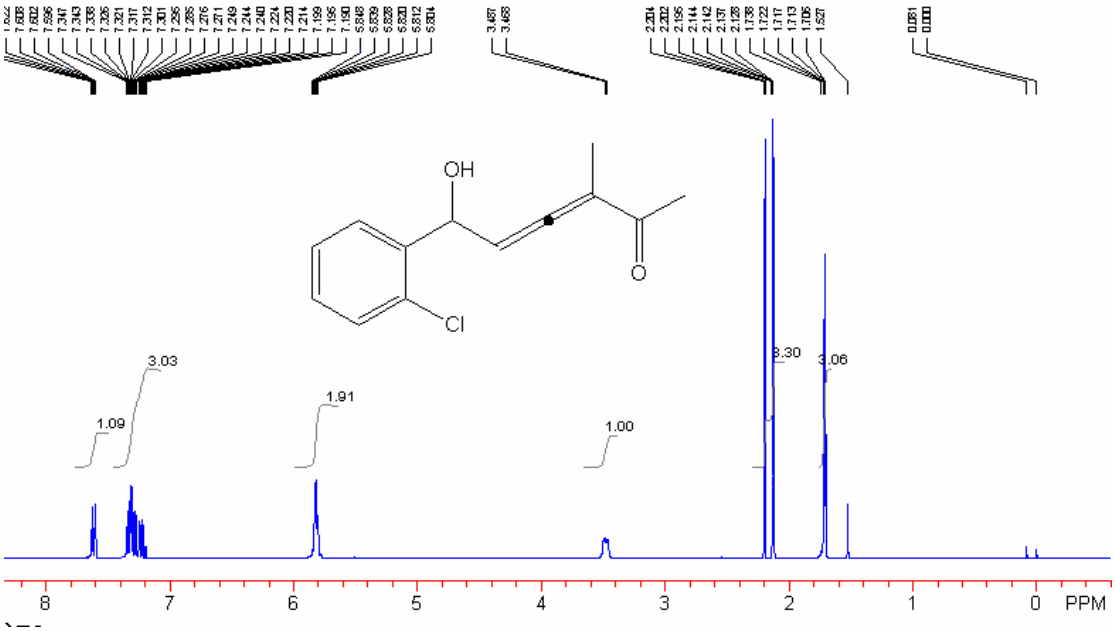
6-(4-Chlorophenyl)-6-hydroxy-3-methylhexa-3,4-dien-2-one 6c: mp. 84-86 ^{o}C; IR (CH_2Cl_2) ν 3417, 1950, 1678, 1665, 1491, 1360, 1264, 1014 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**6c** and (1S, 3S)-**6c**: 1.75 (3H, d, *J* = 2.7 Hz, CH_3), 2.15 (3H, s, CH_3), 2.46 (1H, br s, OH), 5.38 (1H, d, *J* = 6.0 Hz, CH), 5.78-5.80 (1H, m, =CH), 7.34 (4H, m, ArH); (1S, 3R)-**6c** and (1R, 3S)-**6c**: 1.77 (3H, d, *J* = 2.7 Hz, CH_3), 2.24 (3H, s, CH_3), 2.46 (1H, br s, OH), 5.38 (1H, d, *J* = 6.0 Hz, CH), 5.78-5.80 (1H, m, =CH), 7.34 (4H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.20, 13.25, 26.67, 26.74, 71.15, 71.21, 98.60, 98.70, 106.83, 106.95, 127.16, 127.20, 128.64, 128.66, 133.67, 133.69, 140.72 (2C), 198.97 (2C), 211.64, 211.73; MS (EI) *m/e* 237 (M^++ 1, 1.24), 219 (M^+-17, 76.60), 176 (M^+-60, 10.92), 141 (M^+-95, 69.17), 96 (M^+-140, 75.81), 43 (M^+-193, 100); [Found: C, 65.85; H, 5.63%. $C_{13}H_{13}O_2Cl$ requires C, 65.97; H, 5.54%]□

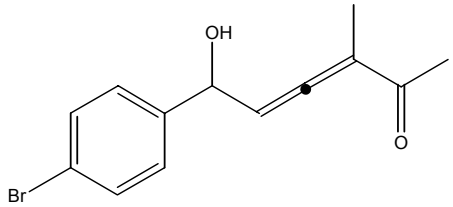


6d

6-(2-Chlorophenyl)-6-hydroxy-3-methylhexa-3,4-dien-2-one 6d: a colorless oil; IR (CH_2Cl_2) ν 3419, 2925, 1951, 1680, 1441, 1360, 1264, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**6d** and (1S, 3S)-**6d**: 1.71 (3H, d, *J* = 1.8 Hz, CH_3), 2.13 (3H, s, CH_3), 3.47 (1H, br s, OH), 5.80-5.84 (2H, m, CH, =CH), 7.21-7.35 (3H, m, ArH), 7.60-7.63 (1H, m, ArH); (1S, 3R)-**6d** and (1R, 3S)-**6d**: 1.72 (3H, d, *J* = 1.5 Hz, CH_3), 2.20 (3H, s, CH_3), 3.47 (1H, br s, OH), 5.80-5.84 (2H, m, CH, =CH), 7.21-7.35 (3H, m, ArH), 7.60-7.63 (1H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.99, 13.13, 26.67, 26.69, 68.28, 68.30, 97.52, 97.54, 106.95, 107.01, 126.94, 127.07, 127.13, 127.14, 128.94, 128.96, 129.30, 129.33, 131.51, 131.62, 139.62 (2C), 199.19 (2C), 211.99, 212.17; MS (EI) *m/e* 236 (M^+, 0.15), 219 (M^+-17, 15.96),

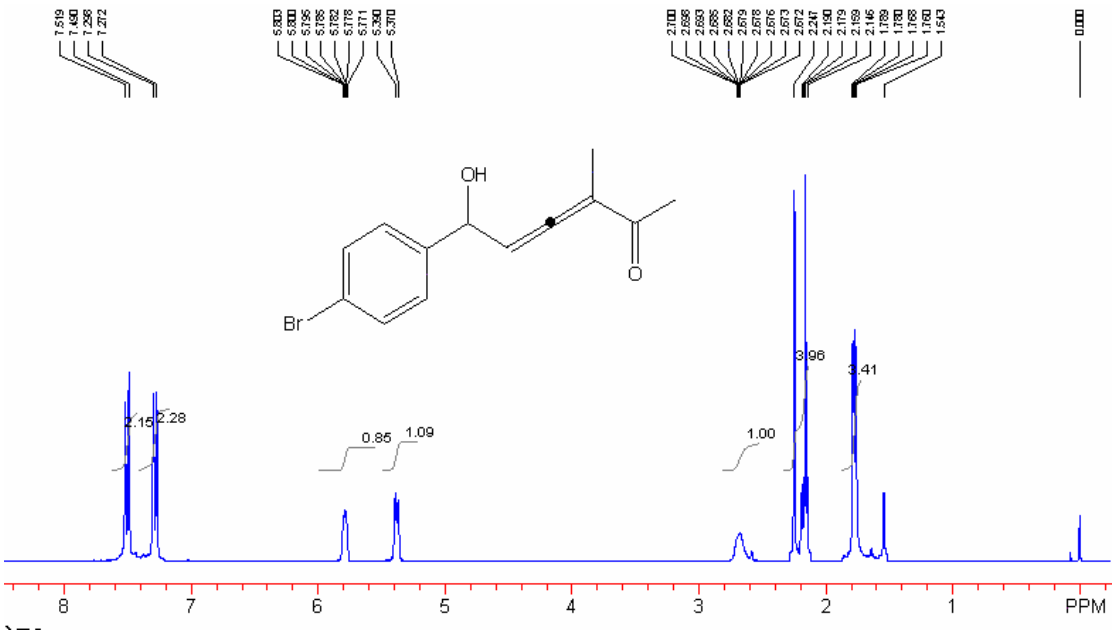
141 (M^+-95, 39.20), 96 (M^+-140, 38.72), 77 (M^+-159, 26.51), 43 (M^+-193, 100); HRMS (EI) calcd. for $C_{13}H_{13}O_2Cl$: 236.0604, Found: 236.0608.

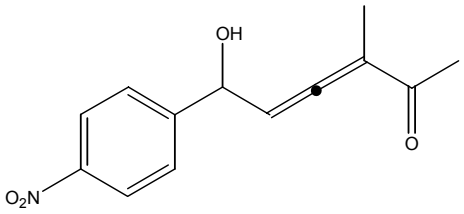




6e

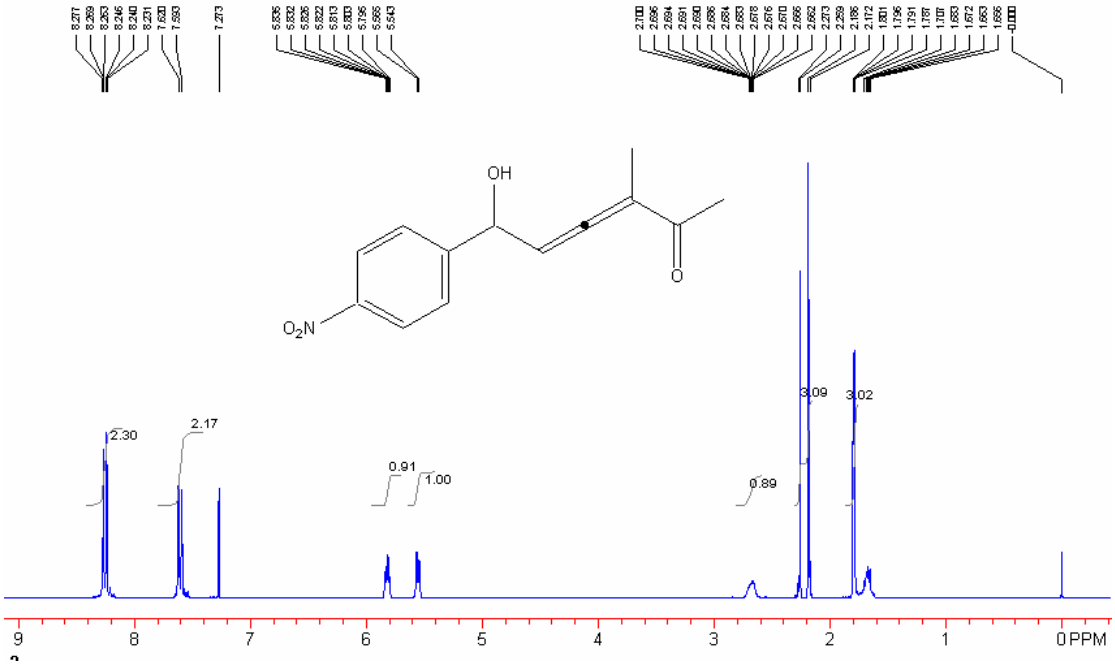
6-(4-Bromophenyl)-6-hydroxy-3-methylhexa-3,4-dien-2-one 6e: mp. 65-68 ^oC; IR (CH_2Cl_2) ν 3423, 1950, 1678, 1591, 1487, 1359, 1261, 1071 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**6e** and (1S, 3S)-**6e**: 1.76 (3H, d, J = 2.7 Hz, CH_3), 2.16 (3H, s, CH_3), 2.68 (1H, br s, OH), 5.38 (1H, d, J = 6.3 Hz, CH), 5.77-5.80 (1H, m, =CH), 7.28 (2H, d, J = 8.4 Hz, ArH), 7.50 (2H, d, J = 8.4 Hz, ArH); (1S, 3R)-**6e** and (1R, 3S)-**6e**: 1.79 (3H, d, J = 2.7 Hz, CH_3), 2.25 (3H, s, CH_3), 2.68 (1H, br s, OH), 5.38 (1H, d, J = 6.3 Hz, CH), 5.77-5.80 (1H, m, =CH), 7.28 (2H, d, J = 8.4 Hz, ArH), 7.50 (2H, d, J = 8.4 Hz, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.20, 13.25, 26.69, 26.75, 71.17, 71.25, 98.52, 98.62, 106.81, 106.94, 121.81 (2C), 127.48, 127.52, 131.57, 131.60, 141.28 (2C), 198.84 (2C), 211.60, 211.71; MS (EI) *m/e* 283 (M^++3, 3.30), 281 (M^++1, 2.93), 193 (M^+-87, 19.65), 185 (M^+-95, 10.97), 183 (M^+-97, 10.02), 149 (M^+-131, 16.99), 84 (M^+-196, 29.52), 43 (M^+-237, 100); HRMS (EI) calcd. for $C_{13}H_{13}O_2BrNa^{+1}$: 302.9991, Found: 303.0003.

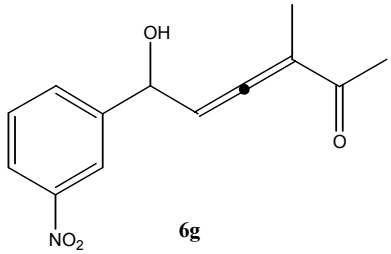




6f

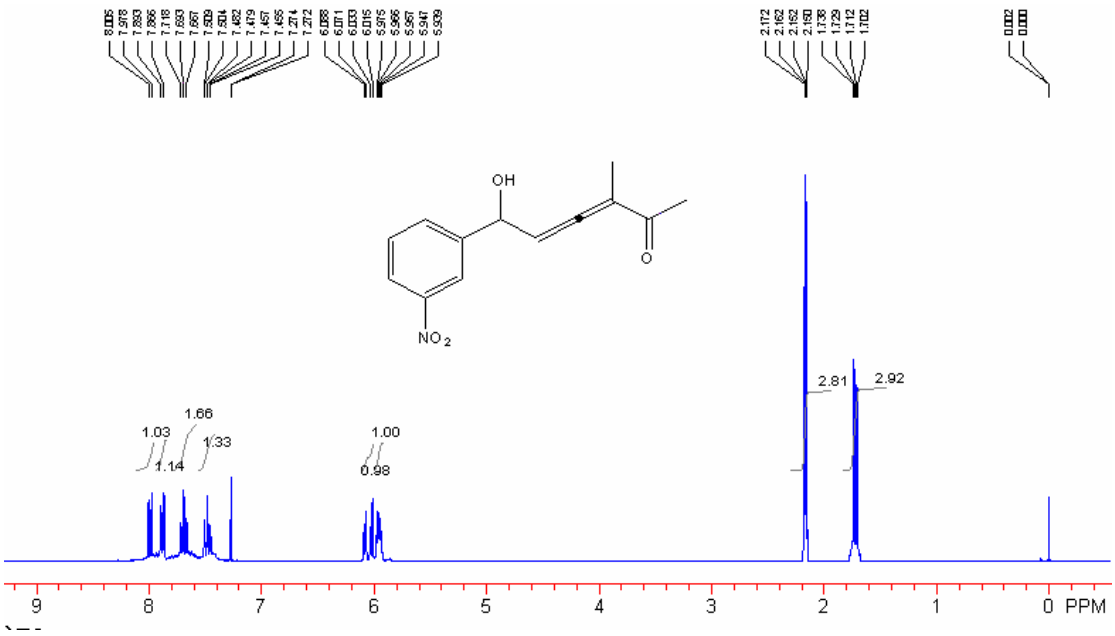
6-Hydroxy-3-methyl-6-(4-nitrophenyl)hexa-3,4-dien-2-one 6f: mp. 118-121 ^{o}C; IR (CH_2Cl_2) ν 3322, 1946, 1655, 1597, 1514, 1344, 1268, 1058 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**6f** and (1S, 3S)-**6f**: 1.79 (3H, d, *J* = 1.2 Hz, CH_3), 2.19 (3H, s, CH_3), 2.67 (1H, br s, OH), 5.55 (1H, d, *J* = 6.6 Hz, CH), 5.80-5.84 (1H, m, =CH), 7.61 (2H, d, *J* = 8.1 Hz, ArH), 8.25 (2H, d, *J* = 8.1 Hz, ArH); (1S, 3R)-**6f** and (1R, 3S)-**6f**: 1.80 (3H, d, *J* = 0.9 Hz, CH_3), 2.26 (3H, s, CH_3), 2.67 (1H, br s, OH), 5.55 (1H, d, *J* = 6.6 Hz, CH), 5.80-5.84 (1H, m, =CH), 7.61 (2H, d, *J* = 8.1 Hz, ArH), 8.25 (2H, d, *J* = 8.1 Hz, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.25, 13.28, 26.77, 26.83, 70.97, 71.02, 98.11, 98.21, 107.22, 107.27, 123.79, 123.81, 126.62, 126.67, 147.41 (2C), 149.30, 149.36, 198.44, 198.51, 211.65, 211.83; MS (EI) *m/e* 247 (M^+, 2.55), 229 (M^+-18, 3.70), 187 (M^+-60, 31.18), 176 (M^+-81□43.53), 152 (M^+-95, 11.19), 43 (M^+-204, 100); HRMS (EI) calcd. for $C_{13}H_{13}O_4N$: 247.0845, Found: 247.0828.

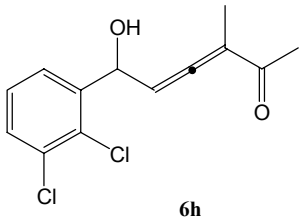




6g

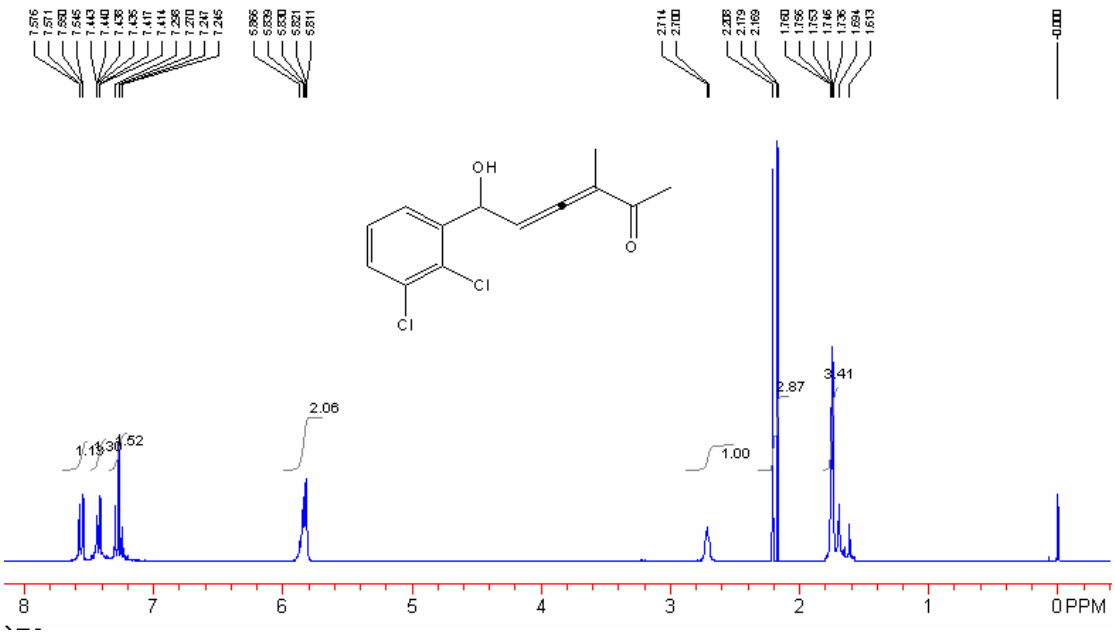
6-Hydroxy-3-methyl-6-(3-nitrophenyl)hexa-3,4-dien-2-one **6g**: a pale yellow oil; IR (CH_2Cl_2) ν 3419, 1951, 1678, 1609, 1526, 1350, 1263, 1099 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**6g** and (1S, 3S)-**6g**: 1.70 (3H, d, *J* = 2.4 Hz, CH_3), 2.16 (3H, s, CH_3), 3.19 (1H, br s, OH), 5.95-5.97 (1H, m, =CH), 6.08 (1H, *J* = 5.4 Hz, CH), 7.46-7.51 (1H, m, ArH), 7.67-7.72 (1H, m, ArH), 7.88 (1H, d, *J* = 8.1 Hz, ArH), 7.99 (1H, d, *J* = 8.1 Hz, ArH); (1S, 3R)-**6g** and (1R, 3S)-**6g**: 1.73 (3H, d, *J* = 2.4 Hz, CH_3), 2.17 (3H, s, CH_3), 3.19 (1H, br s, OH), 5.95-5.97 (1H, m, =CH), 6.03 (1H, *J* = 5.4 Hz, CH), 7.46-7.51 (1H, m, ArH), 7.67-7.72 (1H, m, ArH), 7.88 (1H, d, *J* = 8.1 Hz, ArH), 7.99 (1H, d, *J* = 8.1 Hz, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.99, 13.15, 26.61, 26.64, 67.05, 67.09, 97.84, 97.88, 107.38 (2C), 124.49 (2C), 128.12, 128.14, 128.66 (2C), 133.74, 133.78, 137.71, 137.76, 147.21 (2C), 199.06, 199.08, 211.98, 211.10; MS (EI) *m/e* 247 (M^+, 0.28), 229 (M^+-18, 3.40), 176 (M^+-71, 15.74), 130 (M^+-117, 27.30), 104 (M^+-143, 26.30), 43 (M^+-204, 100); HRMS (EI) calcd. for $C_{13}H_{13}NO_4$: 247.0845, Found: 247.0849.

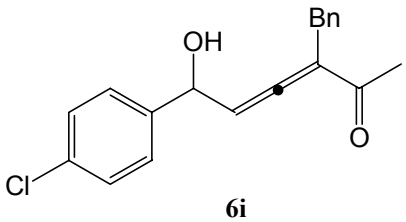




6h

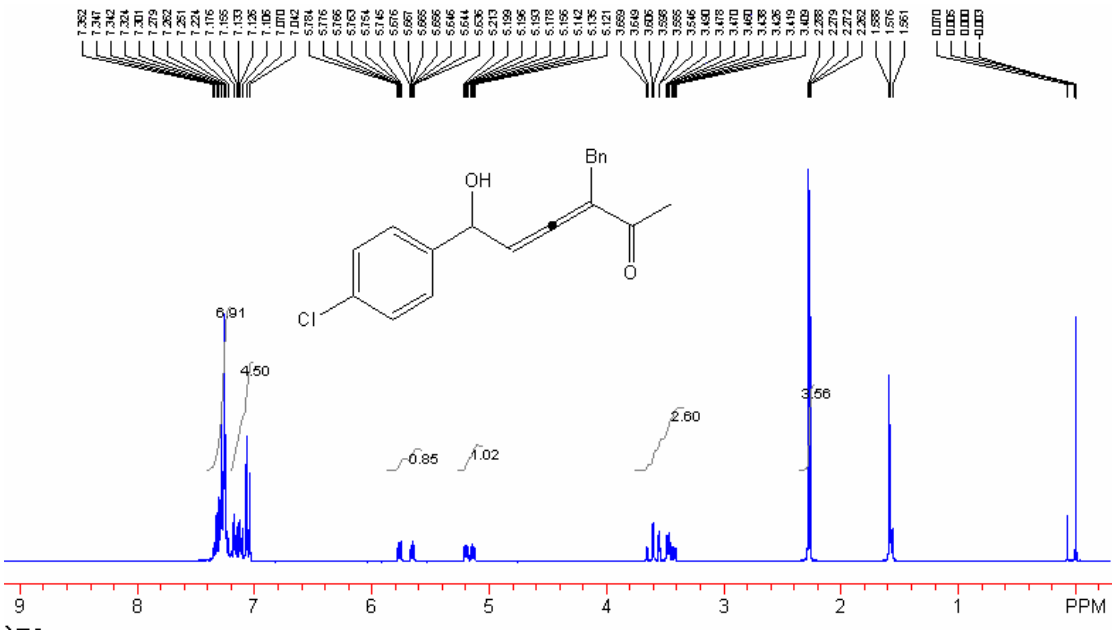
6-(2,3-Dichlorophenyl)-6-hydroxy-3-methylhexa-3,4-dien-2-one 6h: mp. 88-92 ^{o}C; IR (CH_2Cl_2) ν 3424, 1951, 1679, 1450, 1420, 1359, 1262, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**6h** and (1S, 3S)-**6h**: 1.74 (3H, d, *J* = 2.4 Hz, CH_3), 2.17 (3H, s, CH_3), 2.57-2.65 (1H, br s, OH), 5.82-5.86 (2H, m, CH, =CH), 7.25-7.30 (1H, m, ArH), 7.42-7.44 (1H, m, ArH), 7.55-7.58 (1H, m, ArH); (1S, 3R)-**6h** and (1R, 3S)-**6h**: 1.76 (3H, d, *J* = 2.4 Hz, CH_3), 2.21 (3H, s, CH_3), 2.57-2.65 (1H, br s, OH), 5.82-5.86 (2H, m, CH, =CH), 7.25-7.30 (1H, m, ArH), 7.42-7.44 (1H, m, ArH), 7.55-7.58 (1H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.03, 13.25, 26.77, 26.79, 68.79, 68.82, 97.07, 97.14, 107.31 (2C), 124.99 (2C), 125.17 (2C), 129.69, 129.73, 129.91 (2C), 133.03, 133.05, 141.98 (2C), 198.85 (2C), 211.99, 212.16; MS (EI) *m/e* 253 (M^+-17, 1.12), 210 (M^+-60, 3.51), 175 (M^+-95, 26.56), 96 (M^+-174, 47.01), 43 (M^+-227, 100); HRMS (MALDI) calcd. for $C_{13}H_{13}O_2Cl_2^{+1}$: 271.0287, Found: 271.0275.

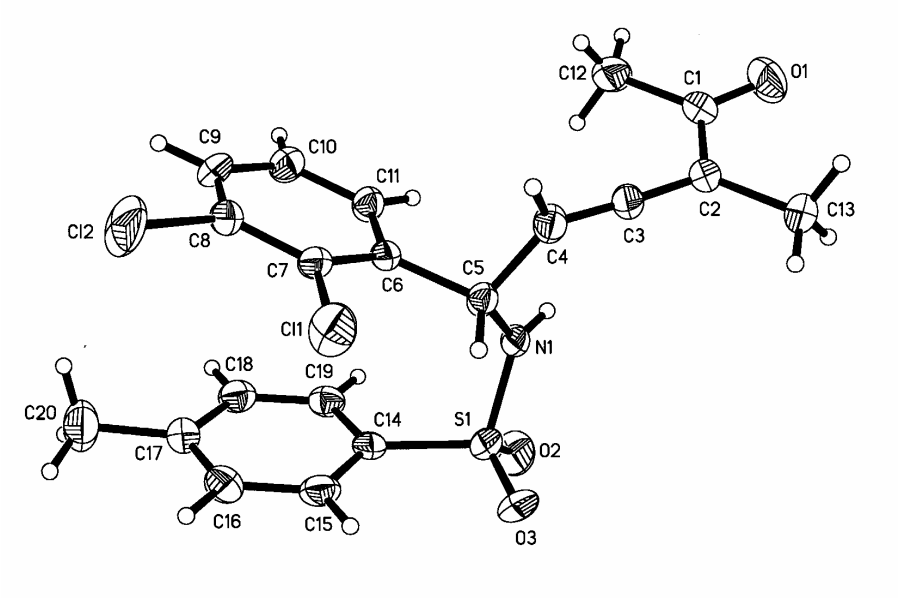




6i

3-Benzyl-6-(4-chlorophenyl)-6-hydroxyhexa-3,4-dien-2-one 6i: mp. 75-79 ^{o}C; IR (CH_2Cl_2) ν 3427, 1947, 1676, 1493, 1453, 1359, 1244, 1090 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1R, 3R)-**6i** and (1S, 3S)-**6i**: 2.23 (3H, s, CH_3), 2.47 (1H, br s, OH), 3.39-3.47 (1H, dm, *J* = 15.3 Hz, CH_2), 3.57 (1H, dm, *J* = 15.3 Hz, CH_2), 5.15 (1H, dd, *J* = 7.2, 7.2 Hz, CH), 5.73-5.75 (1H, m, =CH), 7.02-7.33 (9H, m, ArH); (1S, 3R)-**6i** and (1R, 3S)-**6i**: 2.26 (3H, s, CH_3), 2.47 (1H, br s, OH), 3.39-3.47 (1H, dm, *J* = 15.3 Hz, CH_2), 3.57 (1H, dm, *J* = 15.3 Hz, CH_2), 5.15 (1H, dd, *J* = 7.2, 7.2 Hz, CH), 5.66-5.68 (1H, m, =CH), 7.00-7.32 (9H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 27.11 (2C), 33.04, 33.16, 70.92, 71.05, 100.56, 100.78, 112.23, 112.78, 126.31, 126.36, 127.04, 127.33, 128.29, 128.34, 128.47, 128.58, 128.94, 129.10, 133.43, 133.67, 138.81, 139.03, 140.05, 140.27, 197.66, 197.70, 211.12, 211.30; MS (EI) *m/e* 312 (M^+, 0.72), 295 (M^+-17, 2.43), 251 (M^+-61, 17.72), 217 (M^+-95, 10.10), 172 (M^+-140, 14.14), 77 (M^+-235, 29.70), 43 (M^+-269, 100); HRMS (EI) calcd. for $C_{19}H_{17}O_2Cl$: 312.0917, Found: 312.0907.


OH
Bn
O
Cl
6.91
4.50
0.85
1.02
2.60
3.56
9
8
7
6
5
4
3
2
1
PPM



The crystal data of (1R, 3R)-**3k** and (1S, 3S)-**3k** has been deposited in CCDC with number 266290. Empirical Formula: $C_{20}H_{19}NO_3Cl_2S$; Formula Weight: 424.32; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.510 x 0.495 x 0.107 mm; Crystal System: Monoclinic; Lattice Type: Primitive; Lattice Parameters: a = 8.7617(12)Å, b = 12.4255(16)Å, c = 37.845(5)Å, $\alpha = 90^o$, $\beta = 94.123(3)^o$, $\gamma = 90^o$, V = 4109.5(9)Å^3; Space group: P2(1)/c; Z = 8; D_{calc} = 1.372 g/cm^3; F_{000} = 1760; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0653, 0.1469.

Table 1. Crystal data and structure refinement for cd2509.

Identification code	cd2509
Empirical formula	C20 H19 N O3 Cl2 S
Formula weight	424.32
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 8.7617(12) A alpha = 90 deg. b = 12.4255(16) A beta = 94.123(3) deg. c = 37.845(5) A gamma = 90 deg.
Volume	4109.5(9) A^3
Z, Calculated density	8, 1.372 Mg/m^3
Absorption coefficient	0.437 mm^-1
F(000)	1760
Crystal size	0.510 x 0.495 x 0.107 mm
Theta range for data collection	1.08 to 25.50 deg.
Limiting indices	-10<=h<=10, -14<=k<=15, -45<=l<=41
Reflections collected / unique	21081 / 7614 [R(int) = 0.0938]
Completeness to theta = 25.50	99.6 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.64261
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7614 / 0 / 493
Goodness-of-fit on F^2	0.920
Final R indices [I>2sigma(I)]	R1 = 0.0653, wR2 = 0.1469
R indices (all data)	R1 = 0.1297, wR2 = 0.1770
Largest diff. peak and hole	0.335 and -0.335 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd2509.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	30(2)	3163(1)	3527(1)	56(1)
S(2)	4396(2)	3140(1)	1431(1)	52(1)
Cl(1)	3291(2)	5028(1)	4357(1)	73(1)
Cl(2)	2086(3)	7144(1)	4682(1)	109(1)
Cl(3)	6996(2)	5017(1)	583(1)	78(1)
Cl(4)	5567(3)	7172(1)	278(1)	111(1)
N(1)	1131(4)	4033(3)	3352(1)	44(1)
N(2)	5633(4)	4013(3)	1604(1)	43(1)
O(1)	4045(5)	5194(3)	2150(1)	88(1)
O(2)	-1075(5)	2874(3)	3251(1)	82(1)
O(3)	972(5)	2355(2)	3700(1)	79(1)
O(4)	9210(5)	5212(3)	2802(1)	89(1)
O(5)	3493(4)	2823(3)	1713(1)	73(1)
O(6)	5214(4)	2350(2)	1243(1)	74(1)
C(1)	3666(6)	5302(4)	2449(1)	60(2)
C(2)	4175(6)	4527(4)	2724(1)	51(1)
C(3)	3872(5)	4707(3)	3053(1)	48(1)
C(4)	3651(5)	4922(4)	3379(1)	49(1)
C(5)	2294(5)	4602(3)	3579(1)	40(1)
C(6)	1675(5)	5622(3)	3747(1)	39(1)
C(7)	2102(5)	5870(3)	4096(1)	44(1)
C(8)	1559(6)	6833(4)	4240(1)	56(1)
C(9)	637(6)	7520(4)	4041(1)	57(1)
C(10)	255(6)	7271(4)	3692(1)	54(1)
C(11)	786(5)	6346(3)	3549(1)	45(1)
C(12)	2698(7)	6249(4)	2540(2)	78(2)
C(13)	5107(6)	3565(4)	2621(1)	66(2)
C(14)	-862(5)	3871(3)	3856(1)	44(1)
C(15)	-401(6)	3693(4)	4209(1)	55(1)
C(16)	-1015(6)	4326(4)	4466(1)	58(1)
C(17)	-2066(6)	5119(4)	4378(1)	54(1)
C(18)	-2542(6)	5259(4)	4024(1)	53(1)
C(19)	-1947(6)	4636(4)	3765(1)	48(1)
C(20)	-2660(7)	5841(5)	4662(1)	83(2)
C(21)	8687(7)	5339(4)	2498(2)	67(2)
C(22)	9025(6)	4540(4)	2232(1)	55(1)
C(23)	8521(6)	4713(4)	1899(1)	50(1)
C(24)	8106(6)	4895(4)	1571(1)	50(1)
C(25)	6633(5)	4575(3)	1370(1)	41(1)
C(26)	5912(5)	5612(3)	1208(1)	40(1)
C(27)	6051(5)	5876(3)	856(1)	45(1)
C(28)	5426(6)	6835(4)	721(1)	58(1)
C(29)	4668(6)	7530(4)	928(1)	57(1)
C(30)	4557(6)	7277(4)	1283(1)	56(1)
C(31)	5196(5)	6339(3)	1417(1)	45(1)
C(32)	7711(7)	6294(4)	2399(2)	87(2)
C(33)	9967(7)	3573(4)	2349(1)	68(2)
C(34)	3245(5)	3856(3)	1114(1)	41(1)
C(35)	3438(6)	3710(4)	758(1)	55(1)
C(36)	2656(7)	4387(4)	513(1)	61(2)
C(37)	1719(6)	5199(4)	612(1)	53(1)
C(38)	1528(6)	5312(4)	971(1)	49(1)
C(39)	2284(5)	4660(4)	1223(1)	48(1)
C(40)	988(7)	5980(4)	345(1)	78(2)

Table 3. Bond lengths [A] and angles [deg] for cd2509.

S(1)-O(2)	1.419(4)
S(1)-O(3)	1.428(4)
S(1)-N(1)	1.623(4)
S(1)-C(14)	1.754(5)
S(2)-O(5)	1.429(3)
S(2)-O(6)	1.433(4)
S(2)-N(2)	1.638(4)
S(2)-C(34)	1.752(5)
Cl(1)-C(7)	1.734(5)
Cl(2)-C(8)	1.746(5)
Cl(3)-C(27)	1.737(5)
Cl(4)-C(28)	1.740(5)
N(1)-C(5)	1.468(5)
N(1)-H(1)	0.8600
N(2)-C(25)	1.464(5)
N(2)-H(2)	0.8600
O(1)-C(1)	1.210(5)
O(4)-C(21)	1.218(6)
C(1)-C(2)	1.463(7)
C(1)-C(12)	1.504(7)
C(2)-C(3)	1.313(6)
C(2)-C(13)	1.514(6)
C(3)-C(4)	1.289(6)
C(4)-C(5)	1.510(6)
C(4)-H(4)	0.9300
C(5)-C(6)	1.533(6)
C(5)-H(5)	0.9800
C(6)-C(11)	1.375(6)
C(6)-C(7)	1.383(6)
C(7)-C(8)	1.411(6)
C(8)-C(9)	1.364(7)
C(9)-C(10)	1.376(6)
C(9)-H(9)	0.9300
C(10)-C(11)	1.366(6)
C(10)-H(10)	0.9300
C(11)-H(11)	0.9300
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-C(19)	1.372(6)
C(14)-C(15)	1.383(6)
C(15)-C(16)	1.389(6)
C(15)-H(15)	0.9300
C(16)-C(17)	1.373(7)
C(16)-H(16)	0.9300
C(17)-C(18)	1.384(6)
C(17)-C(20)	1.521(6)
C(18)-C(19)	1.382(6)
C(18)-H(18)	0.9300
C(19)-H(19)	0.9300
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(21)-C(22)	1.461(7)
C(21)-C(32)	1.494(7)
C(22)-C(23)	1.320(6)
C(22)-C(33)	1.506(6)
C(23)-C(24)	1.290(6)
C(24)-C(25)	1.503(6)
C(24)-H(24)	0.9300
C(25)-C(26)	1.543(6)
C(25)-H(25)	0.9800
C(26)-C(31)	1.382(6)
C(26)-C(27)	1.384(5)
C(27)-C(28)	1.392(6)

C(28)-C(29)	1.370(6)
C(29)-C(30)	1.389(6)
C(29)-H(29)	0.9300
C(30)-C(31)	1.375(6)
C(30)-H(30)	0.9300
C(31)-H(31)	0.9300
C(32)-H(32A)	0.9600
C(32)-H(32B)	0.9600
C(32)-H(32C)	0.9600
C(33)-H(33A)	0.9600
C(33)-H(33B)	0.9600
C(33)-H(33C)	0.9600
C(34)-C(35)	1.382(6)
C(34)-C(39)	1.388(6)
C(35)-C(36)	1.395(7)
C(35)-H(35)	0.9300
C(36)-C(37)	1.370(7)
C(36)-H(36)	0.9300
C(37)-C(38)	1.388(6)
C(37)-C(40)	1.509(6)
C(38)-C(39)	1.382(6)
C(38)-H(38)	0.9300
C(39)-H(39)	0.9300
C(40)-H(40A)	0.9600
C(40)-H(40B)	0.9600
C(40)-H(40C)	0.9600

O(2)-S(1)-O(3)	120.0(2)
O(2)-S(1)-N(1)	105.1(2)
O(3)-S(1)-N(1)	108.3(2)
O(2)-S(1)-C(14)	109.6(2)
O(3)-S(1)-C(14)	107.4(2)
N(1)-S(1)-C(14)	105.39(19)
O(5)-S(2)-O(6)	120.3(2)
O(5)-S(2)-N(2)	105.6(2)
O(6)-S(2)-N(2)	108.1(2)
O(5)-S(2)-C(34)	109.2(2)
O(6)-S(2)-C(34)	107.1(2)
N(2)-S(2)-C(34)	105.56(19)
C(5)-N(1)-S(1)	119.2(3)
C(5)-N(1)-H(1)	120.4
S(1)-N(1)-H(1)	120.4
C(25)-N(2)-S(2)	118.8(3)
C(25)-N(2)-H(2)	120.6
S(2)-N(2)-H(2)	120.6
O(1)-C(1)-C(2)	120.0(5)
O(1)-C(1)-C(12)	119.9(5)
C(2)-C(1)-C(12)	120.1(5)
C(3)-C(2)-C(1)	119.4(4)
C(3)-C(2)-C(13)	121.9(5)
C(1)-C(2)-C(13)	118.7(4)
C(4)-C(3)-C(2)	176.3(5)
C(3)-C(4)-C(5)	127.1(4)
C(3)-C(4)-H(4)	116.4
C(5)-C(4)-H(4)	116.4
N(1)-C(5)-C(4)	111.7(3)
N(1)-C(5)-C(6)	112.9(4)
C(4)-C(5)-C(6)	107.7(3)
N(1)-C(5)-H(5)	108.1
C(4)-C(5)-H(5)	108.1
C(6)-C(5)-H(5)	108.1
C(11)-C(6)-C(7)	118.6(4)
C(11)-C(6)-C(5)	121.3(4)
C(7)-C(6)-C(5)	120.0(4)
C(6)-C(7)-C(8)	118.8(4)
C(6)-C(7)-Cl(1)	121.3(3)
C(8)-C(7)-Cl(1)	119.9(4)
C(9)-C(8)-C(7)	121.4(4)
C(9)-C(8)-Cl(2)	119.6(4)
C(7)-C(8)-Cl(2)	118.9(4)
C(8)-C(9)-C(10)	118.8(4)
C(8)-C(9)-H(9)	120.6

C(10)-C(9)-H(9)	120.6
C(11)-C(10)-C(9)	120.3(5)
C(11)-C(10)-H(10)	119.9
C(9)-C(10)-H(10)	119.9
C(10)-C(11)-C(6)	122.0(4)
C(10)-C(11)-H(11)	119.0
C(6)-C(11)-H(11)	119.0
C(1)-C(12)-H(12A)	109.5
C(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(2)-C(13)-H(13A)	109.5
C(2)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(2)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(19)-C(14)-C(15)	120.2(4)
C(19)-C(14)-S(1)	120.3(4)
C(15)-C(14)-S(1)	119.4(4)
C(14)-C(15)-C(16)	118.9(5)
C(14)-C(15)-H(15)	120.5
C(16)-C(15)-H(15)	120.5
C(17)-C(16)-C(15)	121.6(5)
C(17)-C(16)-H(16)	119.2
C(15)-C(16)-H(16)	119.2
C(16)-C(17)-C(18)	118.3(4)
C(16)-C(17)-C(20)	120.7(5)
C(18)-C(17)-C(20)	121.0(5)
C(19)-C(18)-C(17)	121.0(5)
C(19)-C(18)-H(18)	119.5
C(17)-C(18)-H(18)	119.5
C(14)-C(19)-C(18)	119.9(4)
C(14)-C(19)-H(19)	120.1
C(18)-C(19)-H(19)	120.1
C(17)-C(20)-H(20A)	109.5
C(17)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(17)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(4)-C(21)-C(22)	118.9(5)
O(4)-C(21)-C(32)	120.6(5)
C(22)-C(21)-C(32)	120.5(5)
C(23)-C(22)-C(21)	118.4(5)
C(23)-C(22)-C(33)	123.3(5)
C(21)-C(22)-C(33)	118.3(5)
C(24)-C(23)-C(22)	176.8(5)
C(23)-C(24)-C(25)	127.7(4)
C(23)-C(24)-H(24)	116.1
C(25)-C(24)-H(24)	116.1
N(2)-C(25)-C(24)	110.6(3)
N(2)-C(25)-C(26)	113.1(4)
C(24)-C(25)-C(26)	106.9(3)
N(2)-C(25)-H(25)	108.7
C(24)-C(25)-H(25)	108.7
C(26)-C(25)-H(25)	108.7
C(31)-C(26)-C(27)	118.1(4)
C(31)-C(26)-C(25)	120.5(4)
C(27)-C(26)-C(25)	121.3(4)
C(26)-C(27)-C(28)	119.8(4)
C(26)-C(27)-Cl(3)	120.3(3)
C(28)-C(27)-Cl(3)	119.9(3)
C(29)-C(28)-C(27)	121.5(4)
C(29)-C(28)-Cl(4)	118.1(4)
C(27)-C(28)-Cl(4)	120.4(4)
C(28)-C(29)-C(30)	118.8(5)
C(28)-C(29)-H(29)	120.6
C(30)-C(29)-H(29)	120.6
C(31)-C(30)-C(29)	119.6(5)

C(31)-C(30)-H(30)	120.2
C(29)-C(30)-H(30)	120.2
C(30)-C(31)-C(26)	122.2(4)
C(30)-C(31)-H(31)	118.9
C(26)-C(31)-H(31)	118.9
C(21)-C(32)-H(32A)	109.5
C(21)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(21)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(22)-C(33)-H(33A)	109.5
C(22)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
C(22)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
C(35)-C(34)-C(39)	120.2(4)
C(35)-C(34)-S(2)	119.6(4)
C(39)-C(34)-S(2)	119.7(4)
C(34)-C(35)-C(36)	118.7(5)
C(34)-C(35)-H(35)	120.7
C(36)-C(35)-H(35)	120.7
C(37)-C(36)-C(35)	122.6(5)
C(37)-C(36)-H(36)	118.7
C(35)-C(36)-H(36)	118.7
C(36)-C(37)-C(38)	117.2(5)
C(36)-C(37)-C(40)	121.6(5)
C(38)-C(37)-C(40)	121.1(5)
C(39)-C(38)-C(37)	122.0(4)
C(39)-C(38)-H(38)	119.0
C(37)-C(38)-H(38)	119.0
C(38)-C(39)-C(34)	119.2(4)
C(38)-C(39)-H(39)	120.4
C(34)-C(39)-H(39)	120.4
C(37)-C(40)-H(40A)	109.5
C(37)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(37)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd2509.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	71(1)	34(1)	65(1)	-10(1)	25(1)	-9(1)
S(2)	60(1)	34(1)	62(1)	8(1)	-6(1)	-8(1)
Cl(1)	96(1)	75(1)	46(1)	-1(1)	-16(1)	15(1)
Cl(2)	195(2)	81(1)	48(1)	-30(1)	-2(1)	1(1)
Cl(3)	110(1)	75(1)	52(1)	9(1)	32(1)	27(1)
Cl(4)	181(2)	99(1)	55(1)	38(1)	22(1)	33(1)
N(1)	57(3)	45(2)	32(2)	-10(2)	12(2)	-11(2)
N(2)	54(3)	40(2)	35(2)	5(2)	-2(2)	-12(2)
O(1)	116(4)	91(3)	62(2)	17(2)	45(2)	13(3)
O(2)	93(3)	78(3)	77(3)	-41(2)	14(2)	-43(2)
O(3)	108(3)	30(2)	105(3)	13(2)	43(3)	14(2)
O(4)	104(4)	92(3)	67(3)	-15(2)	-25(2)	5(3)
O(5)	73(3)	72(2)	74(2)	38(2)	1(2)	-26(2)
O(6)	89(3)	33(2)	97(3)	-11(2)	-15(2)	10(2)
C(1)	68(4)	51(3)	65(4)	2(3)	28(3)	-8(3)
C(2)	58(3)	41(3)	57(3)	-4(2)	23(3)	-3(3)
C(3)	47(3)	45(3)	53(3)	-9(2)	16(2)	-6(2)
C(4)	45(3)	49(3)	53(3)	-11(2)	8(2)	-3(2)
C(5)	50(3)	37(3)	33(2)	-5(2)	1(2)	2(2)
C(6)	47(3)	36(2)	34(2)	-4(2)	9(2)	-7(2)
C(7)	58(3)	36(3)	37(3)	2(2)	5(2)	-4(2)
C(8)	82(4)	47(3)	39(3)	-10(2)	15(3)	-16(3)
C(9)	73(4)	30(3)	69(4)	-8(3)	16(3)	-3(3)
C(10)	61(4)	43(3)	58(3)	2(3)	7(3)	7(3)
C(11)	57(3)	42(3)	37(3)	-1(2)	3(2)	5(3)
C(12)	86(4)	48(3)	105(5)	17(3)	41(4)	11(3)
C(13)	82(4)	47(3)	73(4)	-7(3)	33(3)	5(3)
C(14)	49(3)	37(3)	46(3)	2(2)	11(2)	-12(2)
C(15)	60(4)	39(3)	67(4)	13(3)	12(3)	5(3)
C(16)	72(4)	60(3)	41(3)	8(3)	3(3)	-1(3)
C(17)	62(4)	47(3)	53(3)	-2(3)	15(3)	2(3)
C(18)	57(3)	46(3)	56(3)	5(3)	5(3)	0(3)
C(19)	54(3)	46(3)	43(3)	8(2)	0(2)	-2(3)
C(20)	97(5)	89(4)	66(4)	-22(3)	19(3)	3(4)
C(21)	69(4)	56(3)	75(4)	-12(3)	-13(3)	-13(3)
C(22)	52(3)	46(3)	65(4)	6(3)	-2(3)	-7(3)
C(23)	47(3)	40(3)	62(3)	10(3)	-2(3)	-10(2)
C(24)	46(3)	41(3)	62(3)	17(3)	6(3)	0(2)
C(25)	55(3)	33(2)	33(2)	4(2)	2(2)	3(2)
C(26)	43(3)	36(2)	40(3)	4(2)	3(2)	-8(2)
C(27)	56(3)	41(3)	37(3)	5(2)	2(2)	1(2)
C(28)	72(4)	55(3)	47(3)	21(3)	7(3)	-4(3)
C(29)	69(4)	33(3)	68(4)	10(3)	3(3)	4(3)
C(30)	64(4)	36(3)	67(3)	1(3)	6(3)	-3(3)
C(31)	60(3)	35(3)	40(3)	2(2)	7(2)	8(2)
C(32)	91(5)	45(3)	120(5)	-25(3)	-36(4)	10(3)
C(33)	90(4)	40(3)	72(4)	7(3)	-18(3)	13(3)
C(34)	49(3)	33(2)	41(3)	0(2)	1(2)	-9(2)
C(35)	65(4)	42(3)	57(3)	-10(3)	5(3)	0(3)
C(36)	88(4)	56(3)	38(3)	-3(3)	6(3)	2(3)
C(37)	63(4)	38(3)	57(3)	8(2)	-2(3)	-7(3)
C(38)	50(3)	40(3)	59(3)	-1(2)	8(3)	2(2)
C(39)	52(3)	49(3)	44(3)	-6(2)	11(2)	-5(3)
C(40)	99(5)	57(3)	74(4)	14(3)	-14(3)	5(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd2509.

	x	y	z	U(eq)
H(1)	1035	4160	3128	53
H(2)	5695	4140	1828	52
H(4)	4411	5319	3504	58
H(5)	2655	4114	3771	48
H(9)	273	8147	4140	68
H(10)	-368	7734	3553	64
H(11)	540	6202	3311	54
H(12A)	3260	6692	2712	117
H(12B)	1779	5996	2636	117
H(12C)	2438	6662	2330	117
H(13A)	6070	3806	2544	99
H(13B)	4558	3181	2432	99
H(13C)	5284	3098	2822	99
H(15)	309	3159	4272	66
H(16)	-706	4210	4703	69
H(18)	-3272	5780	3961	64
H(19)	-2282	4736	3528	57
H(20A)	-2423	5525	4891	125
H(20B)	-3749	5919	4622	125
H(20C)	-2185	6536	4653	125
H(24)	8801	5269	1442	60
H(25)	6867	4088	1178	49
H(29)	4235	8159	833	68
H(30)	4053	7740	1429	67
H(31)	5145	6189	1657	54
H(32A)	7392	6630	2610	131
H(32B)	6827	6066	2254	131
H(32C)	8287	6798	2270	131
H(33A)	9997	3076	2155	102
H(33B)	9516	3228	2543	102
H(33C)	10988	3798	2422	102
H(35)	4076	3170	683	66
H(36)	2776	4283	273	73
H(38)	871	5841	1044	59
H(39)	2150	4759	1462	58
H(40A)	1660	6580	319	116
H(40B)	36	6230	425	116
H(40C)	803	5625	120	116

Table 6. Torsion angles [deg] for cd2509.

O(2)-S(1)-N(1)-C(5)	172.4(3)
O(3)-S(1)-N(1)-C(5)	-58.1(4)
C(14)-S(1)-N(1)-C(5)	56.7(4)
O(5)-S(2)-N(2)-C(25)	-173.9(3)
O(6)-S(2)-N(2)-C(25)	56.1(4)
C(34)-S(2)-N(2)-C(25)	-58.3(4)
O(1)-C(1)-C(2)-C(3)	173.9(5)
C(12)-C(1)-C(2)-C(3)	-4.8(7)
O(1)-C(1)-C(2)-C(13)	-3.2(8)
C(12)-C(1)-C(2)-C(13)	178.2(5)
C(1)-C(2)-C(3)-C(4)	-83(8)
C(13)-C(2)-C(3)-C(4)	94(8)
C(2)-C(3)-C(4)-C(5)	173(8)
S(1)-N(1)-C(5)-C(4)	151.7(3)
S(1)-N(1)-C(5)-C(6)	-86.7(4)
C(3)-C(4)-C(5)-N(1)	-3.2(7)
C(3)-C(4)-C(5)-C(6)	-127.7(5)
N(1)-C(5)-C(6)-C(11)	-45.7(5)
C(4)-C(5)-C(6)-C(11)	78.1(5)
N(1)-C(5)-C(6)-C(7)	139.1(4)
C(4)-C(5)-C(6)-C(7)	-97.1(5)
C(11)-C(6)-C(7)-C(8)	2.5(6)
C(5)-C(6)-C(7)-C(8)	177.8(4)
C(11)-C(6)-C(7)-Cl(1)	-177.1(3)
C(5)-C(6)-C(7)-Cl(1)	-1.8(6)
C(6)-C(7)-C(8)-C(9)	-0.4(7)
Cl(1)-C(7)-C(8)-C(9)	179.2(4)
C(6)-C(7)-C(8)-Cl(2)	179.6(3)
Cl(1)-C(7)-C(8)-Cl(2)	-0.7(6)
C(7)-C(8)-C(9)-C(10)	-1.1(7)
Cl(2)-C(8)-C(9)-C(10)	178.9(4)
C(8)-C(9)-C(10)-C(11)	0.4(7)
C(9)-C(10)-C(11)-C(6)	1.8(7)
C(7)-C(6)-C(11)-C(10)	-3.3(7)
C(5)-C(6)-C(11)-C(10)	-178.5(4)
O(2)-S(1)-C(14)-C(19)	-42.1(4)
O(3)-S(1)-C(14)-C(19)	-174.1(4)
N(1)-S(1)-C(14)-C(19)	70.5(4)
O(2)-S(1)-C(14)-C(15)	141.5(4)
O(3)-S(1)-C(14)-C(15)	9.5(4)
N(1)-S(1)-C(14)-C(15)	-105.8(4)
C(19)-C(14)-C(15)-C(16)	-2.2(7)
S(1)-C(14)-C(15)-C(16)	174.2(4)
C(14)-C(15)-C(16)-C(17)	0.1(7)
C(15)-C(16)-C(17)-C(18)	1.8(8)
C(15)-C(16)-C(17)-C(20)	-176.8(5)
C(16)-C(17)-C(18)-C(19)	-1.6(7)
C(20)-C(17)-C(18)-C(19)	176.9(5)
C(15)-C(14)-C(19)-C(18)	2.3(7)
S(1)-C(14)-C(19)-C(18)	-174.0(4)
C(17)-C(18)-C(19)-C(14)	-0.4(7)
O(4)-C(21)-C(22)-C(23)	-176.4(5)
C(32)-C(21)-C(22)-C(23)	3.8(8)
O(4)-C(21)-C(22)-C(33)	1.9(8)
C(32)-C(21)-C(22)-C(33)	-177.8(5)
C(21)-C(22)-C(23)-C(24)	106(9)
C(33)-C(22)-C(23)-C(24)	-72(9)
C(22)-C(23)-C(24)-C(25)	164(9)
S(2)-N(2)-C(25)-C(24)	-152.6(3)
S(2)-N(2)-C(25)-C(26)	87.5(4)
C(23)-C(24)-C(25)-N(2)	1.1(7)
C(23)-C(24)-C(25)-C(26)	124.7(5)
N(2)-C(25)-C(26)-C(31)	46.2(5)
C(24)-C(25)-C(26)-C(31)	-75.9(5)
N(2)-C(25)-C(26)-C(27)	-138.2(4)
C(24)-C(25)-C(26)-C(27)	99.7(5)
C(31)-C(26)-C(27)-C(28)	-2.3(7)
C(25)-C(26)-C(27)-C(28)	-178.0(4)

C(31)-C(26)-C(27)-Cl(3)	177.8(4)
C(25)-C(26)-C(27)-Cl(3)	2.1(6)
C(26)-C(27)-C(28)-C(29)	-0.1(7)
Cl(3)-C(27)-C(28)-C(29)	179.7(4)
C(26)-C(27)-C(28)-Cl(4)	-179.1(4)
Cl(3)-C(27)-C(28)-Cl(4)	0.7(6)
C(27)-C(28)-C(29)-C(30)	1.5(8)
Cl(4)-C(28)-C(29)-C(30)	-179.4(4)
C(28)-C(29)-C(30)-C(31)	-0.5(7)
C(29)-C(30)-C(31)-C(26)	-2.1(7)
C(27)-C(26)-C(31)-C(30)	3.5(7)
C(25)-C(26)-C(31)-C(30)	179.2(4)
O(5)-S(2)-C(34)-C(35)	-141.6(4)
O(6)-S(2)-C(34)-C(35)	-9.8(4)
N(2)-S(2)-C(34)-C(35)	105.3(4)
O(5)-S(2)-C(34)-C(39)	46.4(4)
O(6)-S(2)-C(34)-C(39)	178.2(3)
N(2)-S(2)-C(34)-C(39)	-66.8(4)
C(39)-C(34)-C(35)-C(36)	0.3(7)
S(2)-C(34)-C(35)-C(36)	-171.7(4)
C(34)-C(35)-C(36)-C(37)	0.8(8)
C(35)-C(36)-C(37)-C(38)	-1.9(8)
C(35)-C(36)-C(37)-C(40)	174.9(5)
C(36)-C(37)-C(38)-C(39)	2.1(7)
C(40)-C(37)-C(38)-C(39)	-174.7(5)
C(37)-C(38)-C(39)-C(34)	-1.1(7)
C(35)-C(34)-C(39)-C(38)	-0.2(7)
S(2)-C(34)-C(39)-C(38)	171.9(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd2509 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)