Supporting Information

Abnormal aza-Baylis-Hillman reaction of *N*-tosylated imines with ethyl 2,3-butadienoate and penta-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. All of the solid compounds reported in this paper gave satisfactory CHN microanalyses 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 200-300 mesh silica gel at increased pressure. The starting materials such as *N*-tosylated imines,[1] ethyl 2,3-butadienoate,[2] and penta-3,4-dien-2-one[3] were prepared according to the literatures.

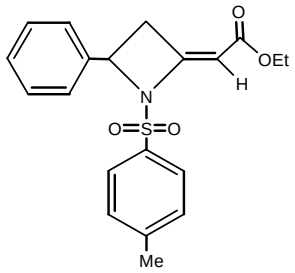
1) B. E. Love, P. S. Raje, T. C. Williams, *Synlett* **1994**, 493.

2) (a) J. C. Anderson, R. j. Cubbon, J. D. Harling, *Tetrahedron: Asymmetry* **2001**, *12*, 923.
(b) H. Jansch, S. Kannenberg, G. Boche, *Eur. J. Org. Chem.* **2001**, 2923.

3) G. Buono, *Synthesis* **1981**, 272.

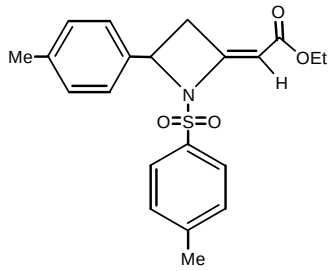
The aza-Baylis-Hillman reaction of *N*-tosylated imines with ethyl 2,3-butadienoate catalyzed by DABCO.

Typical reaction procedure of *N*-tosylated imines with ethyl 2,3-butadienoate at room temperature. To a Schlenk tube with *N*-(*p*-methylbenzenesulfonyl)benzaldimine (65 mg, 0.25 mmol) and DABCO (6 mg, 0.05 mmol) and MS 4A (100 mg) in benzene (0.5 mL) was added ethyl 2,3-butadienoate (34 mg, 0.30 mmol) and the reaction mixture was stirred for 1 h at room temperature (20 ^{o}C). The reaction mixture was washed with water (3 x 10 mL) and extracted with dichloromethane (2 x 10 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= 1/6~1/4) to give adduct **1a** (75 mg, yield 82%) as a colorless solid.



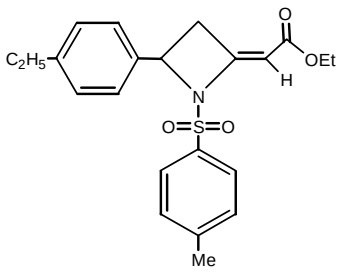
[4-Phenyl-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]-acetic acid ethyl ester 1a.

a colorless solid: mp. 100-103 ^{o}C; IR (CH_2Cl_2) ν 1703 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.27 (3H, t, *J* = 7.2 Hz, CH_3), 2.43 (3H, s, CH_3), 3.10 (1H, ddd, *J* = 16.8, 4.2, 2.4 Hz, CH_2), 3.49 (1H, ddd, *J* = 16.8, 6.9, 1.8 Hz, CH_2), 4.13 (2H, q, *J* = 7.2 Hz, CH_2), 5.19 (1H, dd, *J* = 6.9, 4.2 Hz, CH), 5.84-5.85 (1H, m, =CH), 7.26 (2H, d, *J* = 8.4 Hz, ArH), 7.34 (5H, s, ArH), 7.56 (2H, d, *J* = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.28, 21.55, 37.40, 59.69, 66.04, 94.69, 126.65, 127.30, 128.63, 128.78, 129.75, 134.11, 137.16, 144.81, 158.19, 167.22; MS (EI) *m/z* 371 (M^+, 2.44), 232 (M^+-139, 64.22), 216 (M^+-155, 44.63), 155 (M^+-216, 51.98), 91 (M^+-280, 100); Anal. Calcd. for $C_{20}H_{21}NO_4S$ requires C, 64.68; H, 5.70; N, 3.77%. Found: C, 64.66; H, 5.71; N, 3.56%.



[1-(Toluene-4-sulfonyl)-4-p-tolyl-azetidin-2-ylidene]acetic acid ethyl ester 1b.

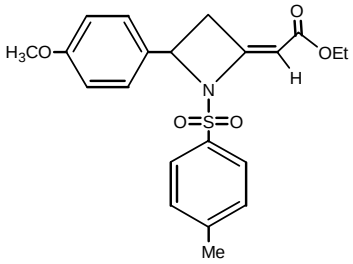
a colorless solid: mp. 135-137 ^{o}C; IR (CH_2Cl_2) ν 1708 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.26 (3H, t, *J* = 7.2 Hz, CH_3), 2.35 (3H, s, CH_3), 2.44 (3H, s, CH_3), 3.09 (1H, ddd, *J* = 17.1, 4.5, 2.1 Hz, CH_2), 3.47 (1H, ddd, *J* = 17.1, 6.9, 2.4 Hz, CH_2), 4.13 (2H, q, *J* = 7.2 Hz, CH_2), 5.15 (1H, dd, *J* = 6.9, 4.5 Hz, CH), 5.83-5.84 (1H, m, =CH), 7.13 (2H, d, *J* = 8.1 Hz, ArH), 7.21-7.28 (4H, m, ArH), 7.57 (2H, d, *J* = 8.1 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.19, 21.03, 21.43, 37.31, 59.54, 65.91, 94.42, 126.54, 127.19, 129.17, 129.62, 134.06, 134.10, 138.57, 144.66, 158.25, 167.11; MS (EI) *m/z* 385 (M^+, 0.63), 340 (M^+-45, 8.31), 230 (M^+-155, 63.12), 157 (M^+-228, 89.01), 155 (M^+-230, 25.70), 91 (M^+-294, 100); Anal. Calcd. for $C_{21}H_{23}NO_4S$ requires C, 65.44; H, 6.02; N, 3.64%. Found: C, 65.37; H, 6.25; N, 3.48%.



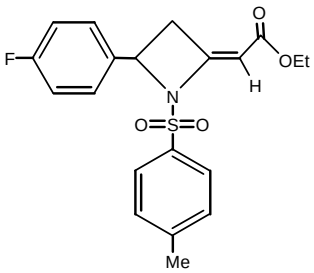
[4-(4-Ethylphenyl)-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]acetic acid ethyl ester 1c.

a colorless solid. Mp. 106-109 ^{o}C; IR (CH_2Cl_2) ν 1707 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.17-1.25 (6H, m, $2CH_3$), 2.38 (3H, s, CH_3), 2.60 (2H, q, *J* = 7.5 Hz, CH_2), 3.07 (1H, ddd, *J* = 16.5, 4.5, 1.8 Hz, CH_2), 3.44 (1H, ddd, *J* = 16.5, 6.9, 1.8 Hz, CH_2), 4.09 (2H, q, *J* = 7.5 Hz, CH_2), 5.12 (1H, dd, *J* = 6.9, 4.5 Hz, CH), 5.79-5.81 (1H, m, =CH), 7.10 (2H, d, *J* = 8.1 Hz, ArH), 7.19-7.21 (4H, m, ArH), 7.51 (2H, d, *J* = 8.1 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75

MHz, TMS) δ 14.31, 15.52, 21.56, 28.54, 37.36, 59.66, 66.07, 94.48, 126.78, 127.31, 128.11, 129.69, 134.29, 134.31, 144.66, 145.06, 158.35, 167.31; MS (EI) *m/z* 399 (M^+, 0.70), 244 (M^+-155, 74.77), 171 (M^+-228, 95.03), 155 (M^+-244, 23.38), 91 (M^+-308, 100); Anal. Calcd. for $C_{22}H_{25}NO_4S$ requires C, 66.15; H, 6.31; N, 3.51%. Found: C, 66.37; H, 6.49; N, 3.33%.

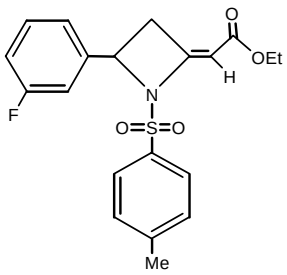


[4-(4-Methoxyphenyl)-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]acetic acid ethyl ester 1d. a colorless solid: mp. 111-115 ^oC; IR (CH_2Cl_2) ν 1706 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.26 (3H, t, *J* = 7.2 Hz, CH_3), 2.43 (3H, s, CH_3), 3.10 (1H, ddd, *J* = 17.1, 4.8, 2.1 Hz, CH_2), 3.48 (1H, ddd, *J* = 17.1, 6.9, 1.8 Hz, CH_2), 3.81 (3H, s, OCH_3), 4.13 (2H, q, *J* = 7.2 Hz, CH_2), 5.16 (1H, dd, *J* = 6.9, 4.8 Hz, CH), 5.81-5.83 (1H, m, =CH), 6.84 (2H, d, *J* = 6.6 Hz, ArH), 7.23-7.26 (4H, m, ArH), 7.55 (2H, d, *J* = 6.6 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.30, 21.55, 37.37, 55.25, 59.66, 65.96, 94.36, 113.95, 127.26, 128.21, 129.09, 129.70, 134.35, 144.68, 158.25, 159.94, 167.31; MS (EI) *m/z* 401 (M^+, 0.65), 246 (M^+-155, 100), 173 (M^+-228, 95.87), 134 (M^+-267, 95.04), 91 (M^+-310, 86.40); Anal. Calcd. for $C_{21}H_{23}NO_5S$ requires C, 62.83; H, 5.78; N, 3.49%. Found: C, 62.69; H, 5.72; N, 3.34%.



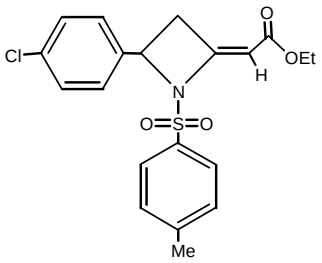
[4-(4-Fluorophenyl)-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]acetic acid ethyl ester 1e. a colorless solid: mp. 103-105 ^oC; IR (CH_2Cl_2) ν 1708 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 300

MHz, TMS) δ 1.27 (3H, t, J = 7.2 Hz, CH_3), 2.44 (3H, s, CH_3), 3.07 (1H, ddd, J = 17.1, 4.5, 2.1 Hz, CH_2), 3.50 (1H, ddd, J = 17.1, 6.9, 2.1 Hz, CH_2), 4.13 (2H, q, J = 7.2 Hz, CH_2), 5.16 (1H, dd, J = 6.9, 4.5 Hz, CH), 5.84-5.86 (1H, m, =CH), 6.99-7.04 (2H, m, ArH), 7.27-7.35 (4H, m, ArH), 7.56-7.60 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.29, 21.57, 37.48, 59.75, 65.29, 94.90, 115.62 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 127.29, 128.56 (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 129.83, 133.14 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 134.09, 144.98, 157.86, 162.81 (d, $^1J_{C\text{-}F}$ = 246.6 Hz), 167.17; MS (EI) *m/z* 389 (M^+, 1.17), 344 (M^+-45, 7.17), 234 (M^+-155, 48.45), 162 (M^+-227, 57.57), 161 (M^+-228, 60.77), 155 (M^+-234, 27.29), 91 (M^+-298, 100); Anal. Calcd. for $C_{20}H_{20}FNO_4S$ requires C, 61.69; H, 5.18; N, 3.60%. Found: C, 61.60; H, 5.09; N, 3.40%.



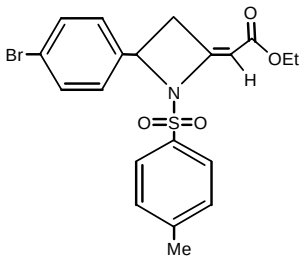
[4-(3-Fluorophenyl)-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]acetic acid ethyl ester 1f.

a colorless solid: mp. 107-109 ^{o}C; IR (CH_2Cl_2) ν 1708 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.29 (3H, t, J = 7.5 Hz, CH_3), 2.44 (3H, s, CH_3), 3.05 (1H, ddd, J = 16.5, 3.9, 1.8 Hz, CH_2), 3.50 (1H, ddd, J = 16.5, 7.5, 2.1 Hz, CH_2), 4.13 (2H, q, J = 7.5 Hz, CH_2), 5.15 (1H, dd, J = 7.5, 3.9 Hz, CH), 5.85-5.87 (1H, m, =CH), 6.99-7.04 (2H, m, ArH), 7.11-7.14 (1H, m, ArH), 7.26-7.32 (3H, m, ArH), 7.58-7.61 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 14.27, 21.55, 37.43, 59.76, 65.17 (d, $^4J_{C\text{-}F}$ = 2.2 Hz), 95.17, 113.46 (d, $^2J_{C\text{-}F}$ = 22.7 Hz), 115.73 (d, $^2J_{C\text{-}F}$ = 21.1 Hz), 122.32 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 127.33, 129.86, 130.32 (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 133.94, 139.88 (d, $^3J_{C\text{-}F}$ = 7.9 Hz), 145.09, 157.71, 162.8 (d, $^1J_{C\text{-}F}$ = 246.8 Hz), 167.07; MS (EI) *m/z* 389 (M^+, 7.17), 234 (M^+-155, 24.36), 161 (M^+-228, 71.39), 155 (M^+-234, 28.60), 91 (M^+-298, 100). Anal. Calcd. for $C_{20}H_{20}FNO_4S$ requires C, 61.69; H, 5.18; N, 3.60%. Found: C, 61.58; H, 5.24; N, 3.42%.



[4-(4-Chlorophenyl)-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]-acetic acid ethyl ester 1g.

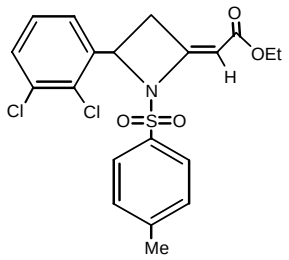
a colorless solid. mp. 108-110 ^{o}C; IR (CH_2Cl_2) ν 1707 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.28 (3H, t, *J* = 7.2 Hz, CH_3), 2.44 (3H, s, CH_3), 3.05 (1H, ddd, *J* = 16.8, 4.2, 2.1 Hz, CH_2), 3.49 (1H, ddd, *J* = 16.8, 7.2, 2.1 Hz, CH_2), 4.13 (2H, q, *J* = 7.2 Hz, CH_2), 5.14 (1H, ddd, *J* = 7.2, 4.2 Hz, CH), 5.85-5.86 (1H, m, =CH), 7.25-7.31 (6H, m, ArH), 7.58 (2H, d, *J* = 8.4 Hz, ArH). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 14.28, 21.59, 37.38, 59.77, 65.18, 95.04, 127.31, 128.02, 128.83, 129.85, 133.96, 134.64, 135.82, 145.06, 157.76, 167.12. MS (EI) *m/z* 405 (M^+, 1.16), 250 (M^+-155, 34.42), 178 (M^+-227, 43.19), 155 (M^+-250, 28.58), 91 (M^+-314, 100). Anal. Calcd. for $C_{20}H_{20}ClNO_4S$ requires C, 59.19; H, 4.97; N, 3.45%. Found: C, 59.35; H, 5.08; N, 3.26%.



[4-(4-Bromophenyl)-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]acetic acid ethyl ester 1h.

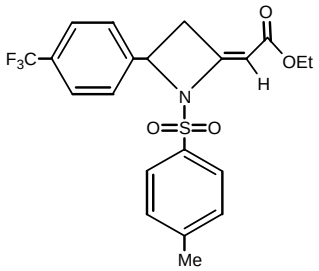
a colorless solid: mp. 135-137 ^{o}C; IR (CH_2Cl_2) ν 1708 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.26 (3H, t, *J* = 7.2 Hz, CH_3), 2.45 (3H, s, CH_3), 3.05 (1H, ddd, *J* = 16.5, 3.9, 2.1 Hz, CH_2), 3.50 (1H, ddd, *J* = 16.5, 6.9, 1.8 Hz, CH_2), 4.13 (2H, q, *J* = 7.2 Hz, CH_2), 5.12 (1H, dd, *J* = 6.9, 3.9 Hz, CH), 5.85-5.86 (1H, m, =CH), 7.20-7.23 (2H, m, ArH), 7.27-7.30 (2H, m, ArH), 7.42-7.46 (2H, m, ArH), 7.56-7.60 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.29, 21.59, 37.30, 59.76, 65.21, 95.04, 122.81, 127.29, 128.30, 129.85, 131.78, 133.94,

136.31, 145.06, 157.74, 167.09; MS (EI) *m/z* 406 (M^+-43, 4.22), 404 (M^+-45, 4.54), 296 (M^+-153, 24.22), 294 (M^+-155, 25.01), 223 (M^+-226, 23.86), 221 (M^+-228, 23.54), 171 (M^+-278, 60.73), 155 (M^+-294, 31.75), 91 (M^+-358, 100); Anal. Calcd. for $C_{20}H_{20}BrNO_4S$ requires C, 53.35; H, 4.48; N, 3.11%. Found: C, 53.29; H, 4.55; N, 2.95%.



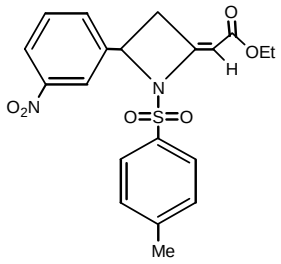
[4-(2,3-Dichlorophenyl)-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]acetic acid ethyl ester 1i.

a colorless solid: mp. 80-82 ^oC; IR (CH_2Cl_2) ν 1710 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.27 (3H, t, *J* = 7.2 Hz, CH_3), 2.48 (3H, s, CH_3), 2.89 (1H, ddd, *J* = 17.1, 4.8, 1.8 Hz, CH_2), 3.53 (1H, ddd, *J* = 17.1, 7.5, 2.4 Hz, CH_2), 4.12 (2H, q, *J* = 7.2 Hz, CH_2), 5.35 (1H, dd, *J* = 7.5, 4.8 Hz, CH), 5.95-5.96 (1H, m, =CH), 7.26-7.32 (1H, m, ArH), 7.38-7.47 (3H, m, ArH), 7.70-7.77 (3H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.23, 21.64, 37.13, 59.86, 62.89, 97.07, 125.26, 127.70, 127.73, 129.59, 130.04, 134.10, 132.55, 133.02, 138.07, 145.51, 157.50, 166.70; MS (EI) *m/z* 441 (M^++2, 4.69), 440 (M^++1, 1.58), 439 (M^+, 6.45), 394 (M^+-45, 4.89), 284 (M^+-155, 9.06), 211 (M^+-228, 31.35), 155 (M^+-284, 34.84), 91 (M^+-348, 100); Anal. Calcd. for $C_{20}H_{19}Cl_2NO_4S$ requires C, 54.56; H, 4.35; N, 3.18%. Found: C, 54.56; H, 4.29; N, 3.04%.



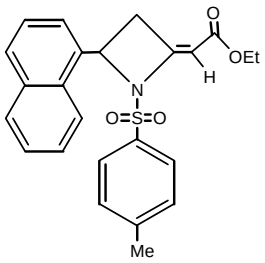
[1-(Toluene-4-sulfonyl)-4-(4-trifluoromethylphenyl)-azetidin-2-ylidene]acetic acid ethyl ester 1j.

a colorless solid: mp. 135-136 ^{o}C; IR (CH_2Cl_2) ν 1707 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.27 (3H, t, *J* = 7.2 Hz, CH_3), 2.44 (3H, s, CH_3), 3.07 (1H, ddd, *J* = 16.5, 4.2, 2.1 Hz, CH_2), 3.53 (1H, ddd, *J* = 16.5, 6.9, 1.8 Hz, CH_2), 4.14 (2H, q, *J* = 7.2 Hz, CH_2), 5.20 (1H, dd, *J* = 6.9, 4.2 Hz, CH), 5.88-5.90 (1H, m, =CH), 7.26-7.29 (2H, m, Ar), 7.44-7.47 (2H, m, Ar), 7.57-7.60 (4H, m, Ar). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 14.27, 21.55, 37.35, 59.84, 64.98, 95.39, 121.97, 125.66 (q, $^{3}J_{C\text{-}F}$ = 3.1 Hz), 126.92, 127.26, 129.87, 130.83 (q, $^{2}J_{C\text{-}F}$ = 32.6 Hz), 133.79, 139.32 (q, $^{1}J_{C\text{-}F}$ = 294.8 Hz), 145.21, 157.56, 167.06; MS (EI) *m/z* 440 (M^{+}+1, 2.05), 439 (M^{+}, 8.23), 284 (M^{+}-155, 11.68), 240 (M^{+}-199, 16.47), 212 (M^{+}-227, 50.04), 155 (M^{+}-284, 30.78), 91 (M^{+}-348, 100). Anal. Calcd. for $C_{21}H_{20}F_3NO_4S$ requires C, 57.40; H, 4.59; N, 3.19%. Found: C, 57.38; H, 4.67; N, 2.99%.



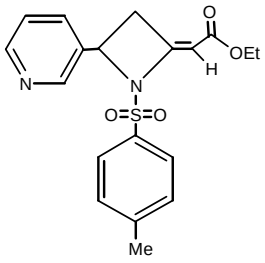
[4-(3-Nitrophenyl)-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]acetic acid ethyl ester 1k.

a colorless solid: mp. 165-167 ^{o}C; IR (CH_2Cl_2) ν 1708 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.28 (3H, t, *J* = 7.2 Hz, CH_3), 2.44 (3H, s, CH_3), 3.08 (1H, ddd, *J* = 16.8, 4.2, 2.1 Hz, CH_2), 3.57 (1H, ddd, *J* = 16.8, 7.5, 2.4 Hz, CH_2), 4.15 (2H, q, *J* = 7.2 Hz, CH_2), 5.24 (1H, dd, *J* = 7.5, 4.2 Hz, CH), 5.91-5.92 (1H, m, =CH), 7.28-7.33 (2H, m, Ar), 7.54-7.65 (3H, m, Ar), 7.77-7.80 (1H, m, Ar), 8.10-8.12 (1H, m, Ar), 8.17-8.21 (1H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.25, 21.55, 37.43, 59.88, 64.47, 95.76, 121.39, 123.63, 127.28, 129.89, 130.01, 132.73, 133.57, 139.59, 145.44, 148.24, 157.08, 166.88; MS (EI) *m/z* 416 (M^{+}, 17.26), 371 (M^{+}-45, 12.05), 261 (M^{+}-155, 7.98), 215 (M^{+}-201, 43.39), 155 (M^{+}-261, 44.21), 91 (M^{+}-325, 100); Anal. Calcd. for $C_{20}H_{20}N_2O_6S$ requires C, 57.69; H, 4.84; N, 6.73%. Found: C, 57.68; H, 4.86; N, 6.29%.



[4-Naphthalen-1-yl-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]acetic acid ethyl ester 1l.

a colorless oil: IR (CH_2Cl_2) ν 1708 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.25 (3H, t, *J* = 7.5 Hz, CH_3), 2.45 (3H, s, CH_3), 3.05 (1H, ddd, *J* = 16.8, 4.8, 2.1 Hz, CH_2), 3.66 (1H, ddd, *J* = 16.8, 7.5, 2.1 Hz, CH_2), 4.12 (2H, q, *J* = 7.5 Hz, CH_2), 5.78 (1H, dd, *J* = 7.5, 4.8 Hz, CH), 6.01-6.03 (1H, m, =CH), 7.31 (2H, d, *J* = 8.4 Hz, Ar), 7.46-7.52 (3H, m, Ar), 7.62-7.65 (1H, m, Ar), 7.71 (2H, d, *J* = 8.4 Hz, Ar), 7.81-7.91 (3H, m, Ar). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 14.26, 21.60, 37.83, 59.76, 63.79, 96.67, 121.82, 123.82, 125.42, 125.78, 126.42, 127.64, 128.67, 129.05, 129.31, 129.92, 133.12, 133.23, 133.49, 145.16, 158.29, 166.97. MS (EI) *m/z* 421 (M^+, 6.06), 376 (M^+-45, 7.40), 266 (M^+-155, 59.43), 193 (M^+-228, 100), 155 (M^+-266, 17.41), 91 (M^+-330, 35.70). HRMS calcd. for $C_{24}H_{23}NO_4S$: 421.1348, Found: 421.1320.



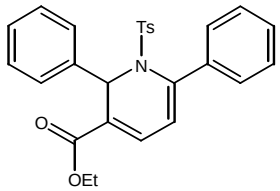
[4-Pyridin-3-yl-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]acetic acid ethyl ester 1m.

a colorless oil. IR (CH_2Cl_2) ν 1708 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.28 (3H, t, *J* = 7.2 Hz, CH_3), 2.45 (3H, s, CH_3), 3.10 (1H, ddd, *J* = 17.1, 4.8, 2.7 Hz, CH_2), 3.53 (1H, ddd, *J* = 17.1, 6.6, 1.8 Hz, CH_2), 4.14 (2H, q, *J* = 7.2 Hz, CH_2), 5.19 (1H, dd, *J* = 6.6, 4.8 Hz, CH), 5.87-5.88 (1H, m, =CH), 7.31-7.36 (3H, m, Ar), 7.62-7.65 (2H, m, Ar), 7.80-7.84 (1H, m, Ar), 8.58-8.62 (2H, m, Ar). ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 14.30, 21.63, 37.15, 59.88, 63.29, 95.60, 123.74, 127.39, 130.03, 133.24, 133.63, 134.29, 145.29, 148.06, 150.02, 157.42, 167.01. MS (EI) *m/z* 372 (M^+, 8.02), 299 (M^+-73, 33.79), 217 (M^+-155, 15.56), 155 (M^+-217, 28.00),

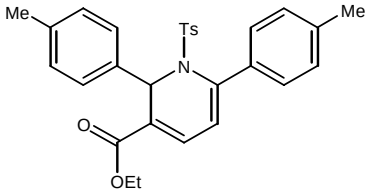
145 (M^+-227, 44.45), 91 (M^+-281, 100). HRMS calcd. for $C_{19}H_{20}N_2O_4S$: 372.1144, Found: 372.1155.

The aza-Baylis-Hillman reaction of *N*-tosylated imines with ethyl 2,3-butadienoate catalyzed by DMAP.

Typical reaction procedure of *N*-tosylated imines with ethyl 2,3-butadienoate at room temperature. To a Schlenk tube with *N*-(*p*-methylbenzenesulfonyl)benzaldimine (65 mg, 0.25 mmol) and DMAP (6 mg, 0.05 mmol) in DCM (0.5 mL) was added ethyl 2,3-butadienoate (34 mg, 0.30 mmol) and the reaction mixture was stirred for 10 min. at room temperature (20 ^{o}C). The reaction mixture was washed with water (3 x 10 mL) and extracted with dichloromethane (2 x 10 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= 1/5) to give adduct **2a** (43 mg, yield 60%) as a colorless solid.

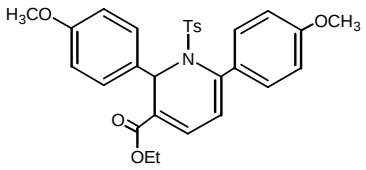


2,6-Diphenyl-1-(toluene-4-sulfonyl)-1,2-dihydropyridine-3-carboxylic acid ethyl ester 2a. a colorless solid. Mp. 130-132 ^{o}C; IR (CH_2Cl_2) ν 1703 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.25 (3H, t, *J* = 6.9 Hz, CH_3), 2.40 (3H, s, CH_3), 4.15 (2H, q, *J* = 6.9 Hz, OCH_2), 6.15 (1H, d, *J* = 5.7 Hz, =CH), 6.52 (1H, s, CH), 6.90 (1H, d, *J* = 5.7 Hz, =CH), 7.17-7.20 (2H, m, ArH), 7.26-7.34 (6H, m, ArH), 7.39-7.45 (4H, m, ArH), 7.56-7.59 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.26, 21.56, 55.98, 60.66, 116.04, 123.90, 127.14, 127.22, 127.27, 128.07, 128.27, 128.38, 129.01, 129.42, 131.75, 135.81, 136.90, 137.58, 141.74, 144.04, 164.37; MS (EI) *m/z* 459 (M^+, 34.43), 382 (M^+-77, 72.12), 304 (M^+-155, 17.04), 274 (M^+-185, 77.13), 232 (M^+-227, 59.52), 155 (M^+-304, 63.89), 91 (M^+-368, 100);. Anal. Calcd. for $C_{27}H_{25}NSO_4$ requires C, 70.57; H, 5.48; N, 3.05%. Found: C, 70.58; H, 5.56; N, 2.93%.



1-(Toluene-4-sulfonyl)-2,6-di-*p*-tolyl-1,2-dihydropyridine-3-carboxylic acid ethyl ester 2b.

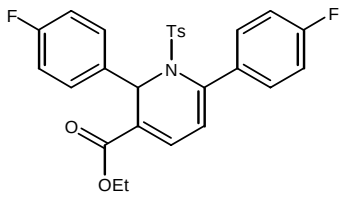
a colorless solid. Mp. 144-146 ^{o}C; IR (CH_2Cl_2) ν 1701 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.24 (3H, t, *J* = 7.2 Hz, CH_3), 2.28 (3H, s, CH_3), 2.32 (3H, s, CH_3), 2.39 (3H, s, CH_3), 4.14 (2H, q, *J* = 7.2 Hz, OCH_2), 6.11 (1H, d, *J* = 5.7 Hz, =CH), 6.48 (1H, s, CH), 6.86 (1H, d, *J* = 5.7 Hz, =CH), 7.08-7.19 (6H, m, ArH), 7.29-7.34 (4H, m, ArH), 7.57 (2H, d, *J* = 6.3 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.28, 21.07, 21.33, 21.55, 55.80, 60.60, 115.30, 123.77, 127.15, 127.18, 127.37, 128.86, 129.02, 129.06, 131.82, 133.88, 134.89, 135.90, 137.94, 139.64, 141.71, 143.94, 164.47; MS (EI) *m/z* 487 (M^+, 100), 396 (M^+-91, 66.09), 332 (M^+-155, 29.72), 288 (M^+-199, 55.63), 260 (M^+-227, 60.39), 155 (M^+-332, 23.72), 91 (M^+-396, 69.93);.Anal. Calcd. for $C_{29}H_{29}NSO_4$ requires C, 71.43; H, 5.99; N, 2.87%. Found: C, 71.25; H, 6.10; N, 2.56%.



2.6-Bis(4-methoxyphenyl)-1-(toluene-4-sulfonyl)-1,2-dihydropyridine-3-carboxylic acid ethyl ester 2c.

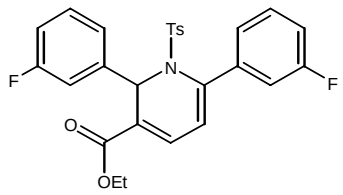
a colorless solid. Mp.152-154 ^{o}C; IR (CH_2Cl_2) ν 1702 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.24 (3H, t, *J* = 7.2 Hz, CH_3), 2.39 (3H, s, CH_3), 3.76 (3H, s, OCH_3), 3.80 (3H, s, OCH_3), 4.14 (2H, q, *J* = 7.2 Hz, CH_2), 6.07 (1H, d, *J* = 6.0 Hz, =CH), 6.46 (1H, s, CH), 6.81-6.84 (4H, m, ArH), 6.86 (1H, d, *J* = 6.0 Hz, =CH), 7.18 (2H, d, *J* = 8.1 Hz, ArH), 7.32-7.37 (4H, m, ArH), 7.56 (2H, d, *J* = 8.1 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.31, 21.58, 55.18, 55.27, 55.67, 60.58, 113.59, 113.75, 114.41, 123.41, 127.18, 128.58, 128.69, 128.87, 129.02, 130.25, 131.92, 135.90, 141.34, 143.94, 159.48, 160.76, 164.51; MS (EI) *m/z* 519 (M^+, 95.65), 364 (M^+-155, 64.33), 320 (M^+-199, 63.22), 291 (M^+-228, 100), 155 (M^+-364, 18.15), 91 (M^+-428, 63.93); Anal. Calcd. for $C_{29}H_{29}NSO_6$ requires C, 67.03; H, 5.63;

N, 2.70%. Found: C, 67.82; H, 5.73; N, 2.64%.



2,6-Bis(4-fluorophenyl)-1-(toluene-4-sulfonyl)-1,2-dihydropyridine-3-carboxylic acid ethyl ester 2d.

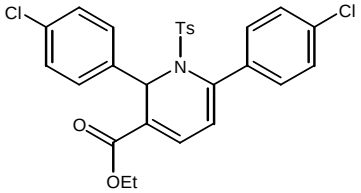
a colorless solid. Mp. 133-135 ^{o}C; IR (CH_2Cl_2) ν 1702 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.26 (3H, t, *J* = 7.2 Hz, CH_3), 2.40 (3H, s, CH_3), 4.15 (2H, q, *J* = 7.2 Hz, CH_2), 6.11 (1H, d, *J* = 5.4 Hz, =CH), 6.47 (1H, s, CH), 6.86 (1H, d, *J* = 5.4 Hz, =CH), 6.97-7.03 (4H, m, ArH), 7.19 (2H, d, *J* = 8.4 Hz, ArH), 7.33-7.41 (4H, m, ArH), 7.55 (2H, d, *J* = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.24, 21.56, 55.39, 60.77, 115.29 (d, $^{1}J_{C-F}$ = 21.8 Hz), 115.43 (d, $^{1}J_{C-F}$ = 21.0 Hz), 123.81, 123.82, 127.08, 128.94 (d, $^{3}J_{C-F}$ = 8.0 Hz), 129.06 (d, $^{3}J_{C-F}$ = 8.6 Hz), 129.17, 131.71, 132.52 (d, $^{4}J_{C-F}$ = 3.1 Hz), 133.60 (d, $^{4}J_{C-F}$ = 2.7 Hz), 135.59, 140.54, 144.30, 162.59 (d, $^{1}J_{C-F}$ = 235.2 Hz), 163.08 (d, $^{1}J_{C-F}$ = 232.0 Hz), 165.18; MS (EI) *m/z* (M^+, 100), 396 (M^+-91, 66.09), 332 (M^+-155, 29.72), 288 (M^+-199, 55.63), 260 (M^+-227, 60.39), 155 (M^+-332, 23.72), 91 (M^+-396, 69.93); Anal. Calcd. for $C_{27}H_{23}NSO_4F_2$ requires C, 65.44; H, 4.68; N, 2.83%. Found: C, 65.43 ; H, 4.58; N, 2.71%.



2,6-Bis(3-fluorophenyl)-1-(toluene-4-sulfonyl)-1,2-dihydropyridine-3-carboxylic acid ethyl ester 2e.

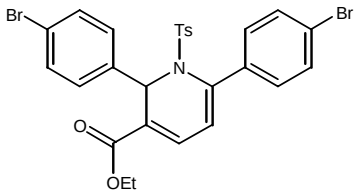
a colorless solid. Mp. 130-132 ^{o}C; IR (CH_2Cl_2) ν 1705 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.25 (3H, t, *J* = 7.2 Hz, CH_3), 2.41 (3H, s, CH_3), 4.16 (2H, q, *J* = 7.2 Hz, OCH_2), 6.18 (1H, d, *J* = 5.4 Hz, =CH), 6.48 (1H, s, CH), 6.90 (1H, d, *J* = 5.4 Hz, =CH), 6.98-7.11 (4H,

m, ArH), 7.17-7.22 (3H, m, ArH), 7.25-7.34 (3H, m, ArH), 7.56-7.58 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.22, 21.55, 55.48 (d, J_{C-F} = 2.0 Hz), 60.87, 113.93 (d, $^2J_{C-F}$ = 16.9 Hz), 114.23 (d, $^2J_{C-F}$ = 16.7 Hz), 115.40 (d, $^2J_{C-F}$ = 21.4 Hz), 116.36 (d, $^2J_{C-F}$ = 21.1 Hz), 116.61, 122.96 (d, $^4J_{C-F}$ = 3.0 Hz), 123.05 (d, $^4J_{C-F}$ = 3.1 Hz), 124.10, 127.10, 129.23, 129.68 (d, $^3J_{C-F}$ = 8.5 Hz), 130.11 (d, $^3J_{C-F}$ = 8.0 Hz), 131.60, 135.46, 139.47 (d, $^3J_{C-F}$ = 8.9 Hz), 139.57 (d, $^3J_{C-F}$ = 11.1 Hz), 140.48 (d, $^4J_{C-F}$ = 2.9 Hz), 144.43, 162.41 (d, $^1J_{C-F}$ = 244.4 Hz), 162.74 (d, $^1J_{C-F}$ = 245.1 Hz), 163.99; MS (EI) *m/z* 495 (M^+, 30.92), 400 (M^+-95, 61.79), 340 (M^+-155, 21.86), 268 (M^+-227, 76.18), 155 (M^+-340, 80.59), 91 (M^+-404, 100);. Anal. Calcd. for $C_{27}H_{23}F_2NSO_4$ requires C, 65.44; H, 4.68; N, 2.83%. Found: C, 65.26; H, 4.38; N, 2.75%.



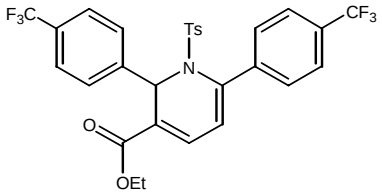
2,6-Bis(4-chlorophenyl)-1-(toluene-4-sulfonyl)-1,2-dihydropyridine-3-carboxylic acid ethyl ester 2f.

a colorless solid. Mp. 188-189 ^oC; IR (CH_2Cl_2) ν 1704 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.25 (3H, t, *J* = 7.2 Hz, CH_3), 2.40 (3H, s, CH_3), 4.14 (2H, q, *J* = 7.2 Hz, OCH_2), 6.14 (1H, d, *J* = 6.0 Hz, =CH), 6.45 (1H, s, CH), 6.89 (1H, d, *J* = 6.0 Hz, =CH), 7.20 (2H, d, *J* = 8.7 Hz, ArH), 7.26-7.36 (8H, m, ArH), 7.55 (2H, d, *J* = 8.7 Hz, ArH), 7.56-7.58 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.22, 21.55, 55.38, 60.83, 116.07, 123.88, 127.07, 128.30, 128.44, 128.66, 128.69, 129.21, 131.66, 134.28, 135.30, 135.45, 135.56, 135.82, 140.49, 144.39, 164.02; MS (EI) *m/z* 531 (M^++4, 4.24), 529 (M^++2, 18.21), 527 (M^+, 25.24), 416 (M^+-109, 53.93), 372 (M^+-155, 17.48), 300 (M^+-227, 53.41), 155 (M^+-372, 73.51), 91 (M^+-436, 100);. Anal. Calcd. for $C_{27}H_{23}Cl_2NSO_4$ requires C, 61.37; H, 4.39; N, 2.65%. Found: C, 61.02; H, 4.31; N, 2.61%.



2,6-Bis(4-bromophenyl)-1-(toluene-4-sulfonyl)-1,2-dihydropyridine-3-carboxylic acid ester 2g.

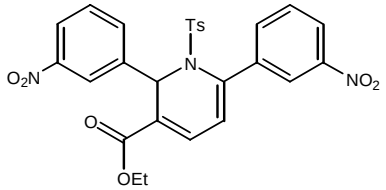
a colorless solid. Mp. 178-181 ^{o}C; IR (CH_2Cl_2) ν 1702 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.25 (3H, t, *J* = 7.2 Hz, CH_3), 2.41 (3H, s, CH_3), 4.15 (2H, q, *J* = 7.2 Hz, OCH_2), 6.15 (1H, d, *J* = 5.7 Hz, =CH), 6.43 (1H, s, CH), 6.89 (1H, d, *J* = 5.7 Hz, =CH), 7.18-7.29 (6H, m, ArH), 7.43-7.47 (4H, m, ArH), 7.53-7.56 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.24, 21.58, 55.45, 60.86, 116.08, 122.54, 123.91, 123.97, 127.09, 128.54, 128.98, 129.22, 131.41, 131.65, 131.67, 135.45, 135.82, 136.24, 140.60, 144.40, 164.02; MS (EI) *m/z* (M^+, 100), 396 (M^+-91, 66.09), 332 (M^+-155, 29.72), 288 (M^+-199, 55.63), 260 (M^+-227, 60.39), 155 (M^+-332, 23.72), 91 (M^+-396, 69.93); Anal. Calcd. for $C_{27}H_{23}Cl_2NSO_4$ requires C, 61.37; H, 4.39; N, 2.65%; Found: C, ; H, 4.31; N, 2.61%.



1-(Toluene-4-sulfonyl)-2,6-bis(4-trifluorophenyl)-1,2-dihydropyridine-3-carboxylic acid ethyl ester 2h.

a colorless oil; IR (CH_2Cl_2) ν 1725 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.27 (3H, t, *J* = 7.2 Hz, CH_3), 2.42 (3H, s, CH_3), 4.16 (2H, q, *J* = 7.2 Hz, OCH_2), 6.24 (1H, d, *J* = 6.0 Hz, =CH), 6.53 (1H, s, CH), 6.95 (1H, d, *J* = 6.0 Hz, =CH), 7.18-7.26 (2H, m, ArH), 7.32-7.35 (1H, m, ArH), 7.48-7.61 (8H, m, ArH), 7.73-7.78 (1H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.24, 21.61, 55.53, 61.05, 117.32, 124.36, 125.27 (q, $J_{C\text{-}F}$ = 3.6 Hz), 125.58 (q, $J_{C\text{-}F}$ = 3.8 Hz), 127.13, 127.38, 127.66, 129.19 (q, $J_{C\text{-}F}$ = 118.2 Hz), 129.37, 129.81 (q, $J_{C\text{-}F}$ =102.5 Hz), 130.95, 131.01, 131.59, 135.36, 140.38, 140.59 (q, $J_{C\text{-}F}$ = 1.8 Hz), 140.81 (q, $J_{C\text{-}F}$ = 1.4 Hz),

144.69, 163.90; MS (EI) *m/z* 595 (M^+, 15.39), 450 (M^+-155, 37.63), 396 (M^+-199, 24.58), 268 (M^+-227, 3.13), 155 (M^+-450, 97.35), 91 (M^+-504, 100); HRMS calcd. for $C_{29}H_{23}F_6NO_4S$: 595.1252, Found: 595.1251.

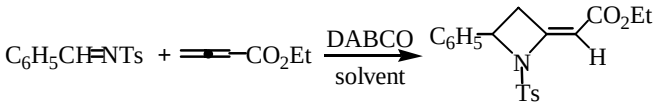


2,6-Bis(3-nitrophenyl)-1-(toluene-4-sulfonyl)-1,2-dihydropyridine-3-carboxylic acid ethyl ester 2i.

a colorless solid. Mp. 152-155 ^oC; IR (CH_2Cl_2) ν 1703 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.28 (3H, t, *J* = 7.2 Hz, CH_3), 2.44 (3H, s, CH_3), 4.19 (2H, q, *J* = 7.2 Hz, OCH_2), 6.34 (1H, d, *J* = 5.4 Hz, =CH), 6.58 (1H, s, CH), 7.01 (1H, d, *J* = 5.4 Hz, =CH), 7.24-7.33 (1H, m, ArH), 7.48-7.69 (5H, m, ArH), 7.80-7.83 (1H, m, ArH), 7.99-8.05 (2H, m, ArH), 8.17-8.25 (3H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.23, 21.64, 55.25, 61.25, 117.61, 121.32, 121.73, 123.88, 124.17, 124.21, 126.37, 127.10, 129.33, 129.56, 129.67, 129.96, 131.75, 133.25, 133.99, 135.04, 138.73, 139.02, 139.33, 145.06, 163.65; MS (EI) *m/z* 549 (M^+, 18.63), 427 (M^+-122, 49.27), 394 (M^+-155, 20.41), 364 (M^+-185, 47.44), 322 (M^+-227, 46.41), 155 (M^+-394, 84.62), 91 (M^+-458, 100); Anal. Calcd. for $C_{27}H_{23}N_3O_8S \cdot CH_2Cl_2$ requires C, 53.04; H, 3.97; N, 6.63%. Found: C, 52.90; H, 4.19; N, 6.48%.

The solvent effects using DABCO and DMAP as a Lewis base promoter in the aza-Baylis-Hillman reaction of *N*-tosylated imines with ethyl 2,3-butadienoate which are not shown in main text due to the limited space.

Table 1. The solvent effect in the aza-Baylis-Hillman reaction of *N*-tosylated imines with ethyl 2,3-butadienoate catalyzed by DABCO in the absence of MS 4A.

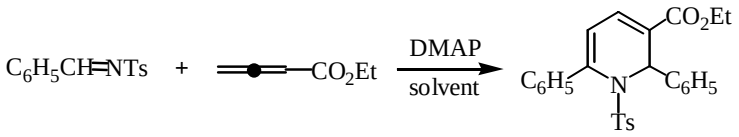


1a

entry	solvent	yield/[%][a] **1a**
1	THF	56
2	DMF	27
3	MeCN	25
4	Et_2O	42
5	CH_2Cl_2	28
6	C_6H_6	57 (82)[b]
7	$Me_2C=O$	54

[a]Isolated yield. [b]In the presence of MS 4A.

Table 2. The solvent effect in the aza-Baylis-Hillman reaction of *N*-tosylated imines with ethyl 2,3-butadienoate catalyzed by DMAP.



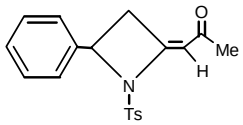
3a

entry	solvent	yield/[%][a] **3a**
1	THF	40
2	C_6H_6	40
3	CH_2Cl_2	60
4	DMF	20
5	MeCN	38
6	Et_2O	23

[a]Isolated yield.

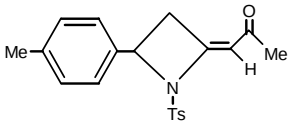
The aza-Baylis-Hillman reaction of *N*-tosylated imines with penta-3,4-dien-2-one catalyzed by DABCO.

Typical reaction procedure of *N*-tosylated imines with penta-3,4-dien-2-one at room temperature. To a Schlenk tube with *N*-(*p*-methylbenzenesulfonyl)benzaldimine (65 mg, 0.25 mmol) and DABCO (6 mg, 0.05 mmol) in DCM (0.5 mL) was added penta-3,4-dien-2-one (25 mg, 0.30 mmol) and the reaction mixture was stirred for 3 h at room temperature (20 ^{o}C). The reaction mixture was washed with water (3 x 10 mL) and extracted with dichloromethane (2 x 10 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= 1/4) to give adduct **3a** (37 mg, yield 43%) as a colorless solid.



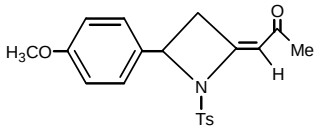
1-[4-Phenyl-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]propan-2-one 3a.

Mp. 123-135 ^{o}C; IR (CH_2Cl_2) ν 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.19 (3H, s, CH_3), 2.43 (3H, s, CH_3), 3.15 (1H, ddd, J = 17.1, 3.9, 1.8 Hz, CH_2), 3.53 (1H, ddd, *J* = 17.1, 6.6, 1.8 Hz, CH_2), 5.23 (1H, dd, *J* = 6.6, 3.9 Hz, CH), 6.27-6.28 (1H, m, =CH), 7.25-7.29 (2H, m, Ar), 7.31 (5H, s, Ar), 7.53-7.56 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.59, 30.97, 38.13, 67.07, 102.50, 126.73, 127.23, 128.66, 128.86, 129.78, 134.27, 136.82, 144.90, 158.25, 197.45; MS (EI) *m/z* 341 (M^+, 0.78), 260 (M^+-81, 1.77), 186 (M^+-155, 3.95), 155 (M^+-186, 14.63), 144 (M^+-197,31.76), 104 (M^+-237, 29.18), 91 (M^+-250, 100); Anal. Calcd. for $C_{19}H_{19}NO_3S$ requires C, 66.85; H, 5.61; N, 4.10%. Found: C, 66.57; H, 5.60; N, 3.95%.



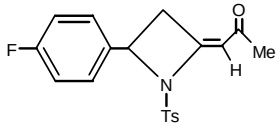
1-[1-(Toluene-4-sulfonyl)-4-*p*-tolyl-azetidin-2-ylidene]propan-2-one 3b.

a colorless oil; IR (CH_2Cl_2) ν 1692 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.20 (3H, s, CH_3), 2.34 (3H, s, CH_3), 2.42 (3H, s, CH_3), 3.13 (1H, ddd, J = 17.1, 3.9, 2.4 Hz, CH_2), 3.50 (1H, ddd, *J* = 17.1, 6.6, 2.1 Hz, CH_2), 5.20 (1H, dd, *J* = 6.6, 3.9 Hz, CH), 6.26-6.27 (1H, m, =CH), 7.11 (2H, d, *J* = 6.9 Hz, Ar), 7.18-7.27 (4H, m, Ar), 7.55 (2H, dd, *J* = 6.9 Hz, 1.8 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.16, 21.58, 30.93, 38.11, 67.05, 102.40, 126.73, 127.24, 129.30, 129.72, 133.83, 134.34, 138.80, 144.83, 158.40, 197.46; MS (EI) *m/z* 355 (M^+, 0.66), 200 (M^+-155, 11.68), 158 (M^+-197, 100), 155 (M^+-200, 16.17), 118 (M^+-237), 91 (M^+-264, 63.57); HRMS calcd. for $C_{20}H_{21}NO_3S$: 355.1242, Found: 355.1246.



1-[4-(4-Methoxyphenyl)-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]propan-2-one 3c.

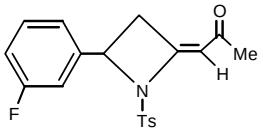
A colorless solid. Mp. 95-97 ^oC; IR (CH_2Cl_2) ν 1701 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.19 (3H, s, CH_3), 2.43 (3H, s, CH_3), 3.15 (1H, ddd, *J* = 16.8, 4.2, 2.1 Hz, CH_2), 3.51 (1H, ddd, *J* = 16.8, 6.9, 2.4 Hz, CH_2), 3.81 (3H, s, OCH_3), 5.21 (1H, dd, *J* = 6.9, 4.2 Hz, CH), 6.25-6.26 (1H, m, =CH), 6.82 (2H, d, *J* = 6.9 Hz, Ar), 7.20-7.27 (4H, m, Ar), 7.51-7.55 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.62, 30.98, 38.12, 55.39, 67.05, 102.27, 114.02, 114.39, 127.25, 127.27, 129.22, 129.75, 144.81, 158.37, 160.05, 197.55; MS (EI) *m/z* 371 (M^+, 3.07), 216 (M^+-155, 20.73), 174 (M^+-197, 100), 155 (M^+-216, 9.46), 91 (M^+-280, 51.30); Anal. Calcd. for $C_{20}H_{21}NO_4S$ requires C, 64.68; H, 5.70; N, 3.77%. Found: C, 64.33; H, 5.65; N, 3.53%.



1-[4-(4-Fluorophenyl)-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]propan-2-one 3d.

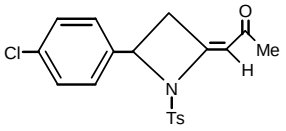
A colorless solid. Mp. 140-142 ^oC; IR (CH_2Cl_2) ν 1692 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 300

MHz, TMS) δ 2.22 (3H, s, CH_3), 2.44 (3H, s, CH_3), 3.12 (1H, ddd, *J* = 17.1, 4.2, 1.8 Hz, CH_2), 3.53 (1H, ddd, *J* = 17.1, 6.9, 2.1 Hz, CH_2), 5.21 (1H, dd, *J* = 6.9, 4.2 Hz, CH), 6.28-6.29 (1H, m, =CH), 6.97-7.03 (2H, m, Ar), 7.26-7.32 (4H, m, Ar), 7.54-7.62 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.59, 30.99, 38.22, 66.31, 102.56, 115.63 (d, $^2J_{C-F}$ = 21.9 Hz), 127.20, 128.62 (d, $^3J_{C-F}$ = 8.4 Hz), 129.85, 132.78 (d, $^4J_{C-F}$ = 3.1 Hz), 134.21, 145.10, 157.92, 162.84 (d, $^1J_{C-F}$ = 247.0 Hz), 197.48; MS (EI) *m/z* 359 (M^+, 2.05), 204 (M^+-155, 13.14), 162 (M^+-197, 100), 155 (M^+-204, 22.06), 91 (M^+-268, 75.49); Anal. Calcd. for $C_{19}H_{18}FNO_3S$ requires C, 63.50; H, 5.05; N, 3.90%. Found: C, 63.35; H, 4.94; N, 3.62%.



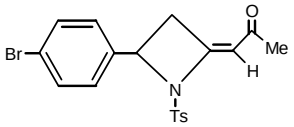
1-[4-(3-Fluoro-phenyl)-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]propan-2-one 3e.

A colorless solid. Mp. 125-127 ^oC; IR (CH_2Cl_2) ν 1692 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.20 (3H, s, CH_3), 2.44 (3H, s, CH_3), 3.10 (1H, ddd, *J* = 17.4, 3.9, 1.2 Hz, CH_2), 3.54 (1H, ddd, *J* = 17.4, 7.2, 1.8 Hz, CH_2), 5.20 (1H, dd, *J* = 7.2, 3.9 Hz, CH), 6.29-6.31 (1H, m, =CH), 6.95-7.04 (2H, m, Ar), 7.10-7.12 (1H, m, Ar), 7.26-7.32 (3H, m, Ar), 7.57-7.60 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.60, 31.02, 38.21, 66.22 (d, *J* = 2.3 Hz), 102.77, 113.53 (d, *J* = 22.5 Hz), 115.82 (d, *J* = 21.1 Hz), 122.41 (d, *J* = 3 Hz), 127.26, 129.89, 130.35 (d, *J* = 8.0 Hz), 134.09, 139.54 (d, *J* = 7.0 Hz), 145.23, 157.80, 162.82 (d, J = 246.2 Hz), 197.45; MS (EI) *m/z* 359 (M^+, 5.07), 204 (M^+-155, 12.52), 162 (M^+-197, 71.41), 155 (M^+-204, 31.54), 91 (M^+-268, 100); Anal. Calcd. for $C_{19}H_{18}FNO_3S$ requires C, 63.50; H, 5.05; N, 3.90%. Found: C, 63.67; H, 5.21; N, 3.63%.



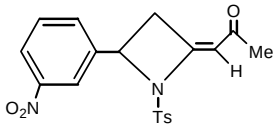
1-[4-(4-Chloro-phenyl)-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]-propan-2-one 3f.

A colorless solid. Mp. 152-153 ^{o}C; IR (CH_2Cl_2) ν 1695 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.19 (3H, s, CH_3), 2.44 (3H, s, CH_3), 3.09 (1H, ddd, *J* = 17.1, 4.2, 2.1 Hz, CH_2), 3.52 (1H, ddd, *J* = 17.1, 7.2, 2.1 Hz, CH_2), 5.19 (1H, dd, *J* = 7.2, 4.2 Hz, CH), 6.28-6.29 (1H, m, =CH), 7.03-7.18 (2H, m, Ar), 7.21-7.30 (4H, m, Ar), 7.54-7.64 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.61, 31.01, 38.12, 66.23, 102.66, 127.23, 128.09, 128.87, 129.88, 134.14, 134.75, 135.46, 145.19, 157.86, 197.48; MS (EI) *m/z* 375 (M^+, 2.07), 220 (M^+-155, 15.13), 180 (M^+-195, 32.27), 178 (M^+-197, 100), 155 (M^+-220, 31.05), 91 (M^+-284, 95.73); Anal. Calcd. for $C_{19}H_{18}ClNO_3S$ requires C, 60.72; H, 4.83; N, 3.73%. Found: C, 60.74; H, 4.92; N, 3.54%.



1-[4-(4-Bromophenyl)-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]propan-2-one 3g.

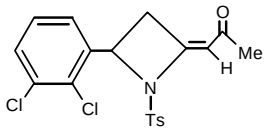
A colorless solid. Mp. 110-113 ^{o}C; IR (CH_2Cl_2) ν 1702 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.22 (3H, s, CH_3), 2.45 (3H, s, CH_3), 3.09 (1H, ddd, *J* = 17.1, 3.9, 1.8 Hz, CH_2), 3.53 (1H, ddd, *J* = 17.1, 6.9, 1.5 Hz, CH_2), 5.17 (1H, dd, *J* = 6.9, 3.9 Hz, CH), 6.28-6.29 (1H, m, =CH), 7.16-7.24 (2H, m, Ar), 7.26-7.34 (2H, m, Ar), 7.42-7.46 (2H, m, Ar), 7.55-7.60 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.63, 31.02, 38.05, 66.26, 102.65, 122.91, 127.22, 128.37, 129.88, 131.82, 134.10, 135.94, 145.20, 157.86, 197.50; MS (EI) *m/z* 422 (M^++3, 3.56), 420 (M^++1, 1.44), 340 (M^+-79, 83.68), 338 (M^+-81, 84.39), 282 (M^+-137, 26.95), 155 (M^+-264, 84.54), 91 (M^+-368, 100); Anal. Calcd. for $C_{19}H_{18}BrNO_3S$ requires C, 54.30; H, 4.32; N, 3.33%. Found: C, 54.93; H, 4.47; N, 2.88%.



1-[4-(3-Nitrophenyl)-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]propan-2-one 3h.

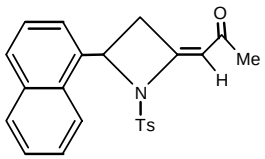
A colorless solid. Mp. 103-105 ^{o}C; IR (CH_2Cl_2) ν 1701 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300

MHz, TMS) δ 2.21 (3H, s, CH_3), 2.44 (3H, s, CH_3), 3.12 (1H, ddd, *J* = 17.1, 4.2, 2.1 Hz, CH_2), 3.60 (1H, ddd, *J* = 17.1, 6.6, 1.2 Hz, CH_2), 5.27-5.31 (1H, m, CH), 6.34 (1H, s, =CH), 7.29-7.31 (2H, m, Ar), 7.53-7.62 (1H, m, Ar), 7.73-7.82 (3H, m, Ar), 8.07 (1H, s, Ar), 8.17-8.20 (1H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.74, 31.33, 38.53, 65.84, 103.45, 121.73, 123.99, 126.60, 129.90, 133.10, 134.07, 139.38, 139.57, 143.73, 145.88, 157.58, 197.92; MS (EI) *m/z* 386 (M^+, 6.02), 231 (M^+-155, 6.31), 171 (M^+-215, 35.90), 155 (M^+-231, 39.15), 91 (M^+-295, 100); HRMS calcd. for $C_{19}H_{18}N_2O_4S$: 386.0936, Found: 386.0920.



1-[4-(2,3-Dichlorophenyl)-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]propan-2-one 3i.

A colorless solid. Mp. 135-137 ^{o}C; IR (CH_2Cl_2) ν 1695 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.18 (3H, s, CH_3), 2.48 (3H, s, CH_3), 2.93 (1H, ddd, *J* = 17.1, 4.2, 2.1 Hz, CH_2), 3.57 (1H, ddd, *J* = 17.1, 7.2, 1.8 Hz, CH_2), 5.40 (1H, dd, *J* = 4.2 Hz, 7.2 Hz, CH), 6.37-6.38 (1H, m, =CH), 7.26-7.31 (1H, m, Ar), 7.37-7.47 (3H, m, Ar), 7.66-7.77 (3H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.71, 31.04, 37.99, 63.89, 104.54, 125.62, 127.68, 127.73, 129.72, 129.94, 130.17, 132.74, 133.16, 137.87, 145.68, 157.57, 197.21; MS (EI) *m/z* 411 (M^++2, 3.49), 409 (M^+, 4.86), 254 (M^+-155, 10.03), 212 (M^+-197, 26.08), 155 (M^+-254, 31.55), 91 (M^+-318, 100); Anal. Calcd. for $C_{19}H_{17}Cl_2NO_3S$ requires C, 55.62; H, 4.18; N, 3.42%. Found: C, 55.66; H, 4.31; N, 3.17%.



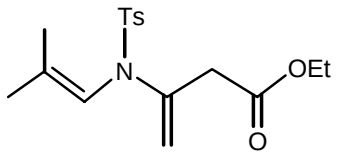
1-[4-Naphthalen-1-yl-1-(toluene-4-sulfonyl)-azetidin-2-ylidene]propan-2-one 3j.

A colorless solid. Mp. 108-110 ^{o}C; IR (CH_2Cl_2) ν 1696 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300

MHz, TMS) δ 2.20 (3H, s, CH_3), 2.46 (3H, s, CH_3), 3.09 (1H, ddd, *J* = 17.1, 4.2, 2.4 Hz, CH_2), 3.70 (1H, ddd, *J* = 17.1, 7.2, 2.4 Hz, CH_2), 5.82 (1H, dd, *J* = 4.2 Hz, 7.2 Hz, CH), 6.44-6.45 (1H, m, =CH), 7.31 (2H, d, *J* = 7.2 Hz, Ar), 7.46-7.51 (3H, m, Ar), 7.61-7.65 (1H, m, Ar), 7.70 (2H, dd, *J* = 7.2 Hz, 1.8 Hz, Ar), 7.81-7.91 (3H, m, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.59, 30.99, 38.62, 64.78, 104.27, 121.86, 123.82, 125.36, 125.80, 126.45, 127.54, 128.73, 129.03, 129.33, 129.92, 132.99, 133.25, 133.50, 145.26, 158.32, 197.28; MS (EI) *m/z* 393 (M^++2, 0.63), 391 (M^+, 3.31), 236 (M^+-155, 16.87), 194 (M^+-197, 100), 155 (M^+-236, 22.61), 153 (M^+-238, 51.33), 91 (M^+-300, 56.29); Anal. Calcd. for $C_{23}H_{21}NO_3S$ requires C, 70.57; H, 5.41; N, 3.58%. Found: C, 70.28; H, 5.31; N, 3.31%.

3-[(2-Methylpropenyl)-(toluene-4-sulfonyl)amino]-but-3-enoic acid ethyl ester 5.

Reaction procedure of *N*-isobutylidene-4-methyl-benzenesulfonamide with ethyl 2,3-butadienoate at room temperature. To a Schlenk tube with *N*-isobutylidene-4-methyl-benzenesulfonamide (112 mg, 0.50 mmol) and DMAP (6 mg, 0.05 mmol) in DCM (0.5 mL) was added ethyl 2,3-butadienoate (56 mg, 0.50 mmol) and the reaction mixture was stirred for 10 min. at room temperature (20 ^{o}C). The reaction mixture was washed with water (3 x 10 mL) and extracted with dichloromethane (2 x 10 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= 1/8) to give adduct **5** (34 mg, yield 20%) as a colorless oil.

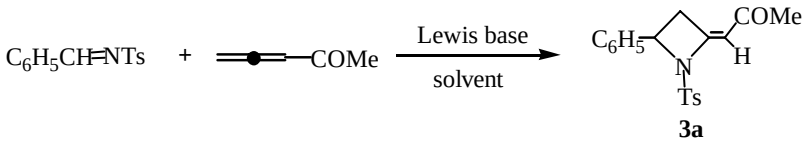


a colorless oil; IR (CH_2Cl_2) ν 1736 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.25 (3H, t, *J* = 7.2 Hz, CH_3), 1.68 (3H, d, *J* = 1.5 Hz, CH_3), 1.73 (3H, d, *J* = 1.5 Hz, CH_3), 2.43 (3H, s, CH_3), 3.17 (2H, d, *J* = 0.6 Hz, CH_2), 4.10 (2H, q, *J* = 7.2 Hz , CH_2), 4.94 (1H, d, *J* = 0.9 Hz, =CH), 4.99 (1H, d, *J* = 0.9 Hz, =CH), 5.58-5.59 (1H, m, =CH), 7.30 (2H, dd, *J* = 7.2 Hz, 0.6 Hz, Ar), 7.70 (2H, dd, *J* = 7.2 Hz, 0.6 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.99, 17.72,

21.44, 22.12, 41.03, 60.79, 112.46, 119.86, 127.76, 129.29, 135.27, 140.30, 140.41, 143.57, 169.83; MS (EI) *m/z* 337 (M^+, 1.80), 273 (M^+-64, 10.34), 182 (M^+-155, 16.41), 168 (M^+-169, 59.11), 155 (M^+-182, 19.32), 108 (M^+-229, 100), 91 (M^+-246, 48.73); HRMS calcd. for $C_{17}H_{23}NO_4S$: 337.1348, Found: 337.1339.

The Lewis base and solvent effects in the aza-Baylis-Hillman reaction of *N*-tosylated imines with penta-3,4-dien-2-one which are not shown in main text due to the limited space.

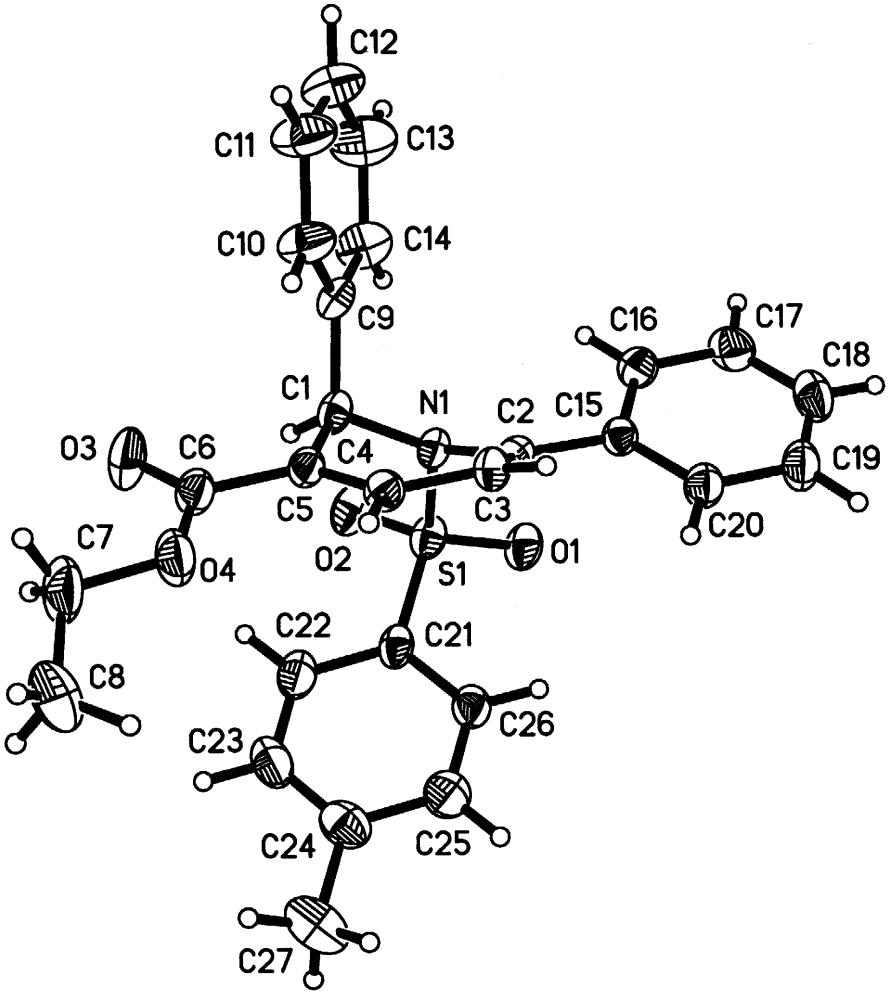
Table 3. The solvent and Lewis base effect in the aza-Baylis-Hillman reaction of *N*-tosylated imines with penta-3,4-dien-2-one catalyzed by Lewis base.



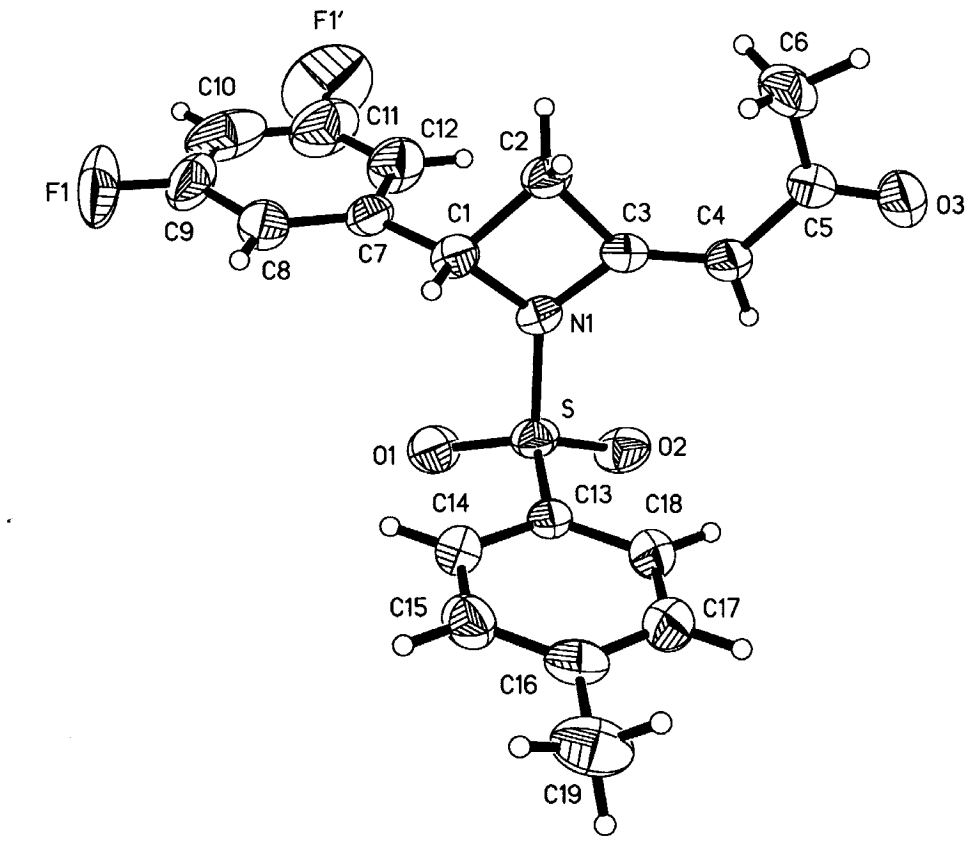
3a

entry	Lewis base	solvent	yield/[%][a)] **3a**
1	DABCO	THF	25
2	DABCO	MeCN	15
3	DABCO	DMF	15
4	DABCO	C_6H_6	16
5	DABCO	CH_2Cl_2	43
6	DABCO	Et_2O	33
7	DABCO	EtOAc	25
8	DMAP	CH_2Cl_2	trace
9	DBU	CH_2Cl_2	trace
10	Et_3N	CH_2Cl_2	trace

[a)]Isolated yield.



The crystal data of **2a** which has been deposited in CCDC with number 211894. Empirical Formula: $C_{27}H_{25}NO_4S$; Formula Weight: 459.54; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.468 x 0.375 x 0.245 mm; Crystal System: Triclinic; Lattice Type: Primitive; Lattice Parameters: a= 7.6675(8)Å, b= 13.8140(15)Å, c= 22.914(3)Å, α= 92.491(2)^o, β= 93.885(2)^o, γ= 98.992(2)^o, V= 2388.1(4)Å^3; Space group: P-1; Z= 4; D_{calc}= 1.278 g/cm^3; F_{000}= 968; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0605, 0.1271.



The crystal data of **3d** which has been deposited in CCDC with number 211895. Empirical Formula: $C_{19}H_{18}NO_3FS$; Formula Weight: 359.40; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.478 x 0.237 x 0.226 mm; Crystal System: Monoclinic; Lattice Type: Primitive; Lattice Parameters: a= 6.3576(9)Å, b= 8.9534(13)Å, c= 31.589(5)Å, α= 90°, β= 91.829(3)°, γ= 90°, V= 1797.2(4)Å^3; Space group: P2(1)/n; Z= 4; D_{calc}= 1.328 g/cm^3; F_{000}= 752; Diffractometer: Rigaku AFC7R; Residuals: R; Rw: 0.0568, 0.1278.