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Supporting Information

Gold(I) Catalyzed Rearrangement of Arylvinylcyclopropenes: A Effect Synthetic Protocol for the Construction of Indene Skeletons

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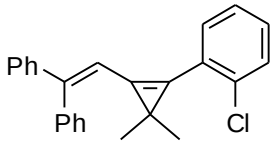
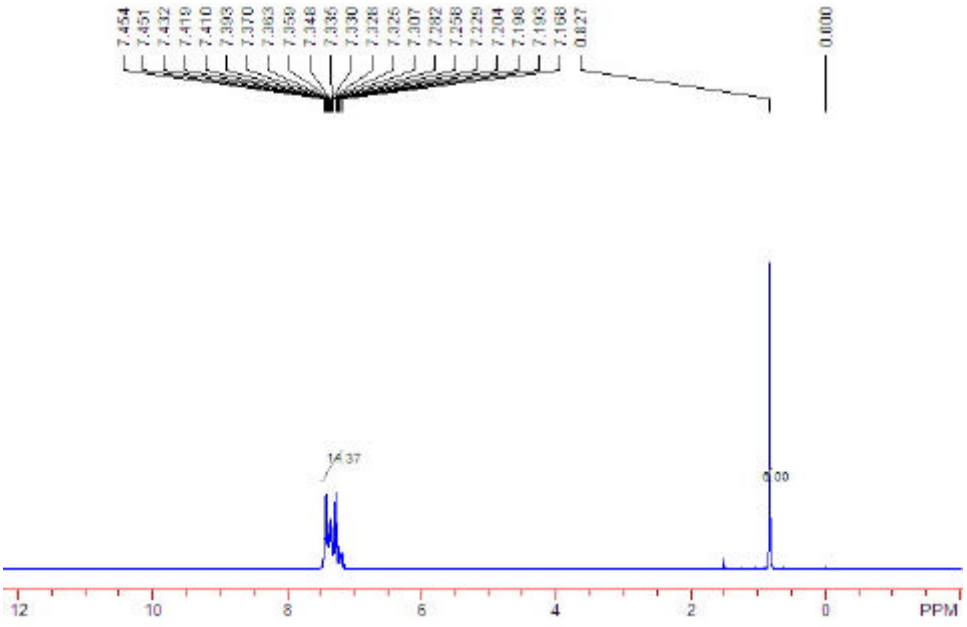
CONTENTS

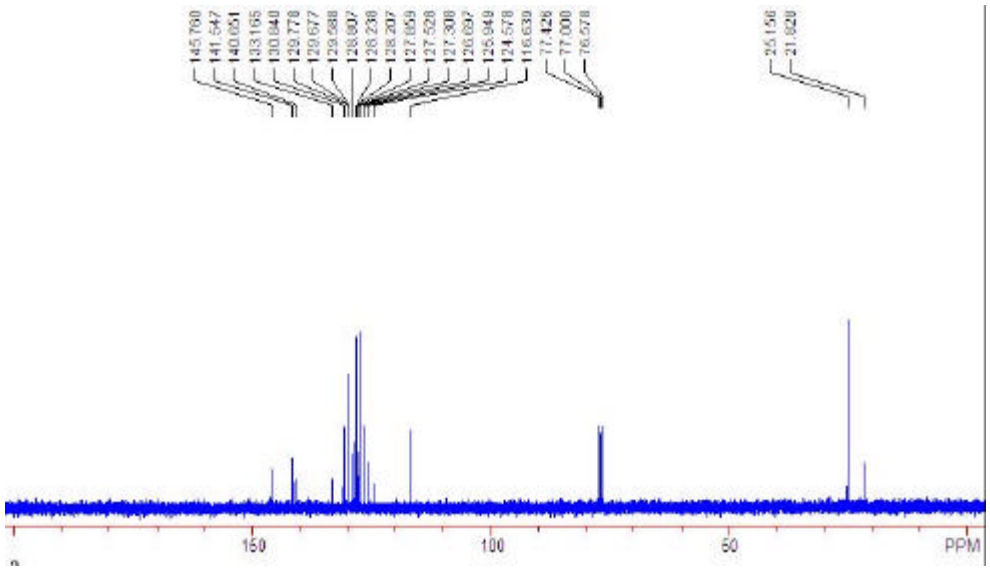
General Remarks. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J*-values are in Hz. Mass spectra were recorded by EI and MALDI methods, and HRMS was measured on a Finnigan MA^+ mass spectrometer. CHN microanalyses were recorded on a Carlo-Erba 1106 analyzer. THF and toluene were distilled from sodium (Na) under argon (Ar) atmosphere. CH_3CN and 1,2-dichloroethane were distilled from CaH_2 under argon (Ar) atmosphere. 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 increased pressure.

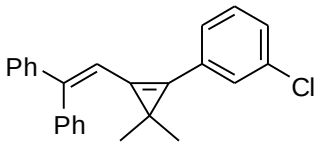
General Procedure. Under an argon atmosphere, arylvinylcyclopropenes **1** (0.2 mmol), $AgSbF_6$ (0.01 mmol), $AuPPh_3Cl$ (0.01 mmol), DBU (0.1 mmol) and DCE (1.0 mL) were added into an Schlenk tube. The reaction mixture was stirred at 50 ^{o}C until the reaction completed. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2).



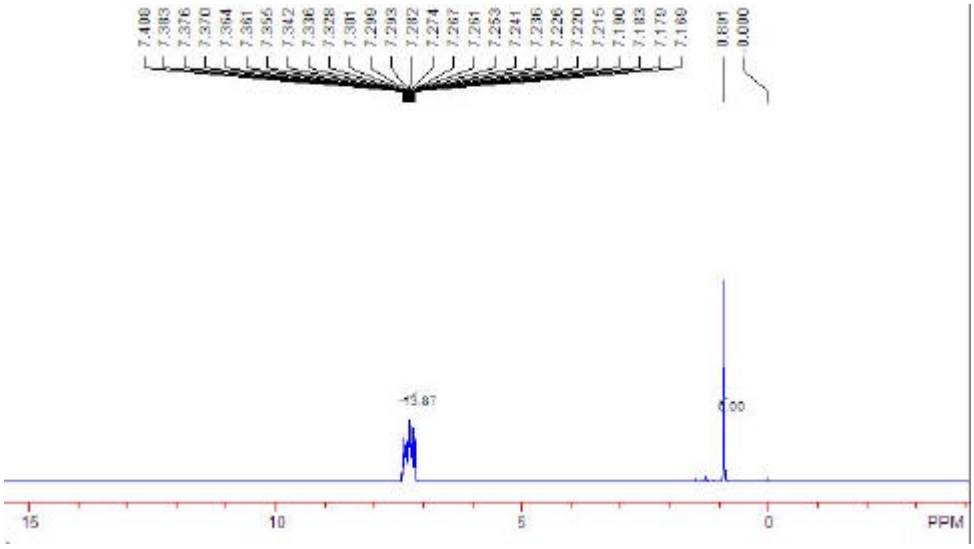
(2-(2-(2-chlorophenyl)-3,3-dimethylcycloprop-1-enyl)ethene-1,1-diyl)dibenzene (1i). A yellow oil; IR (CH_2Cl_2): ν 3056, 3024, 2960, 2917, 2853, 1790, 1770, 1651, 1558, 1539, 1505, 1469, 1361, 1054, 1031, 754, 583 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 0.83 (6H, s, CH_3), 7.17-7.45 (14H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.8, 25.2, 116.6, 124.6, 126.0, 126.7, 127.3, 127.5, 127.9, 128.22, 128.25, 128.8, 129.6, 129.7, 129.8, 130.8, 133.2, 140.7, 141.6, 145.8; MS (EI) *m/z* (%): 356 (22.60) [M^+], 358 (7.94), 357 (6.60), 343 (34.87), 341 (100), 306 (35.90), 291 (36.90), 130 (42.66); HRMS (EI) Calcd. for $C_{25}H_{21}Cl$ (M^+) requires 356.1332, Found: 356.1335.

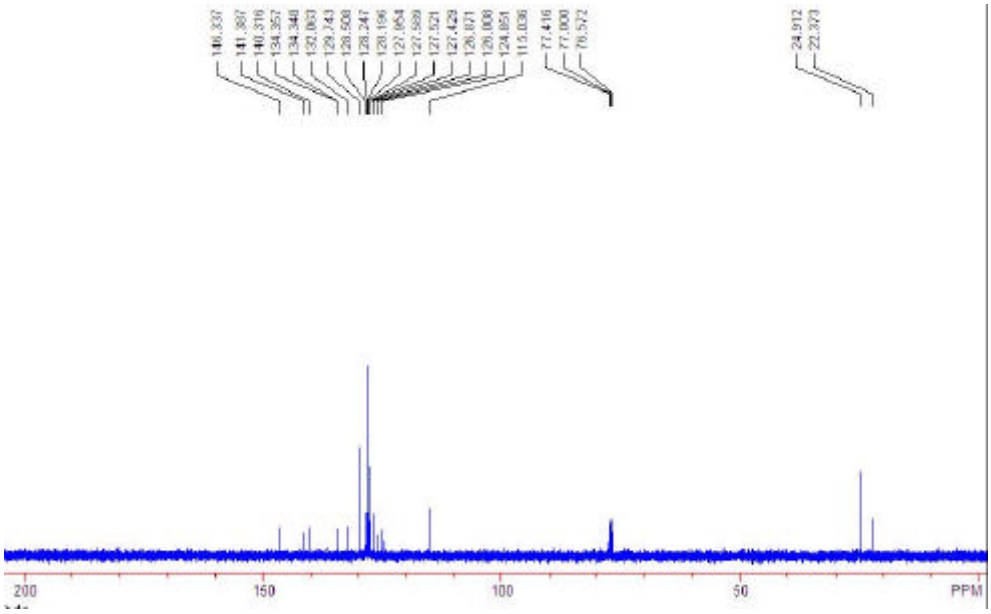


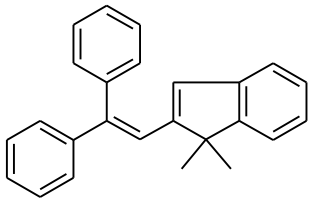




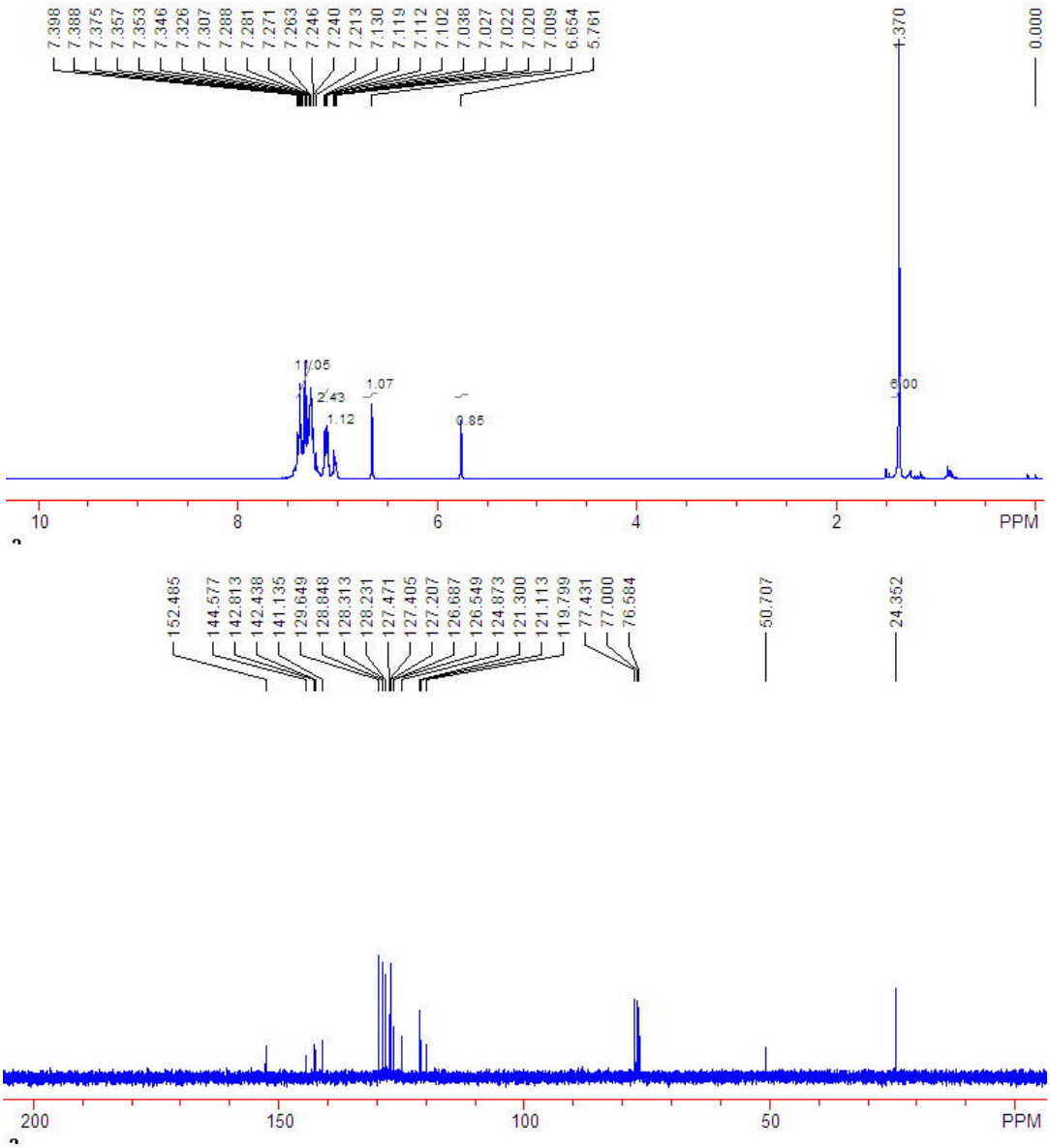
(2-(2-(3-chlorophenyl)-3,3-dimethylcycloprop-1-enyl)ethene-1,1-diyl)dibenzene (1j). A yellow oil; IR (CH_2Cl_2): ν 3058, 3024, 2960, 2930, 2854, 1770, 1732, 1714, 1695, 1590, 1574, 1471, 1455, 984, 762, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 0.89 (6H, s, CH_3), 7.17-7.41 (14H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 22.4, 24.9, 115.0, 124.9, 126.0, 126.9, 127.4, 127.5, 127.6, 128.0, 128.3, 128.5, 129.7, 132.0, 134.4, 140.3, 141.4, 146.3; MS (EI) *m/z* (%): 356 (26.25) [M^+], 358 (9.52), 357 (8.16), 343 (35.89), 341 (100), 306 (33.84), 229 (38.64), 130 (40.98); HRMS (EI) Calcd. for $C_{25}H_{21}Cl$ (M^+) requires 356.1332, Found: 356.1315.

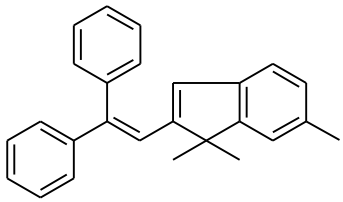






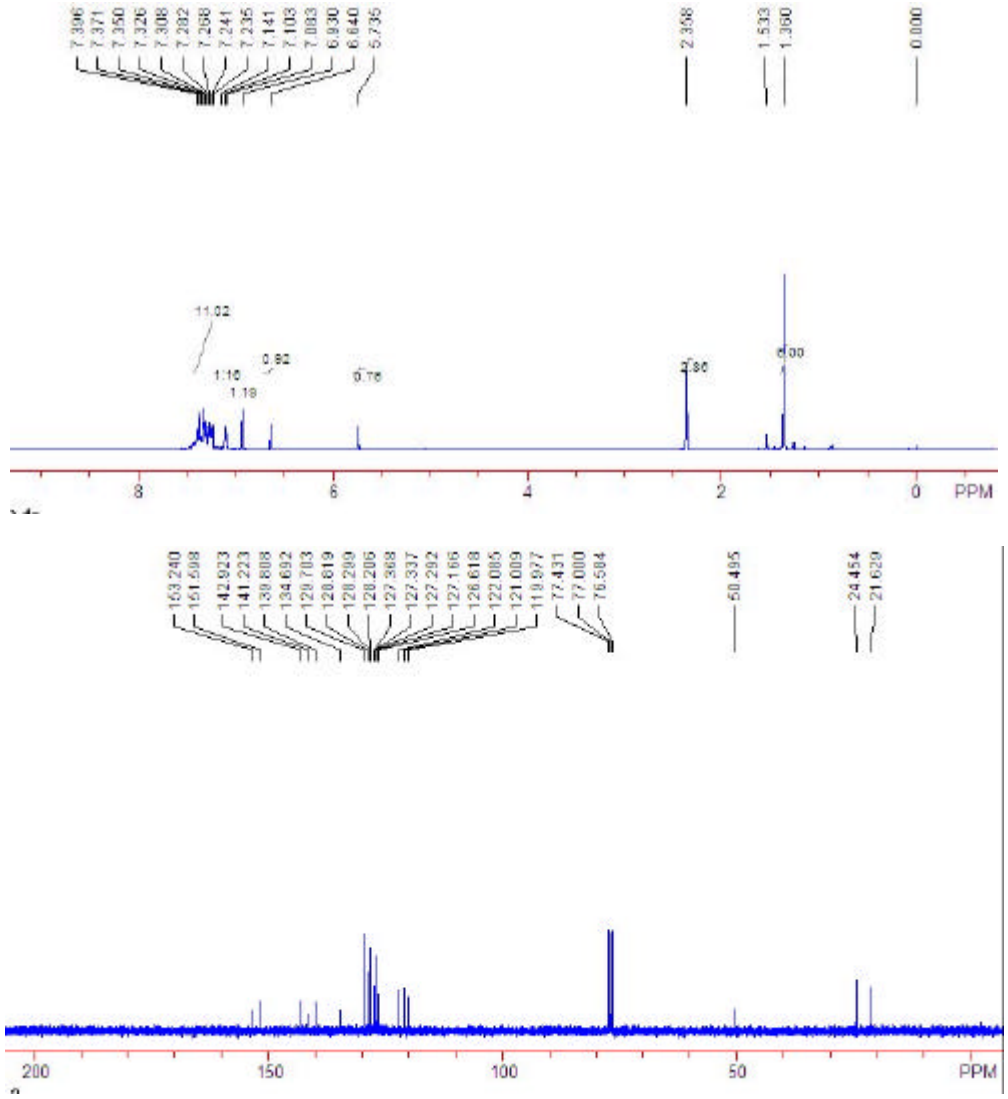
2-(2,2-diphenylvinyl)-1,1-dimethyl-1*H*-indene (2a). A yellow solid, m.p. 87-89 ^{o}C; IR (CH_2Cl_2): ν 3058, 3020, 2959, 2922, 2862, 1598, 1491, 1467, 1443, 1294, 1174, 1154, 1118, 1098, 1073, 890, 749, 699, 639 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.37 (6H, s, CH_3), 5.76 (1H, s, CH), 6.65 (1H, s, CH), 7.01-7.04 (1H, m, Ar), 7.10-7.13 (2H, m, Ar), 7.21-7.40 (11H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 24.4, 50.7, 119.8, 121.1, 121.3, 124.9, 126.5, 126.7, 127.2, 127.4, 127.5, 128.2, 128.3, 128.8, 129.6, 141.1, 142.4, 142.8, 144.6, 152.5, 152.9; MS (EI) *m/z* (%): 322 (100) [M^+], 323 (27.59), 307 (44.77), 292 (26.90), 291 (29.40), 229 (38.18), 215 (24.31), 145 (24.43); Anal. Calcd. for $C_{25}H_{22}$ requires C, 93.12; H, 6.88%. Found: C, 92.72; H, 6.77%.

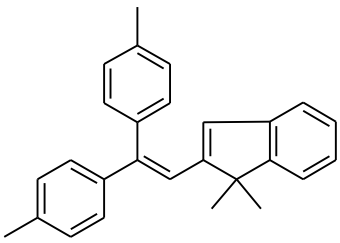




2-(2,2-diphenylvinyl)-1,1,6-trimethyl-1*H*-indene (2b). A yellow oil; IR (CH_2Cl_2): ν 3055, 3022, 2958, 2922, 2859, 1714, 1597, 1495, 1460, 1443, 1538, 1030, 890, 862, 809, 761, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.36 (6H, s, CH_3), 2.36 (3H, s, CH_3), 5.74 (1H, s, CH), 6.64 (1H, s, CH), 6.93 (1H, s, Ar), 7.08-7.14 (1H, m, Ar), 7.24-7.40 (11H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.6, 24.4, 50.5, 120.0, 121.0, 122.1, 126.6, 127.1, 127.2, 127.3, 127.4, 128.2, 128.3, 128.8, 129.7, 134.7, 139.8, 141.2, 142.9, 151.6, 153.2; MS (EI) *m/z*

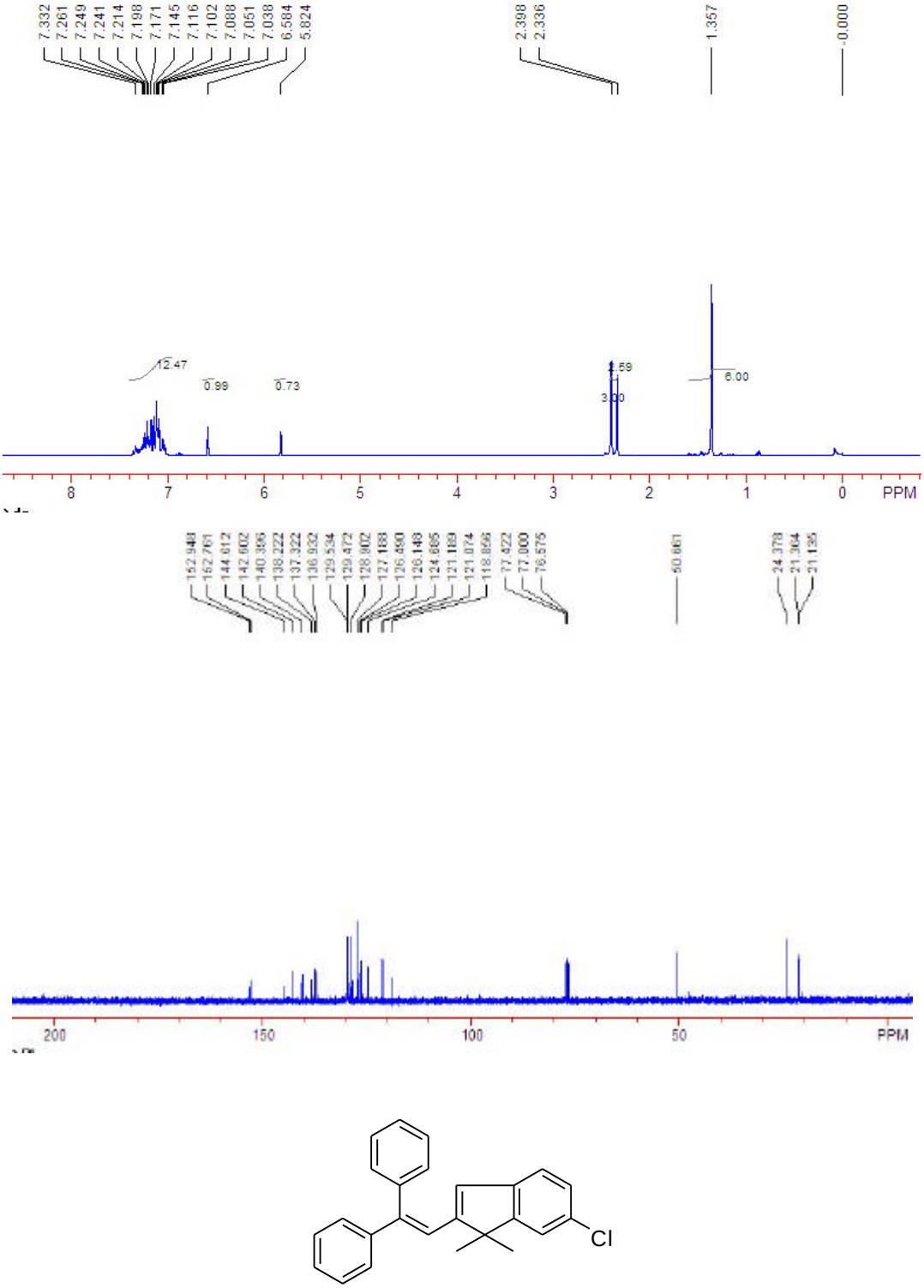
(%): 336 (100) [M^+], 337 (30.08), 334 (39.90), 321 (35.17), 319 (32.18), 243 (24.70), 151 (20.19), 145 (22.07); HRMS (EI) Calcd. for $C_{26}H_{24}$ (M^+) requires 336.1878, Found: 336.1884.





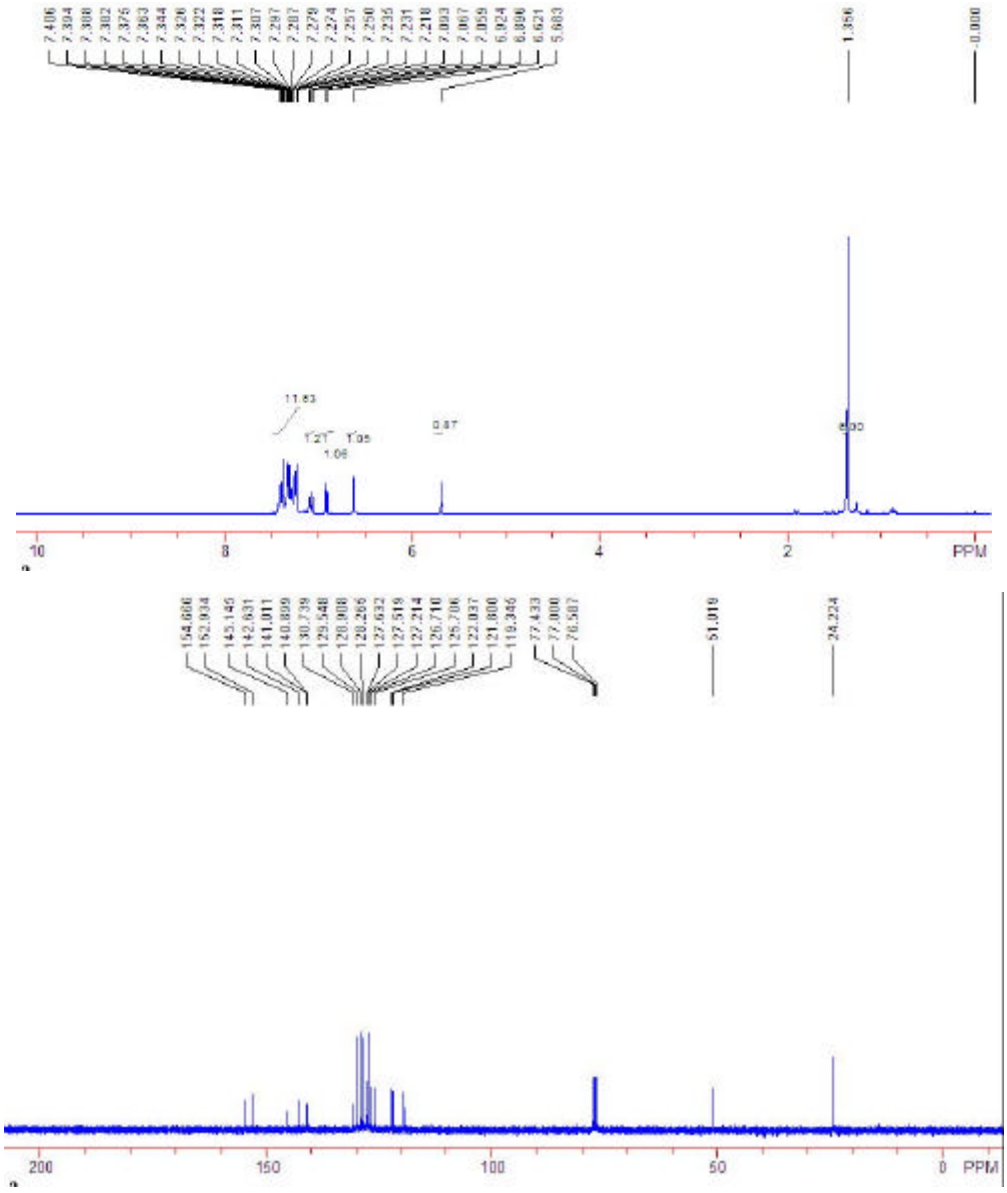
2-(2,2-dip-tolylvinyl)-1,1-dimethyl-1*H*-indene (2c). A yellow solid, m.p. 172-174 ^oC; IR (CH_2Cl_2): ν 2956, 2911, 2844, 1549, 1506, 1459, 1448, 1405, 1365, 1187, 1014, 885, 848, 815, 750, 629, 552 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.36 (6H, s, CH_3), 2.34 (3H, s, CH_3), 2.40 (3H, s, CH_3), 5.82 (1H, s, CH), 6.58 (1H, s, CH), 7.04-7.33 (12H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 21.2, 21.4, 24.4, 50.7, 118.9, 121.1, 121.2, 124.7, 126.1, 126.5, 127.2,

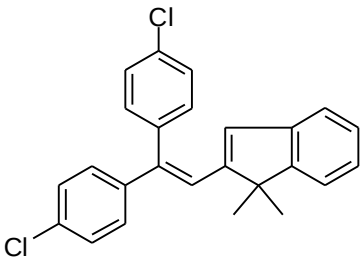
128.9, 129.4, 129.5, 136.9, 137.3, 138.2, 140.4, 142.6, 144.6, 152.8, 153.0; MS (EI) *m/z* (%): 350 (100) [M^+], 351 (29.65), 349 (25.65), 348 (74.48), 335 (23.45), 333 (51.24), 243 (26.34), 151 (35.44); Anal. Calcd. for $C_{27}H_{26}$ requires C, 92.52; H, 7.48; N, 3.03%. Found: C, 92.51; H, 7.31%.



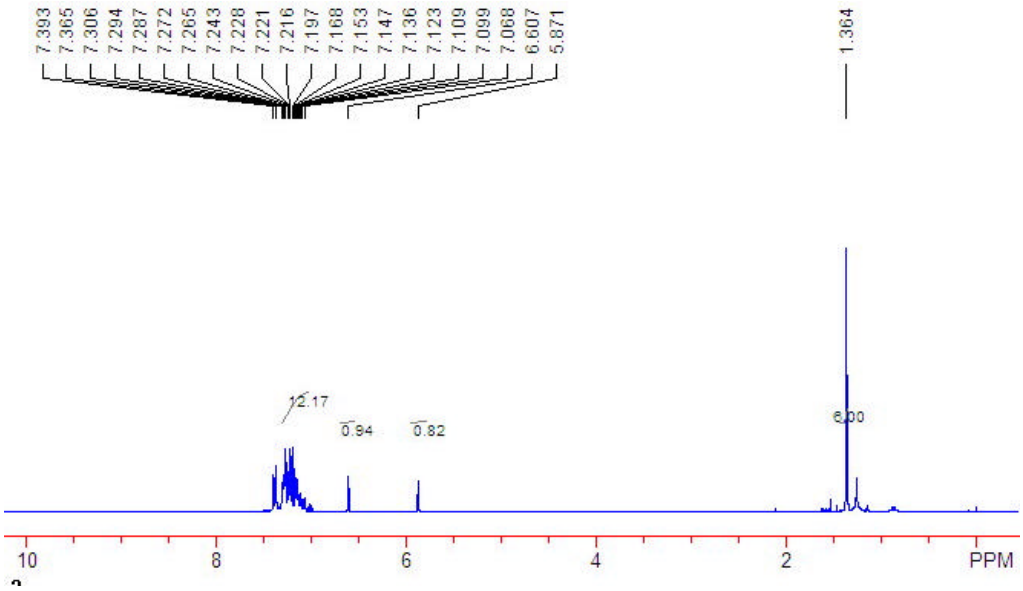
6-chloro-2-(2,2-diphenylvinyl)-1,1-dimethyl-1*H*-indene (2d). A yellow solid, m.p. 118-120

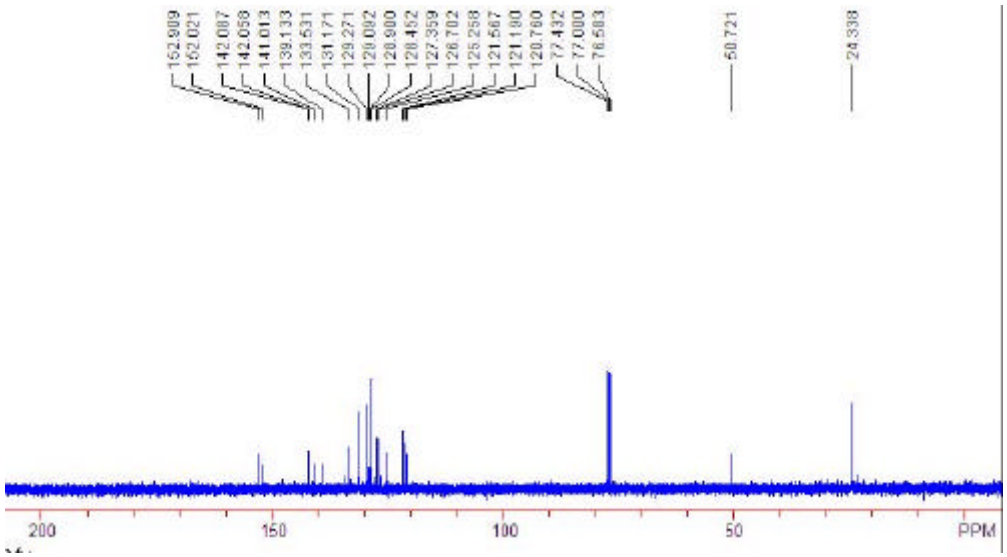
^{o}C; IR (CH_2Cl_2): ν 3056, 3021, 2960, 2924, 2865, 1715, 1682, 1661, 1557, 1494, 1463, 1455, 1445, 1073, 983, 877, 764, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.36 (6H, s, CH_3), 5.68 (1H, s, CH), 6.62 (1H, s, CH), 6.91 (1H, d, *J* = 8.4 Hz, Ar), 7.06 (1H, dd, *J* = 10.2, 2.4 Hz, Ar), 7.21-7.41 (11H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 24.2, 51.0, 119.3, 121.8, 122.0, 125.7, 126.7, 127.2, 127.5, 127.6, 128.3, 128.9, 129.5, 130.7, 140.9, 141.0, 142.6, 145.1, 152.9, 154.7; MS (EI) *m/z* (%): 356 (100) [M^{+}], 358 (35.71), 357 (29.75), 341 (26.30), 291 (38.07), 289 (20.67), 263 (21.81) 145 (24.90); Anal. Calcd. for $C_{25}H_{21}Cl$ requires C, 84.14; H, 5.93 %. Found: C, 84.55; H, 5.87%.

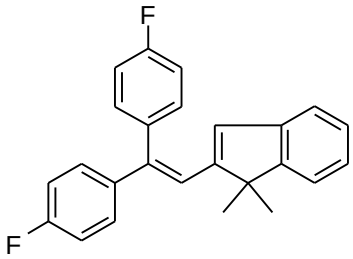




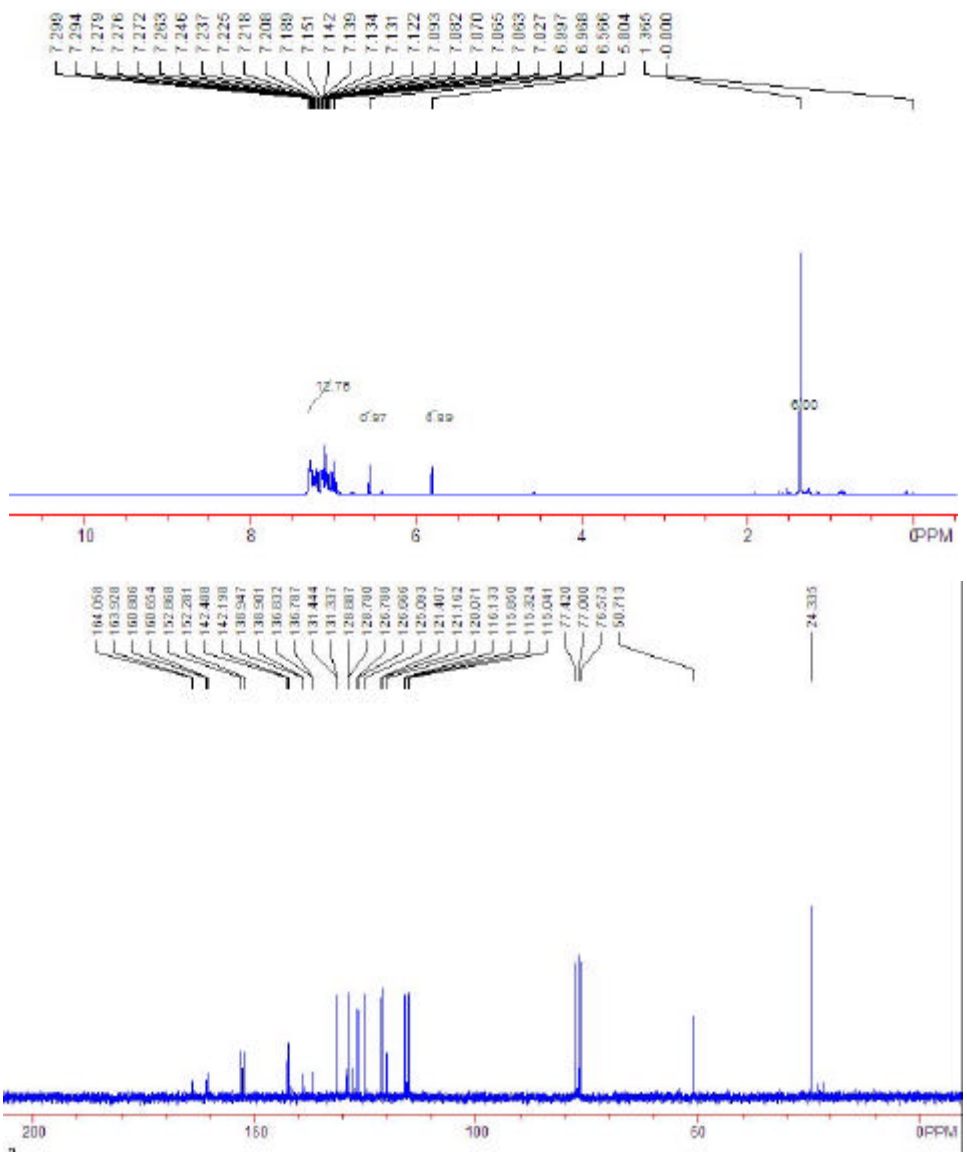
6-chloro-2-(2,2-diphenylvinyl)-1,1-dimethyl-1*H*-indene (2e). A yellow oil; IR (CH_2Cl_2): ν 3064, 2961, 2925, 2858, 1750, 1714, 1589, 1491, 1468, 1362, 1220, 1091, 1015, 829, 753, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.36 (6H, s, CH_3), 5.87 (1H, s, CH), 6.61 (1H, s, CH), 7.07-7.37 (11H, m, Ar), 7.38 (1H, d, *J* = 8.4 Hz, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 24.3, 50.7, 120.8, 121.2, 121.6, 125.3, 126.7, 127.4, 128.5, 128.9, 129.1, 129.3, 131.2, 133.5, 139.1, 141.0, 142.1, 142.2, 152.0, 152.9; MS (EI) *m/z* (%): 390 (100) [M^+], 392 (42.32), 391 (39.66), 388 (92.64), 375 (50.00), 302 (54.27), 151 (93.30), 150 (78.61); HRMS (EI) Calcd. for $C_{25}H_{20}Cl_2$ (M^+) requires 390.0942, Found: 390.0936.

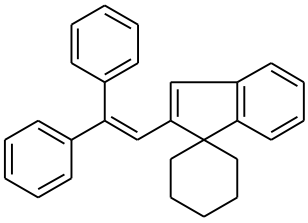






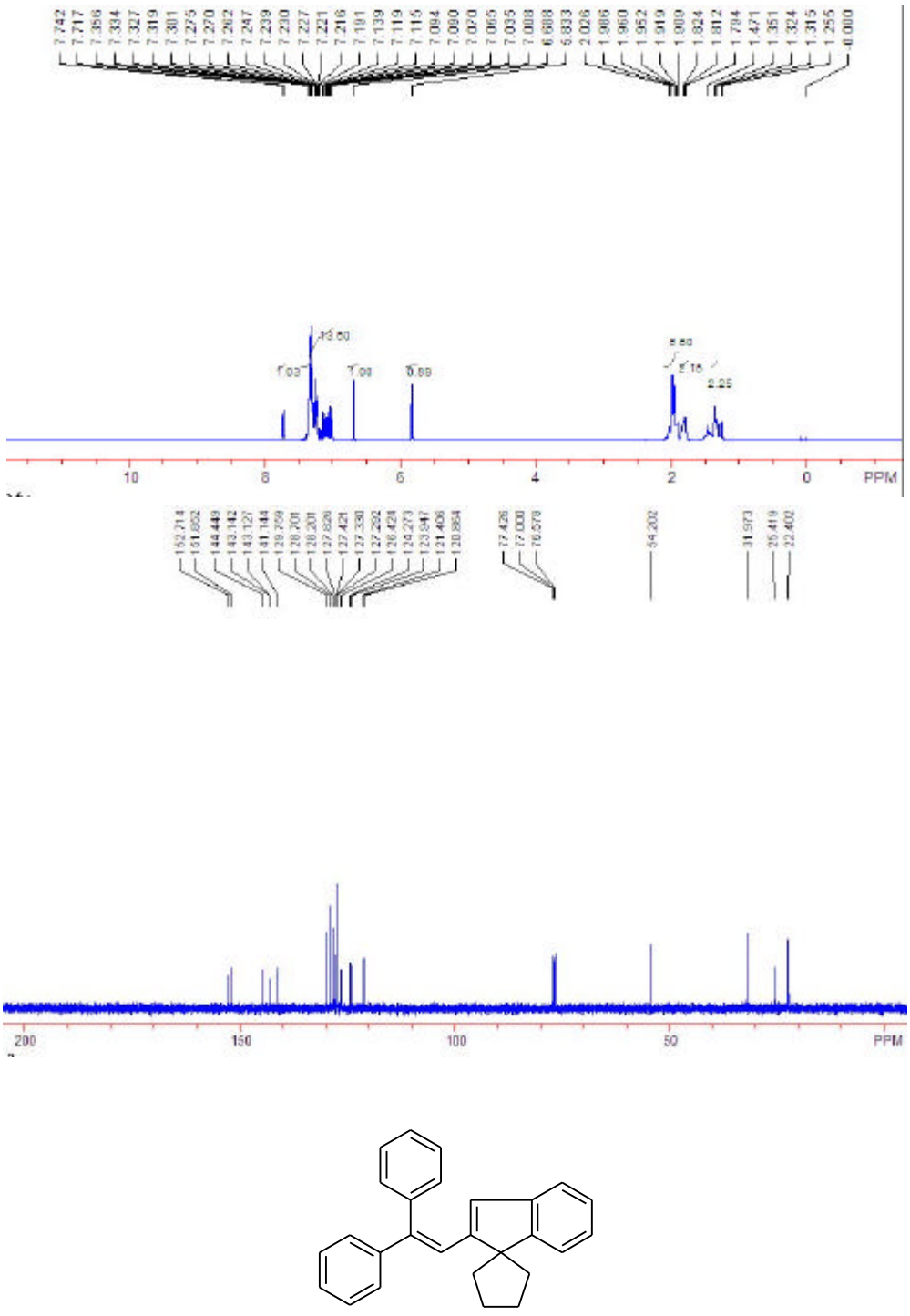
2-(2,2-bis(4-fluorophenyl)vinyl)-1,1-dimethyl-1*H*-indene (2f). A yellow solid, m.p. 129-131 ^{o}C; IR (CH_2Cl_2): ν 3065, 2961, 2924, 2850, 1715, 1651, 1599, 1506, 1455, 1410, 1232, 1154, 1014, 976, 834, 794, 753 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.37 (6H, s, CH_3), 5.80 (1H, s, CH), 6.57 (1H, s, CH), 6.97-7.30 (12H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 24.3, 50.7, 115.2 (d, J_{C-F} = 21.2 Hz), 116.0 (d, J_{C-F} = 21.2 Hz), 120.1, 121.2, 121.4, 125.1, 126.7, 126.8, 128.8 (d, J_{C-F} = 7.4 Hz), 131.4 (d, J_{C-F} = 7.4 Hz), 136.8 (d, J_{C-F} = 3.6 Hz), 138.9 (d, J_{C-F} = 3.6 Hz), 142.2, 142.5, 152.3, 152.9, 162.3 (d, J_{C-F} = 245.6 Hz), 162.4 (d, J_{C-F} = 245.6 Hz); MS (EI) *m/z* (%): 358 (100) [M^{+}], 359 (28.38), 343 (29.07), 328 (18.53), 327 (20.22), 247 (37.05), 233 (16.12), 154 (14.60); Anal. Calcd. for $C_{25}H_{20}F_2$ requires C, 83.77; H, 5.62 %. Found: C, 83.41; H, 5.56%.





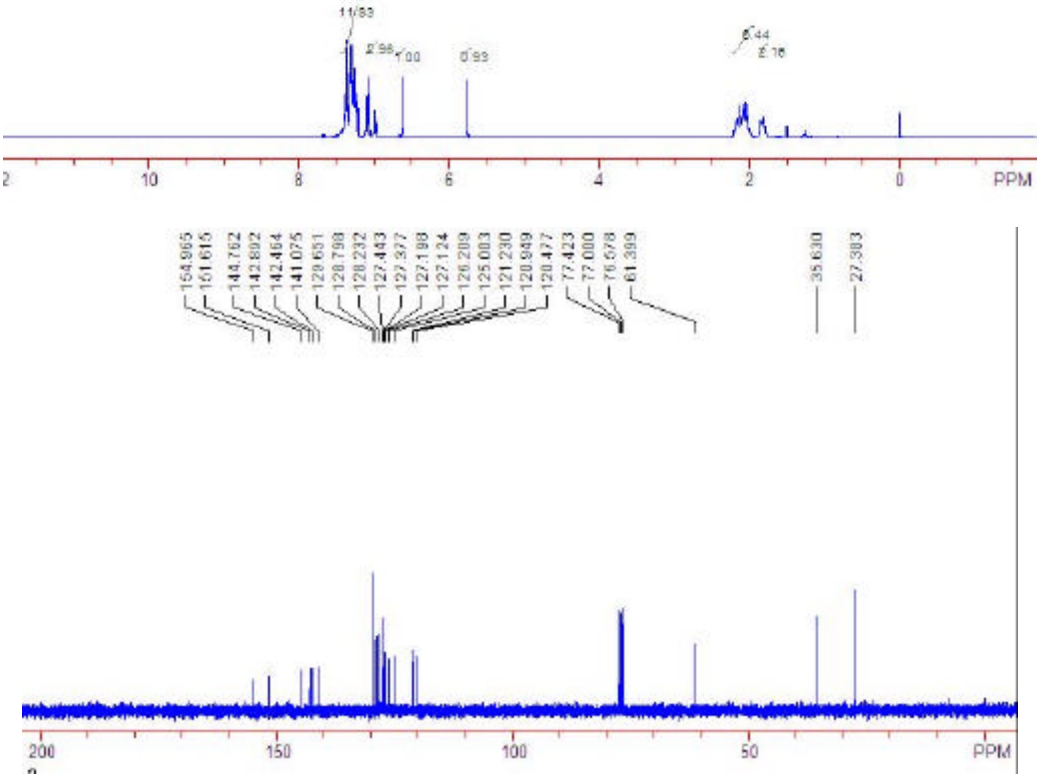
2'-(2,2-diphenylvinyl)spiro[cyclohexane-1,1'-indene] (2g). A yellow solid, m.p. 151-152 ^{o}C; IR (CH_2Cl_2): ν 3057, 3022, 2929, 2865, 2845, 1714, 1699, 1682, 1598, 1557, 1495, 1456, 1360, 1026, 983, 761, 746, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.26-1.47 (2H, m, CH_2), 1.79-1.82 (2H, m, CH_2), 1.91-2.04 (6H, m, CH_2), 5.83 (1H, s, CH), 6.69 (1H, s, CH), 7.01-7.36 (13H, m, Ar), 7.73 (1H, d, *J* = 7.5 Hz, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 22.4, 25.4, 32.0, 54.2, 120.9, 121.4, 123.9, 124.3, 126.4, 127.29, 127.33, 127.4, 127.8, 128.2, 128.7, 129.8,

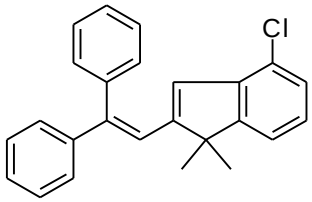
141.2, 143.13, 143.14, 144.5, 151.9, 152.7; MS (EI) *m/z* (%): 362 (100) [M^+], 363 (33.92), 360 (14.17), 305 (16.26), 291 (27.54), 215 (21.81), 151 (13.63), 145 (13.79); Anal. Calcd. for $C_{28}H_{26}$ requires C, 92.77; H, 7.23 %. Found: C, 93.08; H, 7.21%.



2'-(2,2-diphenylvinyl)spiro[cyclopentane-1,1'-indene] (2h). A yellow solid, m.p. 80-82 ^oC; IR (CH_2Cl_2): ν 3059, 3022, 2974, 2852, 1586, 1573, 1488, 1456, 1440, 1361, 1085, 1027, 890, 846, 777, 740, 692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.81-1.86 (2H, m, CH_2), 2.03-2.18 (6H, m, CH_2), 5.76 (1H, s, CH), 6.62 (1H, s, CH), 6.63-7.00 (1H, m, Ar), 7.07-7.11

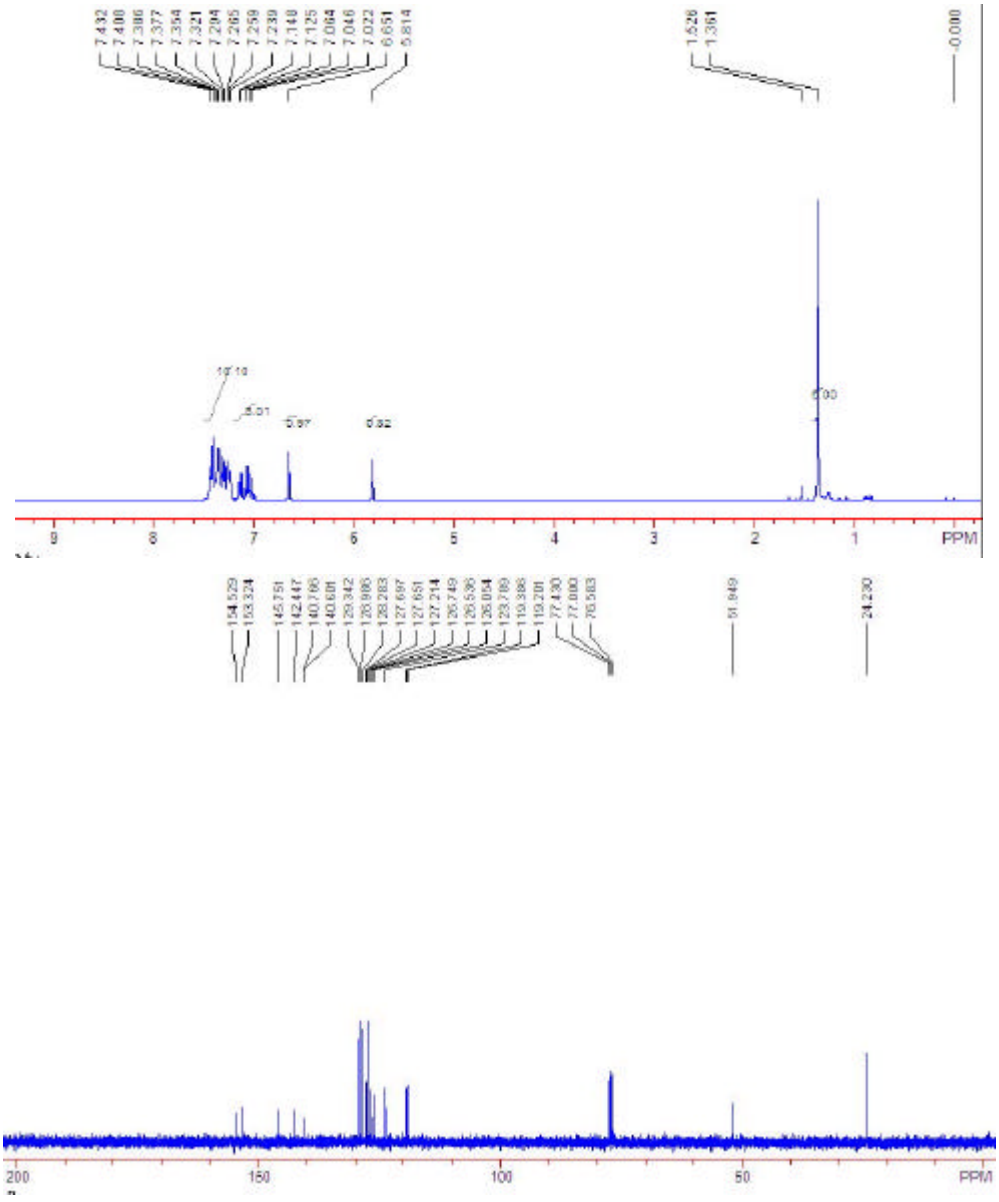
(2H, m, Ar), 7.22-7.41 (11H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 27.4, 35.6, 61.4, 120.5, 121.0, 121.2, 125.0, 126.2, 127.1, 127.2, 127.4, 127.5, 128.2, 128.8, 129.7, 141.1, 142.5, 142.9, 144.8, 151.6, 155.0; MS (EI) *m/z* (%): 348 (100) [M^+], 349 (31.43), 346 (48.18), 305 (19.98), 292 (19.94), 291 (65.36), 151 (24.93), 145 (24.29); Anal. Calcd. for $C_{27}H_{24}$ requires C, 93.06; H, 6.94 %. Found: C, 92.83; H, 6.62 %.

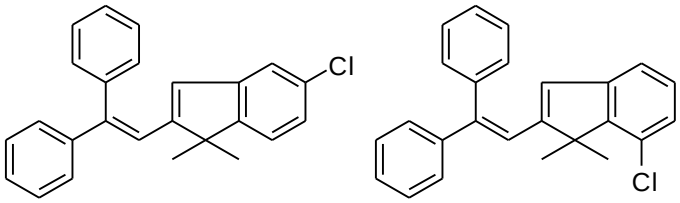




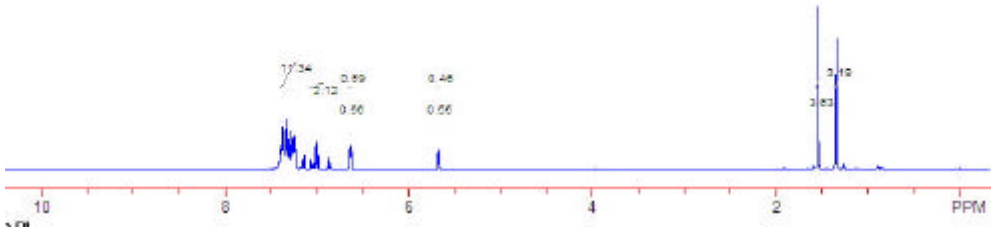
4-chloro-2-(2,2-diphenylvinyl)-1,1-dimethyl-1*H*-indene (2i). A yellow solid, m.p. 156-157 ^{o}C; IR (CH_2Cl_2): ν 3056, 3022, 2952, 2866, 1714, 1699, 1598, 1558, 1489, 1462, 1445, 1219,

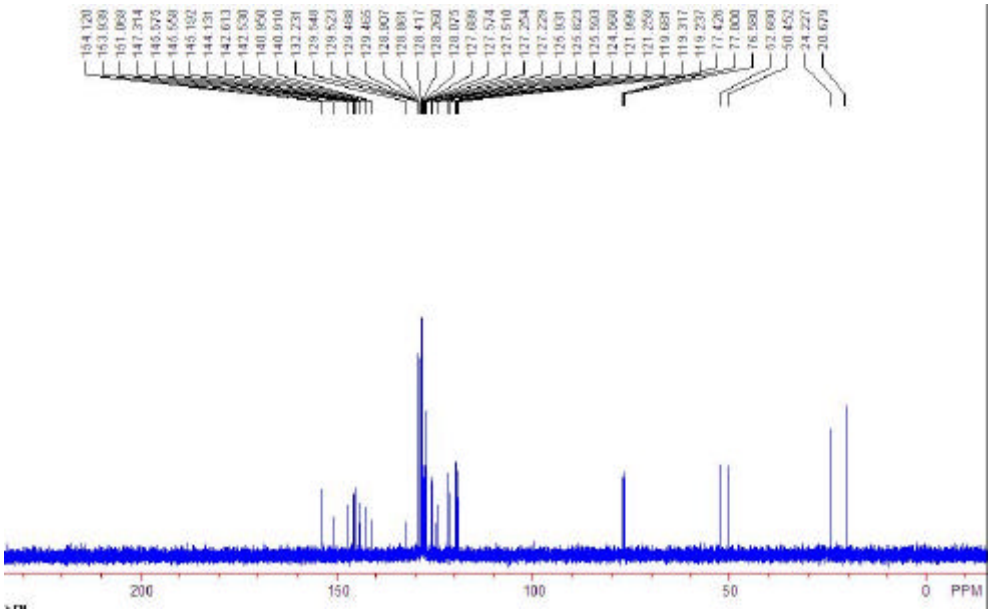
1029, 972, 890, 763, 749, 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.36 (6H, s, CH_3), 5.81 (1H, s, CH), 6.65 (1H, s, CH), 7.02-7.06 (2H, m, Ar), 7.14 (1H, d, *J* = 6.9 Hz, Ar), 7.24-7.43 (10H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 24.2, 52.0, 119.2, 119.4, 123.8, 126.1, 126.5, 126.7, 127.2, 127.65, 127.70, 128.3, 129.0, 129.3, 140.6, 140.8, 142.4, 145.8, 153.3, 154.5; MS (EI) *m/z* (%): 356 (100) [M^+], 358 (38.10), 357 (30.85), 341 (27.08), 291 (29.94), 289 (20.32), 263 (19.27), 145 (29.20); HRMS (EI) Calcd. for $C_{25}H_{21}Cl$ (M^+) requires 356.1332, Found: 356.1328.





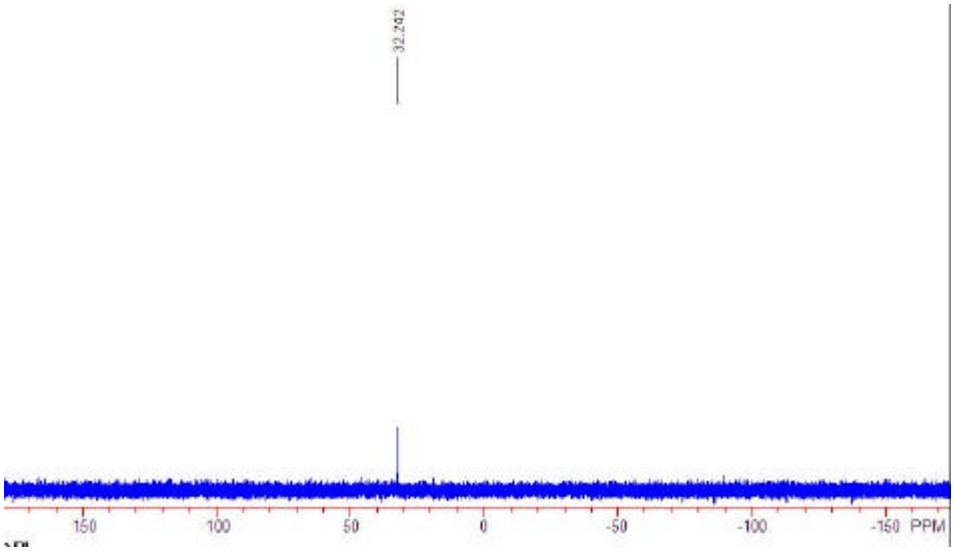
5-chloro-2-(2,2-diphenylvinyl)-1,1-dimethyl-1*H*-indene and 7-chloro-2-(2,2-diphenylvinyl)-1,1-dimethyl-1*H*-indene (2j and 2j'). 1:1 mixtures. A yellow oil; IR (CH_2Cl_2): ν 3057, 2962, 2926, 2865, 1715, 1596, 1491, 1466, 1447, 1359, 1182, 1077, 1030, 959, 762, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.34 and 1.54 (6H, s, CH_3), 5.66 and 5.68 (1H, s, CH), 6.63 and 6.64 (1H, s, CH), 6.86-7.39 (13H, m, Ar); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 20.7, 24.2, 50.5, 52.7, 119.2, 119.3, 119.7, 121.3, 122.0, 124.6, 125.6, 125.8, 125.9, 127.2, 127.3, 127.5, 127.6, 127.7, 128.1, 128.3, 128.4, 128.86, 128.91, 129.47, 129.49, 129.52, 129.55, 132.2, 140.9, 141.0, 142.5, 142.6, 144.1, 145.2, 145.56, 145.58, 147.3, 151.1, 153.9, 154.1; MS (EI) *m/z* (%): 356 (100) [M^+], 358 (37.91), 357 (30.54), 341 (35.38), 291 (36.76), 289 (22.82), 263 (20.54), 145 (28.71); HRMS (EI) Calcd. for $C_{25}H_{21}Cl$ (M^+) requires 356.1332, Found: 356.1336.



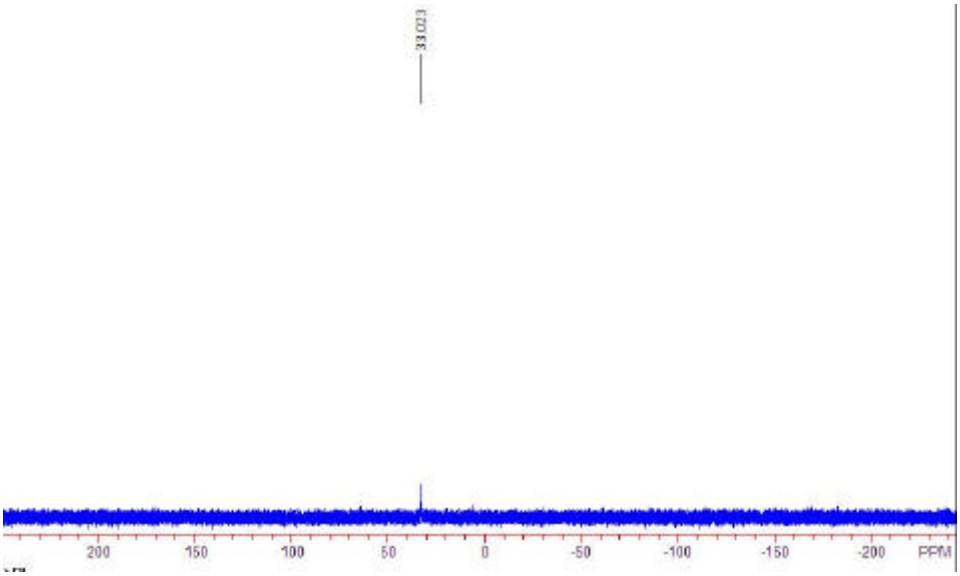

154.120
153.939
151.869
147.314
145.570
145.558
145.192
144.151
142.613
142.530
140.950
140.910
132.231
129.548
129.523
129.488
129.465
128.907
128.861
128.417
128.290
128.075
127.889
127.574
127.510
127.254
127.229
125.831
125.623
125.593
124.868
121.969
121.250
119.881
119.317
119.237
77.426
77.000
76.588
52.690
50.452
24.227
20.679
200
150
100
50
0
PPM

^{31}P NMR spectroscopic trace of $AuPPh_3Cl/AgSbF_6$ in the presence of Et_3N or DBU.

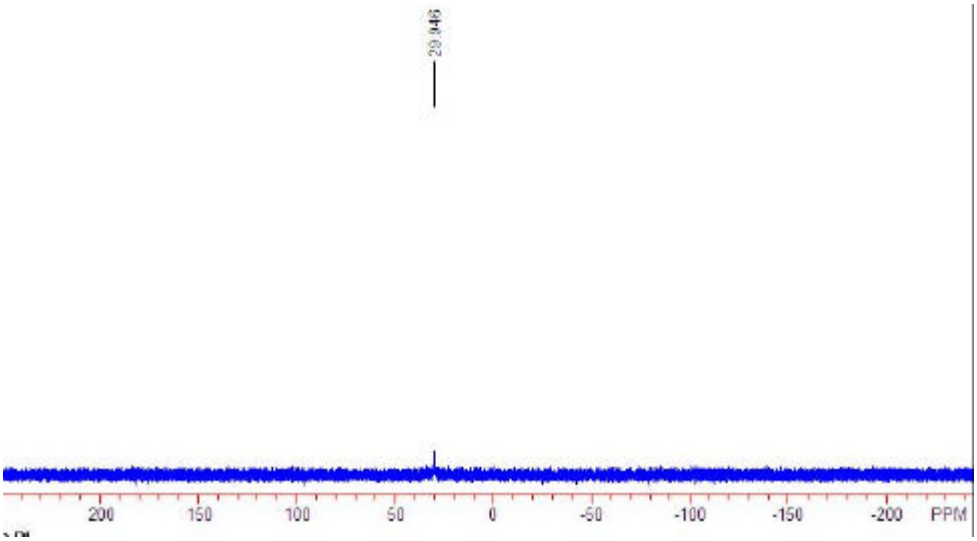
$AuPPh_3Cl/AgSbF_6$ = 0.05 mmol/0.05 mmol, ^{31}P NMR (121 MHz, $CDCl_3$, TMS): δ 32.2.

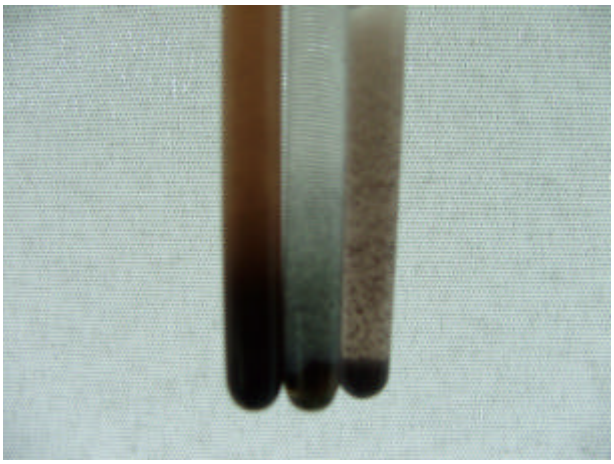


$AuPPh_3Cl/AgSbF_6$/DBU = 0.05mmol/0.05mmol/0.05mmol, ^{31}P NMR (121 MHz, $CDCl_3$, TMS): δ 33.0.



$AuPPh_3Cl/AgSbF_6/Et_3N$ = 0.05mmol/0.05mmol/0.05mmol, ^{31}P NMR (121 MHz, $CDCl_3$, TMS): δ 29.9.





From left to right is $AuPPh_3Cl/AgSbF_6/DBU$, $AuPPh_3Cl/AgSbF_6$ and $AuPPh_3Cl/AgSbF_6/Et_3N$ solution. The colors of the catalyst systems are significantly different, suggesting the coordination between Gold(I) and the bases.