

Lewis Acid-Catalysed Regioselective Hydroheteroarylation of Pentafulvenes

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General Methods

All chemicals were of the best grade commercially available and are used without further purification. All solvents were purified according to standard procedure and dry solvents were obtained according to the literature methods and stored over molecular sieves. Analytical thin layer chromatography was performed on glass plates coated with silica gel containing calcium sulfate binder. Gravity column chromatography was performed using 60-120 or 100-200 mesh silica gel and mixtures of hexane-ethyl acetate were used for elution.

Melting points were determined on a Buchi melting point apparatus and are uncorrected. Proton nuclear magnetic resonance spectra (^1H NMR) were recorded on a Bruker AMX 500 spectrophotometer (CDCl_3 as solvent). Chemical shifts for ^1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform-d (δ 7.25, singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (double doublet); m (multiplet). Coupling constants are reported as J value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform-d (δ 77.03, triplet). For the structural assignment, 2-D NMR experiments were also conducted (^1H - ^1H COSY, ^1H - ^{13}C HSQC, ^1H - ^{13}C HMBC). Mass spectra were recorded under EI/HRMS at 60,000 resolution using Thermo Scientific Exactive mass spectrometer. IR spectra were recorded on Bruker FT-IR spectrometer.

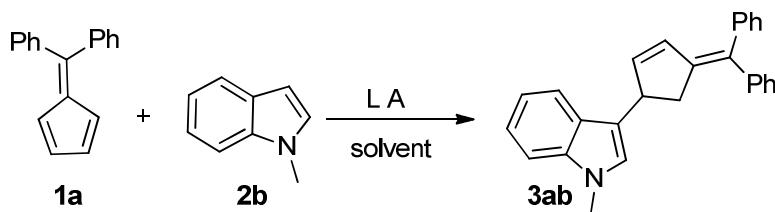
General Procedure for the Lewis acid-catalysed hydroarylation of pentafulvenes

A mixture of pentafulvene (1.0 equiv), indole (1.0 equiv) and Cu(OTf)₂ (2 mol %) were weighed in a reaction tube, CH₃CN (2 mL) was added and allowed to stir at room temperature for 2 hours. The solvent was evaporated in *vacuo* and the residue on silica gel (100-200 mesh) column chromatography with mixtures of hexane-ethyl acetate yielded the products.

Procedure for the Lewis acid-catalysed hydroarylation of alkyl substituted pentafulvenes

A mixture of pentafulvene and indole were weighed in a reaction tube, CH₃CN (2 mL) was added and cooled to 0 °C. To the stirred solution 2 mol % of Cu(OTf)₂ was added and left at 0 °C until the completion of the reaction. The solvent was evaporated in *vacuo* and the residue on silica gel (100-200 mesh) column chromatography with mixtures of hexane-ethyl acetate yielded the products. The products obtained were further purified by HPLC technique.

Table S-1: Optimization of the reaction condition

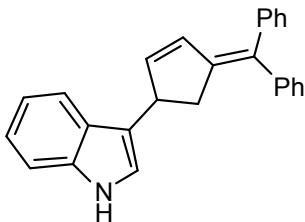


entry	Lewis acid	solvent	yield (%)
1	Sc(OTf) ₃	CH ₃ CN	91
2	Cu(OTf) ₂	CH ₃ CN	99
3	Yb(OTf) ₃	CH ₃ CN	-
4	Zn(OTf) ₂	CH ₃ CN	22
5	Sn(OTf) ₂	CH ₃ CN	93
6	Fe(OTf) ₃	CH ₃ CN	-
7	AgOTf	CH ₃ CN	-
8	BF ₃ OEt ₂	CH ₃ CN	28
9	AlCl ₃	CH ₃ CN	18
10	Cu(OTf) ₂	Toluene	45
11	Cu(OTf) ₂	DCE	25
12	Cu(OTf) ₂	THF	-
13	Cu(OTf) ₂	DMF	-
14	-	CH ₃ CN	-

^a Reaction conditions: fulvene (1.0 equiv), indole (1.0 equiv), Lewis acid (2 mol %) Solvent (2 mL), rt, 2 h.

Characterisation of the products

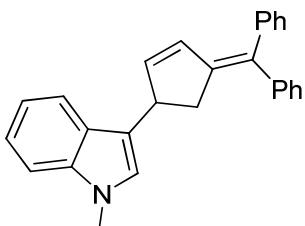
3-(4-(diphenylmethylene)cyclopent-2-enyl)-1H-indole (3aa)



Yield: 44 mg (98%) as colourless foam; $R_f = 0.45$ (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3369, 3053, 2918, 1703, 1595, 1489, 1452, 1339, 1223, 742, 701 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 7.91 (brs, 1H), 7.68 (d, $J = 8$ Hz, 1H), 7.39-7.36 (m, 4H), 7.31-7.20 (m, 7H), 7.16-7.13 (m, 2H), 6.98 (s, 1H), 6.60-6.58 (m, 1H), 6.38-6.37 (m, 1H), 4.43 (brs, 1H), 3.31 (dd, $J_1 = 16.5$ Hz, $J_2 = 7.5$ Hz, 1H), 2.95 (dd, $J_1 = 17$ Hz, $J_2 = 4$ Hz, 1H). **$^{13}\text{C NMR}$** (125 MHz, CDCl_3 , TMS): δ 145.0, 142.9, 141.7, 136.7, 133.4, 132.1, 130.2, 129.5, 128.0, 126.6, 126.5, 126.4, 122.1, 120.5, 119.8, 119.4, 119.3, 111.2, 111.1, 42.1, 39.8.

HRMS (ESI): Calcd for $\text{C}_{26}\text{H}_{21}\text{NNa}$: 370.15717; Found: 370.15695.

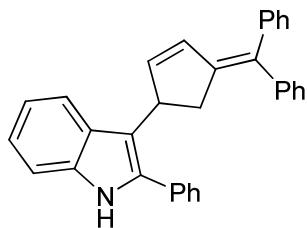
3-(4-(diphenylmethylene)cyclopent-2-enyl)-1-methyl-1H-indole (3ab)



Yield: 46 mg (99%) as colourless foam; $R_f = 0.50$ (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3064, 2902, 2848, 1959, 1878, 1583, 1477, 1361, 1336, 1250, 758, 711 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 7.58 (d, $J = 7.5$ Hz, 1H), 7.32-7.28 (m, 3H), 7.25-7.22 (m, 3H), 7.20-7.18 (m, 5H), 7.15-7.12 (m, 1H), 7.07-7.04 (m, 1H), 6.81 (s, 1H), 6.51 (dd, $J_1 = 5.5$ Hz, $J_2 = 2.5$ Hz, 1H), 6.29 (dd, $J_1 = 5.5$ Hz, $J_2 = 2.5$ Hz, 1H), 4.37-4.35 (m, 1H), 3.73 (s, 3H), 3.24 (dd, $J_1 = 17.5$ Hz, $J_2 = 7.5$ Hz, 1H), 2.87 (dd, $J_1 = 17$ Hz, $J_2 = 4$ Hz, 1H). **$^{13}\text{C NMR}$** (125 MHz, CDCl_3 , TMS): δ 144.9, 142.9, 141.7, 137.4, 133.3, 132.1, 130.2, 130.1, 129.5, 128.0, 127.9, 127.0, 126.4, 126.3, 125.2, 121.7, 119.4, 118.8, 118.3, 109.2, 42.0, 40.1, 32.6.

HRMS (ESI): Calcd for $\text{C}_{27}\text{H}_{23}\text{NNa}$: 384.17282; Found: 384.17228.

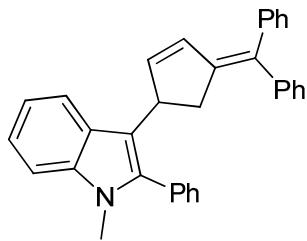
3-(4-(diphenylmethylene)cyclopent-2-enyl)-2-phenyl-1H-indole (3ac)



Yield: 54 mg (99%) as white solid; M.p. = 152-154 °C; R_f . 0.53 (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3864, 3053, 2919, 1599, 1489, 1449, 1308, 742, 699 cm⁻¹. **¹H NMR** (500 MHz, CDCl₃, TMS): δ 7.72 (d, J = 8 Hz, 1H), 7.50-7.47 (m, 2H), 7.43-7.42 (m, 2H), 7.37-7.31 (m, 4H), 7.24-7.22 (m, 8H), 7.19-7.13 (m, 2H), 7.08-7.06 (m, 1H), 6.57 (t, J = 2.5 Hz, 1H), 6.27 (d, J = 5 Hz, 1H), 4.53 (brs, 1H), 3.22 (dd, J_1 = 17 Hz, J_2 = 4.5 Hz, 1H), 3.14 (dd, J_1 = 17 Hz, J_2 = 7.5 Hz, 1H). **¹³C NMR** (125 MHz, CDCl₃, TMS): δ 145.1, 143.0, 142.9, 142.8, 136.3, 134.5, 133.2, 133.0, 132.2, 130.2, 129.5, 128.8, 128.6, 127.9, 127.8, 126.3, 120.5, 119.6, 114.8, 110.9, 42.2, 39.8.

HRMS (ESI): Calcd for C₃₂H₂₅NNa: 446.18847; Found: 446.11809.

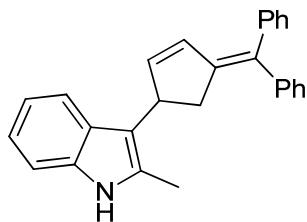
3-(4-(diphenylmethylene)cyclopent-2-enyl)-1-methyl-2-phenyl-1H-indole (3ad)



Yield: 56 mg (99%) as colourless foam; R_f = 0.63 (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3053, 2919, 1599, 1489, 1449, 1308, 1264, 742, 701 cm⁻¹. **¹H NMR** (500 MHz, CDCl₃, TMS): δ 7.72 (d, J = 8 Hz, 1H), 7.50-7.47 (m, 2H), 7.44-7.42 (m, 3H), 7.39-7.32 (m, 3H), 7.27-7.23 (m, 8H), 7.18-7.16 (m, 1H), 7.15-7.12 (m, 1H), 6.54 (dd, J_1 = 7.5 Hz, J_2 = 2 Hz, 1H), 6.25 (dd, J_1 = 7.5 Hz, J_2 = 2 Hz, 1H), 4.26 (brs, 1H), 3.61 (s, 3H), 3.20 (dd, J_1 = 17 Hz, J_2 = 4.5 Hz, 1H), 3.07 (dd, J_1 = 17 Hz, J_2 = 7.5 Hz, 1H). **¹³C NMR** (125 MHz, CDCl₃, TMS): δ 145.3, 143.1, 143.0, 142.9, 137.6, 137.5, 133.0, 131.9, 131.8, 130.9, 130.2, 129.5, 128.4, 128.1, 127.9, 126.5, 126.4, 126.3, 121.8, 120.1, 119.3, 114.9, 109.4, 42.5, 40.1, 30.8.

HRMS (ESI): Calcd for C₃₃H₂₇NNa: 460.20412; Found: 460.20388.

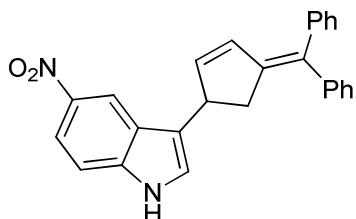
3-(4-(diphenylmethylene)cyclopent-2-en-1-yl)-2-methyl-1H-indole (3ae)



Yield: 52 mg (96%) as colourless foam; $R_f = 0.63$ (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3384, 3048, 2926, 1594, 1491, 1419, 1308, 1265, 740, 699 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 7.62 (brs, 1H), 7.54 (d, $J = 8$ Hz, 1H), 7.33-7.31 (m, 2H), 7.26-7.23 (m, 3H), 7.22-7.20 (m, 5H), 7.14-7.12 (m, 1H), 7.08-7.05 (m, 1H), 7.02-6.99 (m, 1H), 6.55 (dd, $J_1 = 5.5$ Hz, $J_2 = 2.5$ Hz, 1H), 6.24 (dd, $J_1 = 5.5$ Hz, $J_2 = 2.5$ Hz, 1H), 4.36-4.33 (m, 1H), 3.14 (dd, $J_1 = 17$ Hz, $J_2 = 7.5$ Hz, 1H), 2.97 (dd, $J_1 = 17$ Hz, $J_2 = 4.5$ Hz, 1H), 2.36 (s, 3H). **$^{13}\text{C NMR}$** (125 MHz, CDCl_3 , TMS): δ 145.3, 143.0, 142.9, 142.6, 137.8, 135.4, 133.1, 131.9, 130.2, 129.5, 129.0, 128.2, 127.9, 127.7, 126.5, 126.3, 125.3, 121.0, 119.2, 119.0, 113.7, 110.2, 41.8, 39.7, 11.9.

HRMS (ESI): Calcd for $\text{C}_{27}\text{H}_{23}\text{NNa}$: 384.17282; Found: 384.17244.

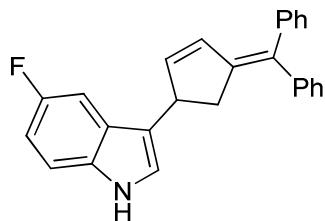
3-(4-(diphenylmethylene)cyclopent-2-enyl)-5-nitro-1H-indole (3af)



Yield: 38 mg (75%) as pale yellow coloured foam; R_f : 0.23 (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3367, 3053, 2922, 1621, 1596, 1516, 1468, 1365, 1330, 1094, 897, 741, 701 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 8.63 (brs, 1H), 8.62-8.13 (m, 1H), 8.12-8.11 (m, 1H), 7.34-7.31 (m, 2H), 7.29-7.19 (m, 6H), 7.14-7.11 (m, 2H), 7.10-7.08 (m, 2H), 6.61-6.59 (m, 1H), 6.30-6.28 (m, 1H), 4.42-4.40 (m, 1H), 3.38 (dd, $J_1 = 17$ Hz, $J_2 = 8.5$ Hz, 1H), 2.80 (dd, $J_1 = 16.5$ Hz, $J_2 = 3$ Hz, 1H). **$^{13}\text{C NMR}$** (125 MHz, CDCl_3 , TMS): δ 144.1, 142.7, 141.6, 140.2, 139.7, 134.2, 133.2, 130.2, 129.4, 128.1, 126.7, 126.6, 126.0, 123.5, 122.6, 117.9, 116.9, 111.2, 41.7, 39.6.

HRMS (ESI): Calcd for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_2\text{Na}$: 415.14225; Found: 415.14170.

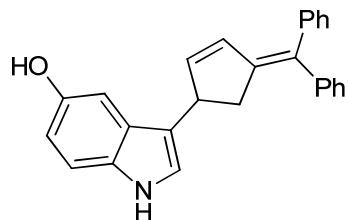
3-(4-(diphenylmethylene)cyclopent-2-enyl)-5-fluoro-1H-indole (3ag)



Yield: 48 mg (100%) as colourless foam; $R_f = 0.38$ (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3661, 3054, 2923, 1705, 1587, 1484, 1453, 1170, 1107, 798, 758, 702 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 7.92 (brs, 1H), 7.37-7.34 (m, 2H), 7.30-7.24 (m, 9H), 7.20-7.18 (m, 1H), 7.03 (s, 1H), 6.97-6.94 (m, 1H), 6.57-6.56 (m, 1H), 6.31-6.30 (m, 1H), 4.35-4.34 (m, 1H), 3.28 (dd, $J_1 = 17$ Hz, $J_2 = 8$ Hz, 1H), 2.86 (dd, $J_1 = 17$ Hz, $J_2 = 4$ Hz, 1H). **$^{13}\text{C NMR}$** (125 MHz, CDCl_3 , TMS): δ 158.5, 144.7, 142.8, 141.1, 133.6, 133.2, 133.0, 132.4, 130.2, 129.4, 129.1, 128.3, 128.0, 126.8, 126.5, 126.4, 122.3, 119.9, 111.8, 111.7, 110.6, 110.4, 104.4, 104.2, 42.0, 39.6.

HRMS (ESI): Calcd for $\text{C}_{26}\text{H}_{20}\text{FNNa}$: 388.14775; Found: 388.14736.

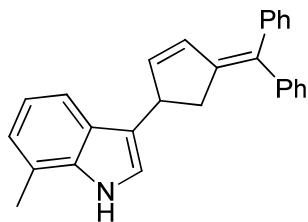
3-(4-(diphenylmethylene)cyclopent-2-enyl)-1H-indol-5-ol (3ah)



Yield: 20 mg (42%) as pale yellow viscous liquid; $R_f = 0.13$ (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3509, 3333, 3051, 2902, 2767, 2351, 1591, 1491, 1443, 1348, 793, 706, 631 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 7.76 (brs, 1H), 7.33-7.24 (m, 2H), 7.23-7.18 (m, 7H), 7.16-7.13 (m, 2H), 6.98 (d, $J = 7$ Hz, 1H), 6.93 (d, $J = 2.5$ Hz, 1H), 6.73 (dd, $J_1 = 8.5$ Hz, $J_2 = 2.5$ Hz, 1H), 6.52 (dd, $J_1 = 5.5$ Hz, $J_2 = 2.5$ Hz, 1H), 6.29 (dd, $J_1 = 5.5$ Hz, $J_2 = 2.5$ Hz, 1H) 4.48 (brs, 1H), 4.31-4.28 (m, 1H), 3.21 (dd, $J_1 = 17$ Hz, $J_2 = 7.5$ Hz, 1H), 2.86 (dd, $J_1 = 16.5$ Hz, $J_2 = 4$ Hz, 1H). **$^{13}\text{C NMR}$** (125 MHz, CDCl_3 , TMS): δ 149.2, 144.8, 142.8, 141.4, 133.5, 132.1, 132.0, 130.2, 129.4, 129.0, 128.2, 127.9, 126.3, 126.5, 127.3, 121.5, 119.2, 111.9, 111.7, 103.9, 42.1, 39.7.

HRMS (ESI): Calcd for $\text{C}_{26}\text{H}_{21}\text{NONa}$: 386.15208; Found: 386.15179.

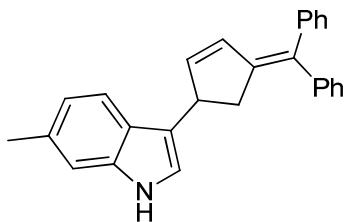
3-(4-(diphenylmethylene)cyclopent-2-enyl)-7-methyl-1H-indole (3aj)



Yield: 32 mg (67%) as pale yellow coloured foam; $R_f = 0.35$ (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3420, 3052, 2921, 2851, 2683, 1590, 1491, 1436, 1339, 1109, 746, 701 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 7.83 (brs, 1H), 7.49 (d, $J = 7.5$ Hz, 1H), 7.36-7.35 (m, 2H), 7.33-7.19 (m, 7H), 7.17-7.16 (m, 1H), 7.06-6.99 (m, 3H), 6.57-6.56 (m, 1H), 6.35(dd, $J_1 = 5.5$ Hz, $J_2 = 2$ Hz, 1H), 4.41-4.40 (m, 1H), 3.28 (dd, $J_1 = 17$ Hz, $J_2 = 8$ Hz, 1H), 2.92 (dd, $J_1 = 17$ Hz, $J_2 = 4$ Hz, 1H), 2.50 (s, 3H). **$^{13}\text{C NMR}$** (125 MHz, CDCl_3 , TMS): δ 144.9, 142.9, 141.6, 136.2, 133.4, 132.1, 130.2, 129.5, 128.2, 127.9, 126.5, 126.3, 126.1, 122.7, 120.4, 120.2, 120.0, 119.6, 117.2, 42.2, 39.9, 16.6.

HRMS (ESI): Calcd for $\text{C}_{27}\text{H}_{23}\text{NNa}$: 384.17282; Found: 384.17251.

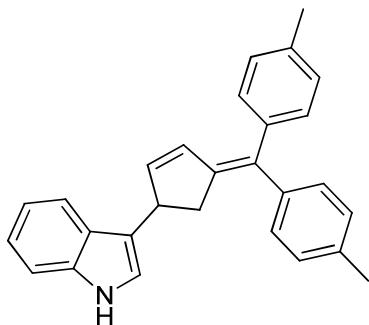
3-(4-(diphenylmethylene)cyclopent-2-enyl)-6-methyl-1H-indole (3ak)



Yield: 29 mg (62%) as pale yellow coloured foam; $R_f = 0.35$ (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3410, 3048, 2918, 1703, 1684, 1590, 1489, 1446, 1341, 758, 700 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 7.79 (brs, 1H), 7.51 (d, $J = 8$ Hz, 1H), 7.36-7.33 (m, 3H), 7.28-7.22 (m, 6H), 7.18-7.14 (m, 3H), 6.95-6.90 (m, 2H), 6.56-6.55 (m, 1H), 4.38-4.37 (m, 1H), 3.27 (dd, $J_1 = 16.5$ Hz, $J_2 = 7.5$ Hz, 1H), 2.91 (dd, $J_1 = 17$ Hz, $J_2 = 4$ Hz, 1H), 2.48 (s, 3H). **$^{13}\text{C NMR}$** (125 MHz, CDCl_3 , TMS): δ 150.0, 142.9, 141.7, 137.2, 133.4, 132.0, 131.8, 130.2, 129.5, 128.2, 127.9, 126.4, 126.3, 124.5, 121.1, 119.6, 119.1, 111.1, 42.2, 39.8, 21.7.

HRMS (ESI): Calcd for $\text{C}_{27}\text{H}_{23}\text{NNa}$: 384.17282; Found: 384.17248.

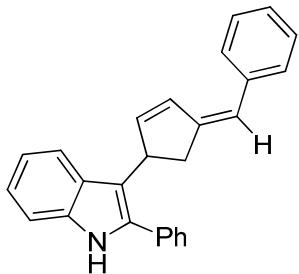
3-(4-(di-p-tolylmethylene)cyclopent-2-en-1-yl)-1H-indole (3ba)



Yield: 36 mg (78%) as colourlss viscous liquid; $R_f = 0.53$ (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3390, 3048, 2920, 1704, 1684, 1590, 1489, 1329, 752, 699 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 7.73 (brs, 1H), 7.59 (d, $J = 8$ Hz, 1H), 7.26 (d, $J = 7.5$ Hz, 1H), 7.16-7.00 (m, 10H), 6.87 (d, $J = 2.5$ Hz, 1H), 6.52(dd, $J_1 = 5.5$ Hz, $J_2 = 2$ Hz, 1H), 6.26-6.25 (m, 1H), 4.36-4.33 (m, 1H), 3.23 (dd, $J_1 = 17$ Hz, $J_2 = 8$ Hz, 1H), 2.86 (dd, $J_1 = 17$ Hz, $J_2 = 4$ Hz, 1H), 2.35 (s, 3H), 2.28 (s, 3H). **$^{13}\text{C NMR}$** (125 MHz, CDCl_3 , TMS): δ 144.2, 140.9, 140.3, 140.2, 136.7, 136.0, 135.8, 133.7, 132.0, 130.2, 129.4, 129.0, 128.7, 126.7, 122.1, 120.3, 120.0, 119.5, 119.4, 111.2, 42.1, 40.0, 21.3, 21.2.

HRMS (ESI): Calcd for $\text{C}_{28}\text{H}_{23}\text{NNa}$: 398.18847; Found: 398.18796.

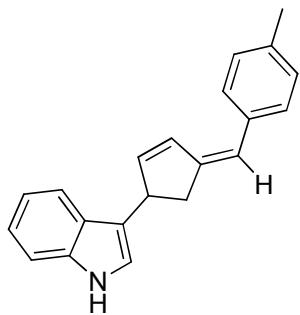
3-(4-benzylidenecyclopent-2-enyl)-2-phenyl-1H-indole (3cc)



Yield: 46 mg (68%) as colourless viscous foam with an isomeric ratio of 10:1; $R_f = 0.58$ (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3379, 3054, 3025, 2931, 1705, 1602, 1488, 1451, 1308, 1157, 1025, 743, 698 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 8.02 (brs, 1H), 7.66-7.60 (m, 3H), 7.56-7.53 (m, 2H), 7.48-7.44 (m, 3H), 7.42-7.40 (m, 1H), 7.38-7.35 (m, 2H), 7.28-7.20 (m, 1H), 7.11-7.08 (m, 1H), 6.60 (s, 1H), 6.57-6.56 (m, 2H), 6.31-6.30 (m, 1H), 4.69-4.68 (m, 1H), 3.45 (dd, $J_1 = 17$ Hz, $J_2 = 7$ Hz, 1H), 3.32-3.28 (d, $J = 15$ Hz, 1H). **$^{13}\text{C NMR}$** (125 MHz, CDCl_3 , TMS): δ 148.8, 141.5, 138.6, 136.3, 134.6, 133.0, 128.9, 128.6, 128.4, 128.1, 128.0, 127.7, 126.0, 122.3, 120.6, 120.4, 119.7, 114.6, 111.0, 43.2, 38.0.

HRMS (ESI): Calcd for $\text{C}_{26}\text{H}_{21}\text{NNa}$: 370.17517; Found: 370.17489.

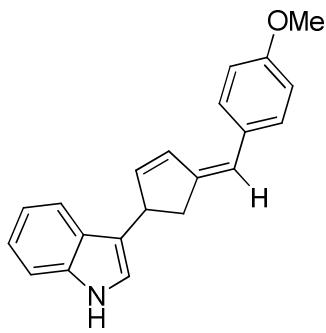
3-(4-(4-methylbenzylidene)cyclopent-2-enyl)-1H-indole (3da)



Yield: 33 mg (65%) as colourless viscous form with an isomeric ratio of 10:1; $R_f = 0.43$ (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3381, 3047, 2930, 1670, 1600, 1568, 1451, 1300, 1100, 870, 742, 690 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 7.88 (brs, 1H), 7.64 (d, $J = 8$ Hz, 1H), 7.35 (d, $J = 8$ Hz, 1H), 7.30-7.28 (m, 2H), 7.23-7.20 (m, 1H), 7.13-7.11 (m, 3H), 6.98 (s, 1H), 6.49-6.46 (m, 2H), 6.30-6.29 (m, 1H), 4.50-4.49 (m, 1H), 3.45 (dd, $J_1 = 17.5$ Hz, $J_2 = 3$ Hz, 1H), 3.00-2.96 (m, 1H), 2.36 (s, 3H). **$^{13}\text{C NMR}$** (125 MHz, CDCl_3 , TMS): δ 147.4, 139.8, 136.7, 136.5, 135.7, 135.5, 129.1, 129.0, 128.0, 126.6, 122.2, 120.5, 120.3, 119.8, 119.4, 111.1, 43.0, 38.1, 21.2.

HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{19}\text{NNa}$: 308.14152; Found: 308.14108.

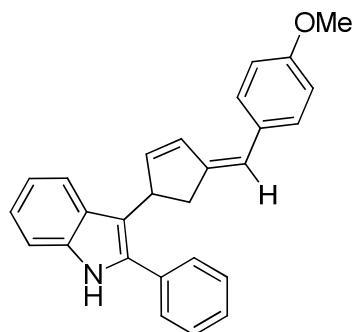
3-(4-(4-methoxybenzylidene)cyclopent-2-enyl)-1H-indole (3ea)



Yield: 18 mg (36%) as colourless viscous foam with an isomeric ratio of 10:1; $R_f = 0.38$ (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3379, 3049, 2925, 1704, 1595, 1504, 1459, 1339, 1247, 1223, 1176, 1030, 742, 700 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 7.93 (brs, 1H), 7.67 (d, $J = 8$ Hz, 1H), 7.39-7.34 (m, 3H), 7.28-7.22 (m, 1H), 7.16-7.13 (m, 1H), 6.99-6.94 (m, 1H), 6.89 (d, $J = 8.5$ Hz, 2 H), 6.50-6.46 (m, 2H), 6.29-6.28 (m, 1H), 4.51-4.50 (m, 1H), 3.83 (s, 3H), 3.46 (dd, $J_1 = 17$ Hz, $J_2 = 7$ Hz, 1H), 2.99-2.96 (m, 1H). **$^{13}\text{C NMR}$** (125 MHz, CDCl_3 , TMS): δ 157.8, 146.3, 139.3, 136.7, 136.5, 131.5, 129.2, 129.1, 126.5, 122.1, 120.5, 120.0, 119.8, 119.4, 113.9, 111.2, 55.3, 43.0, 38.0.

HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{19}\text{NONa}$: 324.13643; Found: 324.13597.

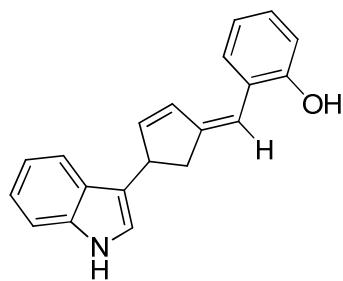
3-(4-(4-methoxybenzylidene)cyclopent-2-enyl)-2-phenyl-1H-indole (3ec)



Yield: 20 mg (32%) as colourless viscous foam with an isomeric ratio of 10:1; $R_f = 0.43$ (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max} : 3385, 3040, 2932, 1673, 1602, 1573, 1452, 1302, 1174, 1104, 870, 742, 688 cm^{-1} . **¹H NMR** (500 MHz, CDCl_3 , TMS): δ 8.03 (s, 1H), 7.61-7.52 (m, 3H), 7.50-7.49 (m, 2H), 7.43-7.41 (m, 1H), 7.40-7.35 (m, 3H), 7.20-7.17 (m, 1H), 7.06-7.03 (m, 1H), 6.93-6.85 (m, 2H), 6.51-6.49 (m, 2H), 6.22-6.21 (m, 1H), 4.64-4.63 (m, 1H), 3.82 (s, 3H), 3.38 (dd, $J_1 = 17.5$ Hz, $J_2 = 8$ Hz, 1H), 3.24-3.21 (m, 1H). **¹³C NMR** (125 MHz, CDCl_3 , TMS): δ 157.8, 146.5, 140.2, 136.3, 134.4, 133.1, 131.5, 129.3, 128.8, 128.7, 127.9, 127.6, 122.3, 120.5, 120.1, 119.6, 114.8, 113.8, 110.9, 55.1, 43.1, 37.9.

HRMS (ESI): Calcd for $\text{C}_{27}\text{H}_{23}\text{NONa}$: 400.16773; Found: 400.16728.

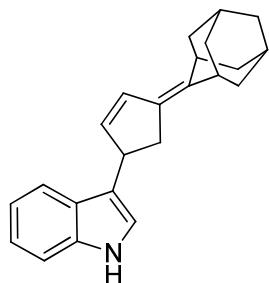
2-((4-(1H-indol-3-yl)cyclopent-2-enylidene)methyl)phenol (3fa)



Yield: 22 mg (44%) as pale yellow viscous liquid; $R_f = 0.15$ (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3412, 3380, 3053, 2926, 1695, 1600, 1454, 1235, 1096, 1015, 742, 699 cm^{-1} . **¹H NMR** (500 MHz, CDCl_3 , TMS): δ 7.96 (brs, 1H), 7.63 (d, $J = 8$ Hz, 1H), 7.38-7.34 (m, 2H), 7.28-7.20 (m, 1H), 7.14-7.08 (m, 2H), 6.98 (s, 1H), 6.89-6.83 (m, 2H), 6.58 (s, 1H), 6.54-6.53 (m, 1H), 6.39-6.37 (m, 1H), 5.14 (brs, 1H), 4.45-4.43 (m, 1H), 3.35-3.29 (m, 1H), 2.87-2.83 (m, 1H). **¹³C NMR** (125 MHz, CDCl_3 , TMS): δ 152.8, 150.7, 141.4, 136.7, 135.6, 128.5, 127.7, 126.5, 125.3, 122.2, 120.5, 119.5, 119.4, 119.3, 115.3, 112.9, 111.2, 42.5, 37.5.

HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{17}\text{NONa}$: 310.12078; Found: 310.12039.

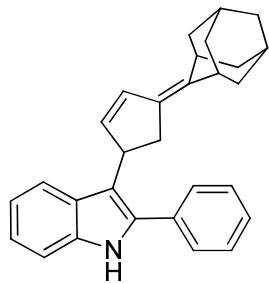
3-(4-(adamantan-2-ylidene)cyclopent-2-en-1-yl)-1H-indole (3ga)



Yield: 28 mg (59%) as colourless viscous liquid; R_f = 0.48 (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3389, 3066, 2931, 2857, 1668, 1620, 1582, 1520, 1455, 1304, 933, 744 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 7.87 (brs, 1H), 7.60 (d, J = 8 Hz, 1H), 7.32 (d, J = 8 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.94 (s, 1H), 6.54-6.53 (m, 1H), 6.08-6.06 (m, 1H), 4.30-4.28 (m, 1H), 3.06 (dd, J_1 = 16 Hz, J_2 = 9 Hz, 1H), 2.94 (brs, 1H), 2.58 (brs, 1H), 2.53 (dd, J_1 = 16 Hz, J_2 = 4 Hz, 1H), 1.96-1.95 (m, 2H), 1.91-1.89 (m, 2H), 1.86-1.82 (m, 6H), 1.74-1.72 (m, 2H). **$^{13}\text{C NMR}$** (125 MHz, CDCl_3 , TMS): δ 138.0, 137.1, 136.7, 131.9, 130.1, 126.6, 121.9, 121.0, 120.0, 119.5, 119.1, 111.0, 41.0, 39.4, 39.2, 38.8, 38.7, 37.3, 35.3, 35.0, 34.6, 28.4, 28.3.

HRMS (ESI): Calcd for $\text{C}_{23}\text{H}_{25}\text{NNa}$: 338.18847; Found: 338.18795.

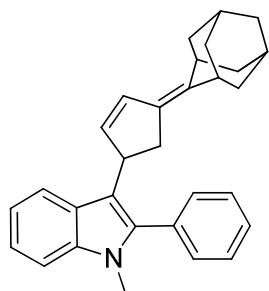
3-(4-(adamantan-2-ylidene)cyclopent-2-en-1-yl)-2-phenyl-1H-indole (3gc)



Yield: 37 mg (62%) as colourless viscous liquid; R_f = 0.54 (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3369, 3060, 2940, 2855, 1670, 1620, 1581, 1520, 1458, 1301, 1291, 1238, 941, 741 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 7.93 (brs, 1H), 7.61 (d, J = 8 Hz, 1H), 7.54-7.52 (m, 2H), 7.47-7.44 (m, 2H), 7.38-7.32 (m, 2H), 7.16-7.13 (m, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.56 (dd, J_1 = 5.5 Hz, J_2 = 2 Hz, 1H), 6.00 (dd, J_1 = 5 Hz, J_2 = 2 Hz, 1H), 4.45-4.43 (m, 1H), 3.00-2.94 (m, 2H), 2.77 (dd, J_1 = 16.5 Hz, J_2 = 4 Hz, 1H), 2.60 (brs, 1H), 2.01-1.96 (m, 3H), 1.93-1.89 (m, 2H), 1.86-1.80 (m, 7H). **$^{13}\text{C NMR}$** (125 MHz, CDCl_3 , TMS): δ 138.2, 138.0, 136.3, 133.9, 133.3, 132.4, 130.0, 128.7, 128.6, 127.9, 127.7, 122.1, 120.8, 119.4, 116.2, 110.7, 41.0, 39.8, 39.3, 39.1, 38.8, 37.4, 35.2, 35.1, 34.7, 28.5, 28.4.

HRMS (ESI): Calcd for C₂₉H₂₉NNa: 414.21977; Found: 414.21928.

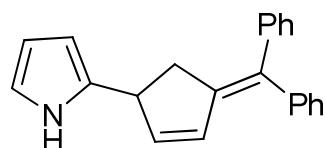
3-(4-(adamantan-2-ylidene)cyclopent-2-en-1-yl)-1-methyl-2-phenyl-1H-indole (3gd)



Yield: 35 mg (57%) as colourless viscous liquid; R_f = 0.54 (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 2981, 2915, 2833, 1671, 1621, 1586, 1542, 1380, 1042, 957, 931, 743 cm⁻¹. **¹H NMR** (500 MHz, CDCl₃, TMS): δ 7.62 (d, *J* = 7.5 Hz, 1H), 7.51-7.47 (m, 2H), 7.45-7.40 (m, 3H), 7.33-7.31 (m, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.07-7.04 (m, 1H), 6.51 (dd, *J*₁ = 5.5 Hz, *J*₂ = 2.5 Hz, 1H), 5.95 (dd, *J*₁ = 5.5 Hz, *J*₂ = 2.5 Hz, 1H), 4.15-4.13 (m, 1H), 3.60 (s, 3H), 2.99 (brs, 1H), 2.89 (dd, *J*₁ = 16.5 Hz, *J*₂ = 9 Hz, 1H), 2.72 (dd, *J*₁ = 16.5 Hz, *J*₂ = 4.5 Hz, 1H), 2.59 (brs, 1H), 2.02-1.81 (m, 12H). **¹³C NMR** (125 MHz, CDCl₃, TMS): δ 138.4, 137.8, 137.5, 137.0, 132.5, 132.1, 130.9, 129.6, 128.3, 127.9, 121.6, 120.4, 119.0, 116.3, 109.2, 41.3, 39.7, 39.0, 38.8, 37.4, 35.3, 35.1, 34.7, 30.8, 30.7, 28.5 ppm.

HRMS (ESI): Calcd for C₃₀H₃₁N: 405.24565; Found: 405.24513.

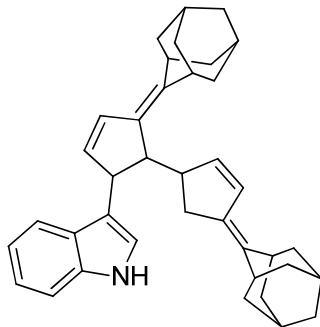
2-(4-(diphenylmethylenecyclopent-2-enyl)-1H-pyrrole (3al)



Yield: 16 mg (40%) as colourless viscous liquid; R_f = 0.13 (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3388, 3054, 2922, 1683, 1596, 1490, 1441, 761, 701 cm⁻¹. **¹H NMR** (500 MHz, CDCl₃, TMS): δ 7.94 (brs, 1H), 7.33-7.26 (m, 2H), 7.25-7.20 (m, 3H), 7.18-7.17 (m, 4H), 6.68 (d, *J* = 1.5 Hz, 1H), 6.51-6.50 (m, 1H), 6.19-6.18 (m, 2H), 6.14-6.12 (m, 1H), 5.95 (brs, 1H), 4.18-4.17 (m, 1H), 3.15 (dd, *J*₁ = 17 Hz, *J*₂ = 8 Hz, 1H), 2.75 (dd, *J*₁ = 16.5 Hz, *J*₂ = 3.5 Hz, 1H). **¹³C NMR** (125 MHz, CDCl₃, TMS): δ 143.8, 142.6, 139.5, 134.8, 134.2, 132.8, 130.1, 129.4, 128.0, 126.6, 126.5, 116.8, 108.4, 104.6, 43.6, 39.8.

HRMS (ESI): Calcd for C₂₂H₁₉NNa: 320.14152; Found: 320.14111.

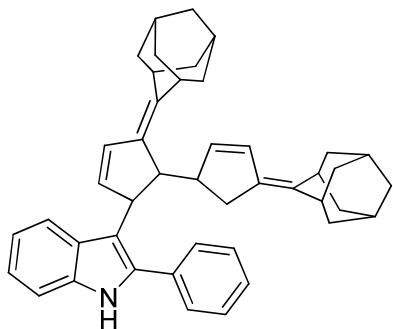
3-(4'-(adamantan-2-ylidene)-5-(adamantan-2-ylidene)-[1,1'-bi(cyclopentane)]-2',3-dien-2-yl)-1H-indole (4ga)



Yield: 44 mg (57%) as colourless viscous liquid; $R_f = 0.48$ (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3356, 3069, 2933, 2857, 1671, 1619, 1582, 1455, 933, 742, 688 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 7.84 (brs, 1H), 7.57 (d, $J = 8\text{ Hz}$, 1H), 7.30 (d, $J = 8\text{ Hz}$, 1H), 7.13 (t, $J = 7.5\text{ Hz}$, 1H), 7.03-6.99 (m, 1H), 6.87 (d, $J = 2\text{ Hz}$, 1H), 6.48 (t, $J = 4\text{ Hz}$, 2H), 5.80 (dd, $J_1 = 9.5\text{ Hz}$, $J_2 = 4.5\text{ Hz}$, 1H), 3.73 (brs, 1H), 3.15-3.14 (m, 1H), 3.07-3.01 (m, 2H), 2.92 (brs, 1H), 2.73 (brs, 1H), 2.58-2.53 (m, 2H), 2.37-2.33 (m, 1H), 2.00-1.77 (m, 24H). **$^{13}\text{C NMR}$** (125 MHz, CDCl_3 , TMS): δ 139.6, 136.7, 136.5, 136.0, 135.9, 132.3, 131.5, 129.3, 126.4, 121.8, 120.9, 120.3, 119.8, 119.0, 110.9, 51.5, 48.6, 42.6, 39.6, 39.5, 39.4, 39.3, 39.1, 38.7, 37.3, 37.2, 35.0, 34.9, 34.6, 34.5, 31.1, 28.5, 28.4.

HRMS (ESI): Calcd for $\text{C}_{38}\text{H}_{43}\text{N}$: 513.33955; Found: 513.33916.

3-(4'-(adamantan-2-ylidene)-5-(adamantan-2-ylidene)-[1,1'-bi(cyclopentane)]-2',3-dien-2-yl)-2-phenyl-1H-indole (4gc)

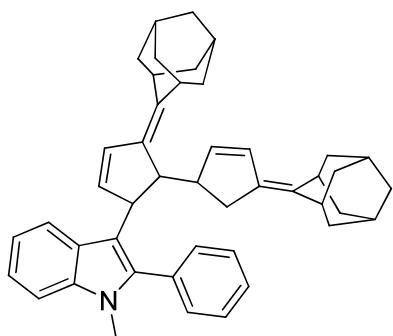


Yield: 52 mg (58%) as colourless viscous liquid; $R_f = 0.54$ (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3048, 2909, 2852, 1589, 1472, 1379, 744, 690 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 7.90 (brs, 1H), 7.64 (d, $J = 8\text{ Hz}$, 1H), 7.51 (d, $J = 7.5\text{ Hz}$, 2H), 7.41-7.38 (m, 2H), 7.31-7.25 (m, 2H), 7.14-7.11 (m, 1H), 6.98 (t, $J = 7.5\text{ Hz}$, 1H), 6.52 (dd, $J_1 = 5\text{ Hz}$, $J_2 = 1.5\text{ Hz}$, 1H),

6.35 (d, $J = 4.5$ Hz, 1H), 5.86 (dd, $J_1 = 5.5$ Hz, $J_2 = 2.5$ Hz, 1H), 5.73 (dd, $J_1 = 5.5$ Hz, $J_2 = 2$ Hz, 1H), 4.03 (brs, 1H), 3.29 (brs, 1H), 3.10 (brs, 1H), 3.06 (brs, 1H), 2.77 (brs, 1H), 2.72 (brs, 1H), 2.47-2.36 (m, 1H), 2.20 (brs, 1H), 2.07 (brs, 1H), 2.02-1.92 (m, 5H), 1.89-1.83 (m, 10H), 1.86-1.80 (m, 4H), 1.77-1.67 (m, 2H), 1.65-1.62 (m, 1H), 1.53-1.51 (m, 1H), 1.50-1.46 (m, 1H), 0.96-1.13 (m, 1H). **^{13}C NMR** (125 MHz, CDCl_3 , TMS): δ 140.5, 138.1, 137.2, 136.9, 136.3, 134.2, 34.0, 132.6, 132.4, 130.3, 129.6, 129.1, 128.8, 128.2, 122.9, 121.8, 120.1, 117.4, 111.5, 50.6, 49.8, 47.1, 43.5, 40.4, 40.3, 40.1, 39.9, 39.8, 39.2, 38.9, 38.1, 35.7, 35.5, 35.4, 35.1, 31.5, 30.5, 29.3, 29.2, 29.1, 29.0.

HRMS (ESI): Calcd for $\text{C}_{44}\text{H}_{47}\text{N}$: 589.37085; Found: 589.37055.

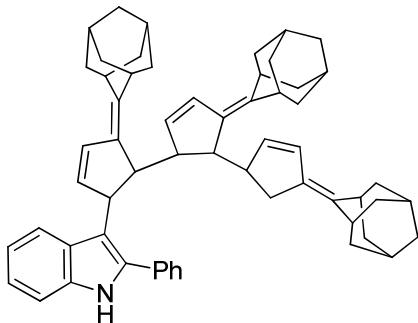
3-(4'-(adamantan-2-ylidene)-5-(adamantan-2-ylidene)-[1,1'-bi(cyclopentane)]-2',3-dien-2-yl)-1-methyl-2-phenyl-1H-indole (4gd)



Yield: 46 mg (50%) as colourless viscous liquid; $R_f = 0.62$ (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3058, 2978, 2908, 1580, 1467, 1445, 1249, 1022, 745 cm^{-1} . **^1H NMR** (500 MHz, CDCl_3 , TMS): δ 7.67-7.65 (m, 1H), 7.45-7.42 (m, 2H), 7.38-7.31 (m, 3H), 7.26-7.19 (m, 1H), 7.03 (t, $J = 7.5$ Hz, 2H), 6.44 (d, $J = 5.5$ Hz, 1H), 6.30 (d, $J = 5$ Hz, 1H), 5.77 (dd, $J_1 = 5.5$ Hz, $J_2 = 2.5$ Hz, 1H), 5.68 (d, $J = 2.5$ Hz, 1H), 3.78 (brs, 1H), 3.60-3.56 (m, 3H), 3.23 (brs, 1H), 3.10-3.03 (m, 2H), 2.76 (brs, 2H), 2.48-2.42 (m, 1H), 2.37 (m, 1H), 2.19 (m, 1H), 2.08-1.52 (m, 24H). **^{13}C NMR** (125 MHz, CDCl_3 , TMS): δ 139.3, 137.4, 136.7, 136.1, 135.7, 132.1, 131.5, 129.1, 128.3, 127.5, 127.3, 126.6, 121.6, 120.6, 118.9, 116.5, 115.6, 109.2, 49.7, 49.4, 43.2, 39.5, 39.2, 38.7, 38.5, 37.4, 34.9, 34.3, 30.9, 30.8, 28.4.

HRMS (ESI): Calcd for $\text{C}_{45}\text{H}_{49}\text{N}$: 603.38650; Found: 603.38596.

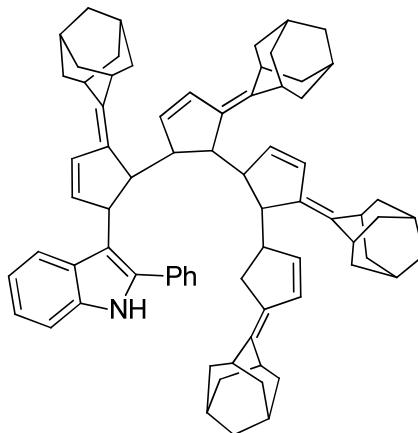
Compound 5gc



Yield: 11 mg (12%) as colourless viscous liquid; 0.62 (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3378, 3058, 2978, 2908, 1580, 1467, 1445, 1022, 745 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 7.89 (brs, 1H), 7.74 (d, J = 8 Hz, 1H), 7.54-7.53 (m, 2H), 7.41-7.38 (m, 2H), 7.32-7.25 (m, 2H), 7.14-7.13 (m, 1H), 7.01-7.00 (m, 1H), 6.45-6.44 (m, 1H), 6.37-6.36 (m, 1H), 6.29-6.28 (m, 1H), 5.91-5.89 (m, 1H), 5.56-5.52 (m, 2H), 3.90 (brs, 1H), 3.27-3.26 (m, 1H), 3.03 (brs, 1H) 2.79 (brs, 1H), 2.74 (brs, 1H), 2.67 (brs, 2H), 2.48-2.45 (m, 3H), 2.33 (brs, 1H), 2.06 (brs, 1H), 2.01-1.95 (m, 8H), 1.90-1.77 (m, 18H), 1.75-1.69 (m, 5H), 1.68-1.63 (m, 2H), 1.61 (brs, 1H), 1.40-1.25 (m, 2H), 0.52-0.46 (m, 1H). **$^{13}\text{C NMR}$** (125 MHz, CDCl_3 , TMS): δ 139.4, 137.9, 137.8, 136.5, 136.2, 136.1, 136.0, 135.9, 134.2, 133.5, 133.4, 132.4, 131.3, 131.2, 128.9, 128.1, 127.3, 122.0, 121.4, 119.2, 116.5, 110.7, 51.3, 50.7, 48.8, 45.4, 42.9, 39.8, 39.7, 39.6, 39.5, 39.4, 39.2, 39.1, 39.0, 38.7, 38.6, 38.5, 38.0, 37.4, 37.2, 35.1, 35.0, 34.9, 34.6, 34.4, 34.1.

HRMS (ESI): Calcd for $\text{C}_{59}\text{H}_{65}\text{N}$: 787.51170; Found: 787.51126.

Compound 6gc



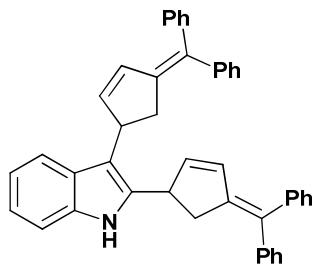
Yield: 12 mg (8%) as colourless viscous liquid; 0.48 (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3212, 3028, 1673, 1584, 1452, 1300, 1248, 1181, 1104, 874, 742, 691 cm^{-1} . **$^1\text{H NMR}$** (500 MHz, CDCl_3 , TMS): δ 7.87 (brs, 1H), 7.71 (d, J = 8 Hz, 1H), 7.50-7.48 (m, 2H), 7.41-7.38 (m, 2H), 7.32-7.28 (m, 2H), 7.14-7.11 (m, 1H), 6.99-6.97 (m, 1H), 6.46-6.44 (m, 1H), 6.27-6.21 (m, 3H), 5.93-5.91 (m, 1H), 5.52-5.50 (m, 1H), 5.42-5.41 (m, 1H), 5.38-5.36 (m, 1H), 3.96 (brs, 1H), 3.06 (brs, 2H), 2.99 (brs, 1H), 2.82 (brs, 1H), 2.77-2.76 (m, 2H), 2.62 (brs, 2H), 2.55-2.53 (m, 3H),

2.47-2.42 (m, 2H), 2.36 (brs, 1H), 2.32 (brs, 1H), 2.03-1.54 (m, 49H). **¹³C NMR** (125 MHz, CDCl₃, TMS): δ 139.5, 138.2, 137.4, 137.0, 136.6, 136.2, 136.1, 136.0, 135.9, 134.8, 134.1, 133.8, 132.4, 131.2, 130.9, 130.5, 129.4, 128.7, 128.1, 127.6, 122.0, 121.3, 119.1, 115.9, 110.4, 51.4, 50.3, 48.5, 46.7, 45.5, 40.0, 39.9, 39.8, 39.6, 39.5, 39.2, 39.1, 38.9, 38.8, 38.7, 38.5, 37.6, 37.5, 37.4, 35.1, 35.0, 34.8, 34.7, 34.6, 34.3, 34.2, 31.0, 28.6, 28.5, 28.4, 28.2, 28.1.

HRMS (ESI): Calcd for C₇₄H₈₃NNa: 1008.64232; Found: 1008.64163.

2,3-bis(4-(diphenylmethylene)cyclopent-2-enyl)-1H-indole (**3aaa**)

Following general procedure for the Lewis acid catalyzed hydroarylation of pentafulvene. The pentafulvene **1a** (30 mg, 1.0 equiv.), indole **2a** (30 mg, 2.0 equiv) and Cu(OTf)₂ (2 mg, 0.006 mmol), in 2 mL acetonitrile at room temperature for 12 hours gave the product **3aaa** (34 mg, 45%) as pale yellow coloured foam. (or) A mixture of compound **3aa** (1.0 equiv), fulvene **1a** (1.0 equiv) and Cu(OTf)₂ (2 mol %) were weighed in a reaction tube, CH₃CN (2 mL) was added and allowed to stir at room temperature for 12 hours. The solvent was evaporated in *vacuo* and the residue on silica gel (100-200 mesh) column chromatography yielded the product **3aaa** (26 mg, 35%) as pale yellow coloured foam.

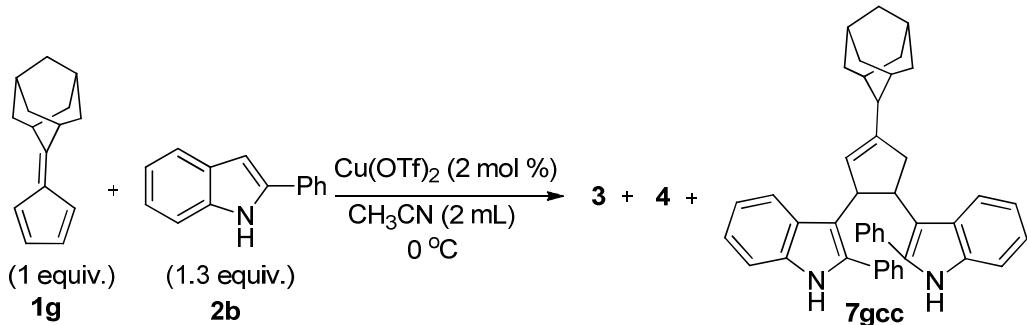


Yield: 39 mg (45%) as pale yellow viscous liquid; R_f = 0.58 (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{max} : 3294, 2857, 2366, 2335, 1647, 1590, 1369, 942, 887, 702 cm⁻¹. **¹H NMR** (500 MHz, CDCl₃, TMS): δ 7.69 (brs, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.33-7.29 (m, 4H), 7.26-7.15 (m, 17H), 7.12-7.00 (m, 2H), 6.62-6.61 (m, 1H), 6.55-6.54 (m, 1H), 6.25-6.21 (m, 1H), 6.17-6.13 (m, 1H), 4.48-4.47 (m, 1H), 4.41-4.40 (m, 1H), 3.13-3.08 (m, 2H), 2.96-2.92 (m, 1H), 2.81-2.77 (m, 1H). **¹³C NMR** (125 MHz, CDCl₃, TMS): δ 145.1, 143.2, 142.5, 142.4, 138.7, 138.6, 136.4, 135.5, 135.4, 133.9, 133.3, 133.2, 132.2, 130.2, 130.1, 129.4, 129.3, 128.1, 128.0, 127.9, 127.7, 126.8, 126.7, 126.5, 126.3, 121.5, 119.4, 119.3, 119.2, 113.3, 110.5, 41.9, 41.5, 40.2, 39.6.

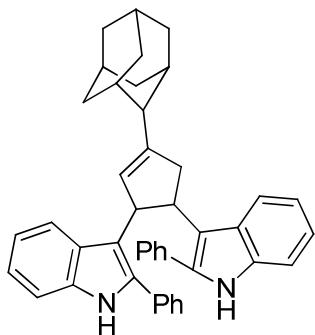
HRMS (ESI): Calcd for C₄₄H₃₅NNa: 600.26672; Found: 600.26609.

Addendum to Table 2

With the increase in the equivalents of indole, adamantanone derived fulvene yielded a minor amount of bis-indole product **7** along with the products **3** and **4**. The proportion of the newly formed product **7** was found to increase with time.

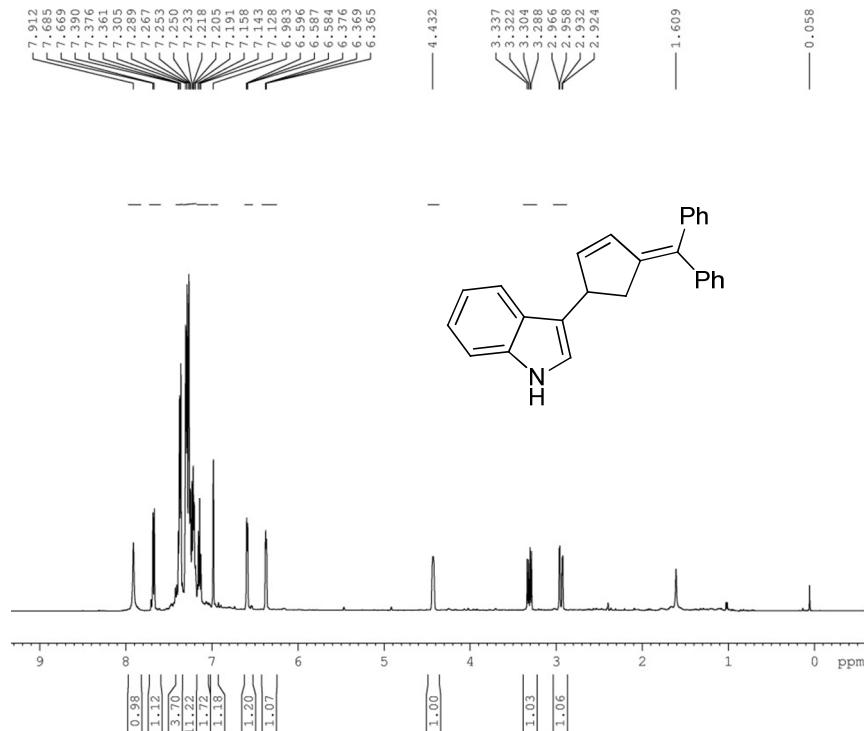


Compound **7gcc**

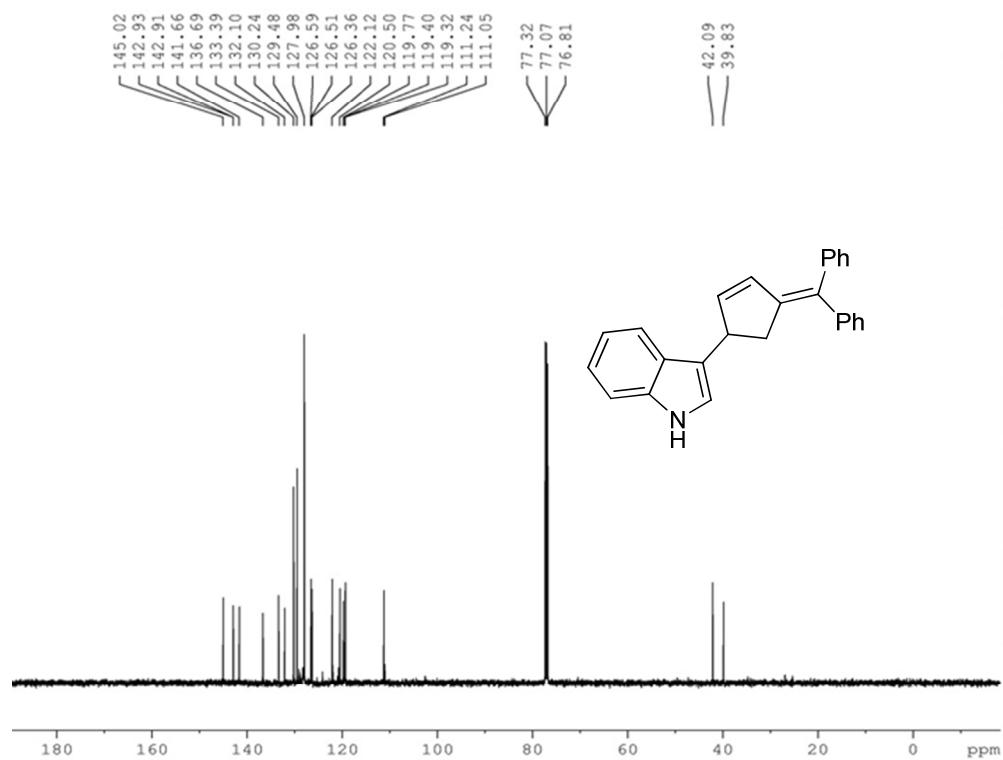


Yield: 13 mg (15%) as pale yellow solid; $R_f = 0.26$ (hexane/ethyl acetate = 4:1). **IR** (Neat) ν_{\max} : 3419, 2903, 2847, 1639, 1487, 1451, 1348, 1309, 1266, 763, 741, 698 cm^{-1} . **1H NMR** (500 MHz, CDCl_3 , TMS): δ 7.88 (m, 2H), 7.80 (d, $J = 8$ Hz, 1H), 7.70 (d, $J = 8$ Hz, 1H), 7.36-7.39 (m, 2H), 7.24-7.19 (m, 2H), 7.10-6.98 (m, 4H), 6.82-6.72 (m, 8H), 5.68 (brs, 1H), 4.93-4.91 (m, 1H), 4.30-4.26 (m, 1H), 3.15-3.10 (m, 1H), 2.80-2.75 (m, 1H), 2.51 (brs, 1H), 2.18-2.03 (m, 4H), 1.91-1.81 (m, 6H), 1.73 (brs, 2H), 1.56-1.51 (m, 2H). **13C NMR** (125 MHz, CDCl_3 , TMS): δ 145.6, 136.4, 136.3, 135.7, 135.5, 133.1, 132.6, 132.5, 128.6, 128.4, 128.3, 128.2, 128.0, 127.4, 127.3, 122.1, 122.0, 121.2, 121.0, 119.4, 119.3, 115.5, 115.4, 111.0, 110.7, 48.8, 46.4, 42.4, 41.0, 39.0, 38.1, 32.8, 31.6, 30.8, 30.6, 28.2, 26.9, 26.6.

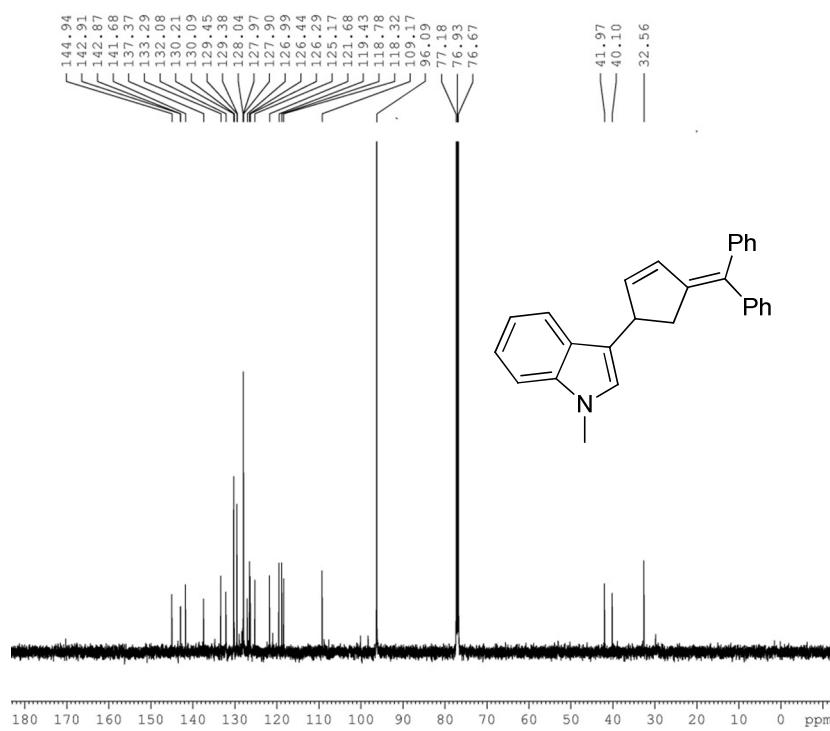
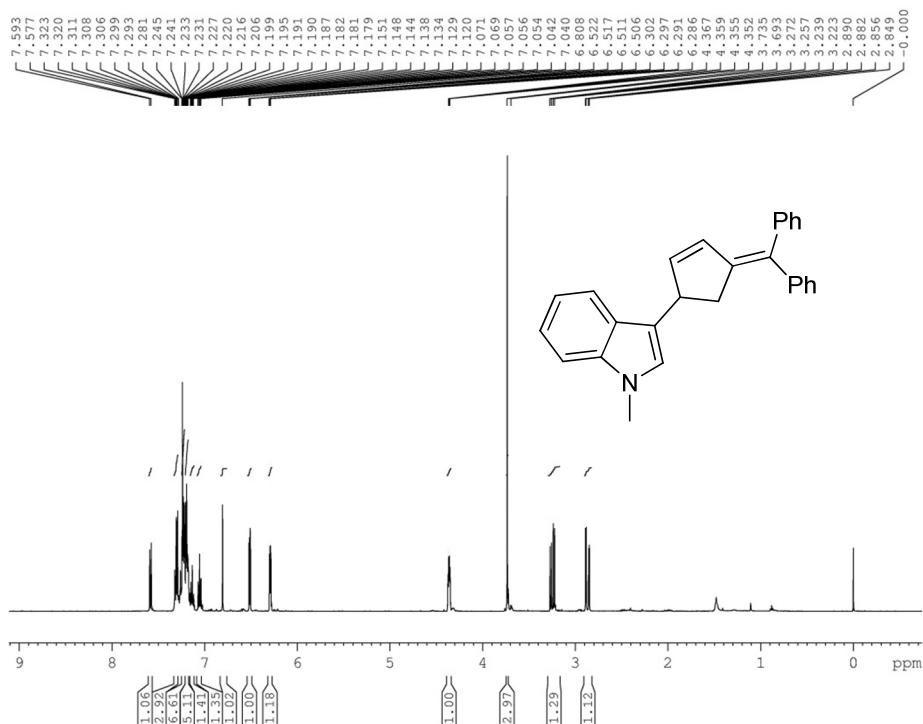
HRMS (ESI): Calcd for $\text{C}_{43}\text{H}_{40}\text{N}_2\text{Na}$: 607.30892; Found: 607.30954.

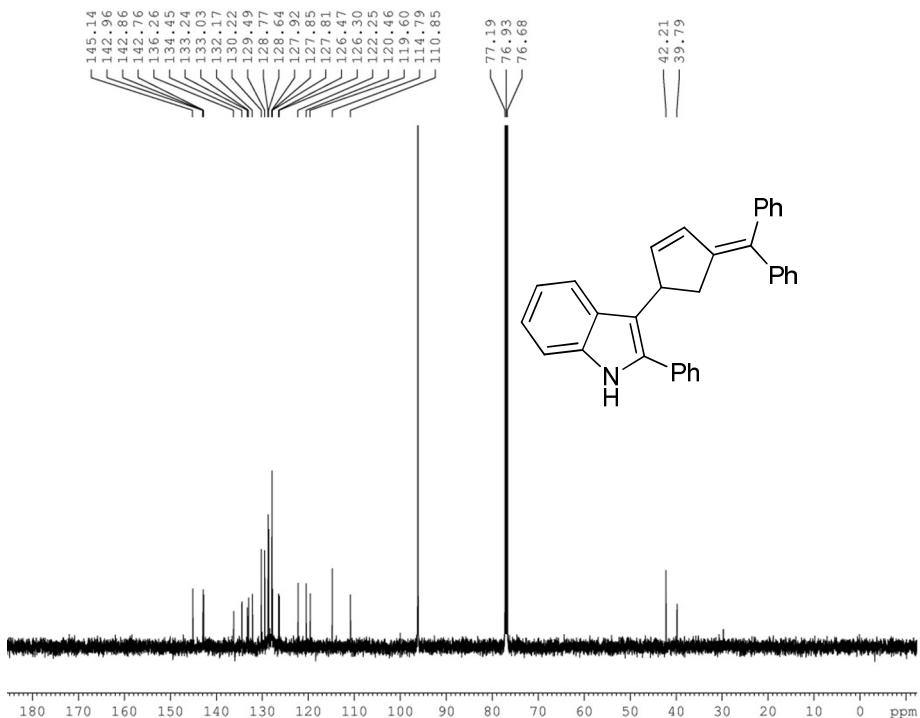
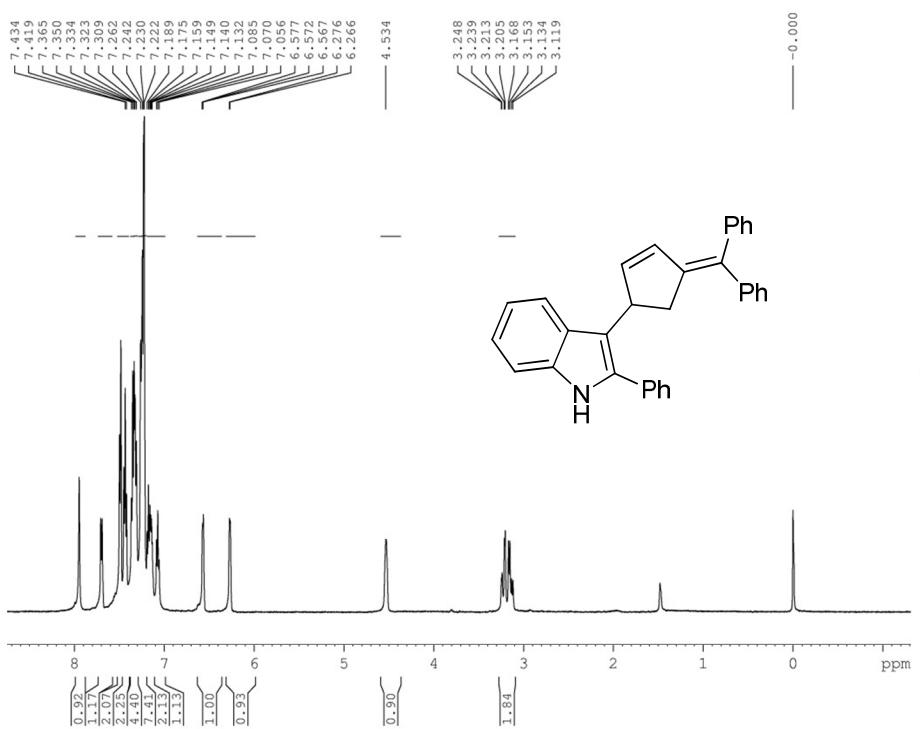


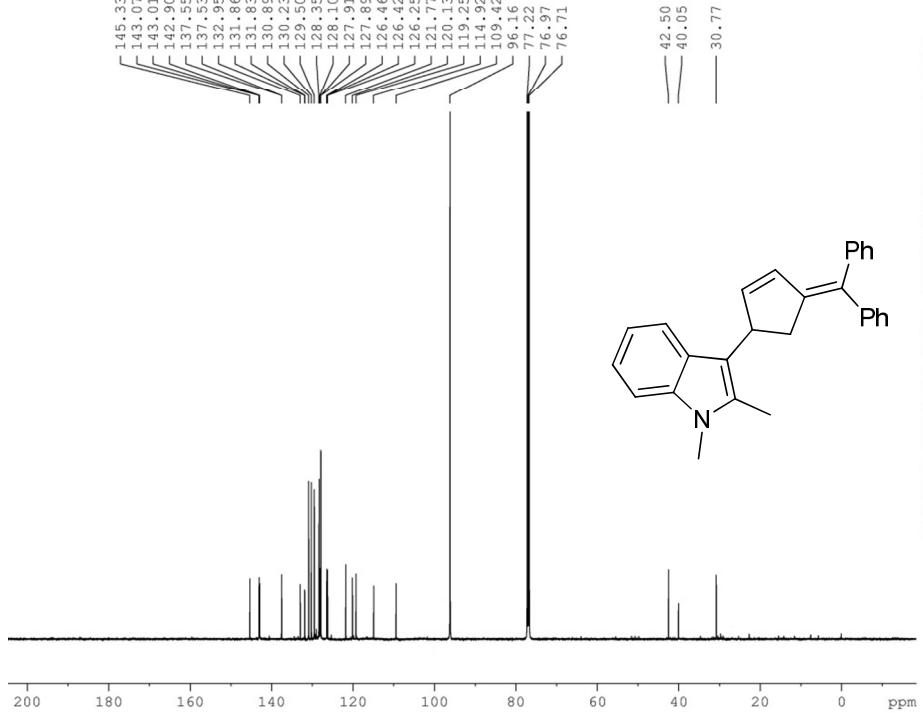
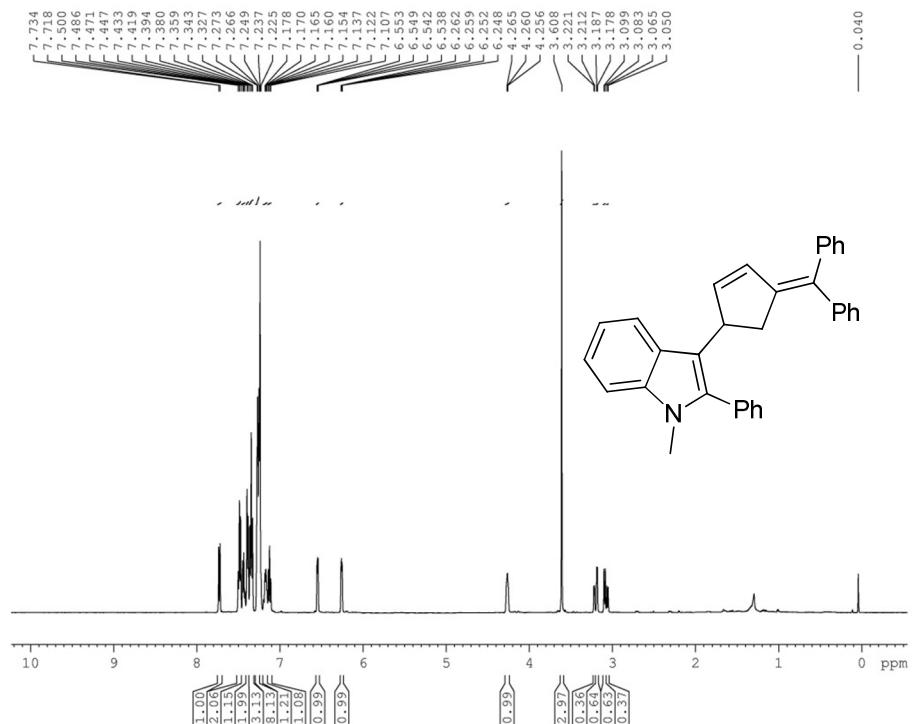
¹H NMR of 3aa



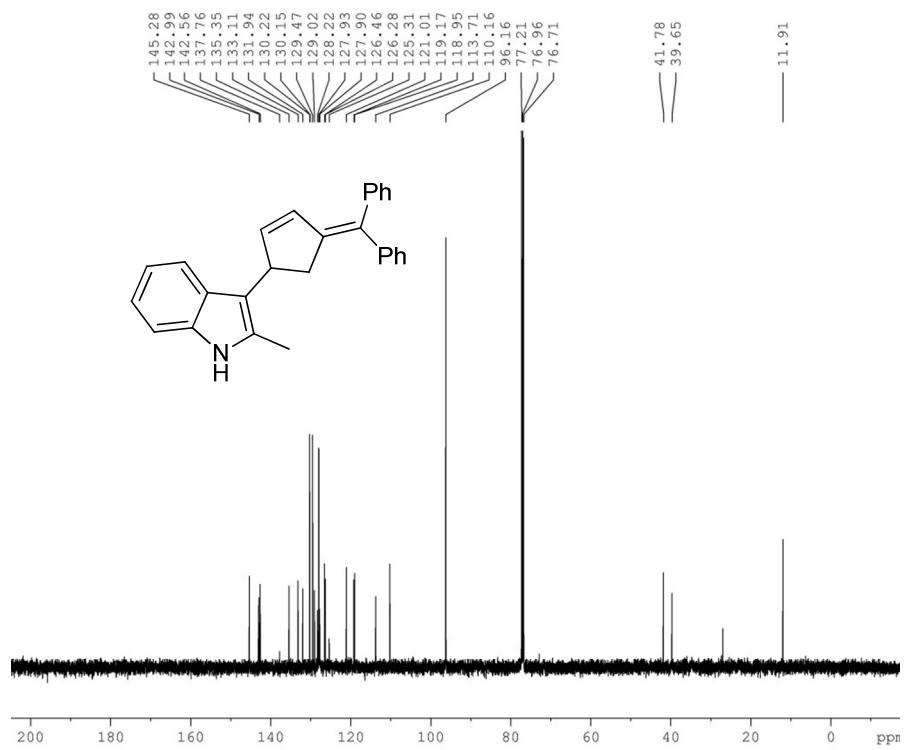
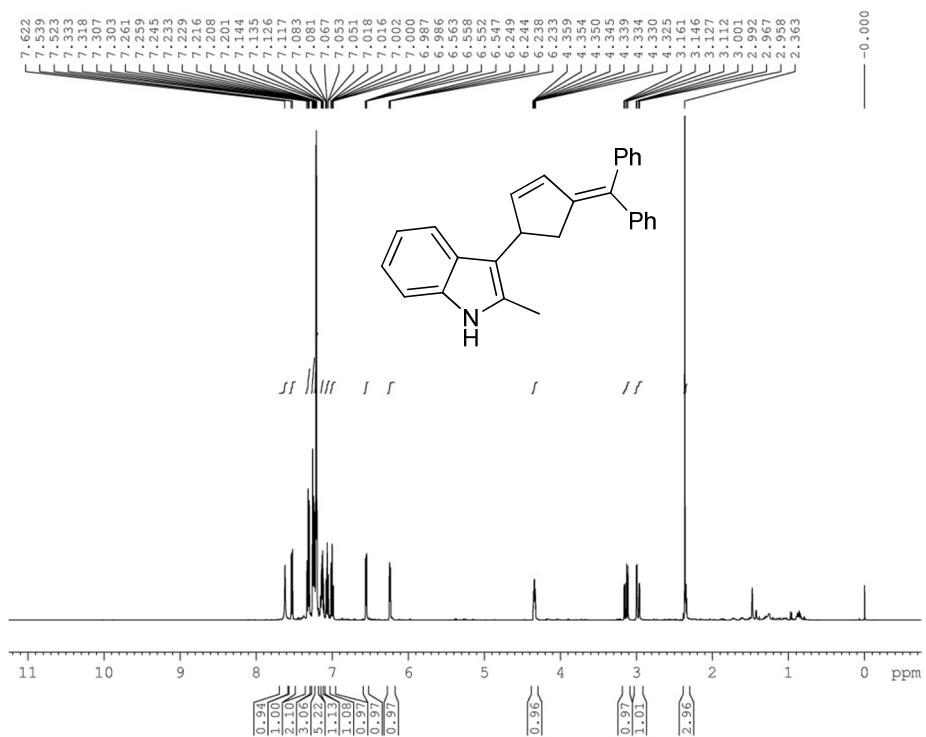
¹³C NMR of 3aa

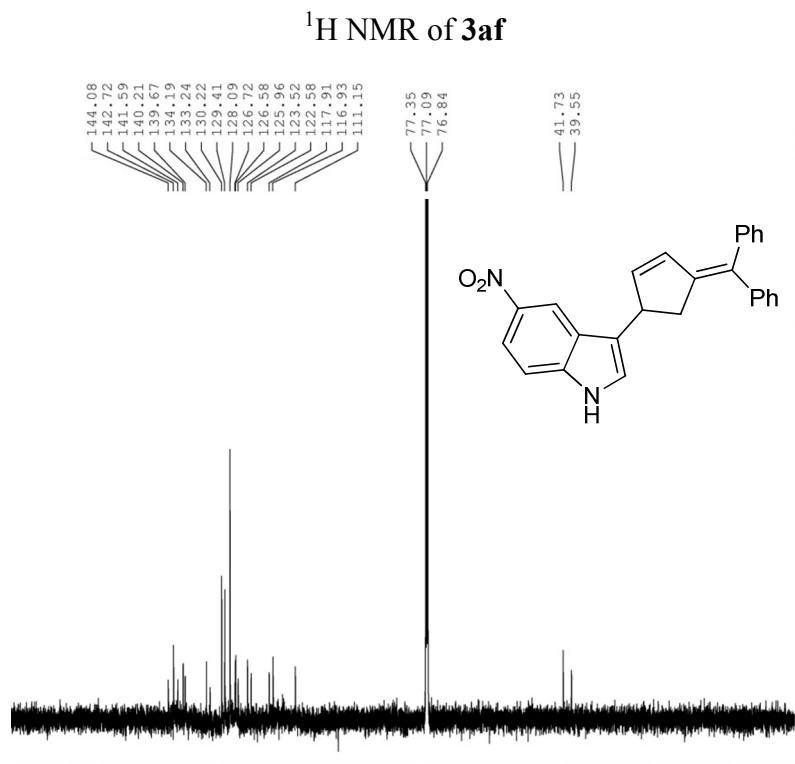
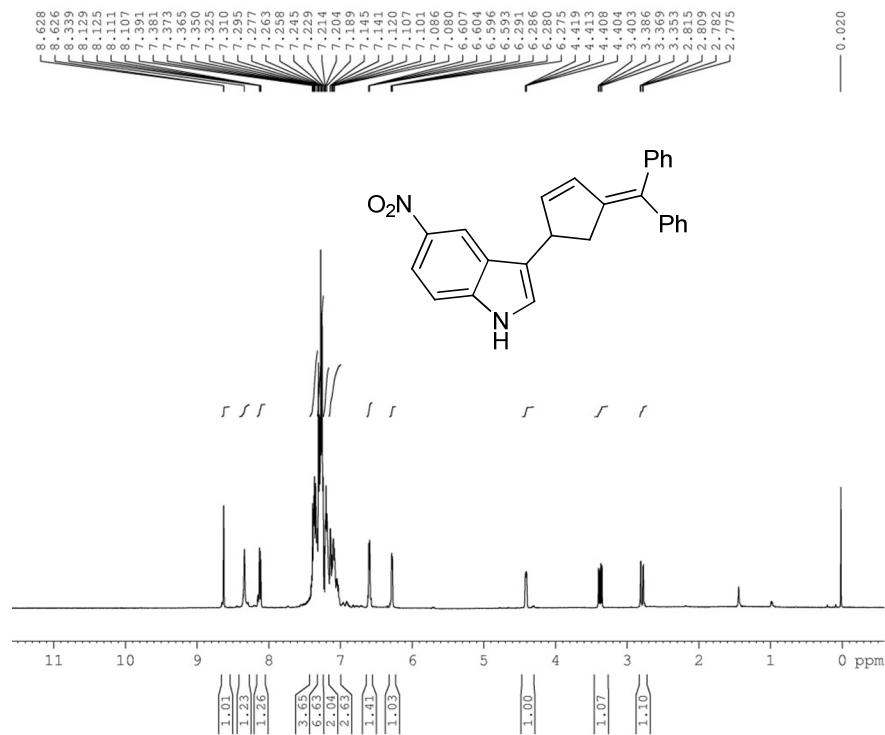


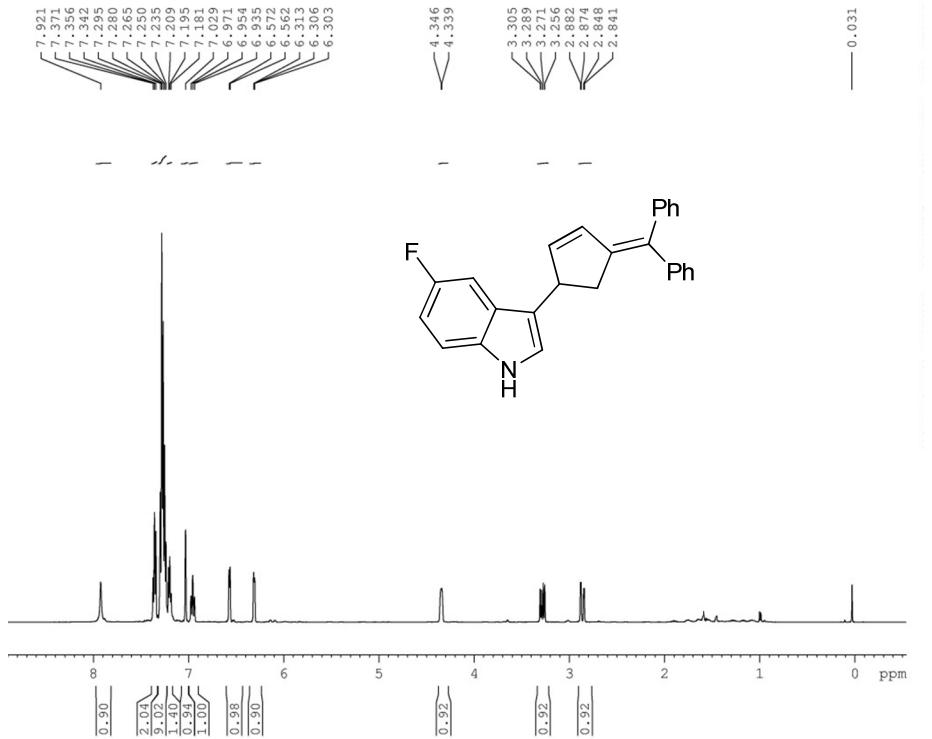




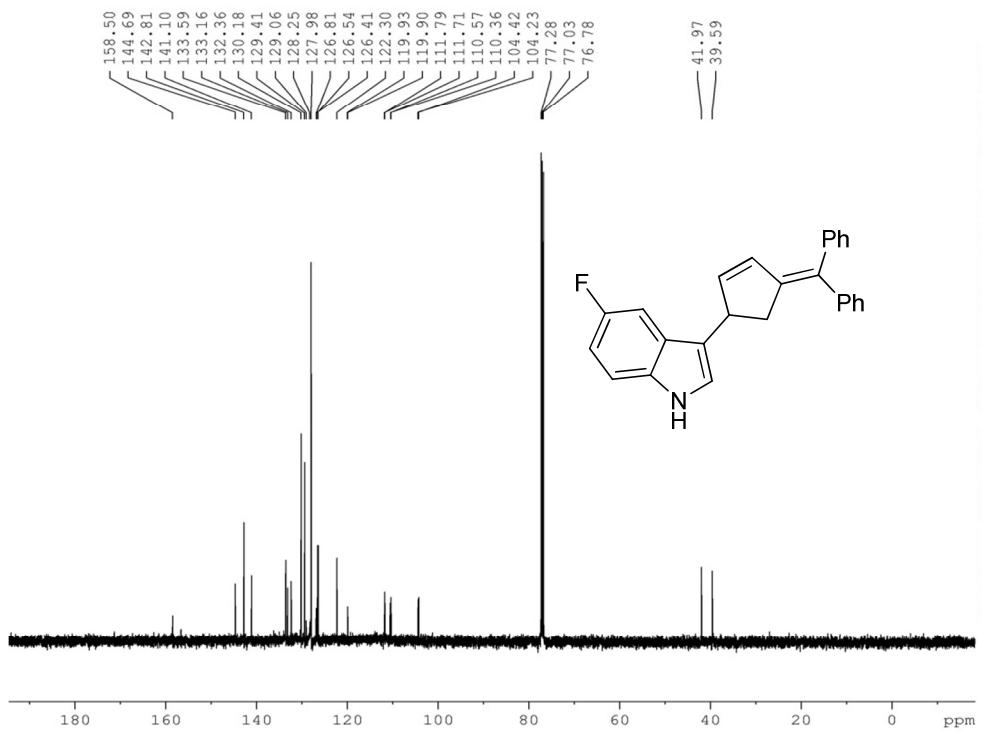
¹³C NMR of 3ad



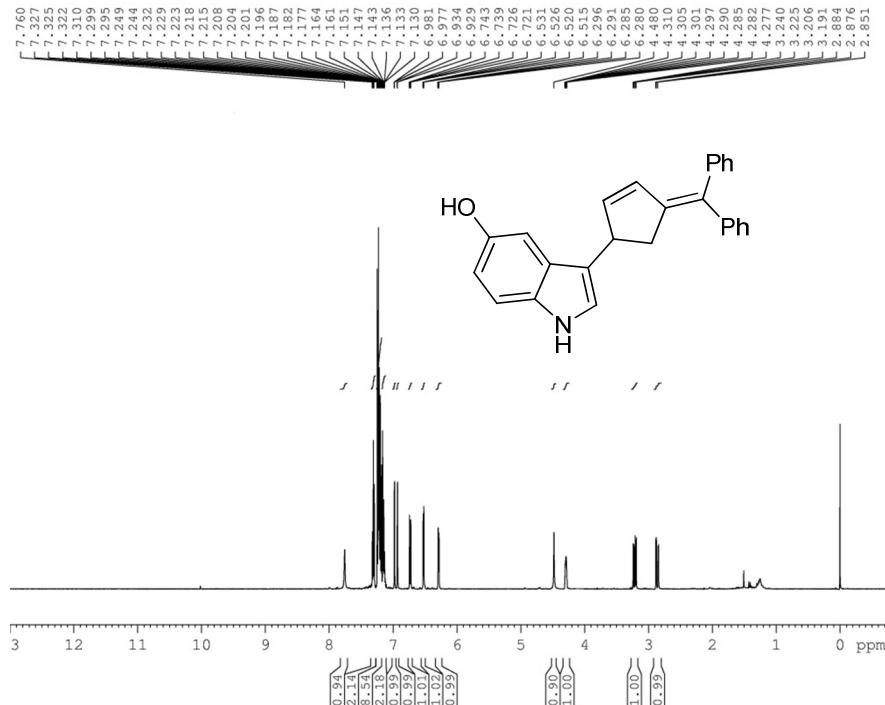




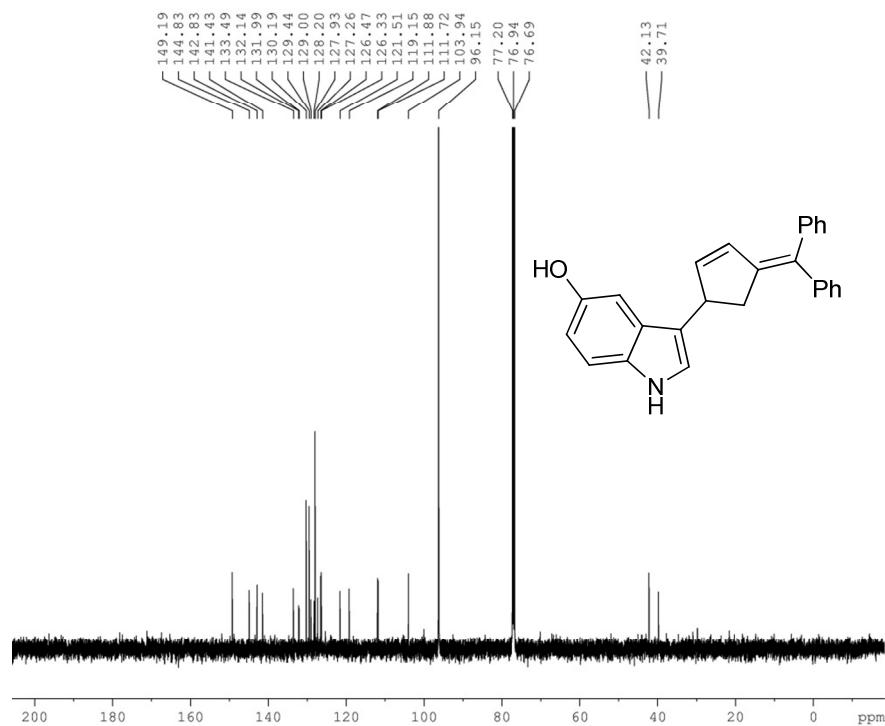
¹H NMR of 3ag



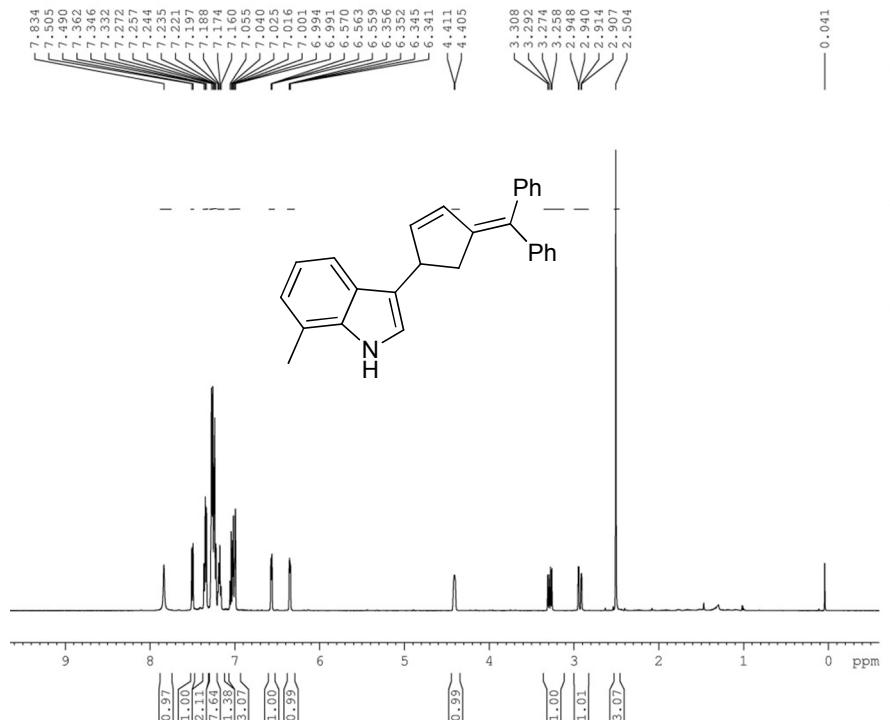
¹H NMR of 3ag



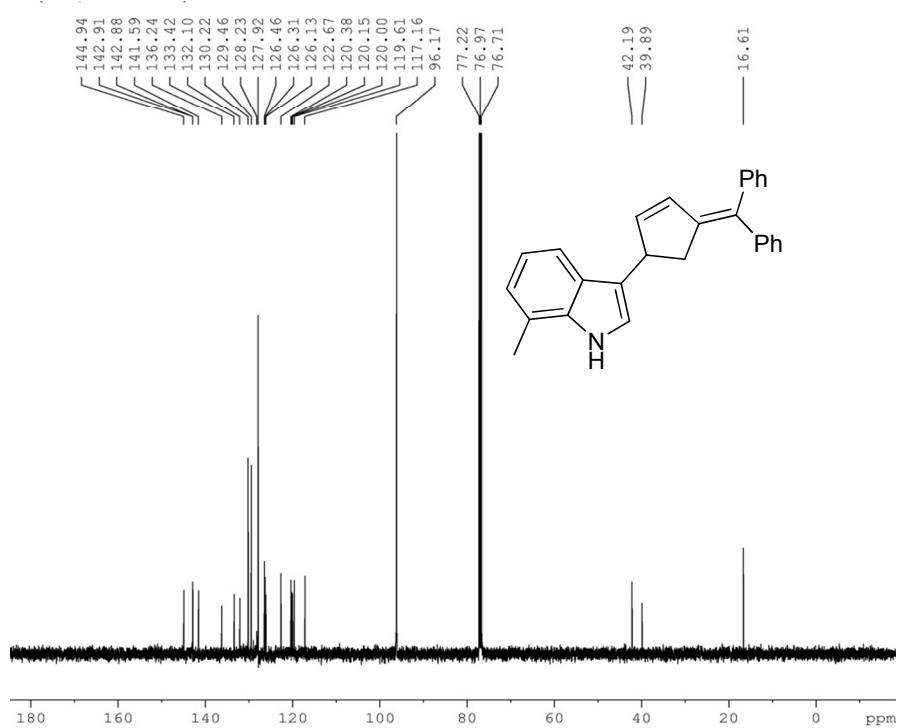
¹H NMR of 3ah



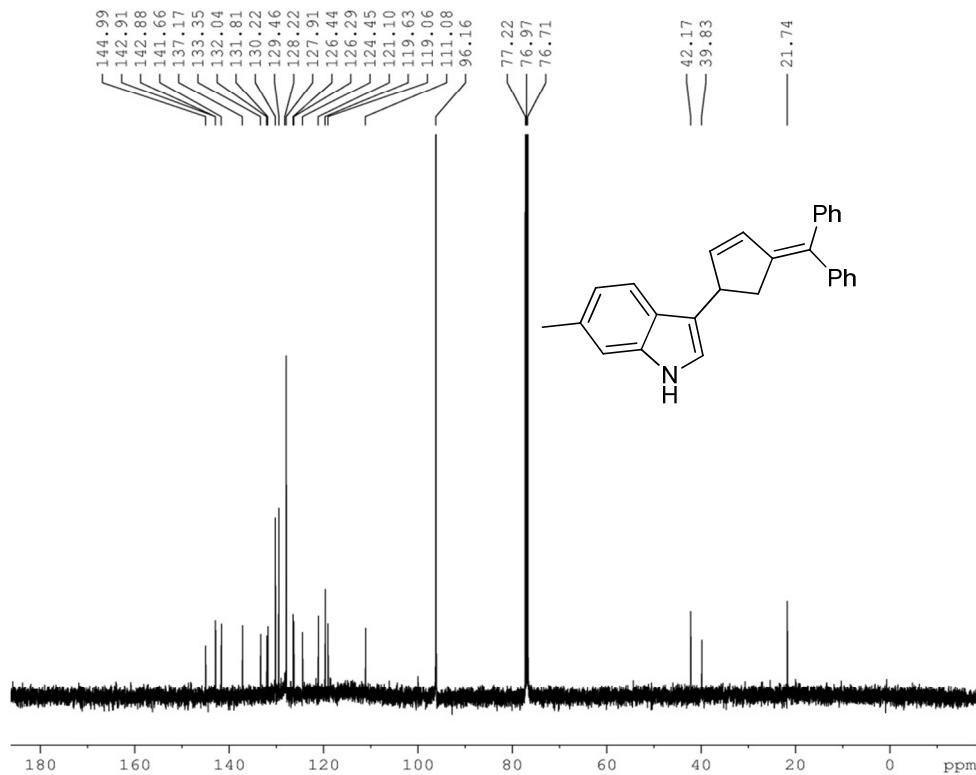
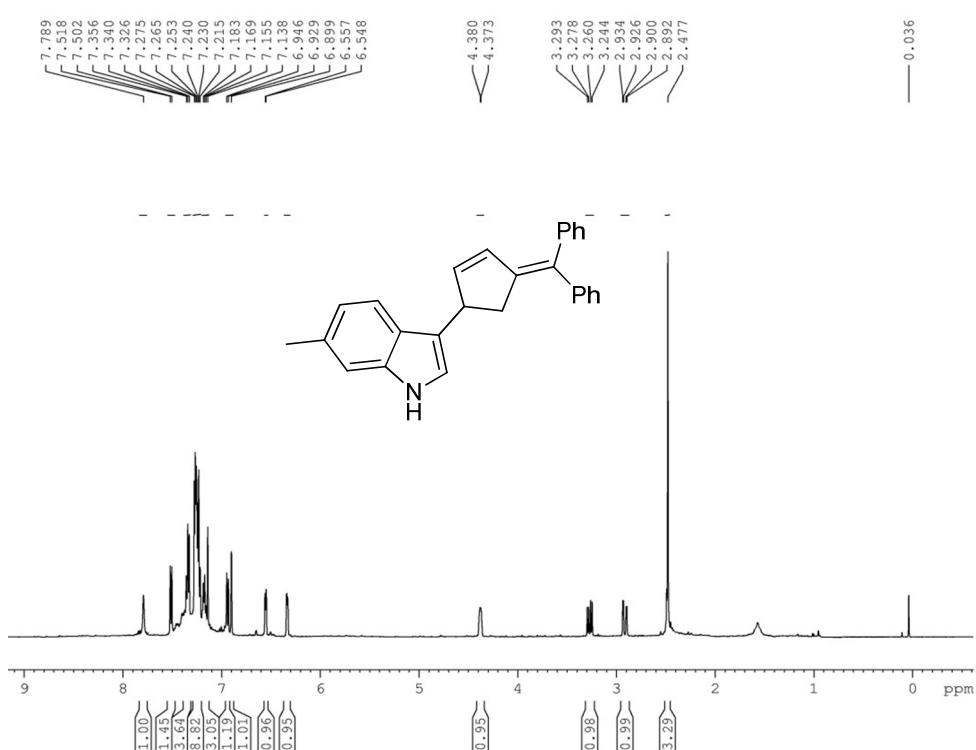
¹³C NMR of 3ah

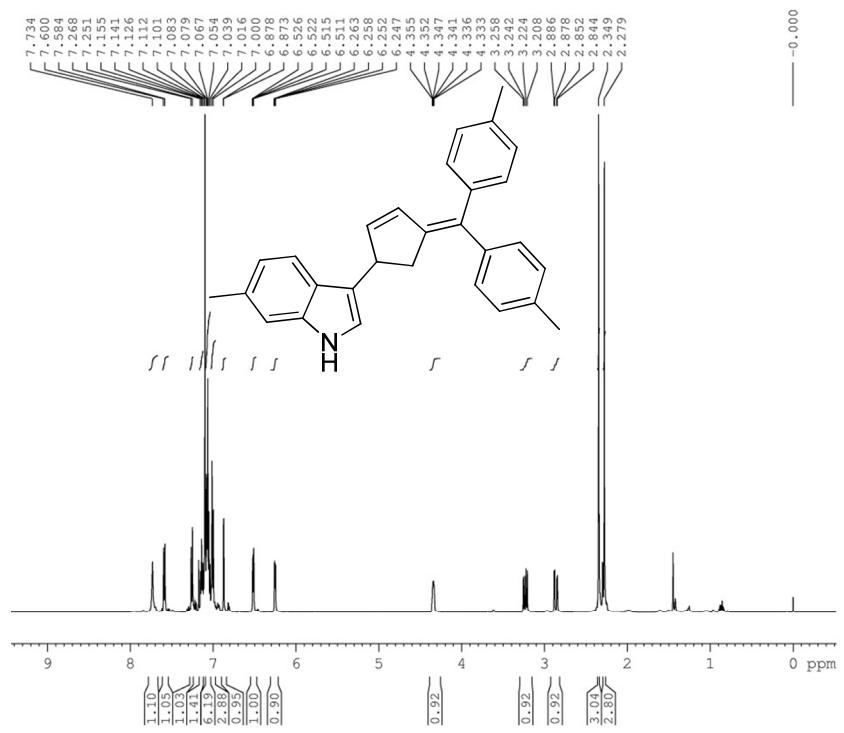


¹H NMR of 3aj

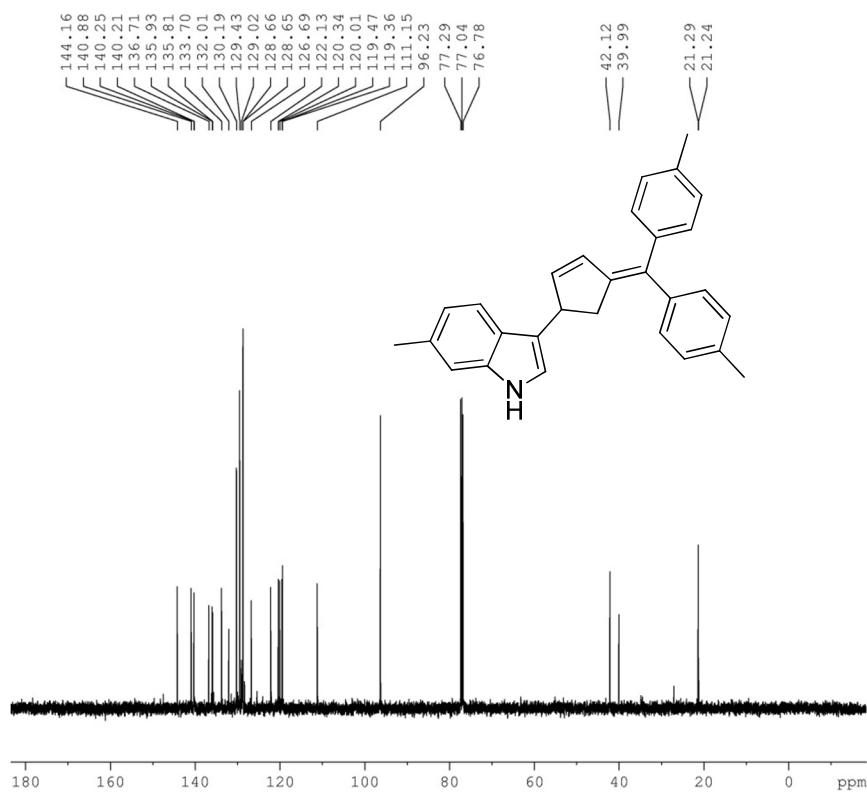


¹³C NMR of **3aj**

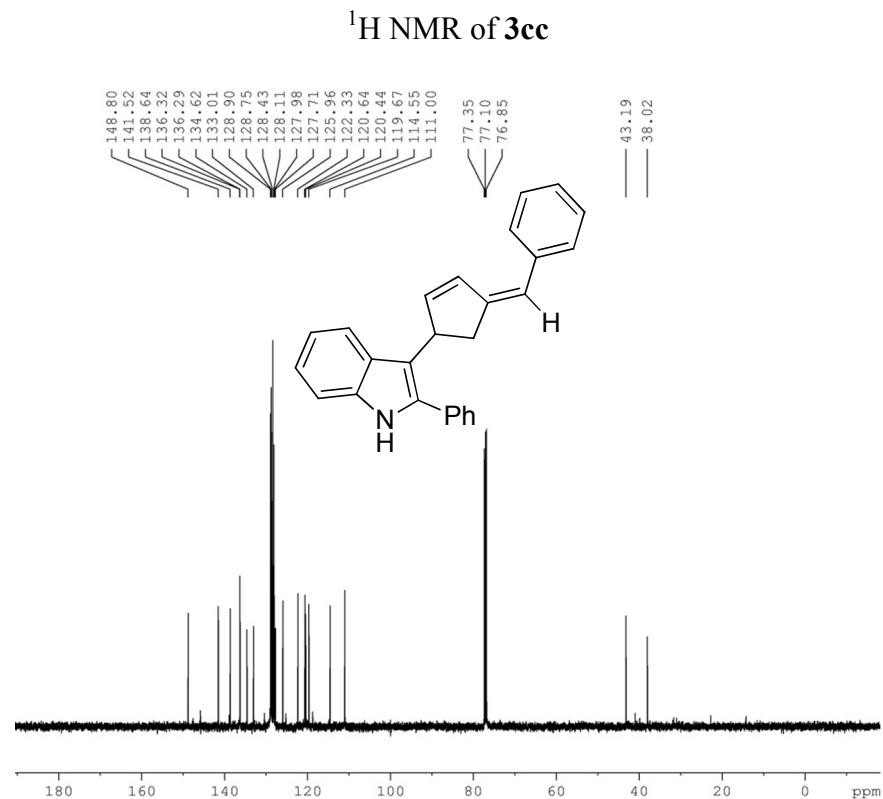
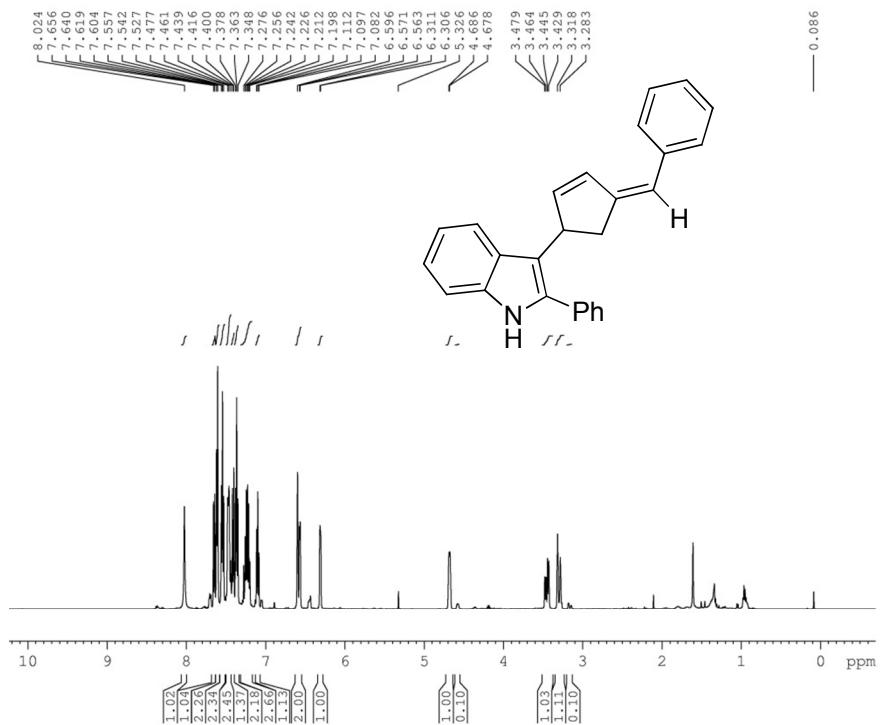


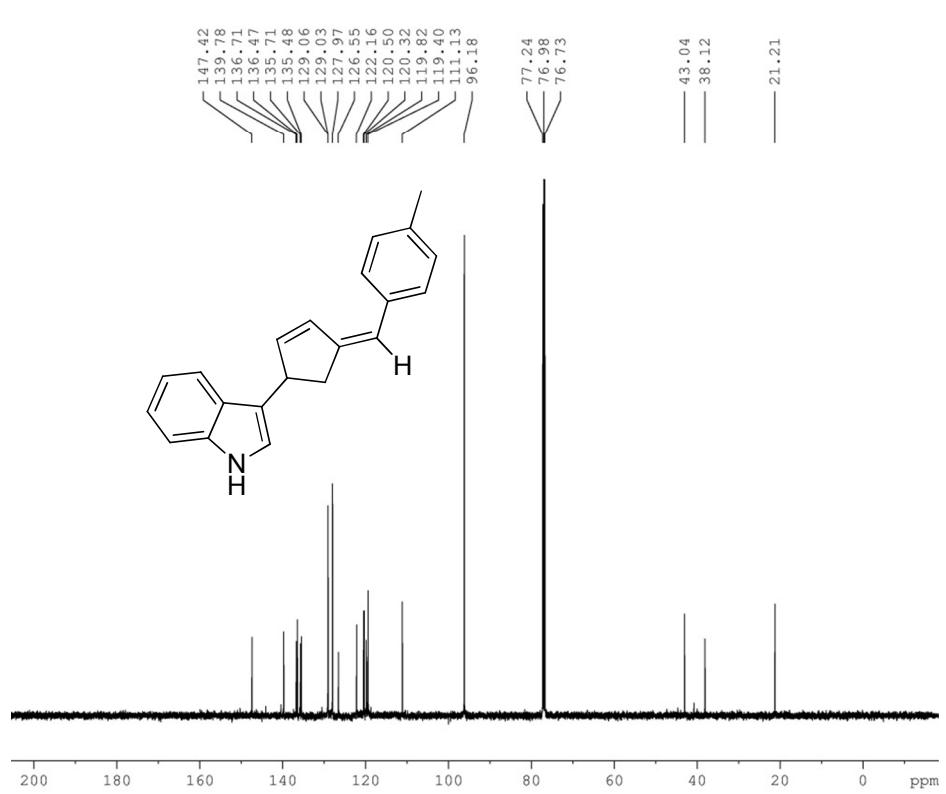
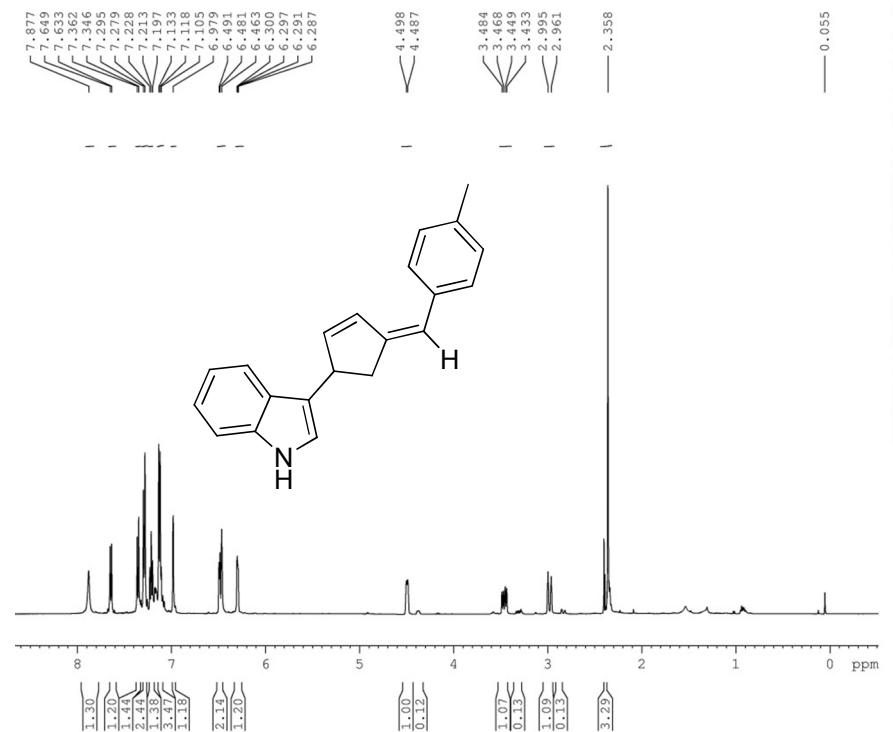


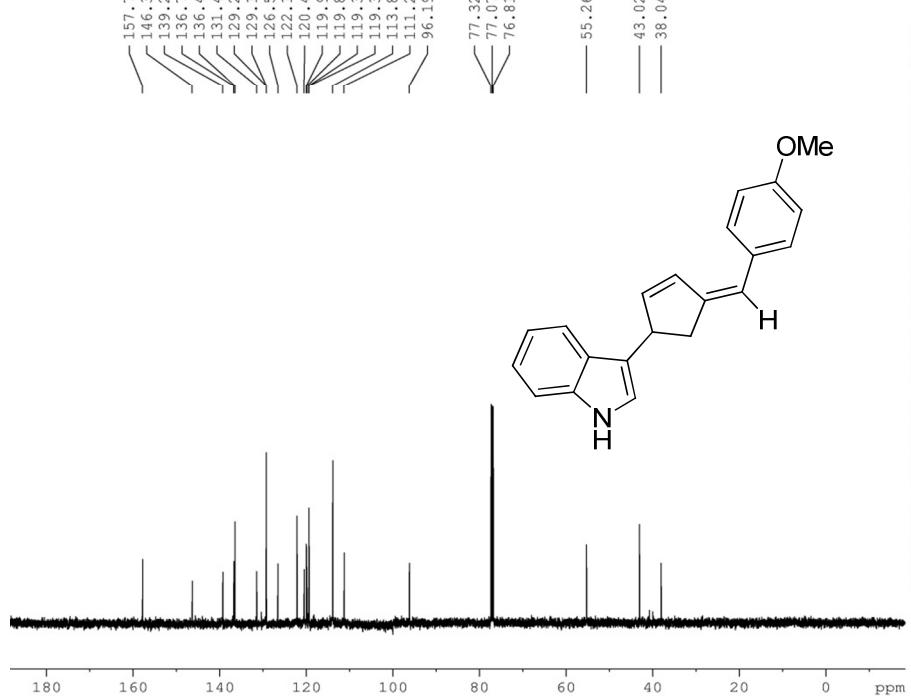
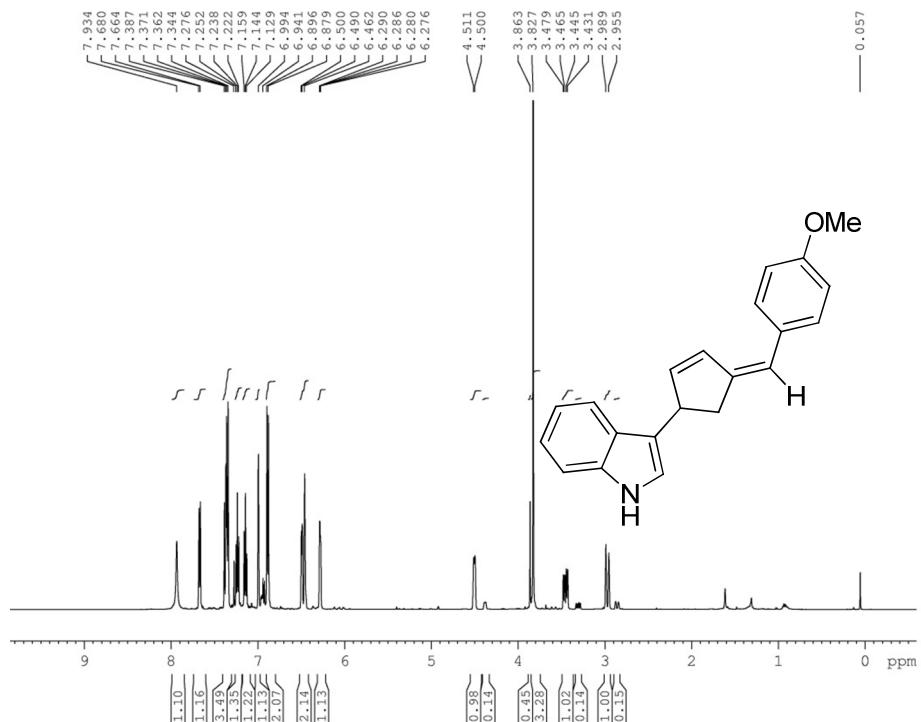
¹H NMR of 3ba

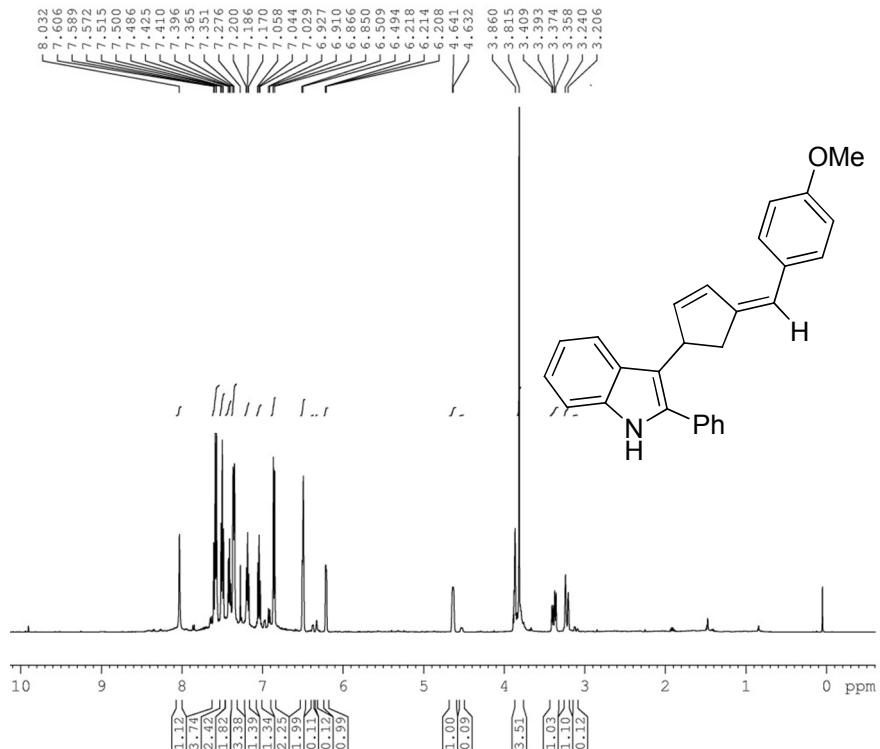


¹³C NMR of **3ba**

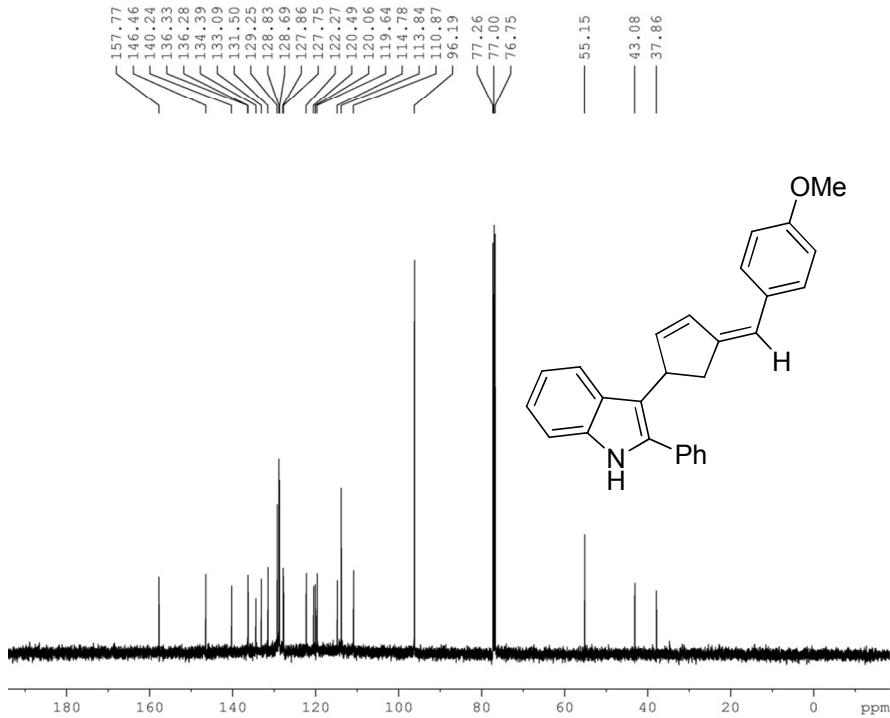




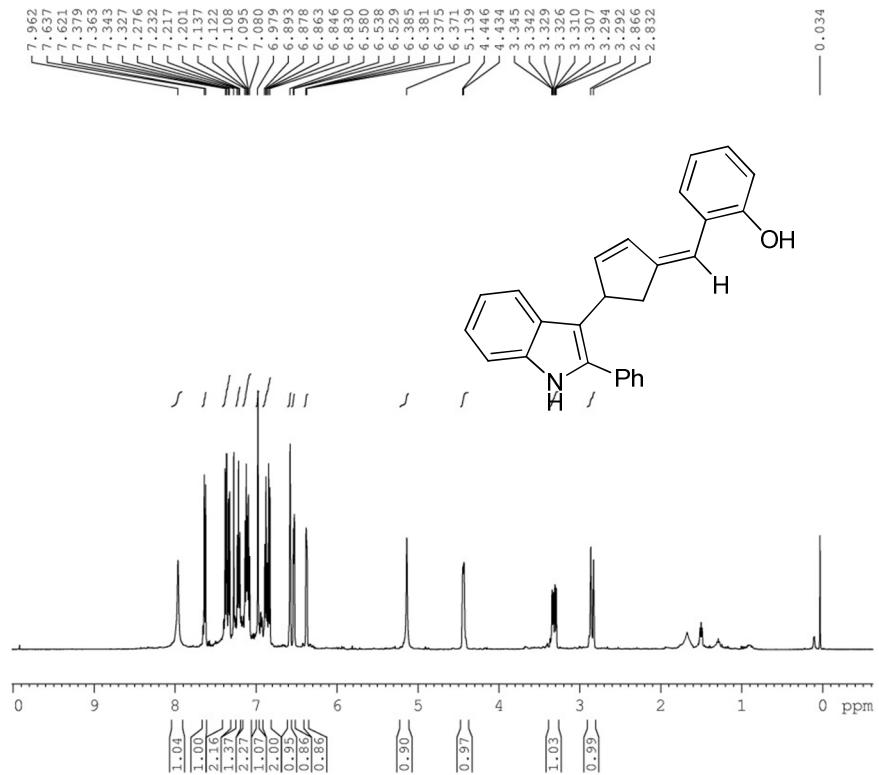




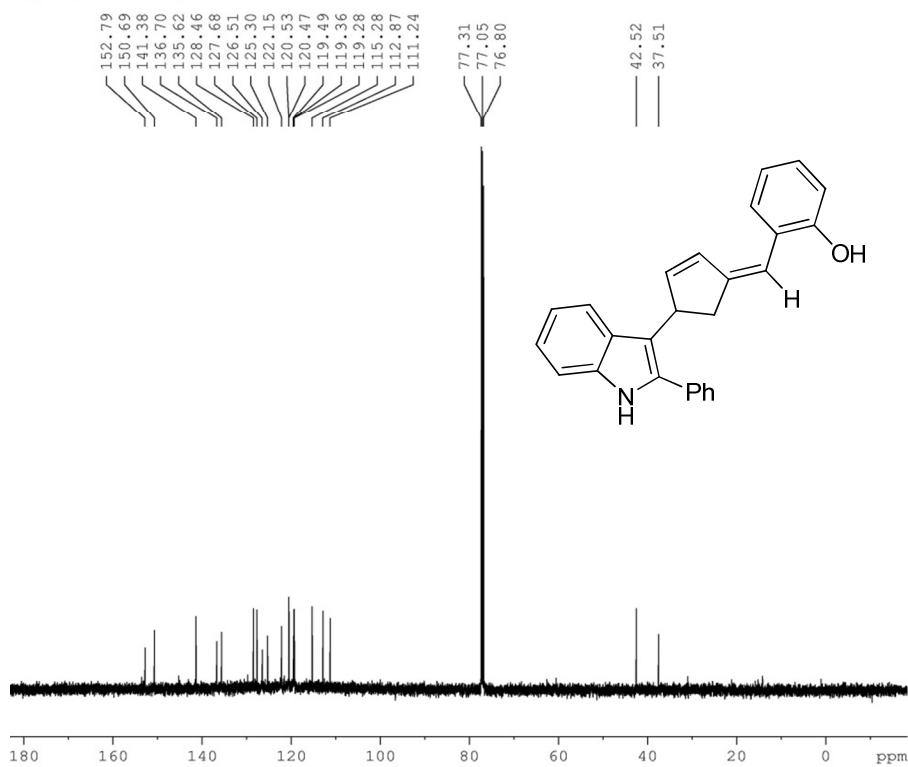
¹H NMR of 3ec



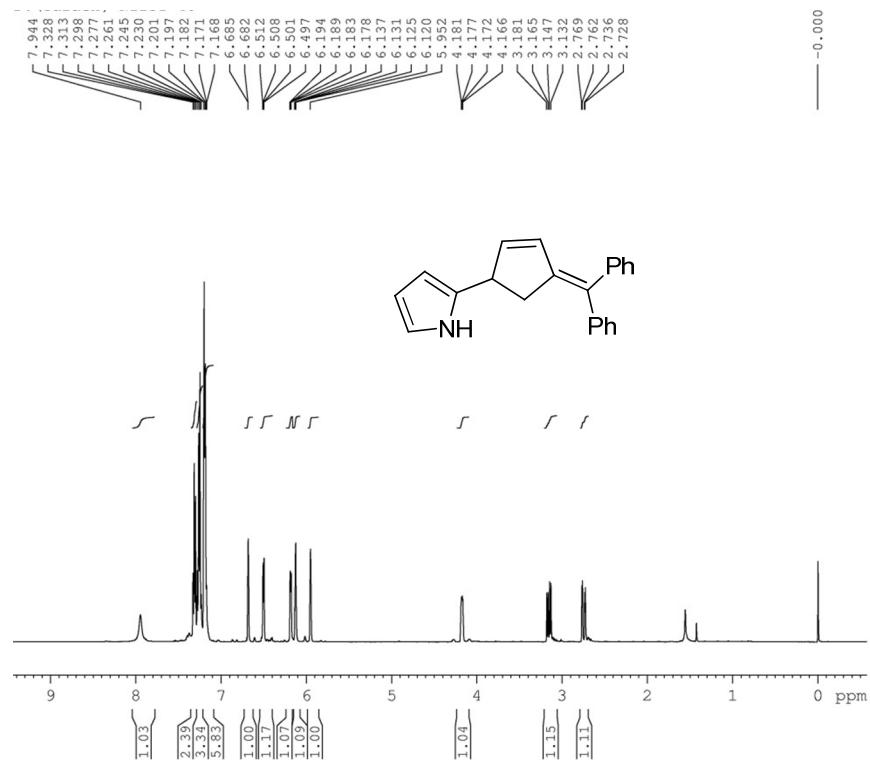
¹³C NMR of 3ec



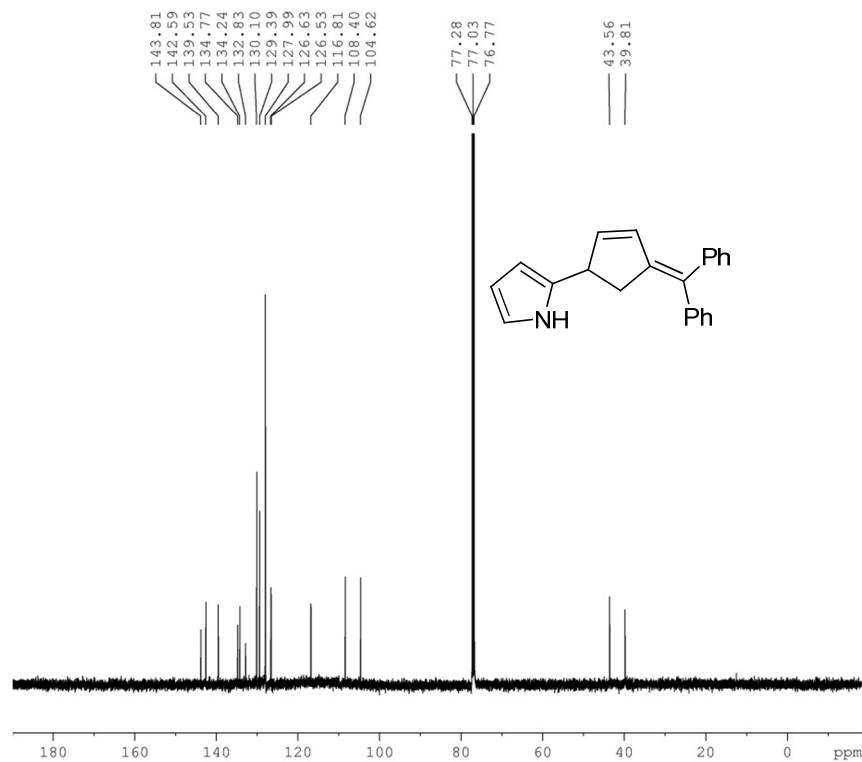
¹H NMR of 3fa



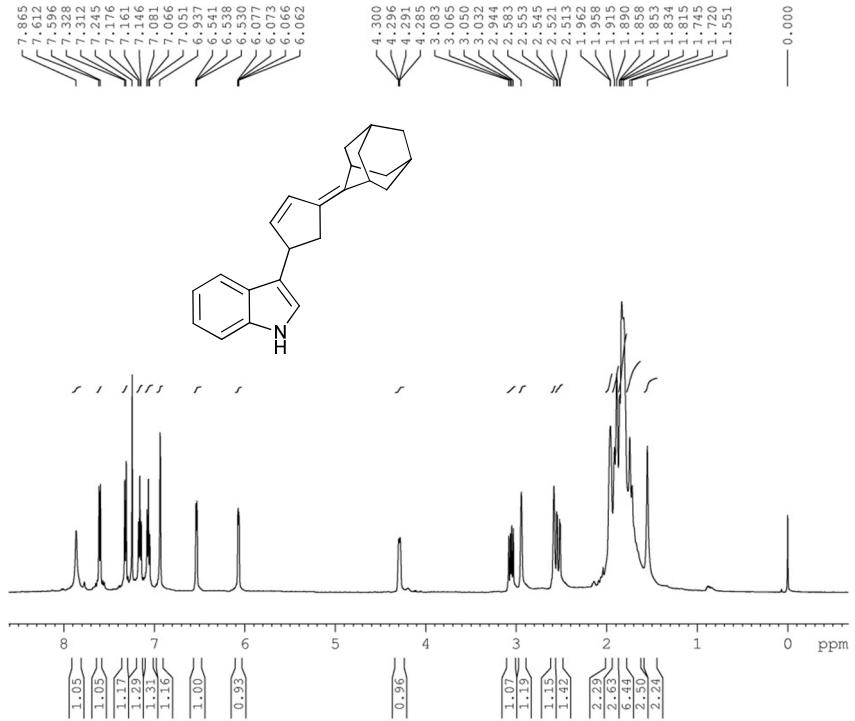
¹³C NMR of 3fa



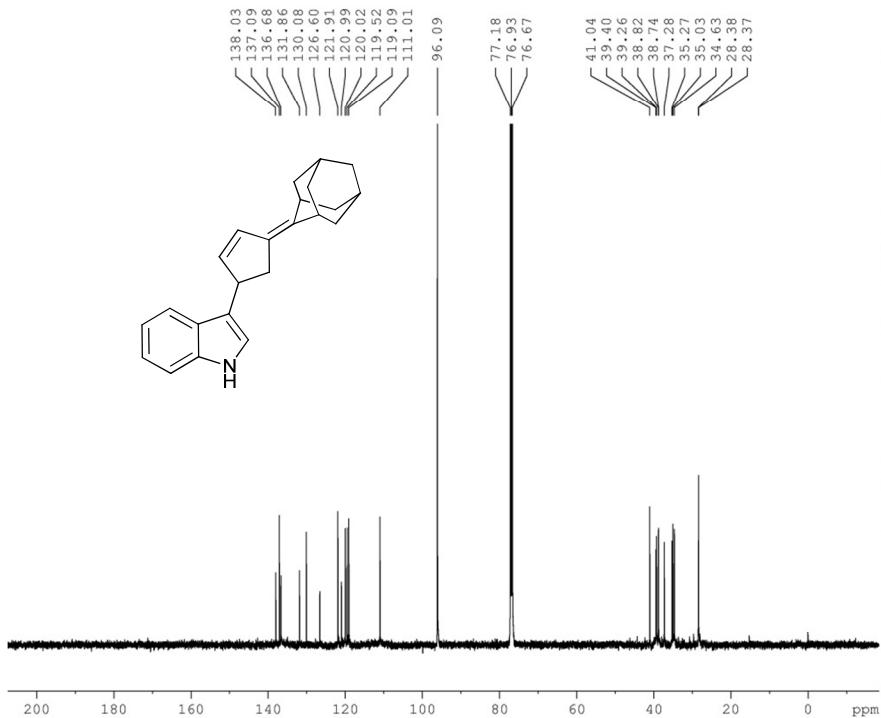
¹H NMR of 3al



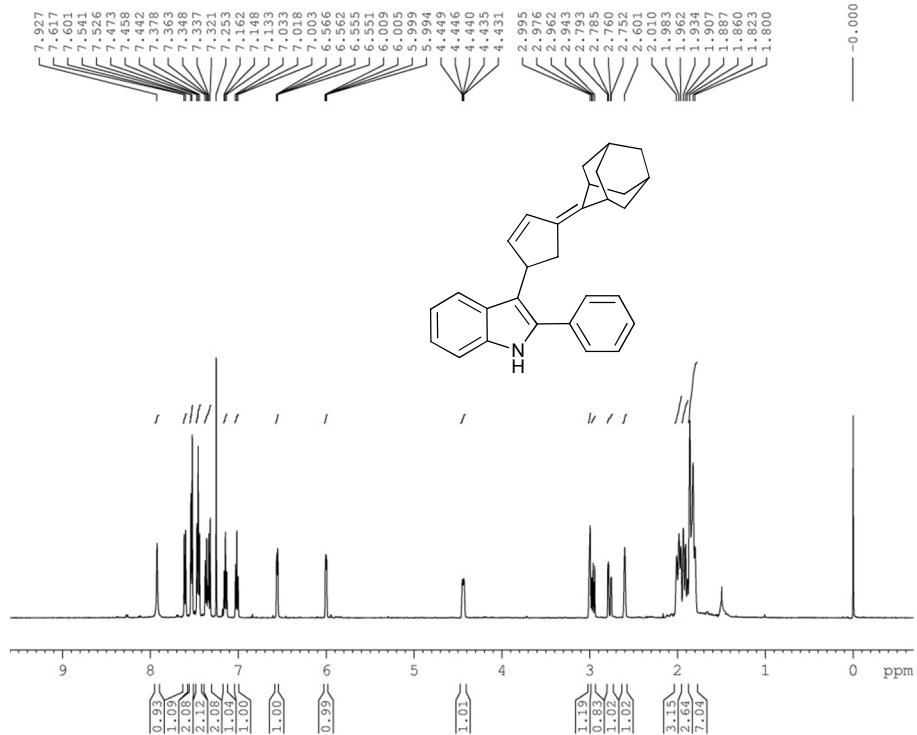
¹³C NMR of 3al



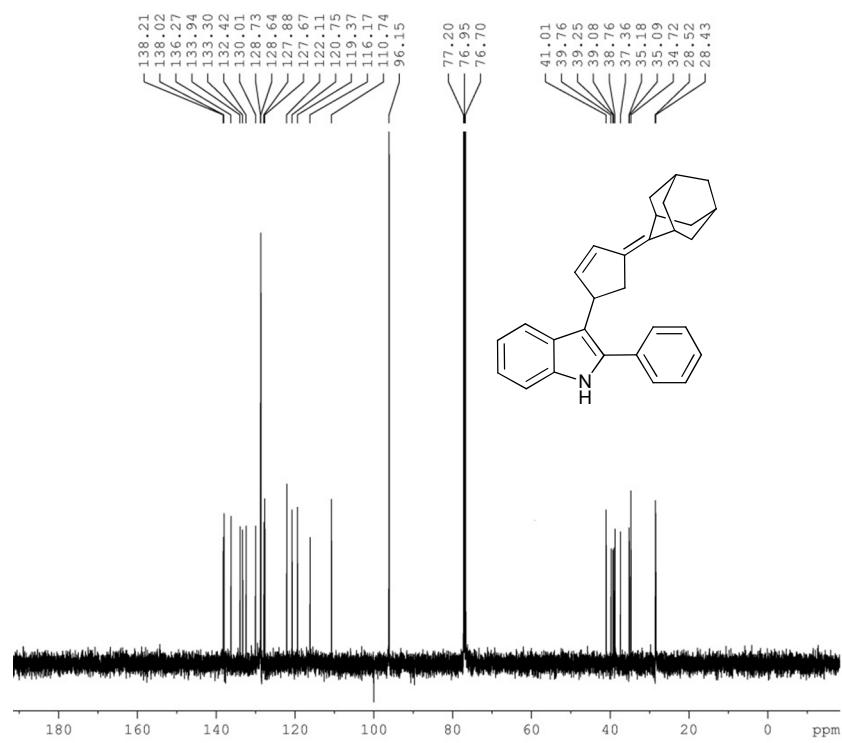
^1H NMR of **3ga**



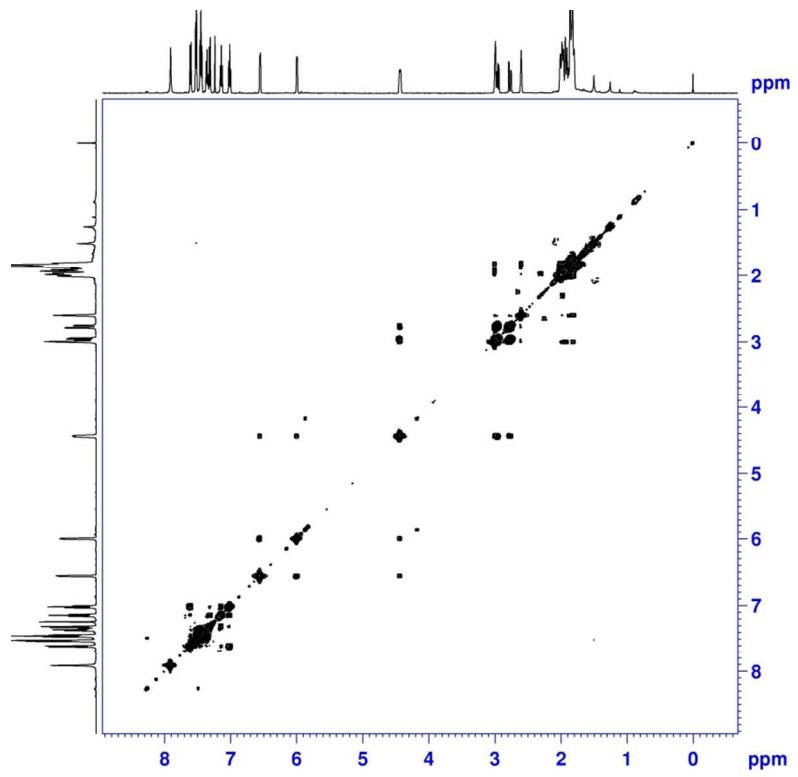
^{13}C NMR of **3ga**



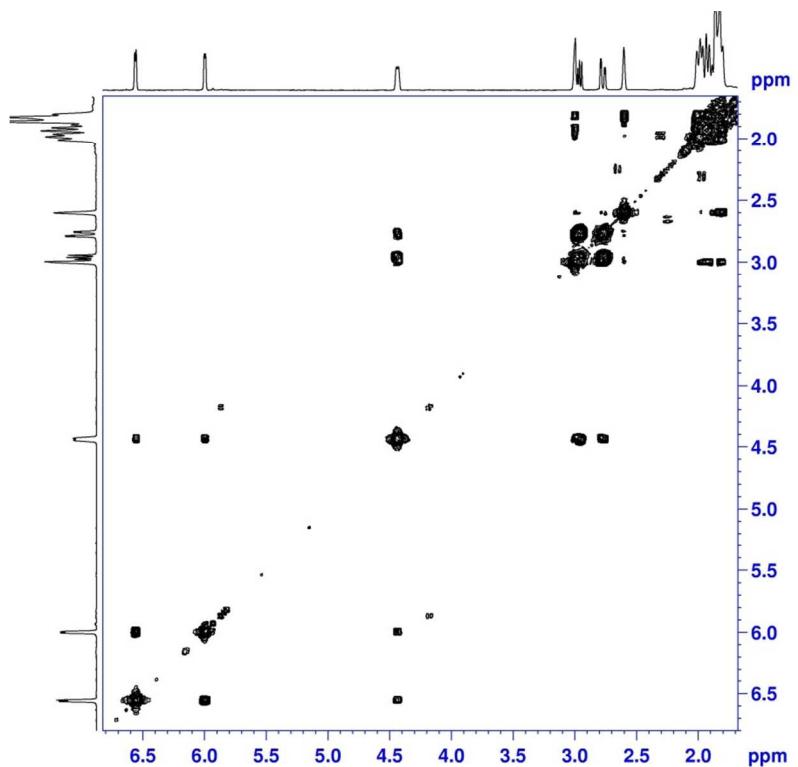
¹H NMR of 3gc



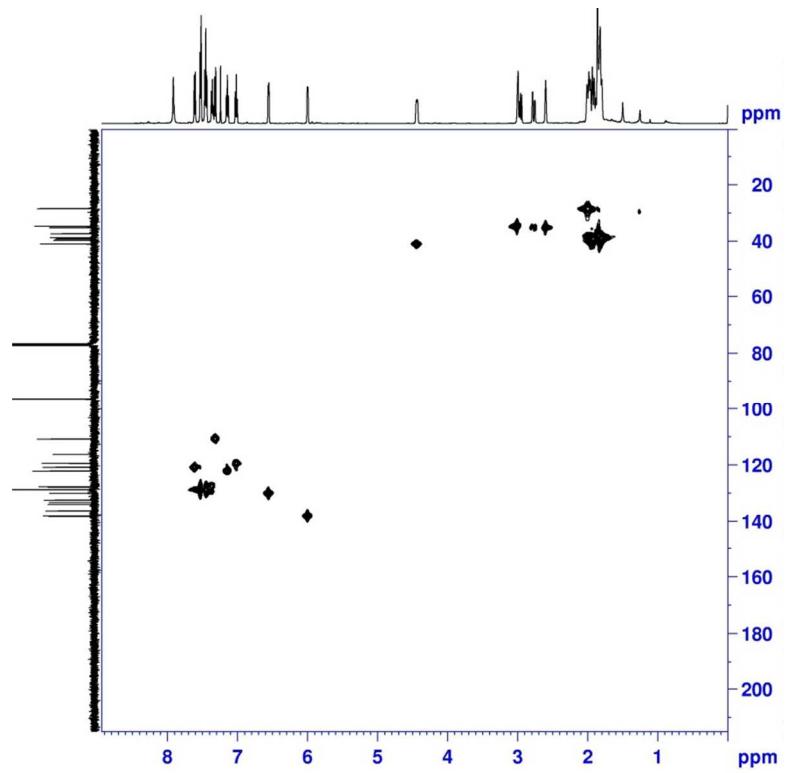
¹³C NMR of 3gc



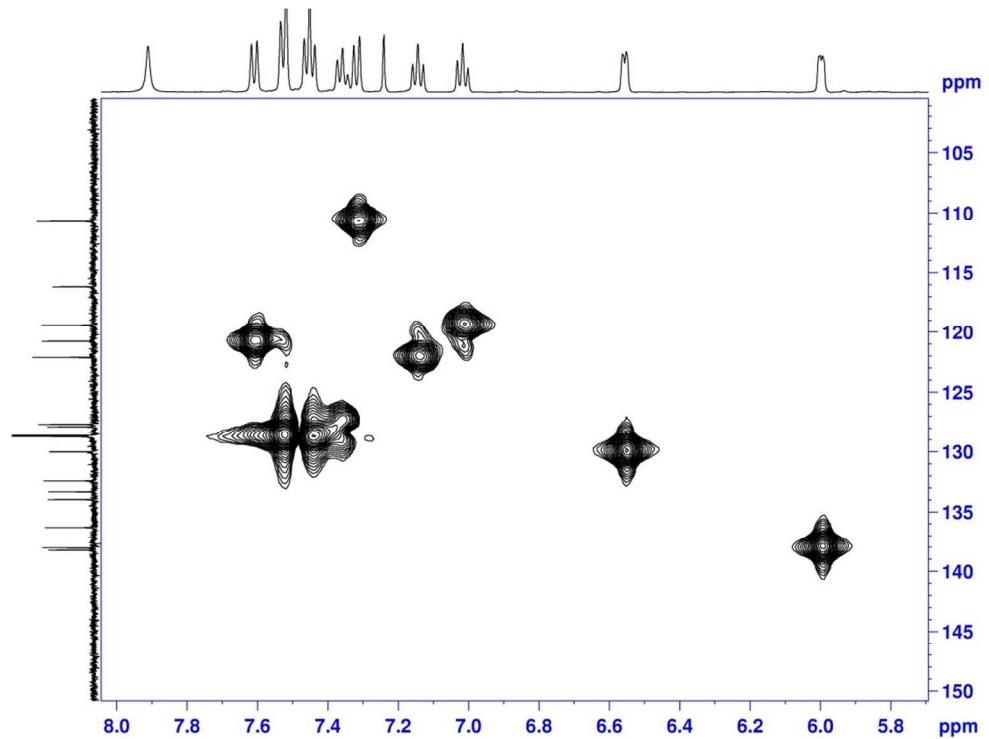
Compound 3gc (COSY)



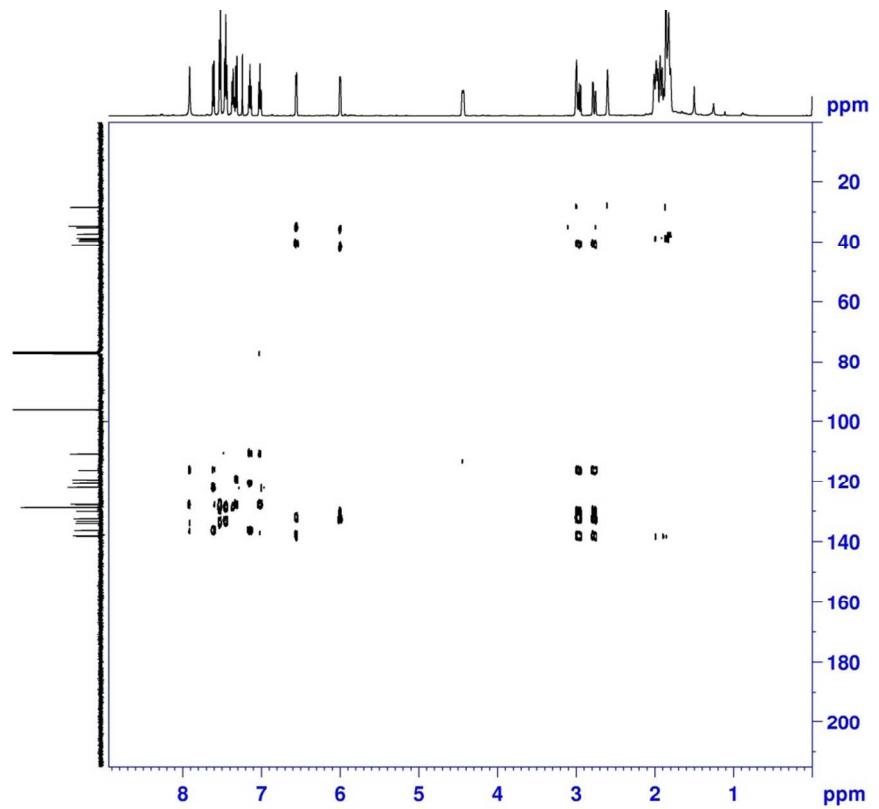
Compound 3gc (COSY)



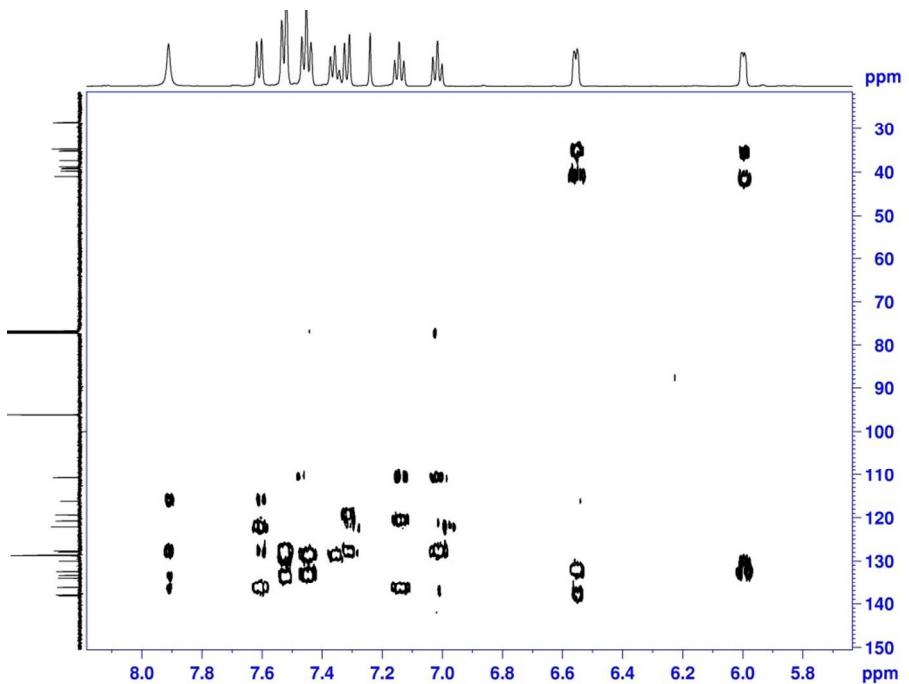
Compound 3gc (HSQC)



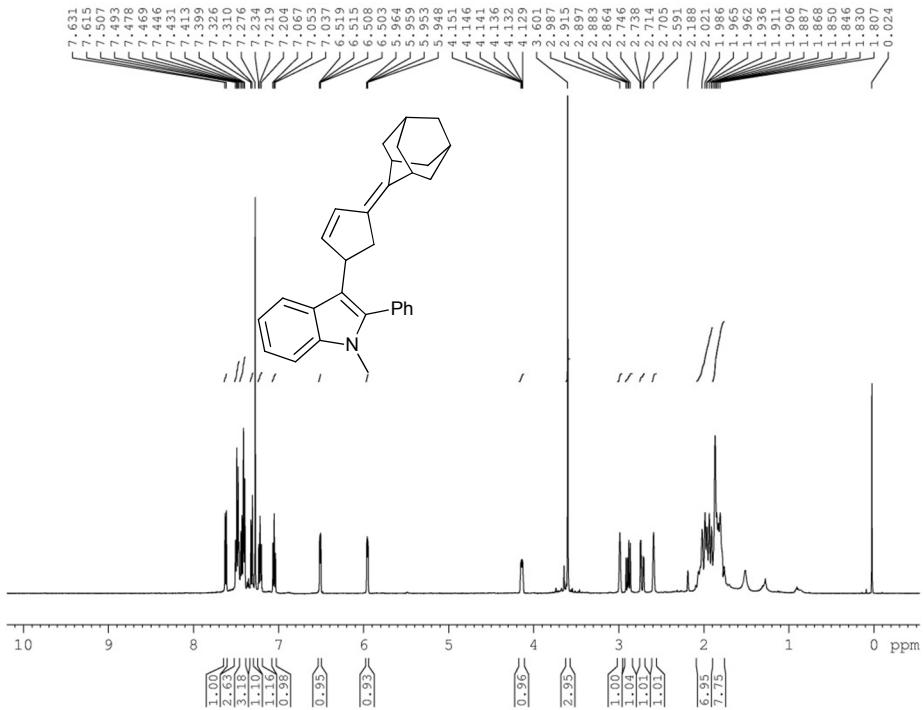
Compound 3gc (HSQC)



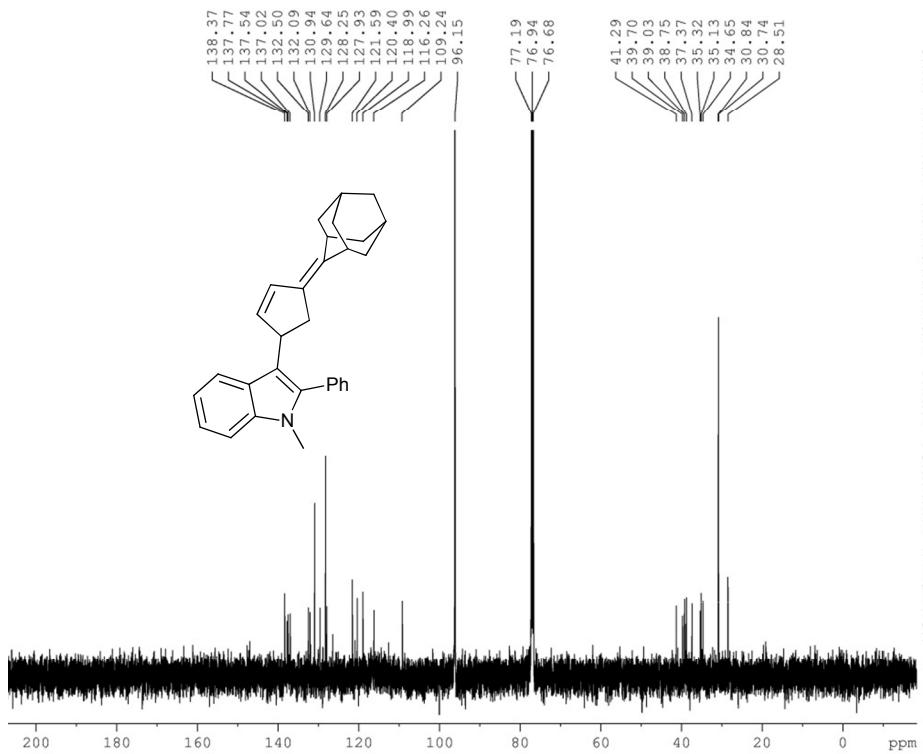
Compound 3gc (HMBC)



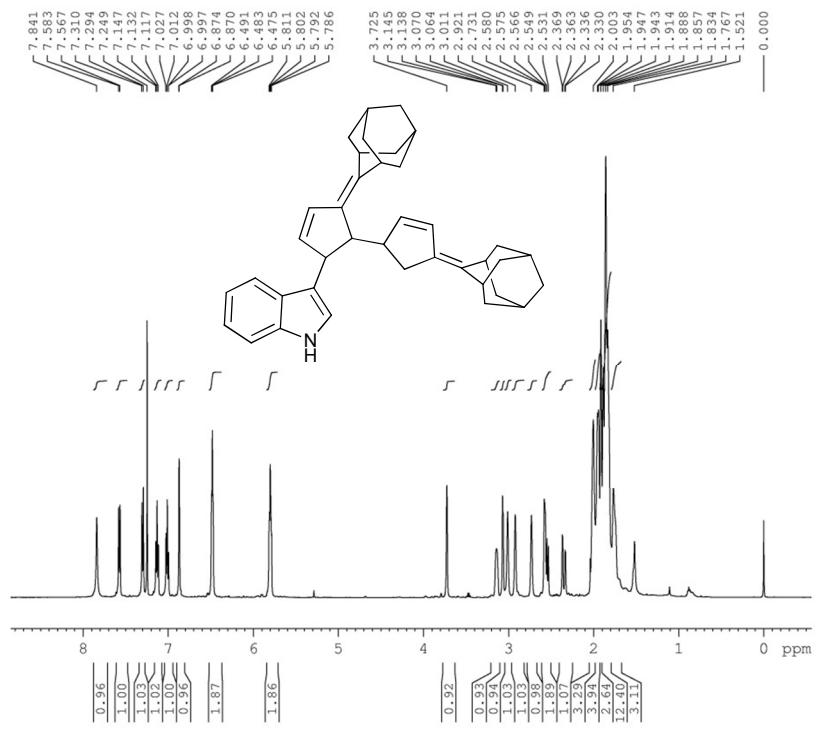
Compound 3gc (HMBC)



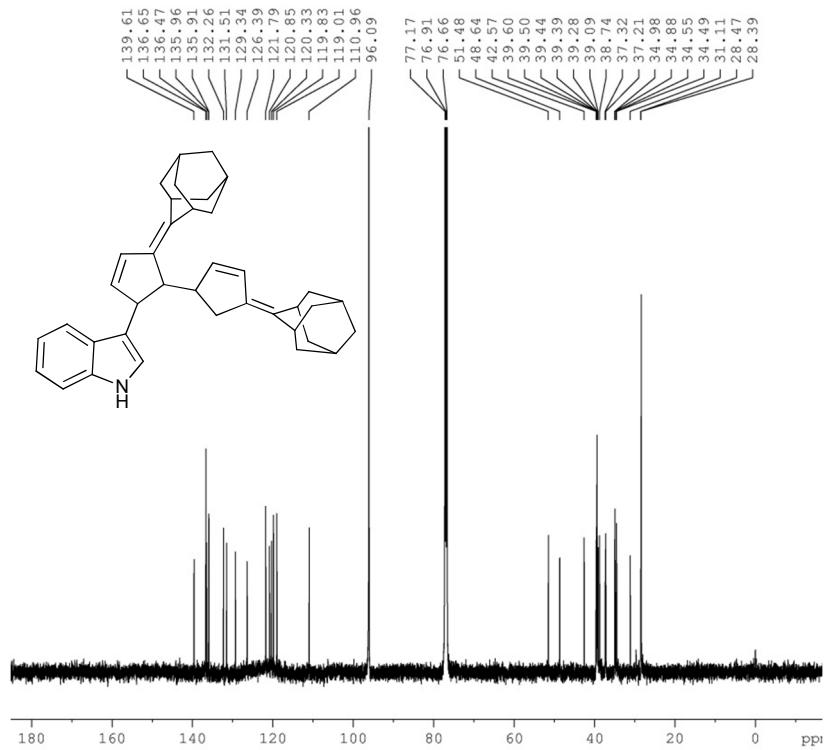
^1H NMR of **3gd**



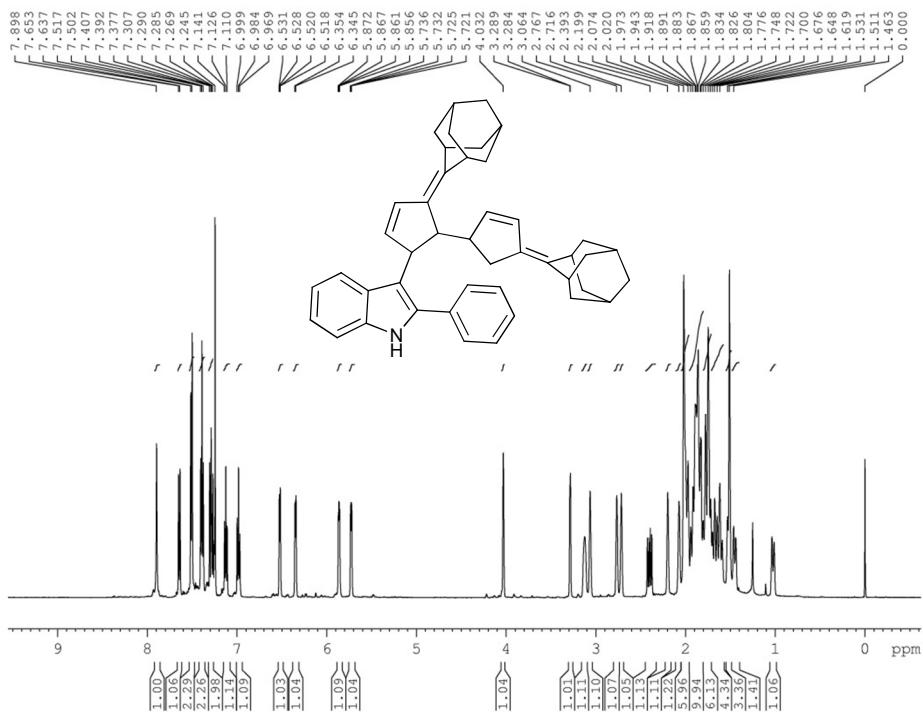
^{13}C NMR of **3gd**



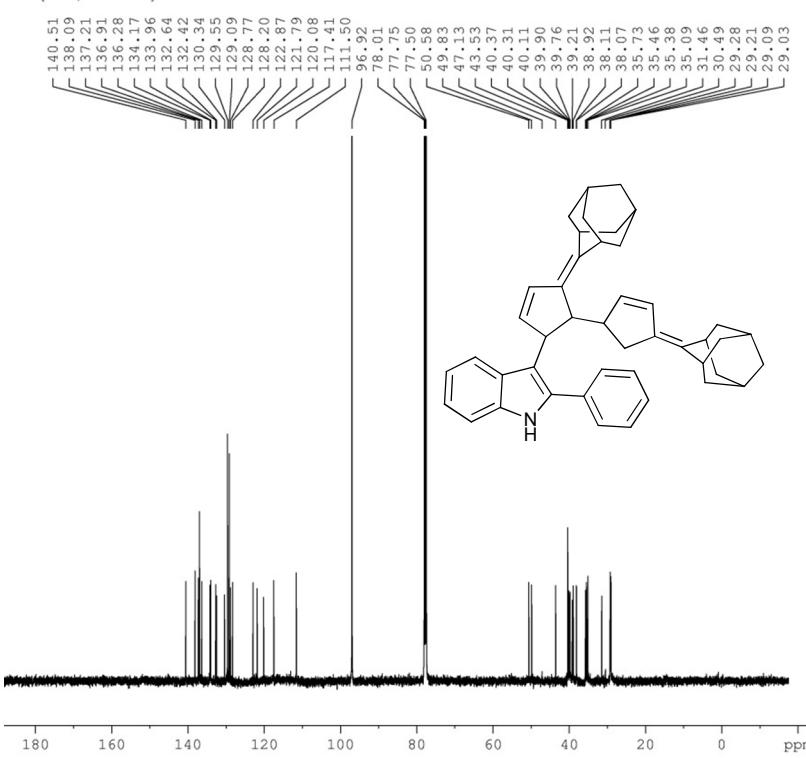
¹H NMR of 4ga



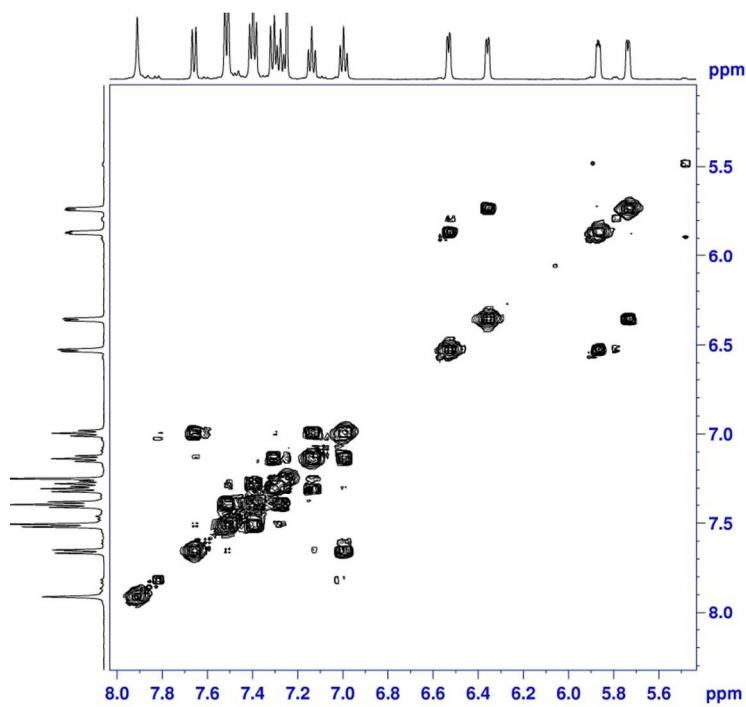
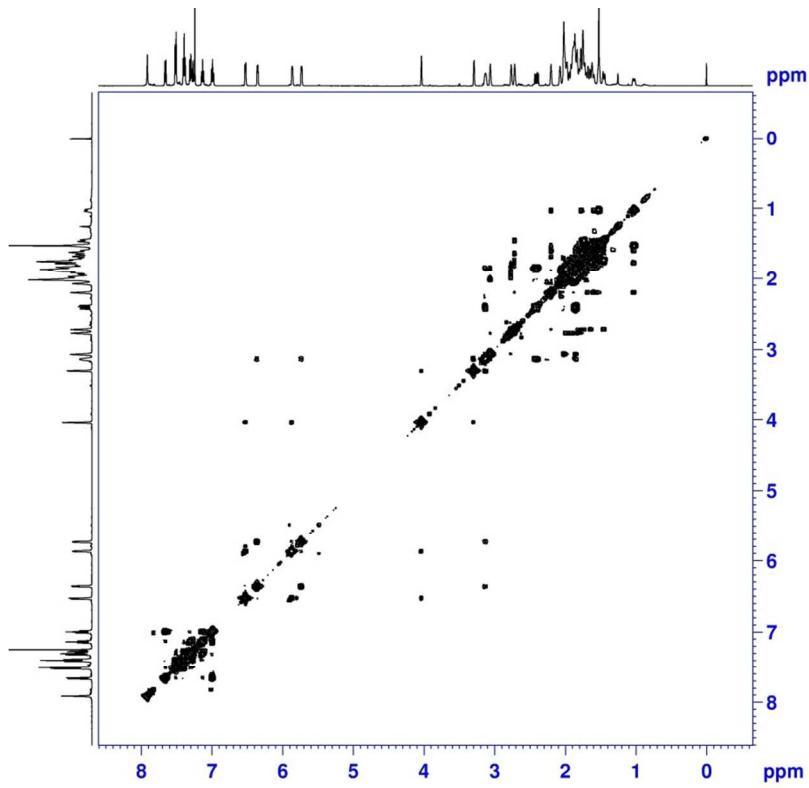
¹³C NMR of 4ga



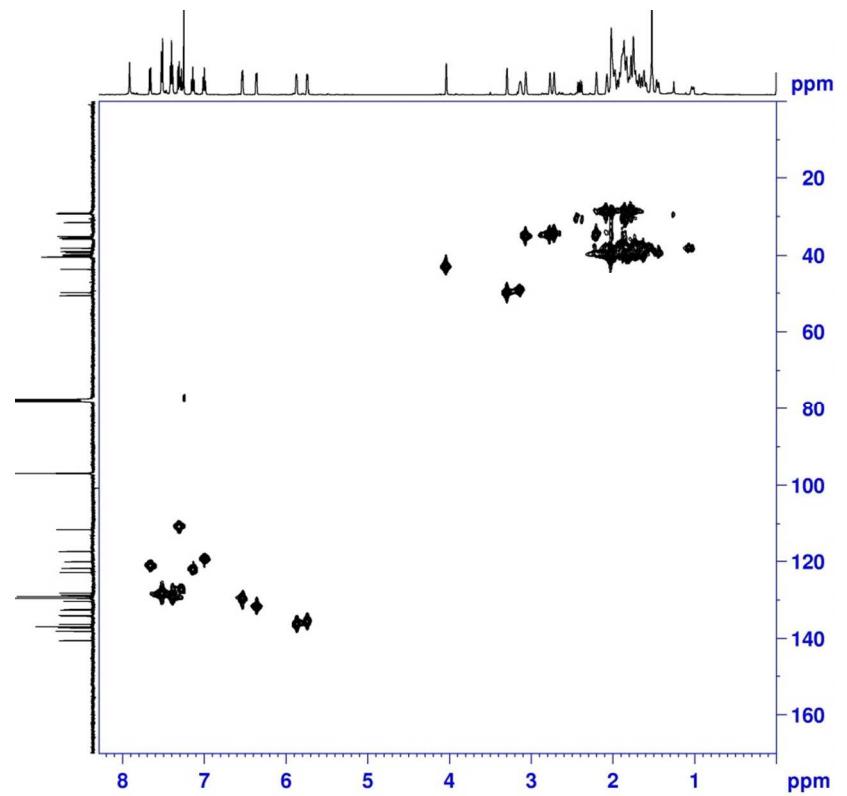
¹H NMR of 4gc



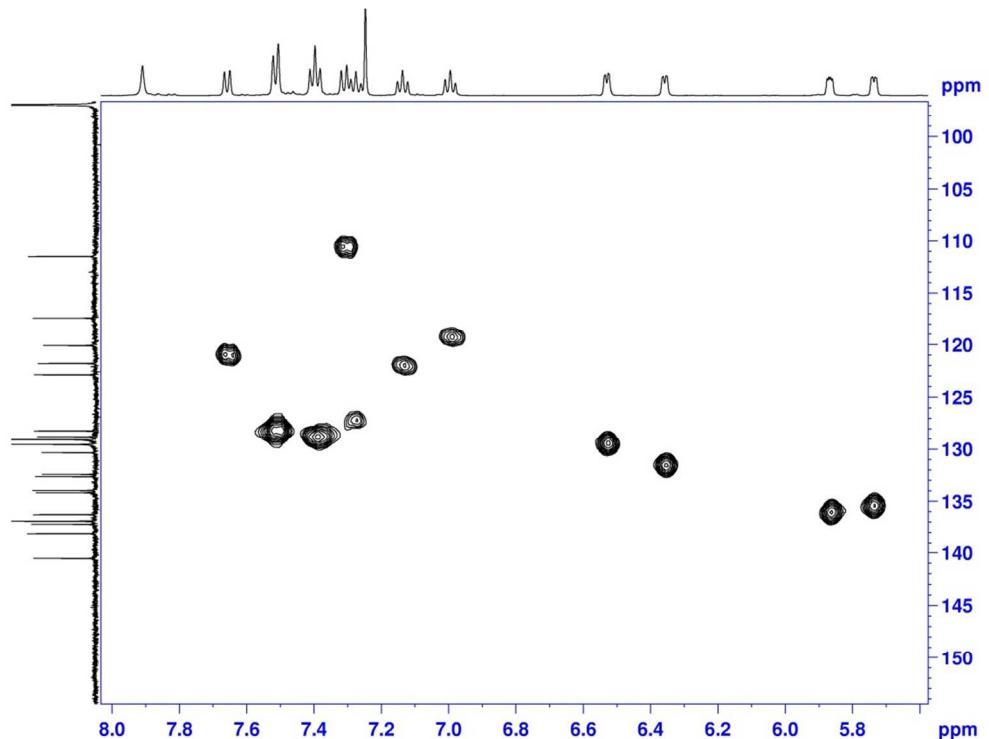
¹³C NMR of 4gc



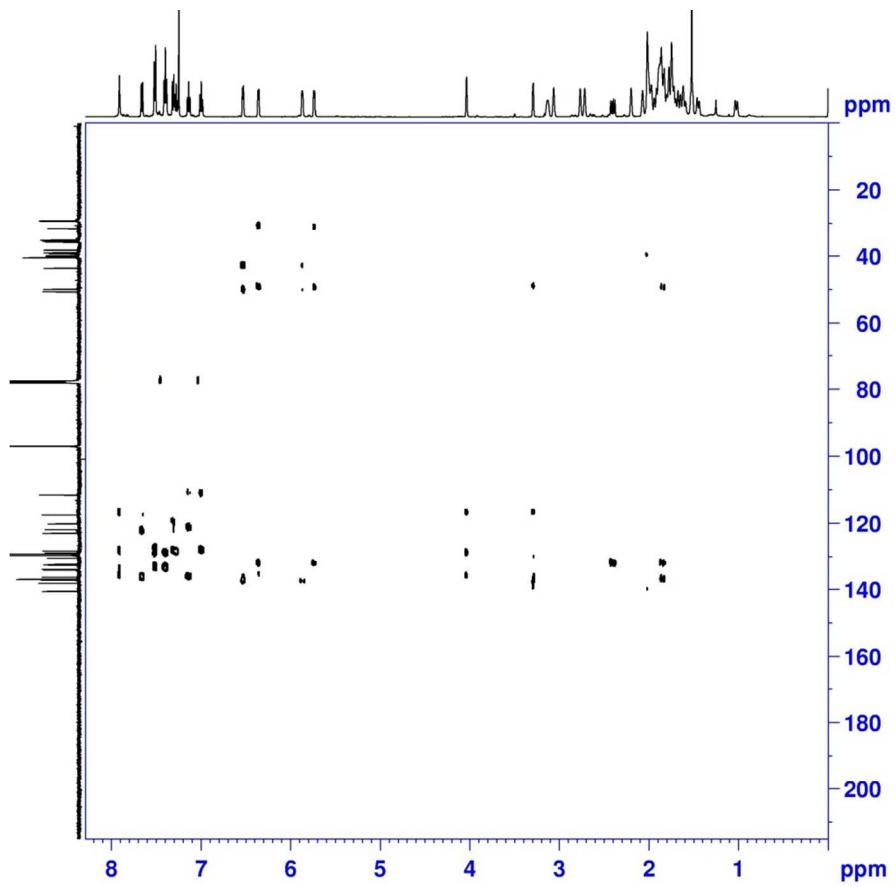
Compound 4gc (COSY)



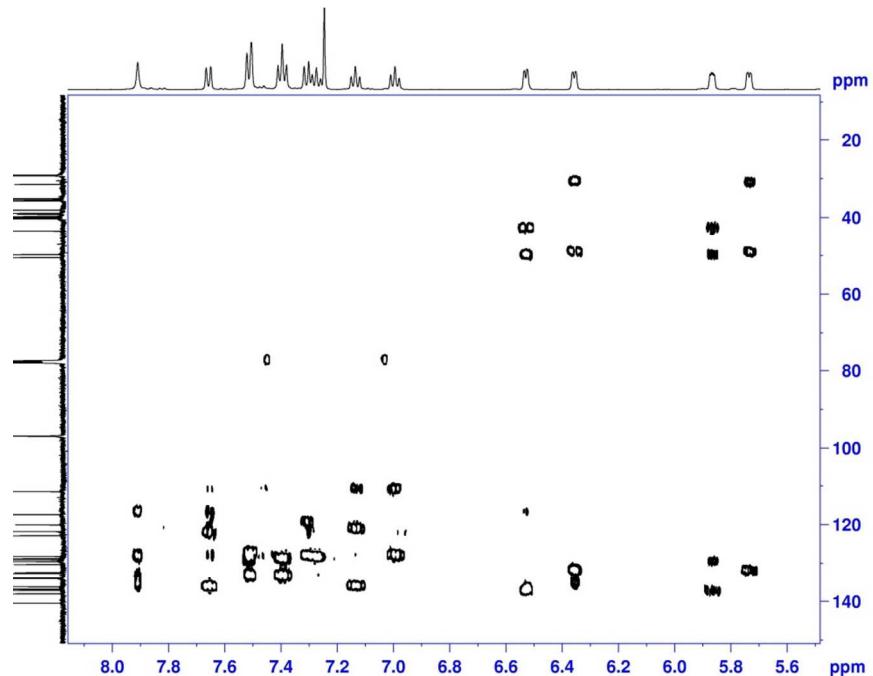
Compound 4gc (HSQC)



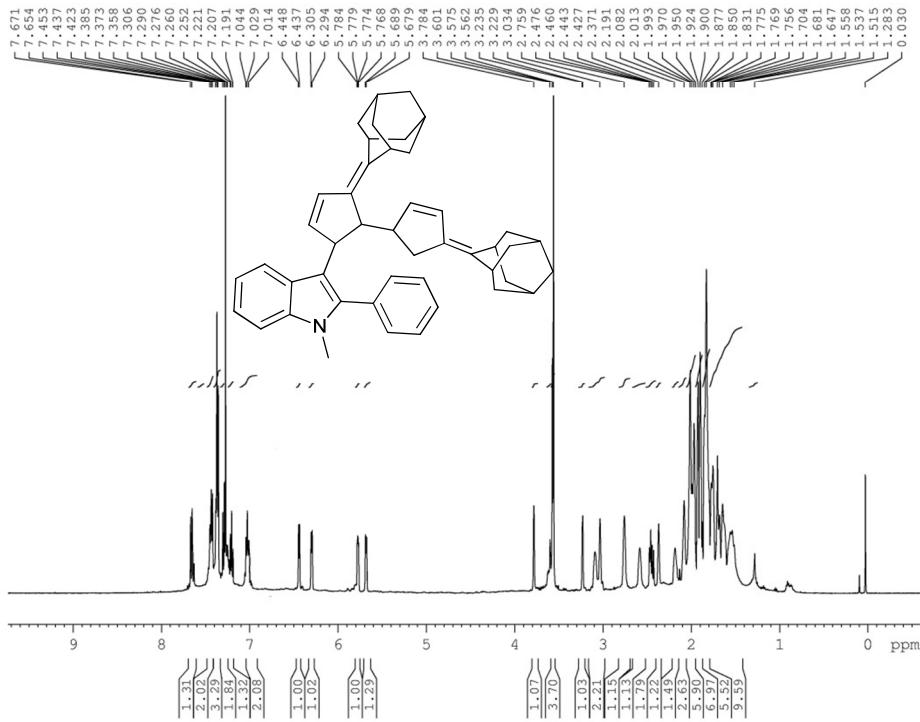
Compound 4gc (HSQC)



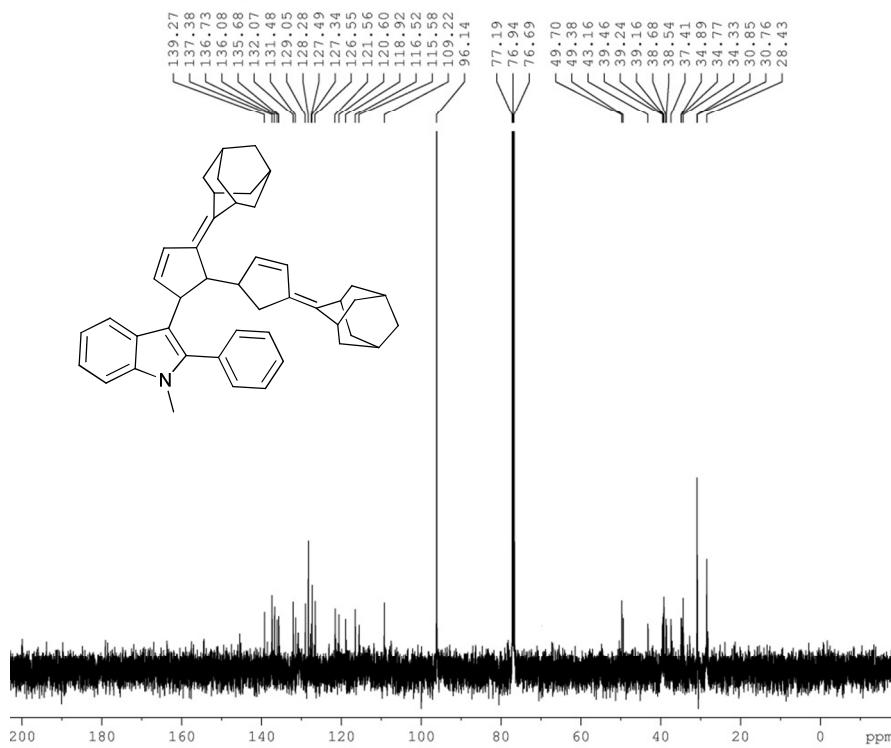
Compound 4gc (HMBC)



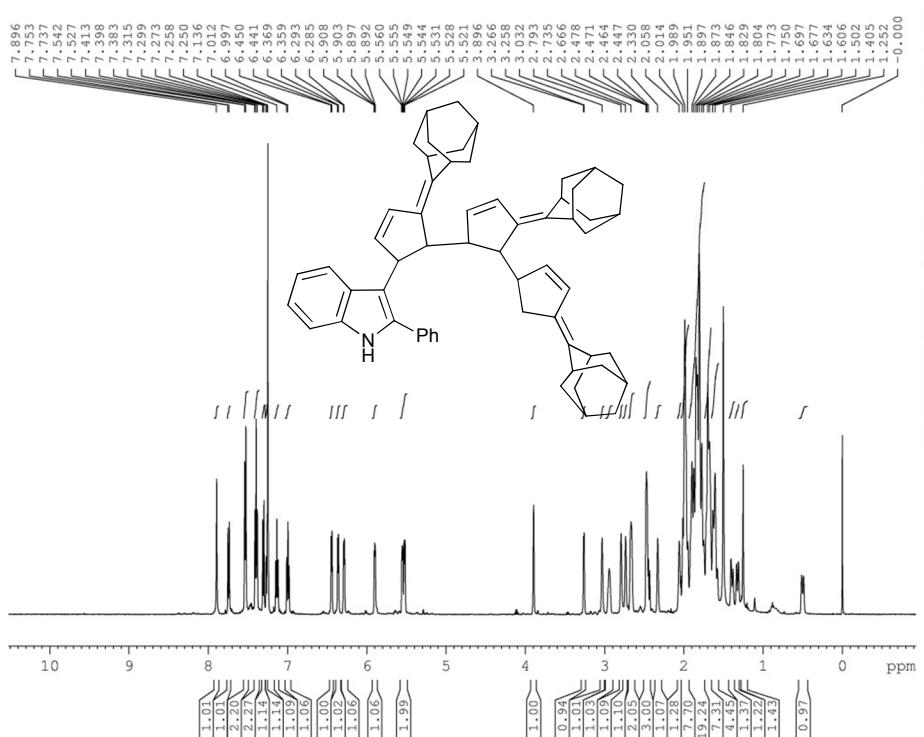
Compound 4gc (HMBC)



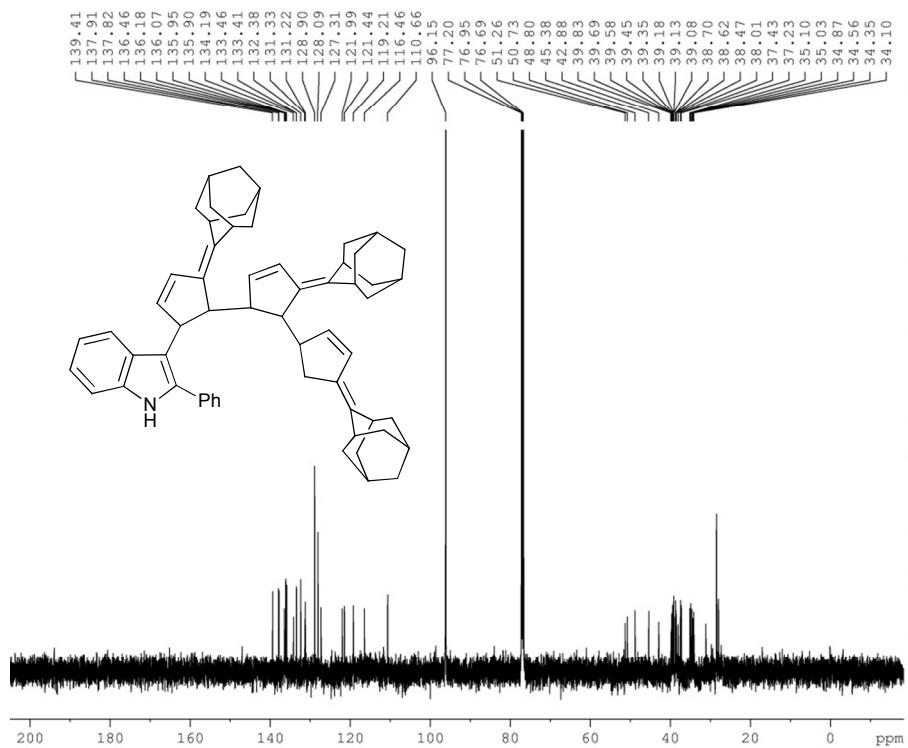
¹H NMR of 4gd



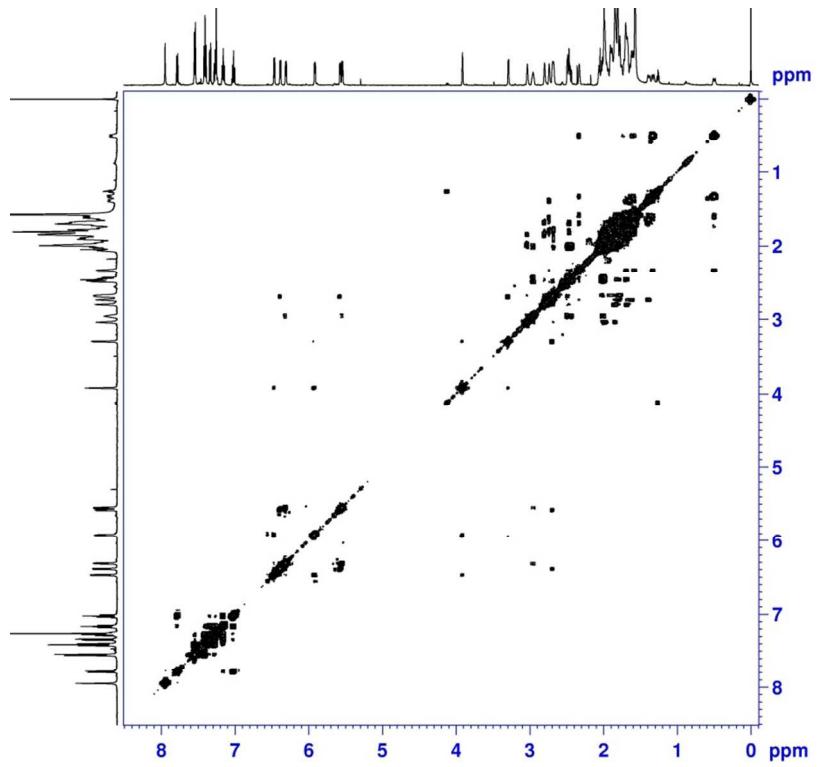
¹³C NMR of 4gd



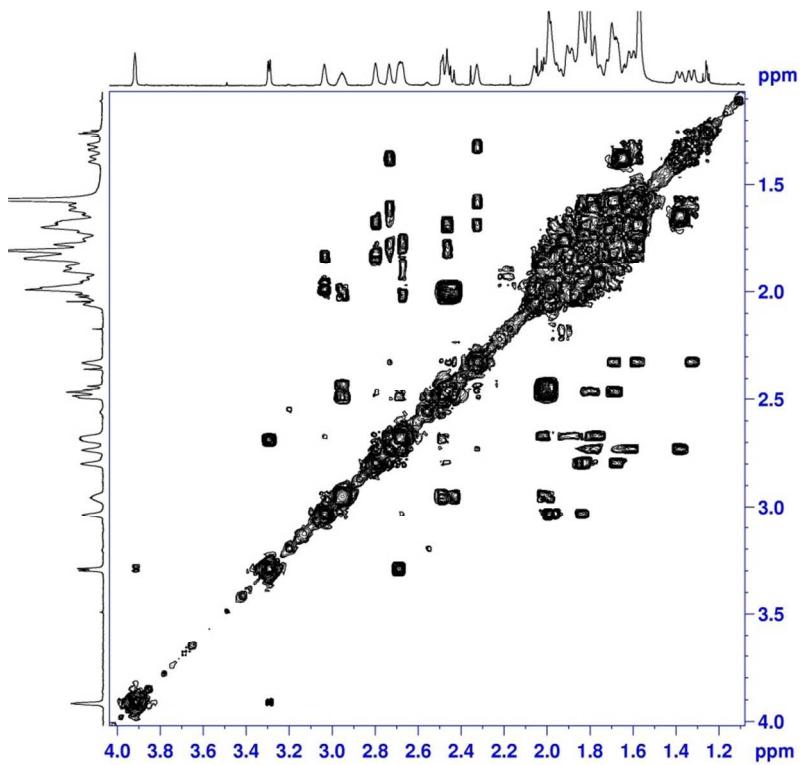
¹H NMR of 5gc



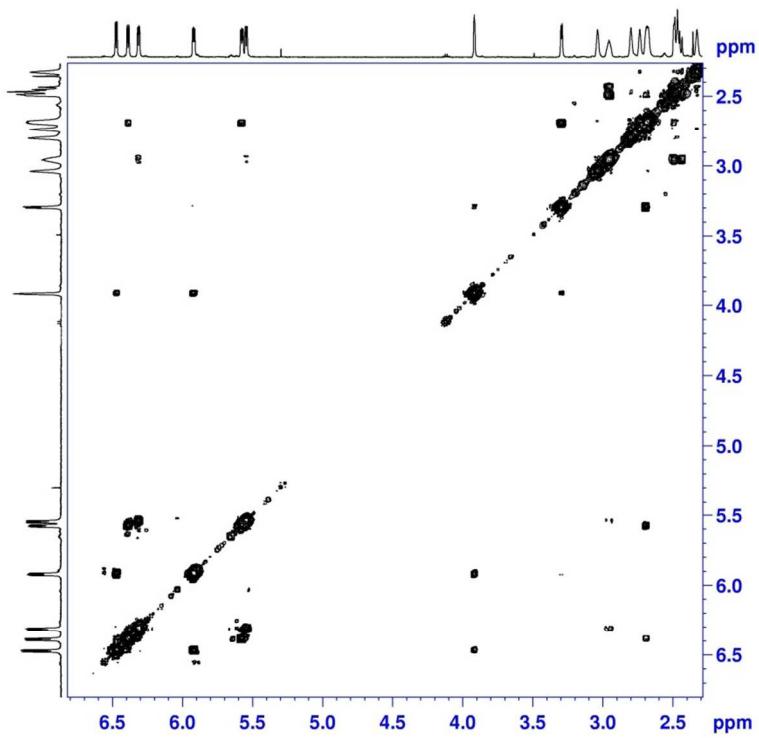
¹³C NMR of 5gc



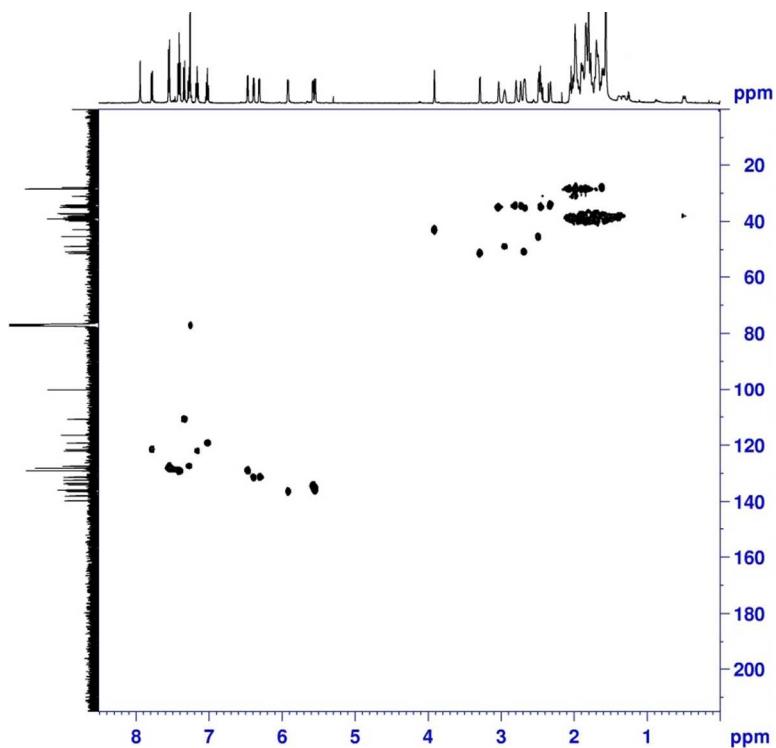
Compound 5gc (COSY)



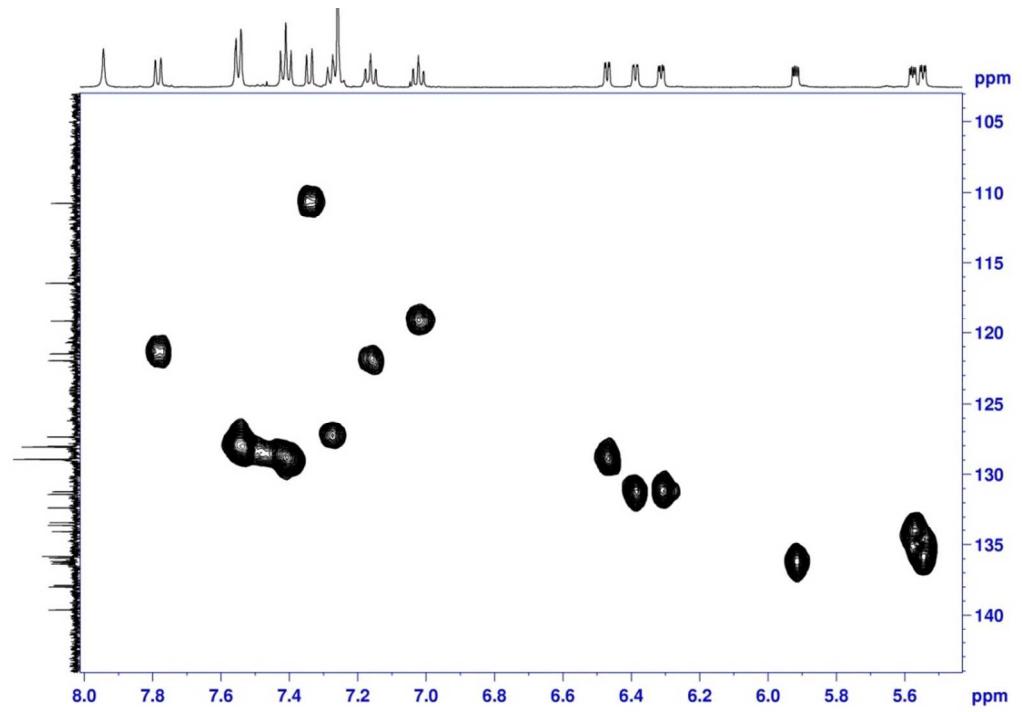
Compound 5gc (COSY)



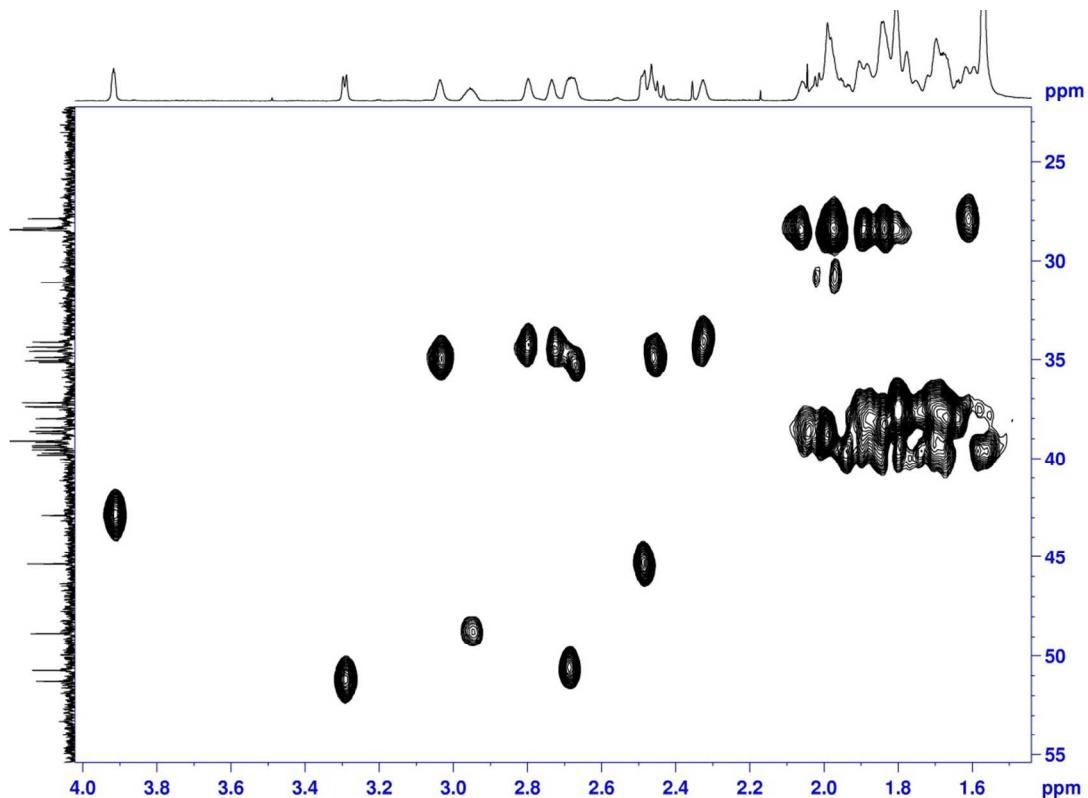
Compound 5gc (COSY)



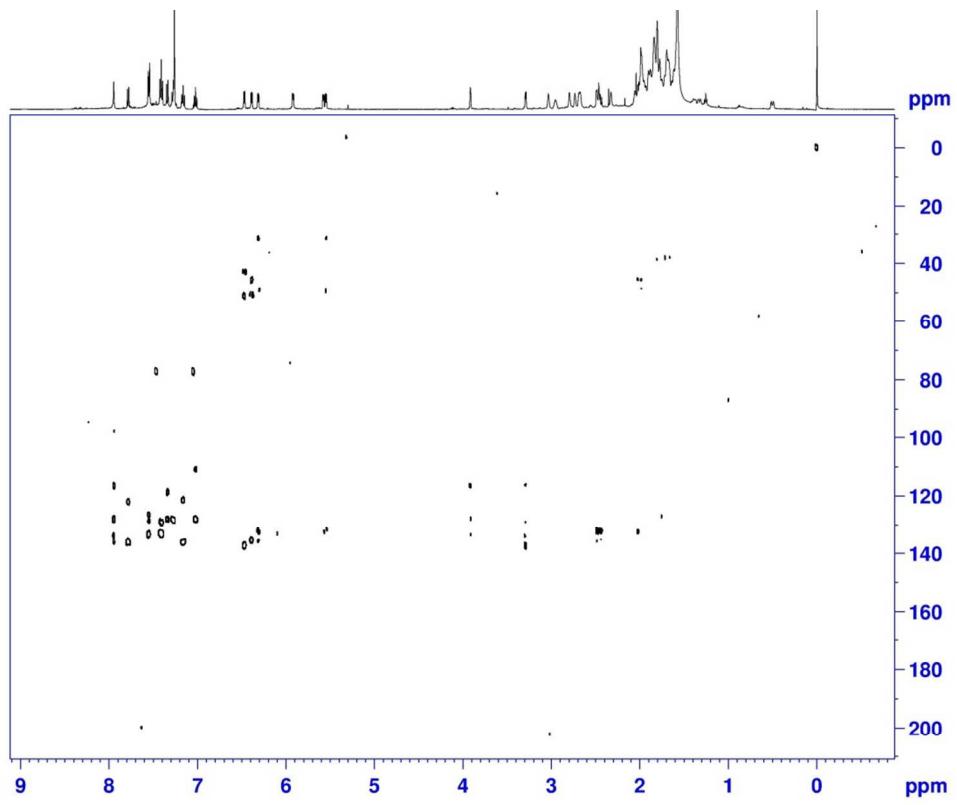
Compound 5gc (HSQC)



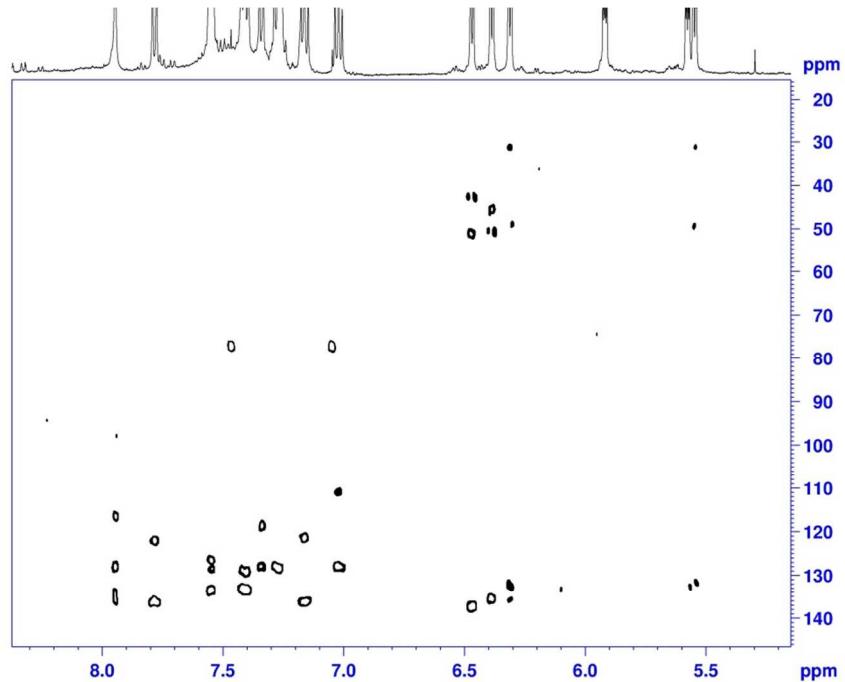
Compound 5gc (HSQC)



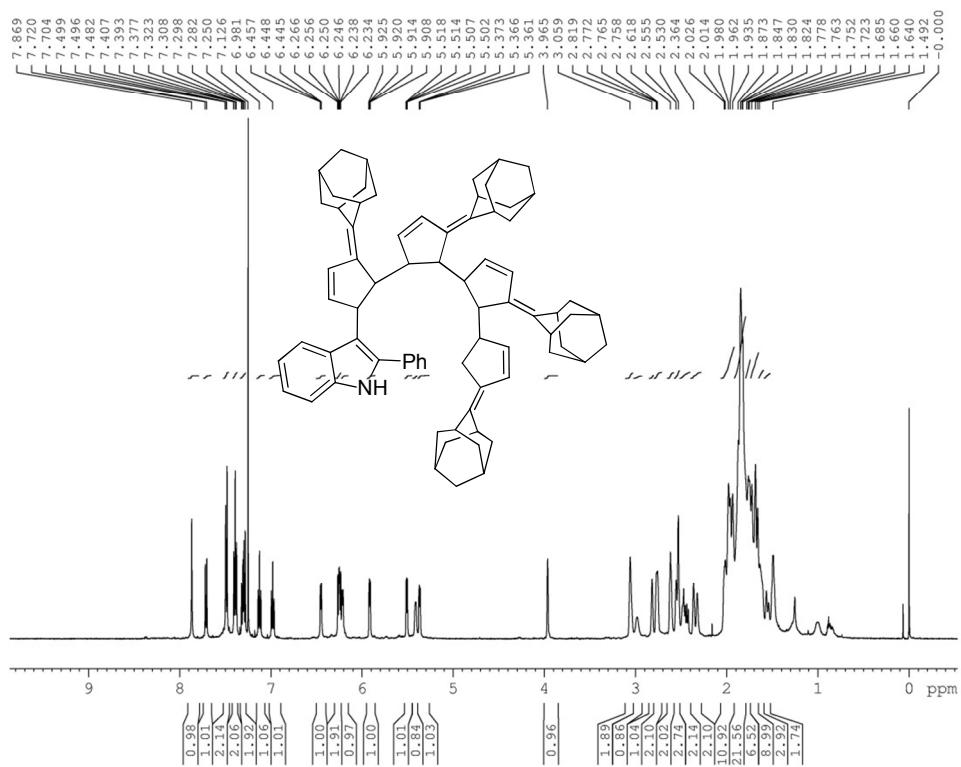
Compound 5gc (HSQC)



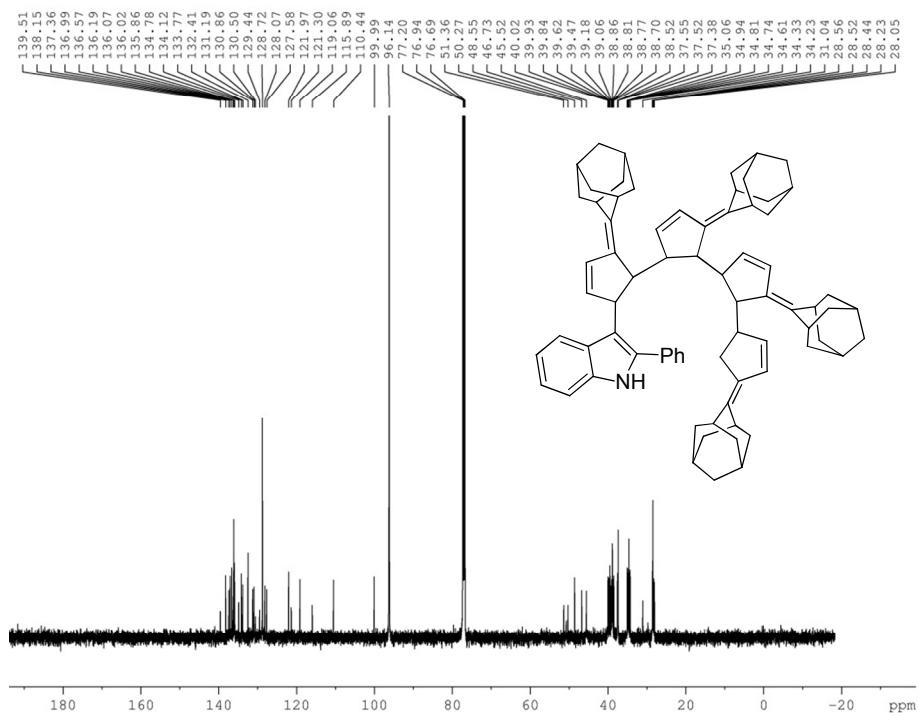
Compound 5gc (¹H NMR)



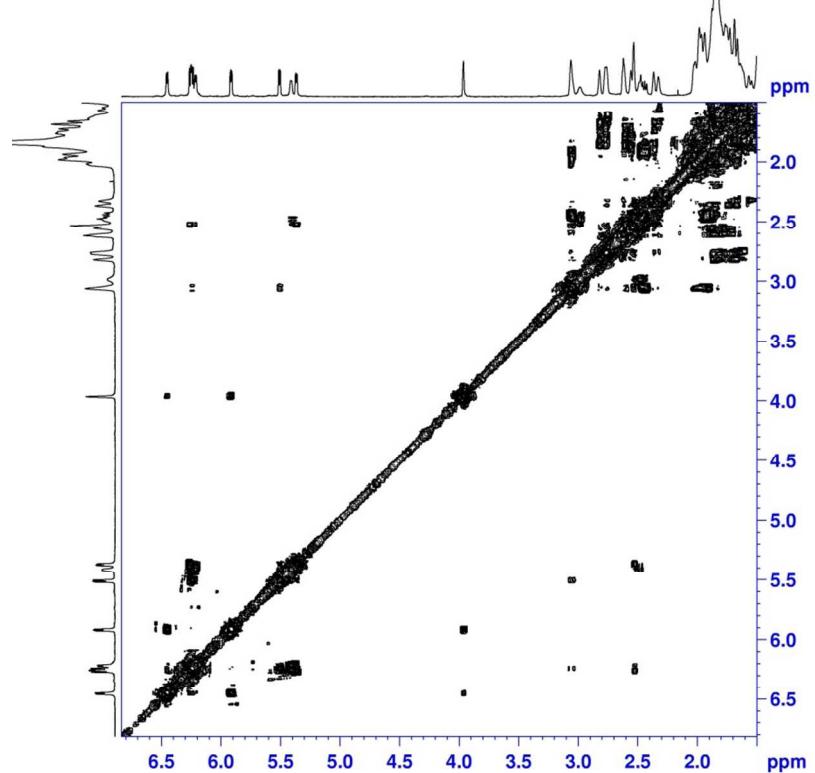
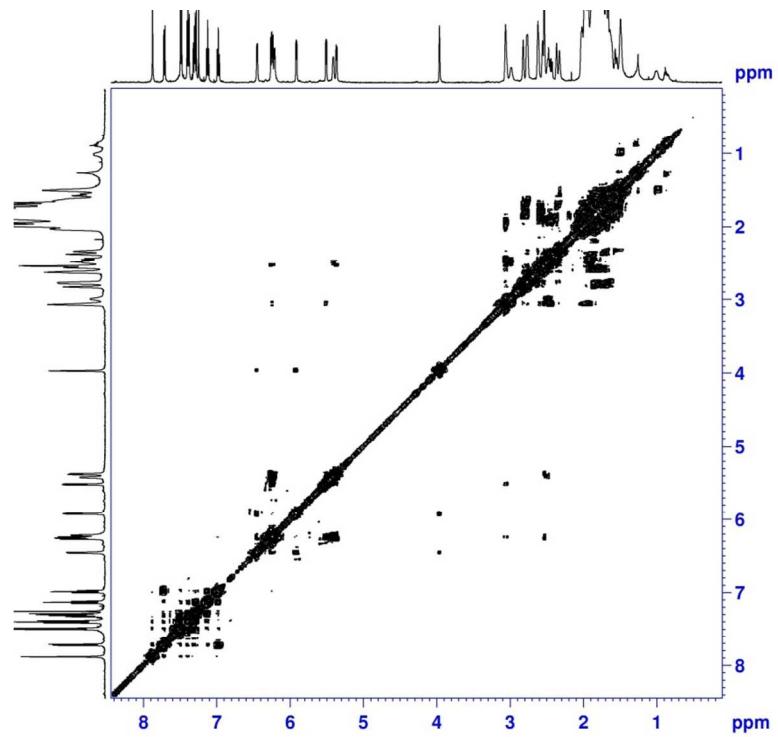
Compound 5gc (HMBC)



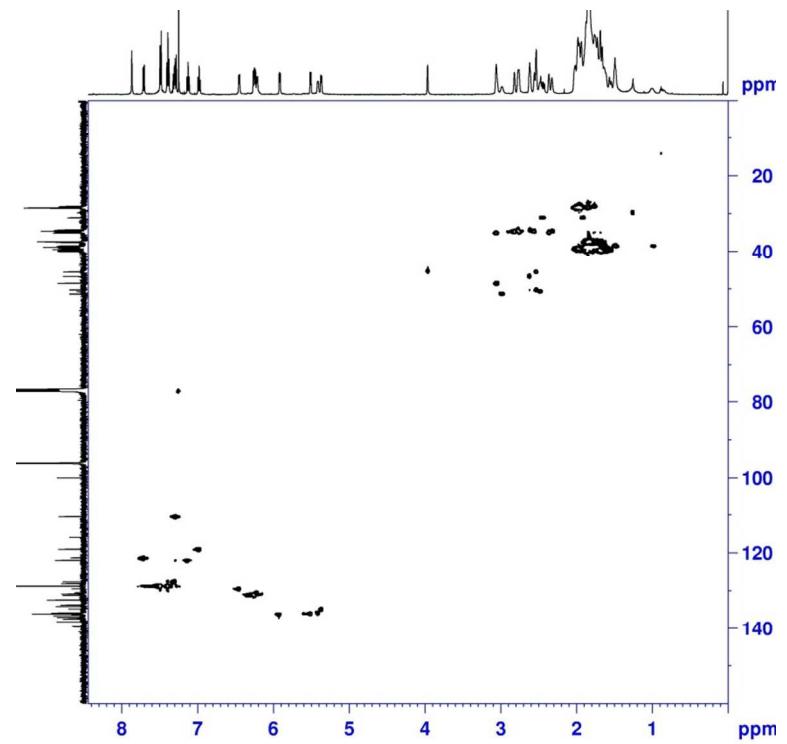
¹H NMR of 6gc



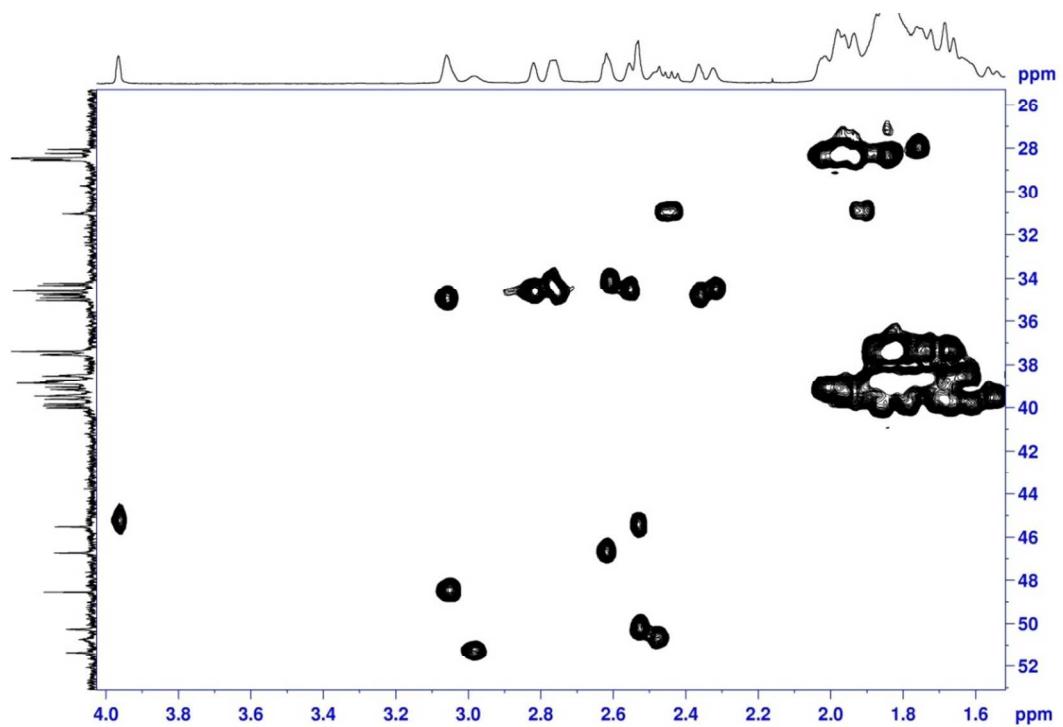
¹³C NMR of 6gc



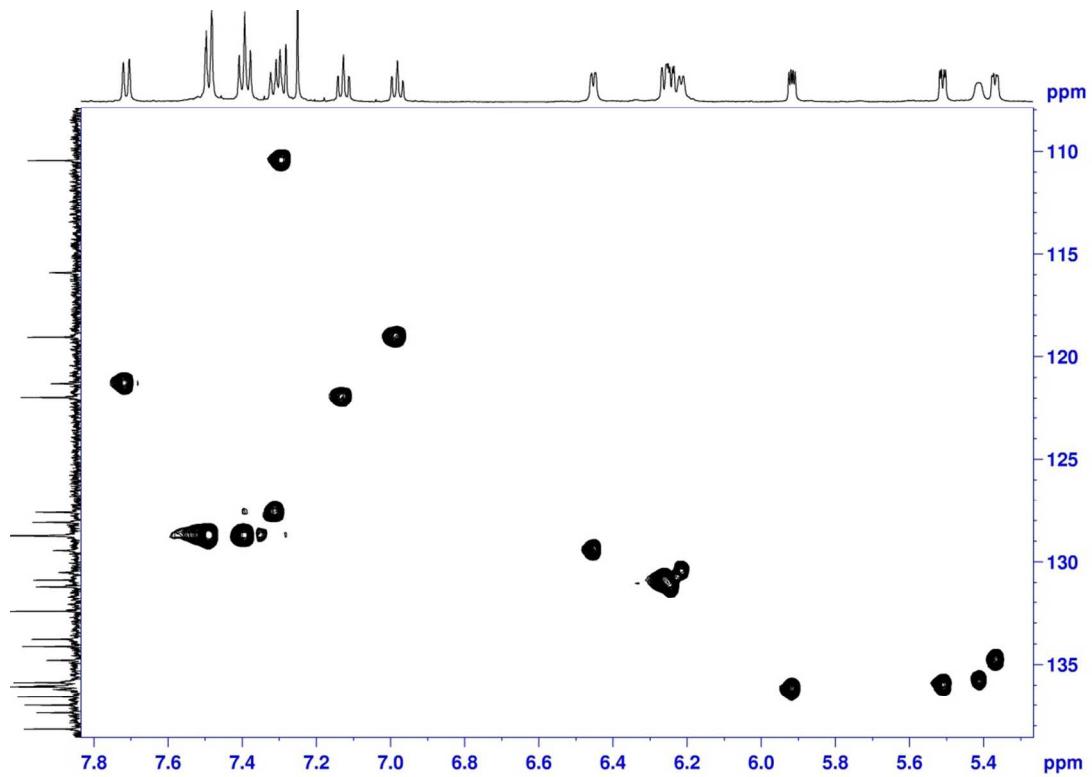
Compound 6gc (COSY)



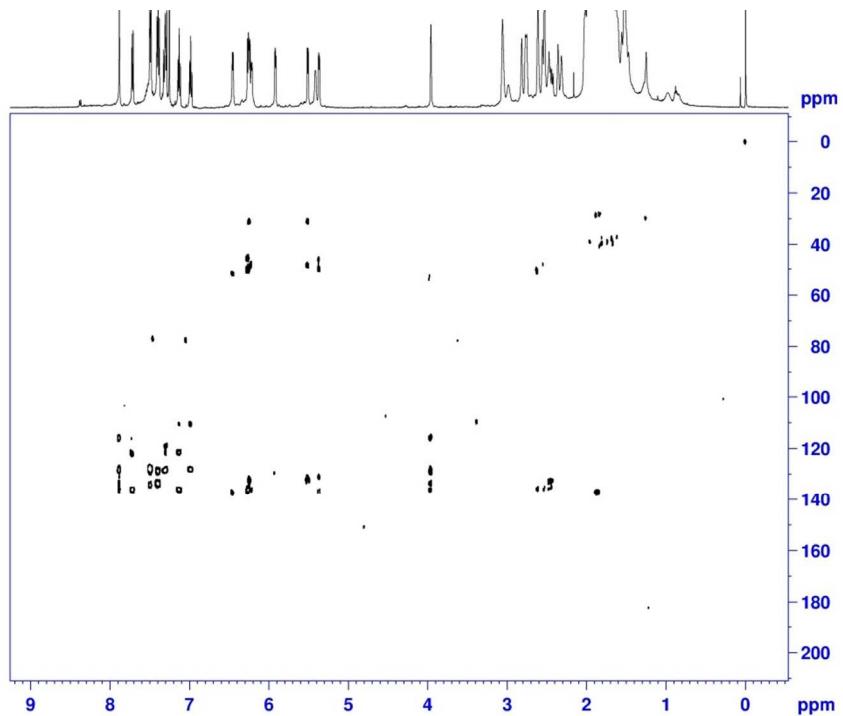
Compound 6gc (HSQC)



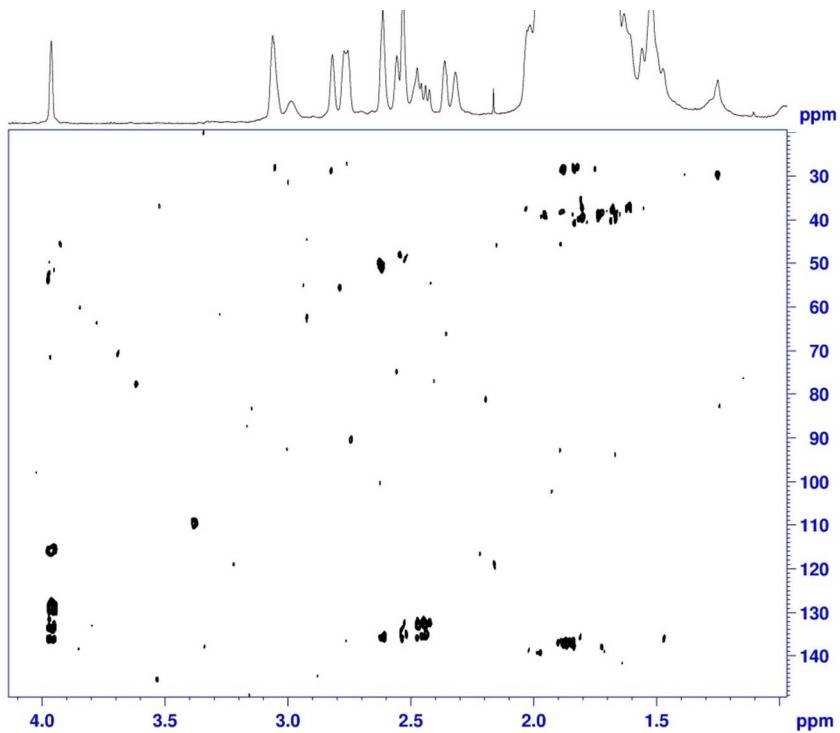
Compound 6gc (HSQC)



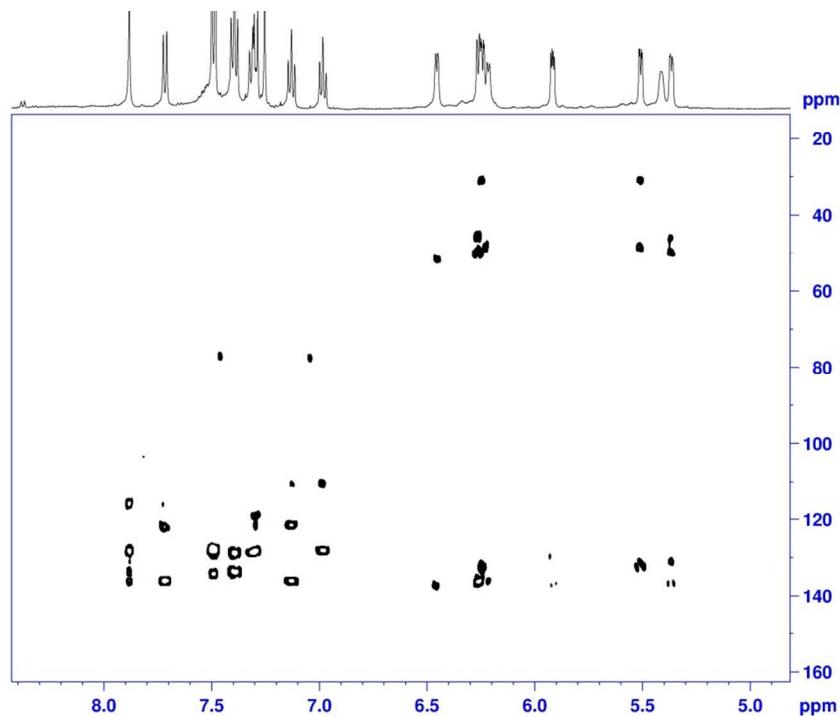
Compound 6gc (HSQC)



Compound 6gc (HMBC)

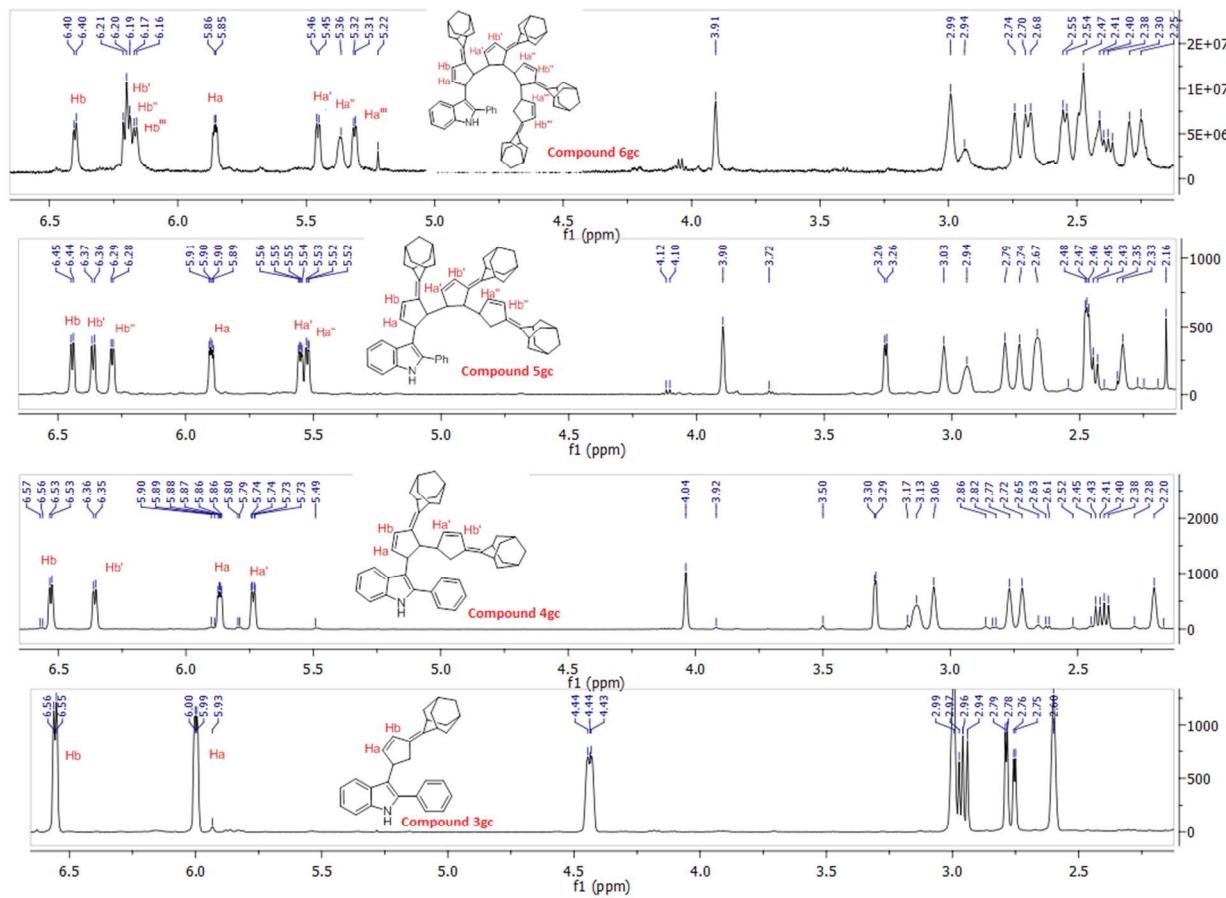


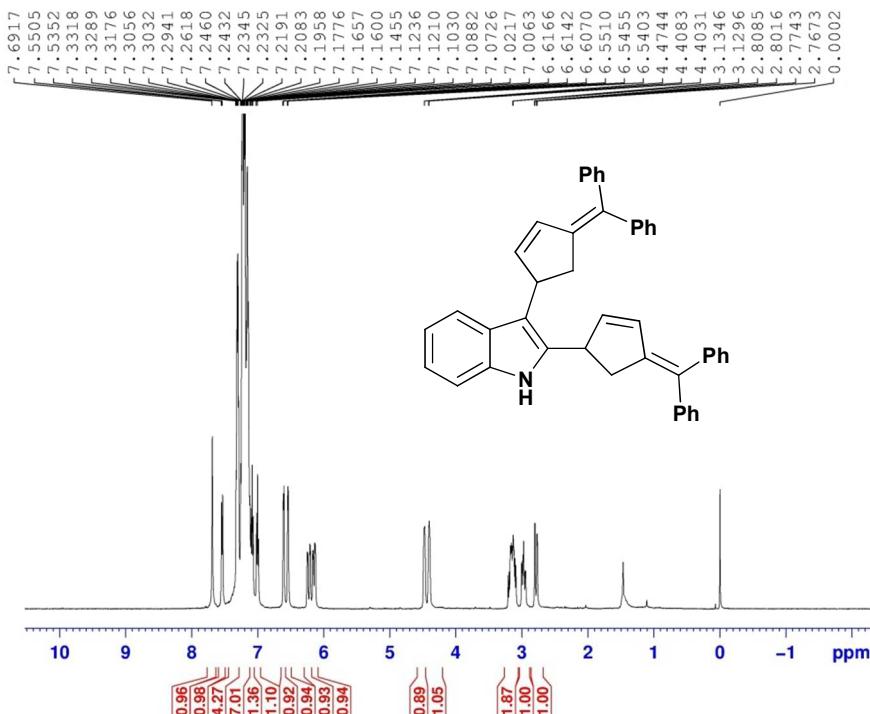
Compound 6gc (¹H NMR)



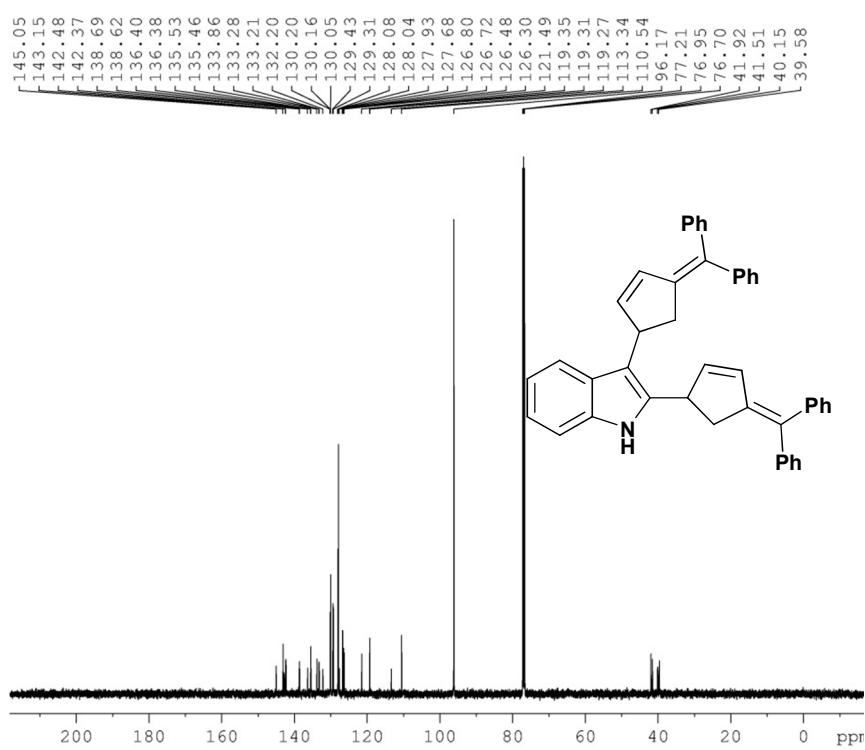
Compound 6gc (¹³C NMR)

Stacked image of ^1H NMR spectra of compounds 3gc, 4gc, 5gc and 6gc

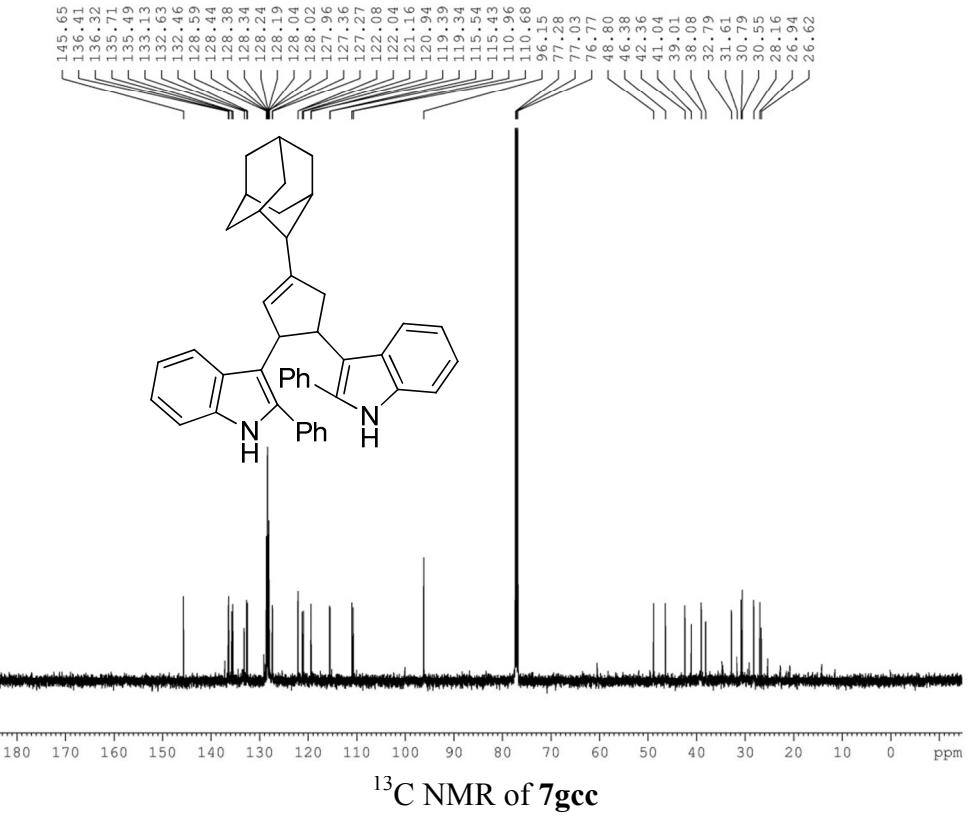
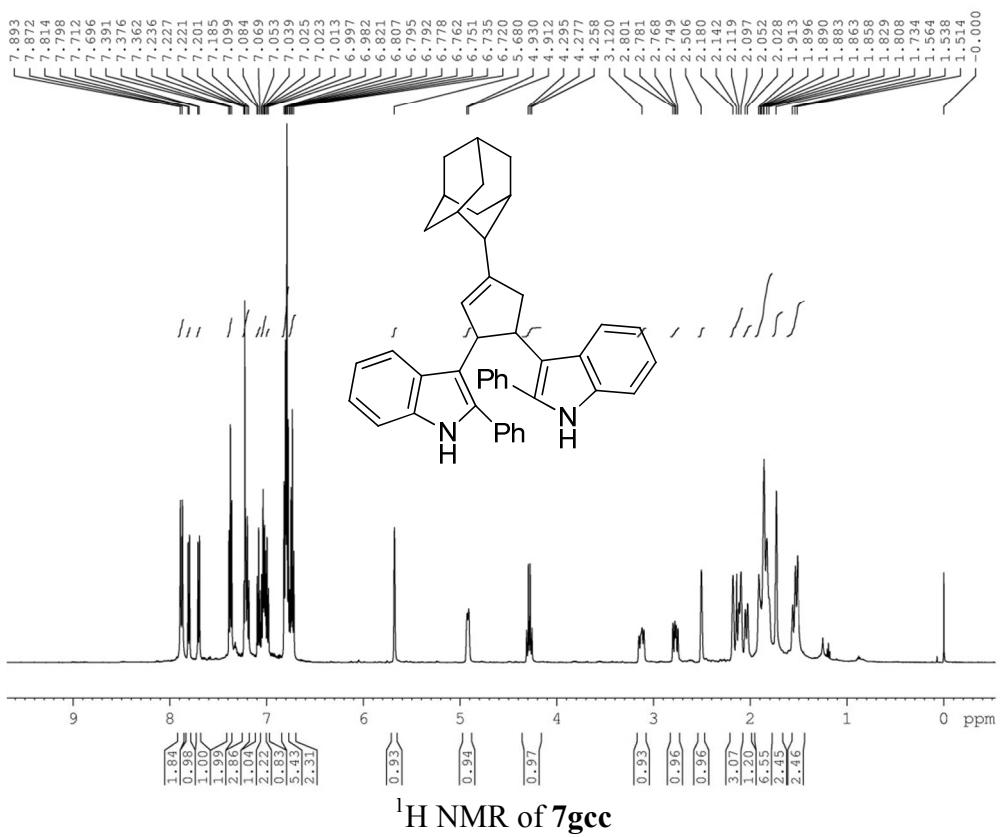




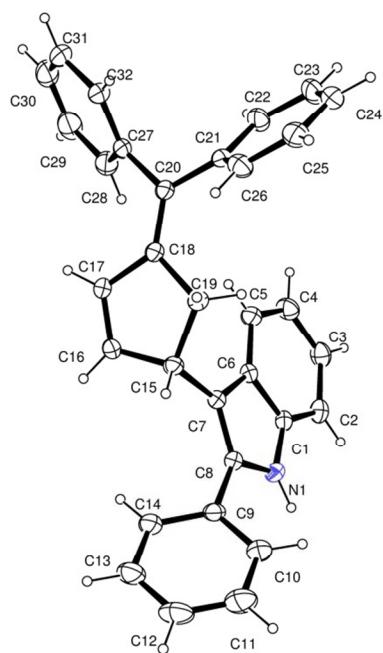
¹H NMR of 3aaa



¹³C NMR of 3aaa



ORTEP Drawing of compound 3ac



CCDC Number: 1034751