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Lewis Acid Catalyzed C-3 Alkylidenecyclopentenylation of Indoles: An Easy Access to Functionalized Indoles and Bisindoles

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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; 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 (^{1}H NMR) were recorded on a Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H 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 (quadret); 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). 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.

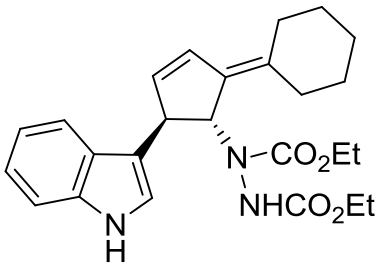
General Procedure for the Lewis acid catalyzed reaction of pentafulvene derived bicyclic hydrazines towards the synthesis of 3.

A mixture of pentafulvene derived bicyclic hydrazine (1.2 eqiuv.), indole (1.0 equiv.) and $Sc(OTf)_3$ (2 mol %) were weighed in a Schlenk tube and degassed for 10 minutes. Dry CH_3CN (2 ml) was added and the reaction mixture was purged with argon and allowed to stir at room temperature for 4 hours. The solvent was evaporated in *vacuo* and the residue on silica gel (100-200 mesh) column chromatography yielded *trans*-3,4-disubstituted alkylidene cyclopentene (**3**) along with minor amount *trans*-3,4-disubstituted bisindolyl product (**4)**

General Procedure for the Lewis acid catalyzed reaction of pentafulvene derived bicyclic hydrazines towards the synthesis of 4.

A mixture of pentafulvene derived bicyclic hydrazine (1.0 eqiuv.), indole (2.0 equiv.) and $Sc(OTf)_3$ (2 mol %) were weighed in a Schlenk tube and degassed for 10 minutes. Dry CH_3CN (2 ml) was added and the reaction mixture was purged with argon and allowed to stir at room temperature for 4 hours. The solvent was evaporated in *vacuo* and the residue on silica gel (100-200 mesh) column chromatography yielded *trans*-3,4-disubstituted bisindolyl product (**4)** along with minor amount *trans*-3,4-disubstituted *trans*-3,4-disubstituted alkylidene cyclopentene.

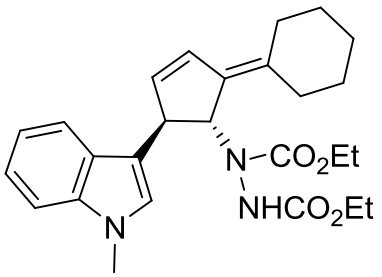
Diethyl 1-(2-cyclohexylidene-5-(1H-indol-3-yl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3aa)



Yield: 73%; pale yellow solid; M. p. 122–124 ^{o}C; R_f: 0.31 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3334, 3054, 2976, 2920, 2853, 1709, 1586, 1458, 1410, 1330, 1220, 1120, 1052, 920, 745cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.10 (brs, 1H), 7.68 (brs, 1H), 7.29-7.23 (m, 1H), 7.16- 7.13 (m, 1H), 7.06-7.03 (m, 1H), 6.84 (s, 1H), 6.53(d, *J* = 6 Hz, 1H), 6.26 (brs, 1H), 6.04 (brs, 1H), 5.34- 5.12 (m, 1H), 4.50-4.40(m, 1H), 4.24-4.17 (m, 4H), 2.39-2.33 (m, 2H), 2.08- 2.07 (m, 2H), 1.66-1.53 (m, 6H), 1.30-1.29 (m, 5H), 1.02 (brs, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.6, 155.1, 136.7, 136.2, 134.0, 129.7, 126.6, 121.9, 120.0, 119.2, 118.1, 110.0, 65.4, 64.1, 62.4, 61.9, 47.4, 32.0, 31.0, 28.4, 28.1, 26.6, 14.5, 14.2.

HRMS (ESI): Calcd for $C_{25}H_{31}N_3O_4Na$: 460.22123; Found: 460.22171.

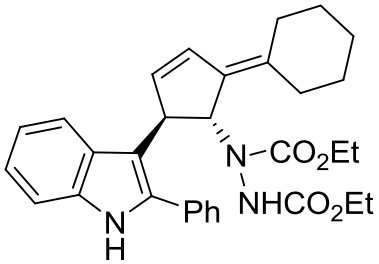
Diethyl 1-(2-cyclohexylidene-5-(1-methyl-1H-indol-3-yl) cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3ab)



Yield: 75%; pale yellow solid; M. p. 120–122^{o}C, R_f: 0.33 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3323, 3055, 2981, 2932, 2855, 1710, 1619, 1583, 1513, 1458, 1415, 1339, 1302, 1227, 1096, 1061, 920, 743cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.68 (brs, 1H), 7.25-7.23 (m, 2H), 7.05 (t, *J* = 7Hz,1H), 6.73 (s, 1H), 6.53(d, J=5.5, 1H), 6.23 (brs, 1H), 6.04 (s, 1H), 5.31-5.09 (m, 1H), 4.49-4.39 (m, 1H), 4.24-4.18 (m, 4H), 3.72 (s, 3H), 2.38-2.34 (m, 2H), 2.07-2.03 (m, 2H), 1.61-1.53 (m, 6H), 1.31-1.26 (m, 5H), 1.05-1.04 (brs, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.4, 155.1, 137.4, 133.7, 129.6, 127.0, 125.7, 121.5, 120.1, 118.7, 109.1, 108.8, 65.5, 62.3, 61.8, 47.5, 32.5, 31.9, 28.3, 28.0, 26.5, 14.5.

HRMS (ESI): Calcd for $C_{26}H_{33}N_3O_4Na$: 474.23688; Found: 474.23764

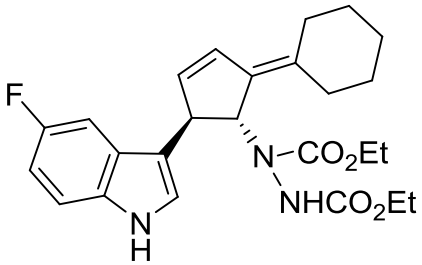
Diethyl 1-(2-cyclohexylidene-5-(2-phenyl-1H-indol-3-yl) cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3ac)



Yield: 78%; yellow viscous liquid; R_f: 0.36 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3324, 2980, 2930, 2854, 1701, 1519, 1472, 1420, 1382, 1332, 1261, 1233, 1097, 1060 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.16 (brs, 1H), 7.60-7.25 (m, 6H), 7.19-7.03 (m, 2H), 7.03 (d, *J* = 7Hz, 1H), 6.55 (brs, 1H), 6.20-6.03 (m, 1H), 5.91 (brs, 1H), 5.59-5.45 (m, 1H), 4.68-4.53 (m, 1H), 4.16-4.12 (m, 4H), 2.58 (brs, 1H), 2.39-2.12 (m, 3H), 1.75-1.59 (m,6H), 1.29-0.88 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.2, 155.4, 137.7, 136.3, 134.7, 132.8, 129.0, 128.6, 128.2, 127.6, 125.3, 121.9, 120.3, 119.4, 110.9, 62.4, 61.7, 60.3, 48.3, 34.6, 32.1, 26.9, 26.7, 21.5, 14.5, 14.2.

HRMS (ESI): Calcd for $C_{31}H_{35}N_3O_4Na$: 536.25253; Found: 536.25289.

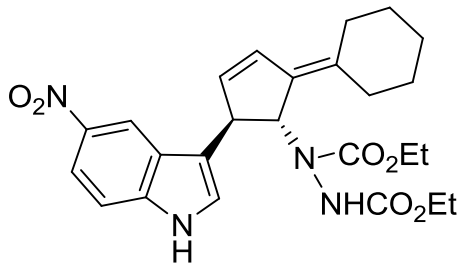
Diethyl 1-(2-cyclohexylidene-5-(5-fluoro-1H-indol-3-yl) cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3ad)



Yield: 61%; colourless viscous liquid; R_f: 0.26 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3363, 3277, 3054, 2984, 2931, 2854, 1711, 1582, 1500, 1149, 1411, 1330, 1120, 1050, 1010, 919, 744cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.26 (s, 1H), 7.34 (brs, 1H), 7.27-7.22 (m, 1H), 6.96-6.92 (brs, 1H), 6.65-6.56 (m, 2H), 6.40-6.31 (m, 1H), 6.02 (d, J = 3.5Hz,1H), 5.32-5.11 (m, 1H), 4.46-4.18 (m, 5H), 2.41- 2.33 (m, 2H), 2.07-2.05 (m, 2H), 1.62-1.45 (m, 6H), 1.35-1.07 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 158.5, 156.8, 155.3, 136.9, 133.3, 130.0, 126.9, 123.1, 118.1, 111.5, 110.3, 104.9, 65.4, 62.6, 62.3, 47.5, 32.0, 31.1, 28.3, 28.0, 26.5, 14.4.

HRMS (ESI): Calcd for $C_{25}H_{30}FN_3O_4Na$: 478.21180; Found: 478.21223.

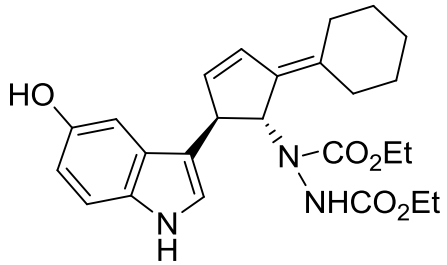
Diethyl 1-(-2-cyclohexylidene-5-(5-nitro-1H-indol-3-yl) cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3ae)



Yield: 59%; pale yellow solid; M. p. 132–134 ^{o}C. R_f: 0.22 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3365, 3071, 2960, 2852, 1712, 1623, 1582, 1469, 1410, 1380, 1318, 1245, 1173, 1115, 1058, 743 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 9.22 (brs, 1H), 8.56(s, 1H), 7.92 (brs, 1H), 7.17-7.13 (m, 1H), 6.92-6.82 (m, 1H), 6.61 (d, 1H, *J* = 4.5Hz), 6.34 (brs, 1H), 5.98 (brs, 1H), 5.39-5.17 (m, 1H), 4.49-4.23 (m, 5H), 2.56-2.06 (m, 4H), 1.76-1.22 (m, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.3, 155.6, 141.3, 139.8, 137.7, 130.1, 129.0, 128.2, 125.5, 125.3, 124.2, 117.6, 117.2, 111.0, 64.3, 62.9, 62.2, 47.5, 32.1, 31.3, 28.2, 26.6, 21.5, 14.5, 14.2.

HRMS (ESI): Calcd for $C_{25}H_{30}N_4O_6Na$: 505.20630; Found: 505.20668.

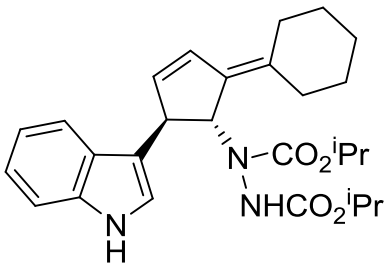
Diethyl 1-(2-cyclohexylidene-5-(5-hydroxy-1H-indol-3-yl) cyclopent-3-enyl) hydrazine-1,2-dicarboxylate. (3af)



Yield: 56%; pale yellow viscous liquid; R_f: 0.17 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3380, 3280, 3054, 2976, 2928, 2853, 1709, 1586, 1499, 1149, 1410, 1330, 1220, 1120, 1052, 1011, 920, 745cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.89 (brs, 1H), 7.23-7.15 (m, 2H), 6.79-6.77 (m, 1H), 6.56-6.28 (m, 2H), 6.05 (brs, 1H), 5.32-5.09 (m,1H), 4.45-4.11 (m, 5H), 2.37-2.33 (m, 2H), 2.07-2.06 (m, 2H), 1.60-1.38 (m, 6H), 1.29-1.13 (m, 5H), 0.99 (brs, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 155.2, 154.5, 147.5, 135.8, 135.0, 134.3, 127.2, 126.8, 125.3, 111.9, 111.8, 108.5, 104.5, 64.9, 62.8, 62.2, 41.9, 32.0, 28.2, 26.5, 19.4, 19.2, 14.5.

HRMS (ESI): Calcd for $C_{25}H_{31}N_3O_5Na$: 476.21614; Found: 476.21658.

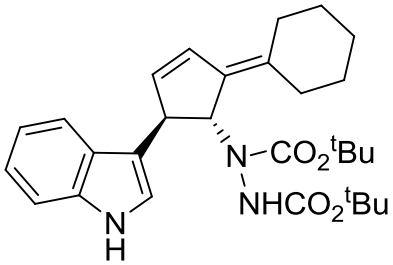
Diisopropyl 1-(2-cyclohexylidene-5-(1H-indol-3-yl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3ba)



Yield: 72%; pale yellow viscous liquid; R_f: 0.33 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3331, 3068, 2981, 2932, 2857, 1688, 1621, 1583, 1514, 1462, 1380, 1304, 1238, 1108, 1042, 957, 931, 743 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.16 (brs, 1H), 7.75-7.71 (m, 1H), 7.31-7.23 (m, 1H), 7.18-7.05 (m, 2H), 6.88 (brs, 1H), 6.56-6.27 (m, 2H), 6.07 (brs, 1H), 5.34-5.14 (m, 1H), 5.00-4.95 (m, 2H), 4.53-4.43 (m, 1H), 2.36 (brs, 2H), 2.09-1.81 (m, 2H), 1.61-1.51 (m, 6H), 1.44-1.22 (m, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.5, 154.7, 136.8, 133.8, 129.8, 129.0, 128.2, 126.7, 125.3, 121.7, 119.1, 110.9, 69.9, 69.5, 63.9, 47.2, 31.6, 30.8, 29.7, 28.3, 26.9, 22.7, 22.4, 22.1.

HRMS (ESI): Calcd for $C_{27}H_{35}N_3O_5Na$: 488.25253; Found: 488.25286.

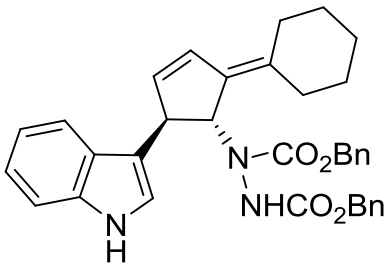
Di-tert-butyl 1-(2-cyclohexylidene-5-(1H-indol-3-yl) cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3ca)



Yield: 42%; pale yellow viscous liquid; R_f: 0.40 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3375, 3078, 2992, 2943, 2836, 1690, 1610, 1583, 1565, 1468, 1462, 1400, 1316, 1238, 1152, 1123, 969, 938, 746 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.00 (d, *J* = 11Hz,1H), 7.99-7.79 (m, 1H), 7.32-7.28 (m, 1H), 7.20-7.06 (m, 2H), 6.87 (s, 1H), 6.55 (d, *J* = 5.5Hz, 1H), 6.15-6.00 (m, 2H), 5.30-5.08 (m, 1H), 4.54-4.44 (m, 1H), 2.37 (brs, 2H), 2.12 (brs, 2H), 1.63-1.53 (m, 24H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 155.7, 154.0, 136.7, 136.5, 126.7, 122.1, 121.8, 119.2, 118.2, 111.1, 110.9, 110.7, 81.3, 80.7, 65.5, 44.3, 32.0, 31.1, 28.3, 28.2, 28.0, 26.6.

HRMS (ESI): Calcd for $C_{29}H_{39}N_3O_4Na$: 516.28383; Found: 516.28414.

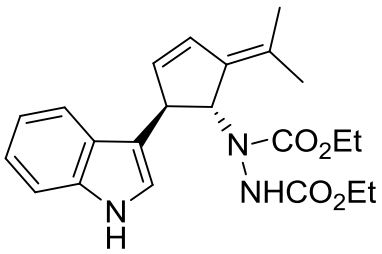
Dibenzyl 1-(2-cyclohexylidene-5-(1H-indol-3-yl) cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3da)



Yield: 39%; yellow viscous liquid; R_f: 0.31 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3358, 3059, 3027, 2920, 2858, 1702, 1580, 1489, 1449, 1400, 1311, 1281, 1050, 1000, 743cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.28 (brs, 1H),7.66 (brs, 1H), 7.39-6.90 (m, 13H), 6.75 (brs, 2H), 6.46 (s, 1H), 5.98-5.86 (m, 1H), 5.36 -5.05 (m, 5H), 4.52-4.29 (m, 1H), 2.36-2.32 (m, 2H), 2.02-1.94 (m, 2H), 1.56-1.26 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.4, 154.8, 136.7, 135.8, 133.4, 128.6, 128.5, 128.3, 128.2, 127.9, 126.6, 122.0, 121.2, 119.9, 119.4, 117.5, 110.9, 68.1, 67.6, 47.5, 32.0, 31.0, 28.3, 28.0, 26.5.

HRMS (ESI): Calcd for $C_{35}H_{35}N_3O_4Na$: 584.25253; Found: 584.25288.

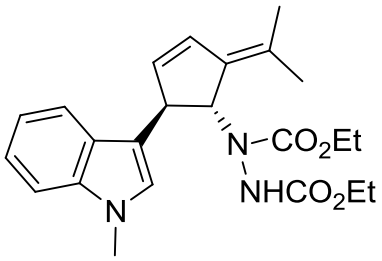
Diethyl 1-(2-(1H-indol-3-yl)-5-(propan-2-ylidene) cyclopent-3-enyl) hydrazine-1,2-dicarboxylate. (3ea)



Yield: 69%; colourless viscous liquid; R_f: 0.29 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3317, 3056, 2982, 2931, 1719, 1620, 1582, 1512, 1415, 1382, 1229, 1096, 1062, 744 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.30 (s, 1H), 7.71 (brs, 1H), 7.34-7.27 (m, 1H), 7.19-7.08 (m, 2H), 6.86-6.78 (m, 2H), 6.52 (d, 1H, *J* = 5Hz), 6.05 (s, 1H), 5.35-5.14 (m, 1H), 4.53-4.18 (m, 5H), 1.89 (s, 3H), 1.67 (brs, 3H), 1.29-1.26 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.9, 155.8, 136.8, 136.6, 135.5, 129.0, 126.7, 125.3, 121.7, 119.9, 119.1, 119.0, 117.9, 111.3, 66.0, 62.6, 62.2, 47.6, 21.5, 14.4.

HRMS (ESI): Calcd for $C_{22}H_{27}N_3O_4Na$: 420.18993; Found: 420.18866.

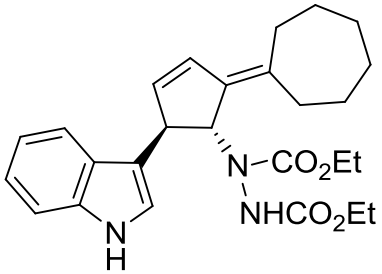
Diethyl 1-(2-(1-methyl-1H-indol-3-yl)-5-(propan-2-ylidene) cyclopent-3-enyl) hydrazine -1,2-dicarboxylate. (3eb)



Yield: 65%; colourless solid; M. p. 124–126 ^{o}C, R_f: 0.33 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3385, 3055, 2981, 2924, 1707, 1611, 1474, 1413, 1379, 1321, 1265, 1219, 1163, 1122, 1061, 1021, 933, 739 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.73 (s, 1H), 7.29-7.23 (m, 2H), 7.10 (t, *J* = 7Hz, 1H), 6.77 (brs, 1H), 6.53 (d, *J* = 5Hz, 1H), 6.39 (brs, 1H), 6.07 (s, 1H), 5.36-5.14 (m, 1H), 4.53-4.20 (m, 5H), 3.73 (s, 3H), 1.90 (s, 3H), 1.69 (s, 3H), 1.31-1.05 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.7, 155.6, 137.5, 136.7, 135.6, 130.5, 128.3, 127.1, 125.9, 121.6, 120.1, 118.8, 116.7, 109.0, 66.2, 62.5, 61.9, 47.5, 32.6, 21.5, 13.8.

HRMS (ESI): Calcd for $C_{23}H_{29}N_3O_4Na$: 434.20588; Found: 434.20615.

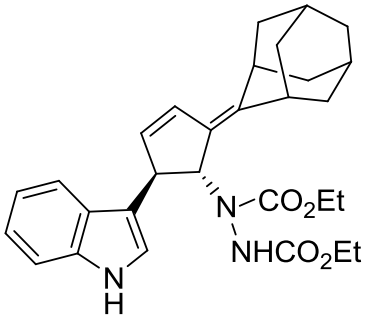
Diethyl 1-(2-cycloheptylidene-5-(1H-indol-3-yl)cyclopent-3-enyl)hydrazine-1,2-dicarboxylate. (3fa)



Yield: 70%; colourless viscous liquid; R_f: 0.31 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3348, 3056, 2924, 2853, 1708, 1617, 1458, 1414, 1380, 1226, 1177, 1121, 1061, 741cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.09 (brs, 1H), 7.66 (brs, 1H),7.28 (brs, 1H), 7.16-7.04(m 2H), 6.84 (brs, 1H), 6.51 (d, *J* = 5.5Hz, 1H), 6.25-6.21 (m, 1H), 6.04 (brs, 1H), 5.33-5.11 (m, 1H), 4.50-4.18 (m, 5H), 2.50-2.41 (m, 2H), 2.20-2.16 (brs, 2H), 1.71-1.03 (m, 14H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.3, 155.5, 136.8, 129.0, 128.2, 126.6, 125.3, 121.7, 119.0, 119.0, 111.1, 62.4, 61.9, 47.6, 32.7, 32.3, 29.1, 28.2, 27.6, 14.5, 14.2.

HRMS (ESI): Calcd for $C_{26}H_{33}N_3O_4Na$: 474.23688; Found: 474.23714.

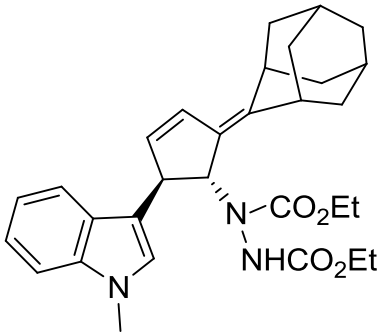
Compound 3ga



Yield: 66%; colourless viscous liquid; R_f: 0.33 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3323, 3057, 2920, 2848, 1713, 1620, 1475, 1413, 1381, 1305, 1294, 1216, 1116, 1085, 1065, 1025, 742 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.21 (brs, 1H), 7.70 (brs, 1H), 7.32-7.25 (m, 2H), 7.20-7.05 (m, 3H), 6.86 (brs, 1H), 6.56 (d, *J* =5.5Hz, 1H), 6.29 (brs, 1H), 6.05 (brs, 1H), 5.39-5.16 (m, 1H), 4.53-4.41 (m, 1H), 4.30-4.13(m, 4H), 3.06 (brs,1H), 2.59 (brs,1H), 2.08-1.64 (m, 12H), 1.35-1.08 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.7, 155.2, 144.4, 136.5, 130.2, 129.0, 128.3, 126.6, 125.3, 121.4, 121.1, 119.9, 119.0, 117.1, 111.1, 63.8, 62.5, 62.0, 47.6, 39.9, 39.5, 39.1, 37.0, 35.1, 34.4, 28.1, 28.0, 21.5, 14.6.

HRMS (ESI): Calcd for $C_{29}H_{35}N_3O_4$: 512.25253; Found: 515.25290.

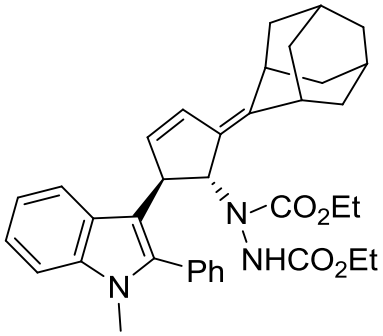
Compound 3gb



Yield: 70%; pale yellow viscous liquid; R_f: 0.36 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3315, 3054, 2910, 2852, 1711, 1612, 1472, 1413, 1379, 1305, 1221, 1124, 1061, 1019, 740 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.71 (brs, 1H), 7.7-7.21 (m, 2H), 7.07 (t, *J* = 7Hz, 1H), 6.80 (brs, 1H), 6.55 (d, *J* = 5.5Hz, 1H), 6.25 (brs, 1H), 6.05 (s, 1H), 5.35-5.12 (m, 1H), 4.53-4.28 (m, 1H), 4.23-4.13 (m, 4H), 3.75 (s, 3H), 3.05 (s, 1H), 2.58 (brs, 1H), 2.02-1.63 (m, 12H), 1.37-1.09 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.6, 154.9, 137.4, 130.2, 127.1, 125.8, 121.5, 120.2, 118.7, 108.9, 62.3, 61.9, 47.2, 39.6, 37.0, 35.1, 34.7, 32.6, 28.1, 26.9, 25.3, 22.9, 20.8, 14.9.

HRMS (ESI): Calcd for $C_{30}H_{37}N_3O_4Na$: 526.26818; Found: 526.26862.

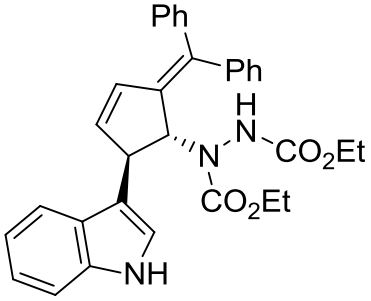
Compound 3gc



Yield: 66%; pale yellow viscous liquid; R_f: 0.38 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3378, 3058, 2978, 2908, 2848, 1756, 1704, 1467, 1445, 1409, 1379, 1364, 1338, 1308, 1277, 1248, 1218, 1172, 1157, 1097, 1062, 1022cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.58-7.44 (m, 6H), 7.33-7.19 (m, 3H), 7.04 (brs,1H), 6.50-6.42 (m, 1H), 6.12-5.81 (m, 2H), 5.45 (brs, 1H), 4.25-4.15 (m, 4H), 3.58 (s, 3H), 3.06 (brs, 1H), 2.65-2.61 (m, 1H), 2.03-1.85 (m, 10H), 1.59-1.25 (m, 2H), 1.01-0.87 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.4, 155.3, 137.4, 131.3, 130.6, 128.1, 128.0, 121.5, 120.2, 119.0, 113.5, 109.3, 65.9, 62.3, 61.7, 47.8, 39.5, 39.4 37.0, 35.1, 34.6, 30.8, 28.2, 28.1, 14.7.

HRMS (ESI): Calcd for $C_{36}H_{41}N_3O_4Na$: 602.29948; Found: 602.29977.

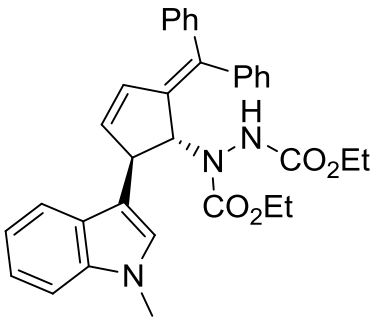
Diethyl 1-(2-(diphenylmethylene)-5-(1-methyl-1H-indol-3-yl)cyclopent-3-enyl)hydrazine -1,2-dicarboxylate. (3ha)



Yield: 62%; pale yellow solid, M. p. 182–184^{o}C; R_f: 0.24 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3362, 3051, 2968, 2911, 2852, 1736, 1710, 1552, 1514, 1467, 1454, 1411, 1384, 1364, 1308, 1287, 1243, 1231, 1168, 1157, 1069, 1063, 1022, 742cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.85-7.79 (m, 1H), 7.42-7.03 (m, 12H), 6.90-6.59 (m, 3H), 6.32-6.22 (brs, 1H), 6.04-5.91 (m, 2H), 5.08 (brs, 1H), 4.23-4.13 (m, 4H), 3.92-3.73 (m, 1H), 1.35-1.01 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.0, 154.7, 142.5, 142.4, 141.3, 140.8, 137.4, 130.0, 129.9, 128.6, 128.2, 127.7, 127.4, 126.8, 121.6, 120.2, 119.1, 116.9, 115.5, 110.2, 65.6, 62.0, 61.8, 47.9, 14.8.

HRMS (ESI): Calcd for $C_{32}H_{31}N_3O_4Na$: 544.22123; Found: 544.22151.

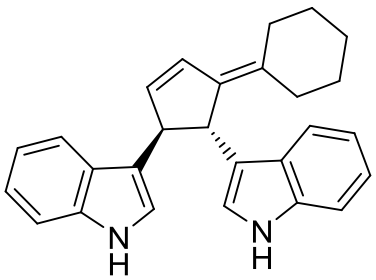
Diethyl 1-(2-(diphenylmethylene)-5-(1-methyl-1H-indol-3-yl)cyclopent-3-enyl)hydrazine -1,2-dicarboxylate. (3hb)



Yield: 68%; yellow viscous liquid; R_f: 0.29 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3340, 3068, 2981, 2932, 2857, 1688, 1621, 1602, 1583, 1555, 1514, 1462, 1380, 1315, 1238, 1108, 1042, 931, 743 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.79 (brs, 1H), 7.34-7.19 (m, 14H), 7.09-6.97 (m, 2H), 6.61-6.55 (m, 1H), 6.32 (brs, 1H), 5.82-5.56 (m, 2H), 4.70-4.65 (m, 1H), 4.25-4.15 (m, 4H), 3.76 (brs, 3H), 1.32- 1.29 (m, 4H), 1.03 (brs, 1H), 0.69 (brs, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 156.9, 154.9, 142.6, 142.3, 141.3, 140.7, 137.4, 130.0, 129.9, 128.5, 128.1, 127.4, 127.3, 127.1, 126.6, 121.4, 120.2, 118.8, 116.0, 115.3, 108.9, 65.5, 62.0, 61.8, 47.6, 32.6, 14.5,13.8.

HRMS (ESI): Calcd for $C_{33}H_{33}N_3O_4Na$: 558.23688; Found: 558.23721.

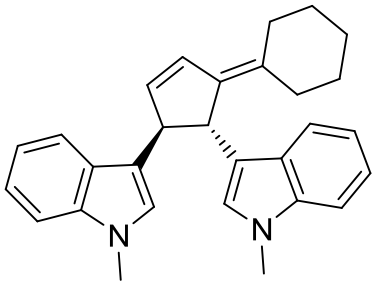
3, 3'-(5-Cyclohexylidenecyclopent-3-ene-1, 2-diyl)bis(1H-indole) (4aa)



Yield: 64%; pale yellow coloured solid. M. p. 152–156^{o}C; R_f: 0.43 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3405, 2922, 2851, 2362, 2349, 1590, 1459, 1421, 1364, 1120, 1033 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.93 (s, 1H), 7.85 (s, 1H), 7.61-7.57 (m, 2H), 7.38-7.34 (m, 2H), 7.22-7.17 (m, 2H), 7.09-6.94 (m, 4H), 6.78 (d, J = 5.5Hz, 1H), 6.04 (dd, J_1 = 5.5Hz, J_2 = 2.5Hz, 1H), 4.32 (brs, 1H), 4.19 (brs, 1H), 2.46 (t, J = 6 Hz, 2H), 2.04-1.97 (m, 2H), 1.67-1.29 (m, 6H). **^{13}C NMR**(125MHz,$CDCl_3$, TMS): δ139.1, 136.9, 135.9, 133.0, 129.9, 129.1, 128.3, 126.7, 126.6 , 125.4, 121.9, 121.8, 121.0, 120.9, 120.2, 120.1, 119.6, 118.9, 111.2, 111.0, 52.3, 45.8, 32.1, 31.8, 28.6, 27.7, 26.9.

HRMS (ESI): Calcd for $C_{27}H_{26}N_2Na$: 401.19937; Found: 401.19968.

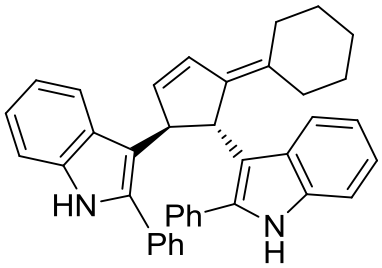
3,3'-(5-Cyclohexylidenecyclopent-3-ene-1,2-diyl)bis(1-methyl-1H-indole) (4ab)



Yield: 58%; pale yellow viscous liquid; R_f: 0.48 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 2935, 2855, 2358, 2353, 1680, 1595, 1449, 1431, 1358, 1156, 1120, 1033 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.56-7.52 (m, 2H), 7.28-7.16 (m, 4H), 7.14-6.99 (m, 2H), 6.83 (s, 1H), 6.75 (s, 1H), 6.71 (dd, *J*1 = 5.5Hz, *J*2 = 1Hz, 1H), 5.97 (dd, *J*1 = 5.5Hz, *J*2= 2.5Hz, 1H), 4.26 (s, 1H), 4.11 (s, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 2.45-2.41 (m, 2H), 2.02-2.00 (m, 1H), 1.94-1.92 (m, 1H), 1.63-1.45 (m, 4H), 1.34-1.31 (m, 1H), 1.18-1.17 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 139.2, 137.5, 137.4, 136.1, 132.8, 129.6, 129.0, 128.2, 127.1, 126.9, 125.6, 125.3, 121.5, 121.3, 120.4, 120.3, 120.2, 118.8, 118.6, 118.3, 109.1, 108.9, 52.3, 45.7, 32.6, 32.5, 32.0, 31.9, 28.6, 27.7, 26.9.

HRMS (ESI): Calcd for $C_{29}H_{30}N_2Na$: 429.23067; Found: 429.23102.

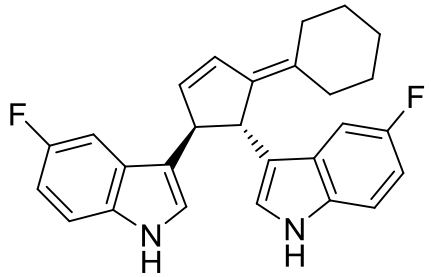
3,3'-(5-Cyclohexylidenecyclopent-3-ene-1,2-diyl)bis(2-phenyl-1H-indole) (4ac)



Yield: 54%; Pale yellow solid. M. p 160–164^{o}C; R_f: 0.52 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3342, 3075, 2953, 2912, 2857, 1695, 1611, 1514, 1462, 1380, 1238, 1100, 1030, 931, 740 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.98 (s, 1H), 7.88 (s, 1H), 7.68 (d, *J* = 8Hz, 1H), 7.59 (d, *J* = 8Hz, 1H), 7.42-7.37 (m, 4H), 7.28-6.80 (m, 13H), 6.14 (m, 1H), 4.76 (brs, 1H), 4.71 (brs, 1H), 2.51-2.49 (m, 1H), 2.38-2.18(m, 1H), 1.83-1.07 (m, 8H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 138.4, 136.5, 136.4, 136.3, 135.1, 134.5, 133.4, 132.6, 132.5, 130.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.4, 127.3, 122.3, 122.2, 121.3, 120.9, 119.6, 119.2, 117.3, 114.7, 110.5, 110.3, 50.6, 44.8, 32.5, 30.8, 28.6, 27.1, 26.8.

HRMS (ESI): Calcd for $C_{39}H_{34}N_2Na$: 553.26197; Found: 553.26233.

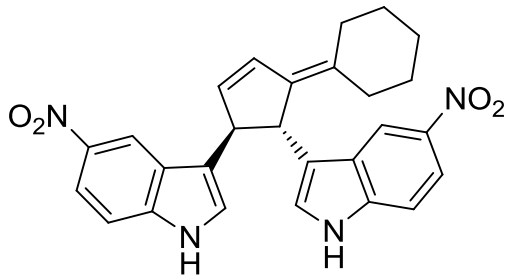
3,3'-(5-Cyclohexylidenecyclopent-3-ene-1,2-diyl)bis(5-fluoro-1H-indole). (4ad)



Yield: 52%; pale yellow viscous liquid; R_f: 0.40 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3356, 3052, 2978, 2939, 2849, 1689, 1619, 1583, 1514, 1462, 1415, 1402, 1380, 1304, 1238, 1111, 1047, 942, 740 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.03 (s, 1H), 7.94 (s, 1H), 7.31-7.20 (m, 4H), 7.07 (s, 1H), 7.00-6.77 (m, 4H), 6.00 (t, 1H, *J* = 3Hz), 4.22 (s, 1H), 4.09 (s, 1H), 2.46- 2.42 (m, 2H), 2.06-2.04 (m, 1H), 1.96- 1.94 (m, 1H), 1.67- 1.44 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 158.5, 156.7, 138.5, 135.3, 133.8, 133.5, 130.3, 126.9, 122.9, 122.7, 121.9, 120.3, 111.7, 111.6, 110.5, 110.3, 110.2, 105.2, 105.0, 45.6, 32.0, 31.8, 28.5, 27.6, 26.8.

HRMS (ESI): Calcd for $C_{27}H_{24}F_2N_2Na$: 437.18052; Found: 437.18088.

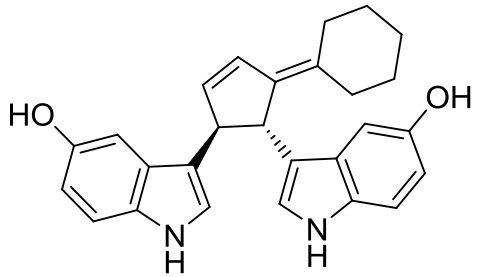
3,3'-(5-Cyclohexylidenecyclopent-3-ene-1,2-diyl)bis(5-nitro-1H-indole) . (4ae)



Yield: 48%; orange red viscous liquid; R_f: 0.40 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3326, 3056, 2955, 2932, 2850, 1675, 1629, 1583, 1457, 1385, 1300, 1238, 1100, 1040, 931, 7445 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 8.91 (s, 1H), 8.74 (s, 1H), 8.53-8.52 (m, 2H), 8.12- 8.09 (m, 2H), 7.45-7.41 (m, 2H), 7.26 (d, *J* = 10.5Hz, 1H), 7.14 (s, 1H), 6.86 (d, *J* = 5.5Hz, 1H), 5.99 (d, *J* = 4.5Hz, 1H), 4.33 (s, 1H), 4.22 (brs, 1H), 2.61-2.58 (m, 1H), 2.44-2.42 (m, 1H), 2.07-2.04 (m, 1H), 1.93-1.90 (m, 1H), 1.89-1.37 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 141.4, 141.2, 140.1, 140.0, 137.6, 135.1, 134.6, 130.9, 125.9, 125.7, 124.1, 124.0, 123.8, 122.2, 117.7, 117.6, 117.5, 112.9, 111.3, 52.3, 45.7, 32.1, 32.0, 28.2, 27.7, 26.7.

HRMS (ESI): Calcd for $C_{27}H_{24}N_2O_4Na$: 491.16952; Found: 491.16993.

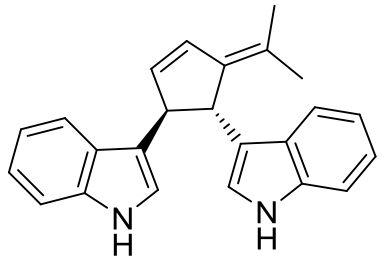
3,3'-(5-Cyclohexylidenecyclopent-3-ene-1,2-diyl)bis(1H-indol-5-ol). (4af)



Yield: 39%; pale yellow viscous liquid; R_f: 0.19 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3339, 3061, 2990, 2940, 2842, 1680, 1623, 1580, 1514, 1380, 1302, 1240, 1110, 1042, 931, 740 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.87 (brs, 1H), 7.78 (brs, 1H), 7.27-7.22 (m, 2H), 7.03-6.98 (m, 3H), 6.92 (d *J* = 2Hz, 1H), 6.81-6.74 (m 3H) ,6.01-6.00 (dd, J_1 = 6 Hz, J_2 = 3 Hz, 1H), 4.82 (d, *J* = 6.5Hz, 2H), 4.16 (s, 1H), 4.07(s, 1H), 2.45-2.39 (m, 2H), 1.99-1.94 (m, 2H),1.50-1.44 (m 3H), 1.33-0.87 (m 5H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 149.1, 148.9, 138.8, 135.6, 133.1, 132.1, 130.0, 127.3, 122.2, 121.3, 119.8, 111.8, 111.7, 111.6, 111.6, 104.8, 104.7, 51.7, 45.8, 32.0, 31.8, 28.6, 27.6, 26.8.

HRMS (ESI): Calcd for $C_{27}H_{26}N_2O_2Na$: 433.18920; Found: 433.18954.

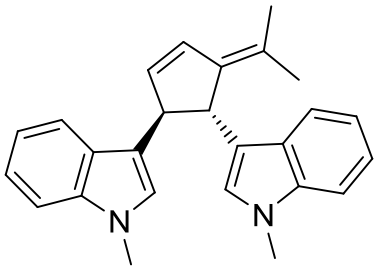
3,3'-(5-(Propan-2-ylidene)cyclopent-3-ene-1,2-diyl)bis(1H-indole). (4ea)



Yield: 64%; colourless viscous liquid; R_f: 0.45 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3315, 2920, 2857, 2377, 1648, 1590, 1520, 1468, 1367, 1160, 1119, 1037cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.99 (s, 1H), 7.92 (s, 1H), 7.60-7.56 (m, 2H), 7.40- 7.37 (m, 2H), 7.23-7.18 (m, 3H), 7.09-7.05 (m, 3H), 7.00 (s, 1H), 6.94 (s, 1H), 6.74 (dd, 1H, J_1 = 5.5Hz, J_2 = 2Hz), 6.05 (dd, 1H, J_1 = 5.5Hz, J_2 = 2.5Hz), 4.28 (s, 1H), 4.22 (s, 1H), 1.93 (s, 3H), 1.61 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 141.9, 137.1, 136.9, 135.8, 130.4, 127.3, 126.8, 125.8,125.7, 124.4, 121.5, 121.3, 120.5, 120.3, 120.0, 118.4, 118.2, 117.9, 110.8, 110.7, 52.4, 46.4, 21.3

HRMS (ESI): Calcd for $C_{24}H_{22}N_2Na$: 361.16807; Found: 361.16848

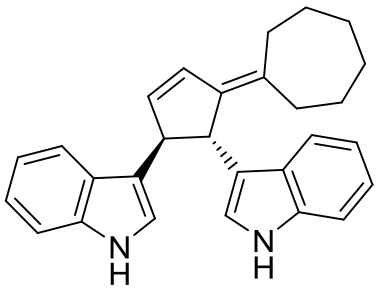
3,3'-(5-(Propan-2-ylidene)cyclopent-3-ene-1,2-diyl)bis(1-methyl-1H-indole). (4eb)



Yield: 56%; pale yellow solid, M. p. 162–164^{o}C; R_f: 0.50 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 2925, 2852, 2371, 1649, 1586, 1523, 1465, 1364, 1254, 1167, 1122, 1042cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.66-7.61 (m, 2H), 7.38-7.31 (m, 2H), 7.29- 7.27 (m, 2H), 7.14-7.09 (m, 2H), 6.90 (s, 1H), 6.83 (s, 1H), 6.78 (dd, 1H, J_1= 5.5Hz, J_2= 2Hz,) 6.09 (dd, H, J_1 = 5.5Hz, J_2 = 2.5Hz), 4.32 (s, 1H), 4.25 (s, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 1.99 (s, 3H), 1.60 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 142.2, 137.6, 137.5, 135.9, 130.5, 127.1, 127.0, 125.9, 125.7, 124.4, 121.5, 121.3, 120.3, 120.2, 119.9, 118.8, 118.7, 118.4, 109.2, 109.1, 52.6, 46.6, 31.7, 21.4.

HRMS (ESI): Calcd for $C_{26}H_{26}N_2Na$: 389.19937; Found: 389.19969.

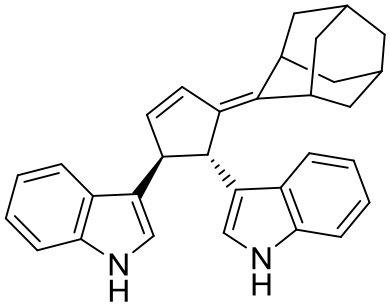
3,3'-(5-Cycloheptylidenecyclopent-3-ene-1,2-diyl)bis(1H-indole). (4fa)



Yield: 53%; colourless viscous liquid; R_f: 0.43 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3408, 3056, 2923, 2853, 1703, 1619, 1583, 1517, 1485, 1455, 1338, 1227, 1095, 1012, 741cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.97 (s, 1H), 7.89 (s, 1H),7.59-7.57 (d, J= 8Hz, 2H), 7.37-7.34 (m, 2H), 7.21-7.16 (m, 2H), 7.07-7.05 (m, 2H), 6.98-6.93 (m, 2H), 6.76 (dd, J_1 = 5.5Hz, J_2 = 2.5Hz, 1H), 6.04 (dd, J_1 = 5.5Hz, J_2 = 3 Hz, 1H), 4.27 (s, 1H), 4.18 (brs, 1H), 2.57-2.51 (m, 2H), 2.25-2.19 (m, 1H), 2.07-2.06 (m, 1H), 1.72-1.29 (m, 8H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 142.1, 136.9, 136.7, 135.9, 134.3, 130.4, 129.0, 128.2, 126.7, 126.6, 121.9, 121.5,120.8, 120.7,120.2, 120.1, 119.2,119.0, 111.0, 110.9, 52.5, 46.1, 32.8, 32.5, 29.8, 28.8, 27.2, 26.9.

HRMS (ESI): Calcd for $C_{28}H_{28}N_2Na$: 415.21502; Found: 415.21538.

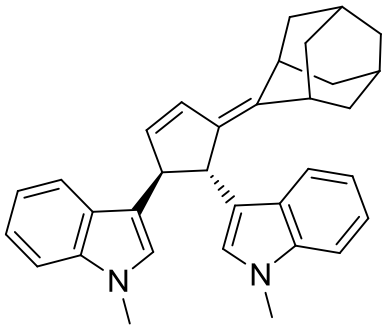
Compound **4ga**



Yield: 58%; colourless viscous liquid; R_f: 0.43 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3289, 3066, 2931, 2857, 1668, 1620, 1582, 1520, 1455, 1304, 1238, 933, 744 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.88 (s, 1H), 7.79 (s, 1H), 7.62 (d, *J* = 8Hz, 1H), 7.55 (d, *J* = 8Hz, 1H), 7.54-7.21 (m, 2H), 7.19-7.13 (m, 2H), 7.05- 6.93 (m, 4H), 6.72-6.71 (m, 1H), 5.94 (dd, J_1 = 5.5Hz, J_2 = 3Hz, 1H), 4.30 (s, 1H), 4.11 (brs, 1H), 3.12 (brs, 1H), 2.49 (brs, 1H), 2.04-1.68 (m, 9H), 1.53-1.43 (m, 2H), 0.88-0.84 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 140.8, 137.8, 137.0, 136.9, 135.4, 135.2, 129.5, 129.1, 128.3, 126.8, 126.5, 125.4, 122.0, 121.8, 120.9, 120.4, 119.2, 118.9, 111.2, 111.1, 52.4, 45.2, 39.8, 39.4, 38.2, 37.3, 35.1, 34.8, 28.4, 21.6.

HRMS (ESI): Calcd for $C_{31}H_{30}N_2Na$: 453.23067; Found: 453.23101.

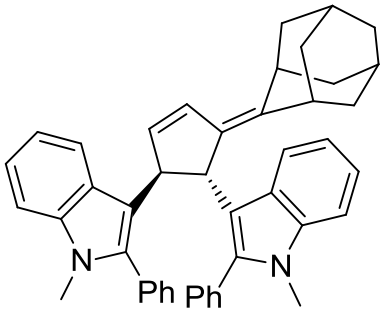
Compound **4gb**



Yield: 55%; colourless viscous liquid; R_f: 0.48 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3090, 2950, 2932, 2857, 1688, 1621, 1583, 1514, 1462, 1380, 1304, 1238, 1108, 1042, 957, 931, 743 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.65 (d, *J* = 8Hz, 1H), 7.58 (d, *J* = 8Hz, 1H), 7.33-7.20 (m, 6H), 7.08-7.02 (m, 2H), 6.89 (s, 1H), 6.83 (s, 1H), 6.73 (d, *J* = 5.5Hz, 1H), 5.95 (t, *J* = 2.5Hz, 1H), 4.32 (s, 1H), 4.13 (s, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.17 (s, 1H), 2.53 (s, 1H), 2.01-1.58 (m, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 140.6, 137.6, 135.6, 135.2, 129.2, 127.2, 127.0, 125.6, 125.5, 121.5, 120.5, 120.3, 118.8, 118.8, 118.6, 109.1, 108.9, 52.5, 45.2, 39.8, 39.3, 38.2, 37.3, 35.0, 34.4, 32.6, 32.5, 28.4, 28.3.

HRMS (ESI): Calcd for $C_{33}H_{34}N_2Na$: 481.26197; Found: 481.26141

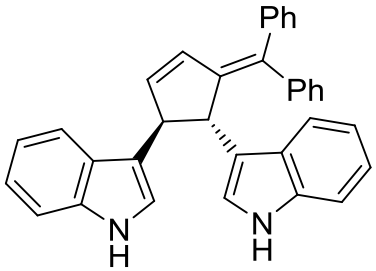
Compound **4gc**



Yield: 74%; colourless viscous liquid; R_f: 0.55 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 2981, 2915, 2833, 1671, 1621, 1586, 1542, 1380, 1300, 1238, 1042, 957, 931, 743 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.62-7.47 (m, 6H), 7.38-6.96 (m, 12H), 6.66 (dd, J_1=5.5 Hz, J_2=2.5 Hz, 1H), 6.04 (dd, J_1=5.5 Hz, J_2= 2.5 Hz, 1H), 4.41 (brs, 1H), 4.22 (brs, 1H), 3.61 (s, 3H), 3.57 (s, 3H), 2.98 (brs, 1H), 2.32 (brs, 1H), 1.83-1.50 (m, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 140.2, 137.9, 137.4, 136.2, 135.8, 134.6, 133.9, 133.4, 131.3, 130.5, 129.7, 128.7, 128.2, 127.7, 127.5, 126.6, 125.3, 122.3, 121.4, 120.3, 119.5, 119.1, 119.0, 117.5, 115.2, 108.9, 108.7, 51.0, 45.3, 39.3, 38.9, 37.8, 37.4, 34.9, 33.1, 30.9, 28.1.

HRMS (ESI): Calcd for $C_{45}H_{42}N_2Na$: 633.32457; Found: 633.32486.

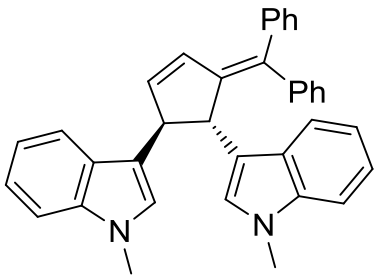
3,3'-(5-(Diphenylmethylene)cyclopent-3-ene-1,2-diyl)bis(1H-indole). 4ha



Yield: 84%; pale yellow solid, M.p. 154-156^{o}C; R_f: 0.43 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3294, 2857, 2366, 2335, 1647, 1590, 1369, 1120, 1037, 702 cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.90 (s, 1H), 7.67-7.51 (m, 3H), 7.37-7.06 (m, 9H), 6.98-6.78 (m, 9H), 6.40 (d, J = 4 Hz, 1H), 6.24 (brs, 1H), 4.51-4.49 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 148.1, 143.2, 142.6, 140.4, 136.8, 136.5, 135.0, 133.1, 129.8, 129.3, 127.9, 127.4, 126.7, 126.5, 126.2, 125.9, 122.0, 121.5, 120.8, 120.1, 119.8, 119.5, 119.3, 119.0, 118.9, 111.1, 110.9, 57.7, 48.5.

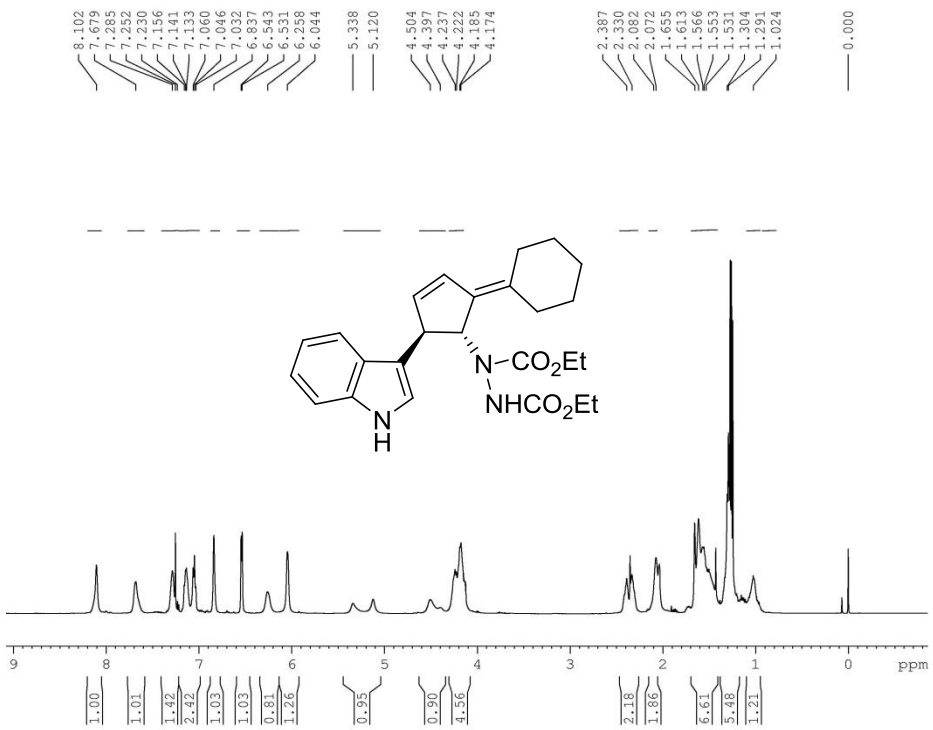
HRMS (ESI): Calcd for $C_{34}H_{26}N_2Na$: 485.19937; Found: 485.19969.

3,3'-(5-(Diphenylmethylene)cyclopent-3-ene-1,2-diyl)bis(1-methyl-1H-indole). (4hb)

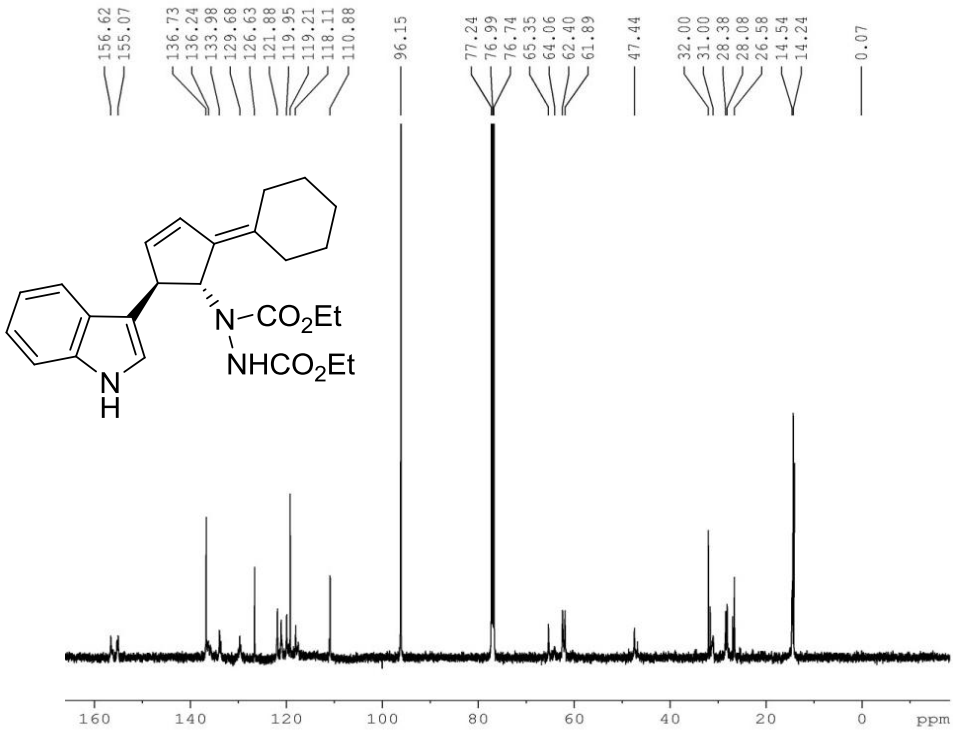


Yield: 81%; yellow solid, M.p. 160-162^{o}C; R_f: 0.48 (hexane/ethyl acetate = 3:1). **IR** (Neat) ν_{max}: 3053, 2927, 1709, 1688, 1613, 1513, 1469, 1427, 1372, 1328, 1242, 1156, 1130, 1013, 740cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$, TMS): **δ** 7.78-7.76 (m,2H), 7.72-7.30 (m, 9H), 7.20-6.99 (m, 6H), 6.87 (brs, 3H), 6.52 (t, J = 3Hz, 1H), 6.09 (dd, J_1= 4 Hz, J_2= 2.5 Hz, 1H), 4.66 (brs, 1H), 4.57-4.54 (m, 1H), 3.81 (s, 3H), 3.58 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, TMS): **δ** 148.8, 143.3, 143.0, 140.8, 137.6, 137.3, 134.9, 132.9, 129.9, 129.3,129.2, 128.4, 128.0, 127.4, 127.2, 127.2, 126.8, 126.5, 125.8, 125.7, 121.7, 121.1, 120.3, 120.0, 118.9, 118.4, 118.1, 117.6, 109.3, 109.1, 51.8, 48.9, 32.6, 32.2.

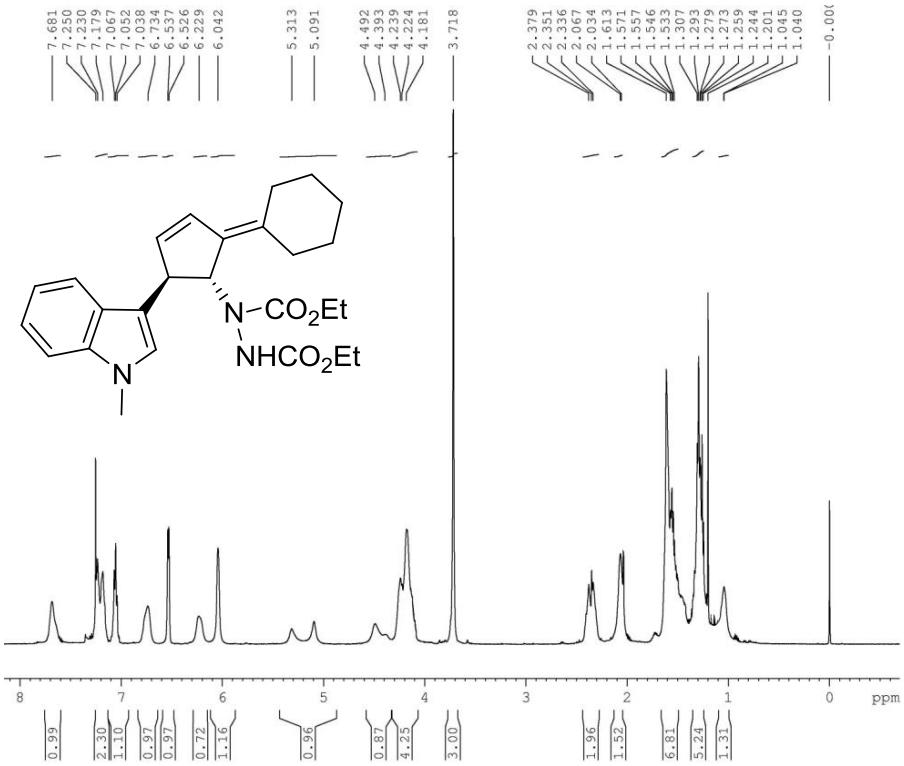
MS (ESI): Calcd for $C_{36}H_{30}N_2Na$: 513.23067; Found: 513.23098.



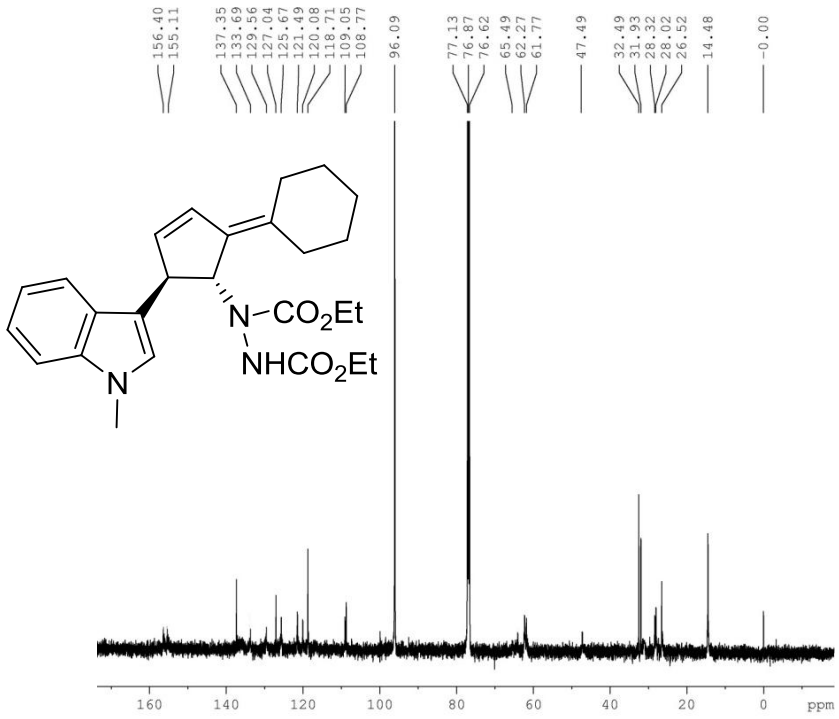
^{1}H NMR of 3aa



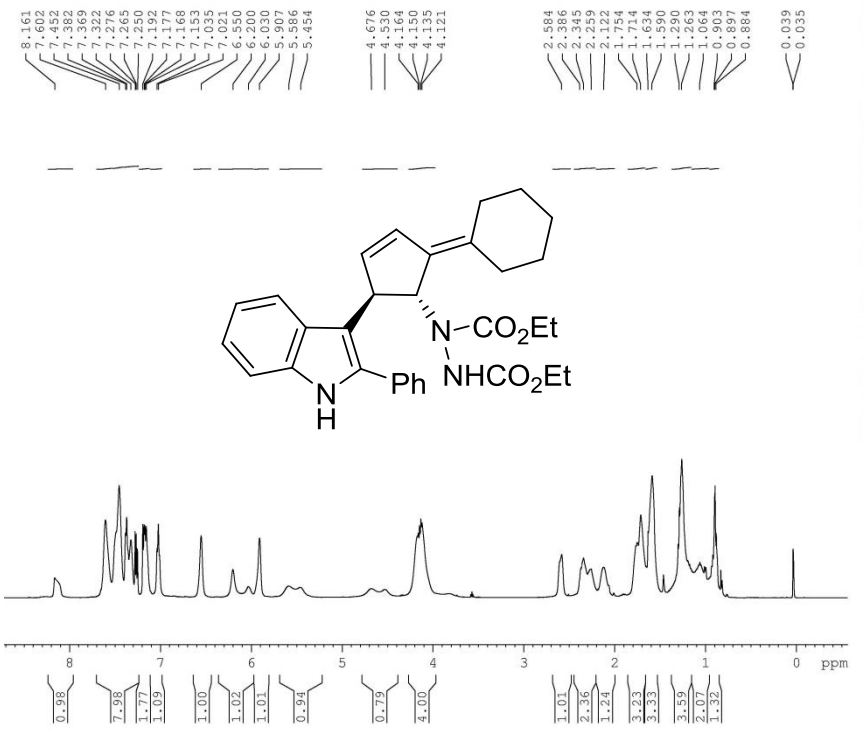
^{13}C NMR of 3aa



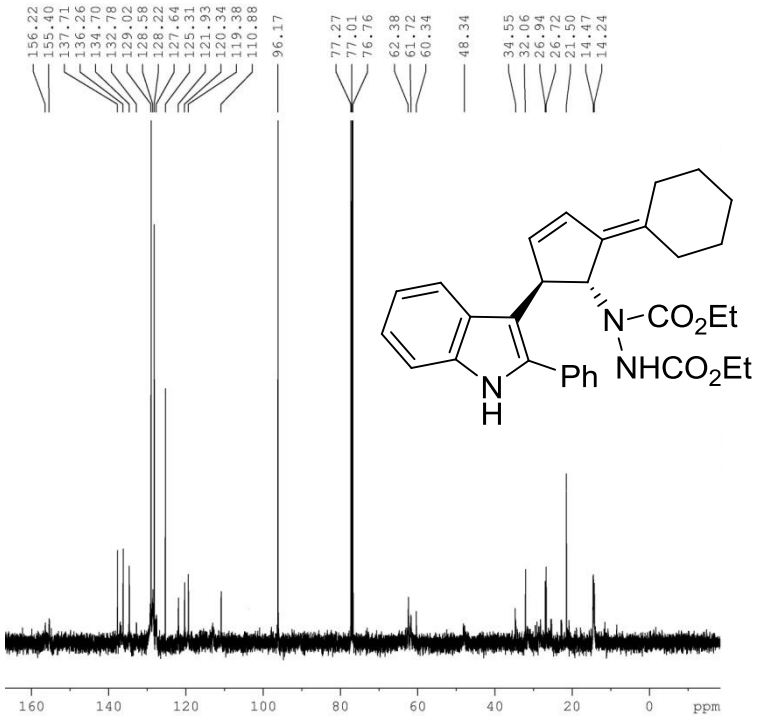
^{1}H NMR of 3ab



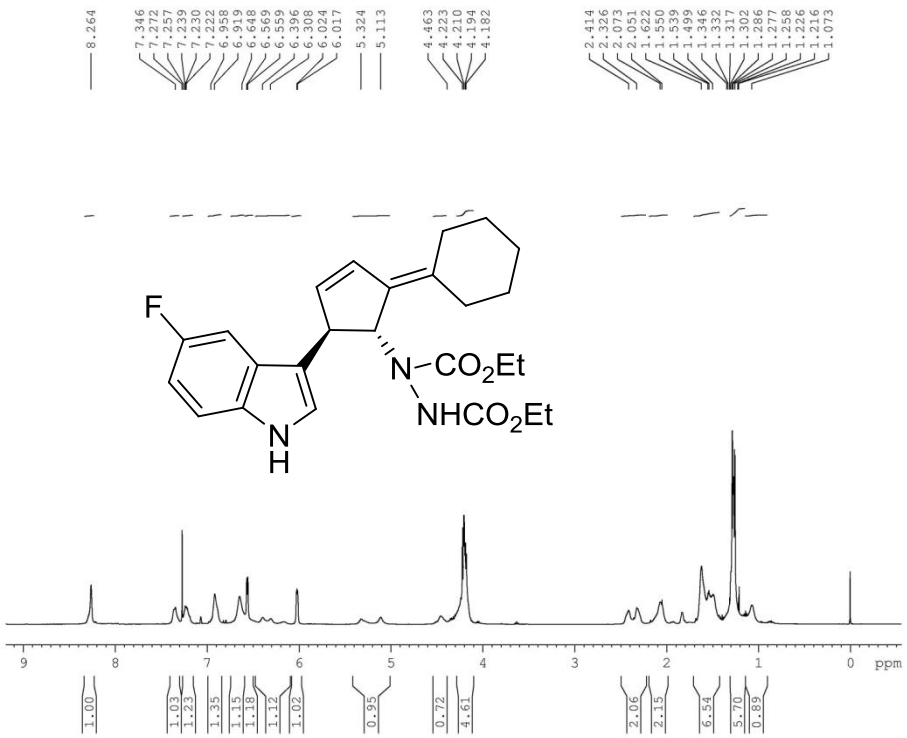
^{13}C NMR of 3ab



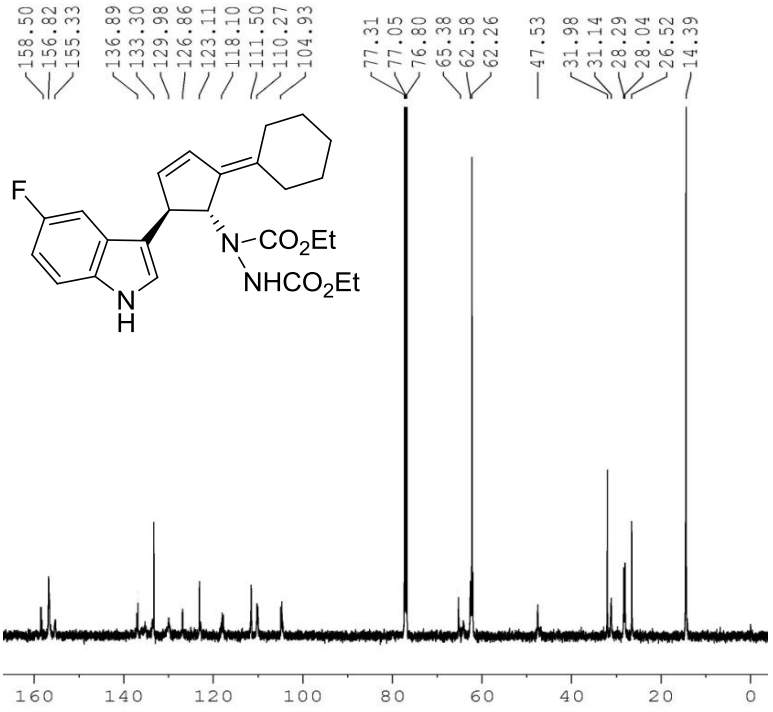
^{1}H NMR of 3ac



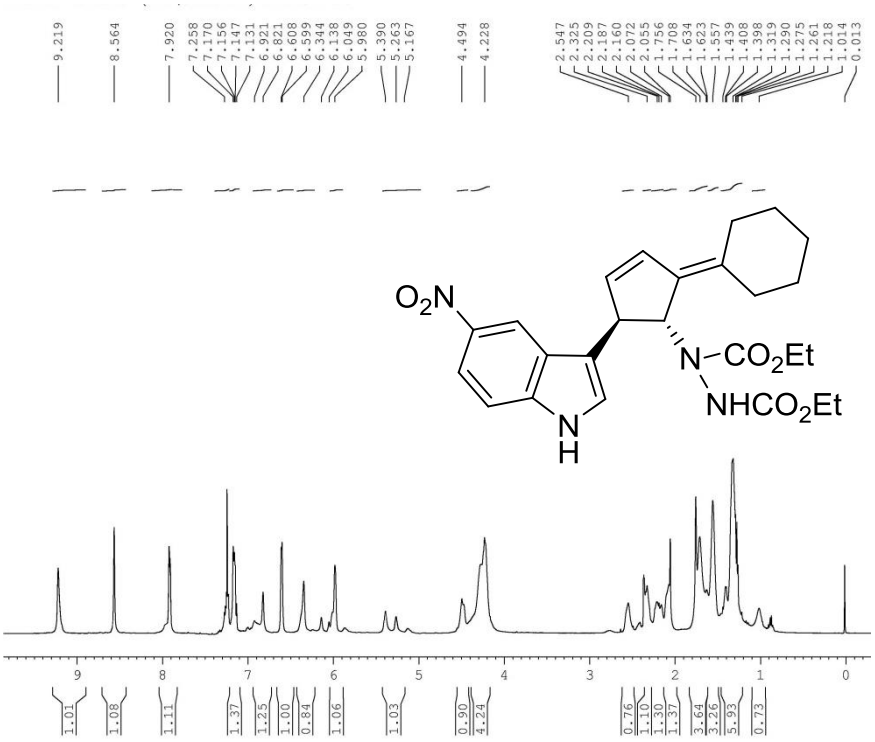
^{13}H NMR of 3ac



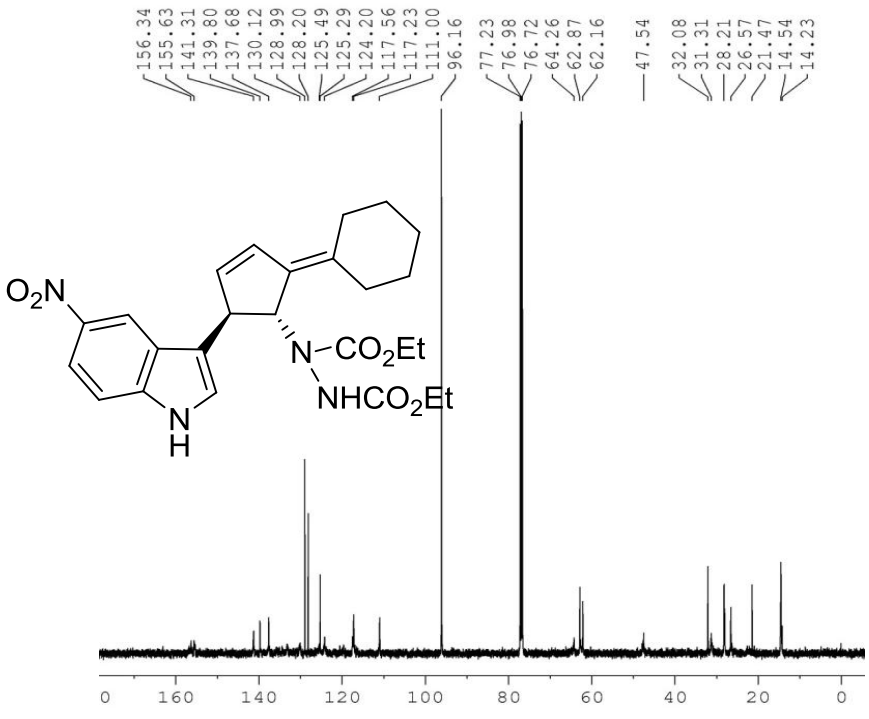
^{1}H NMR of 3ad



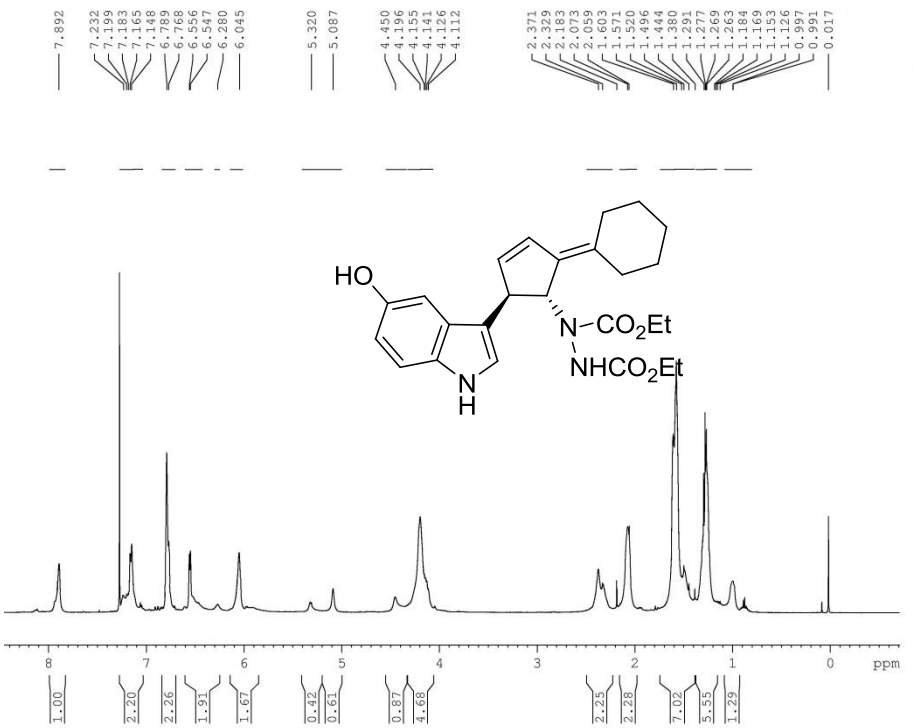
^{13}C NMR of 3ad



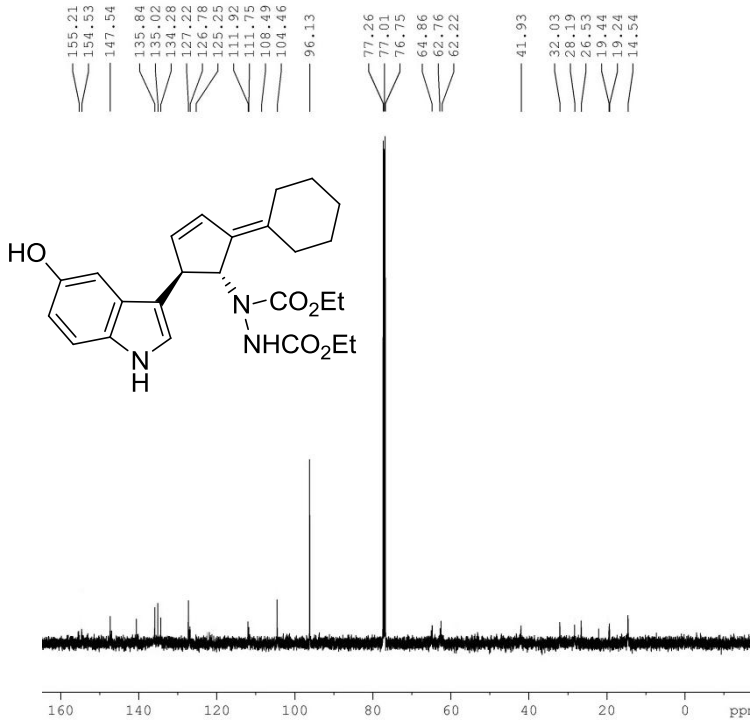
^{1}H NMR of 3ae



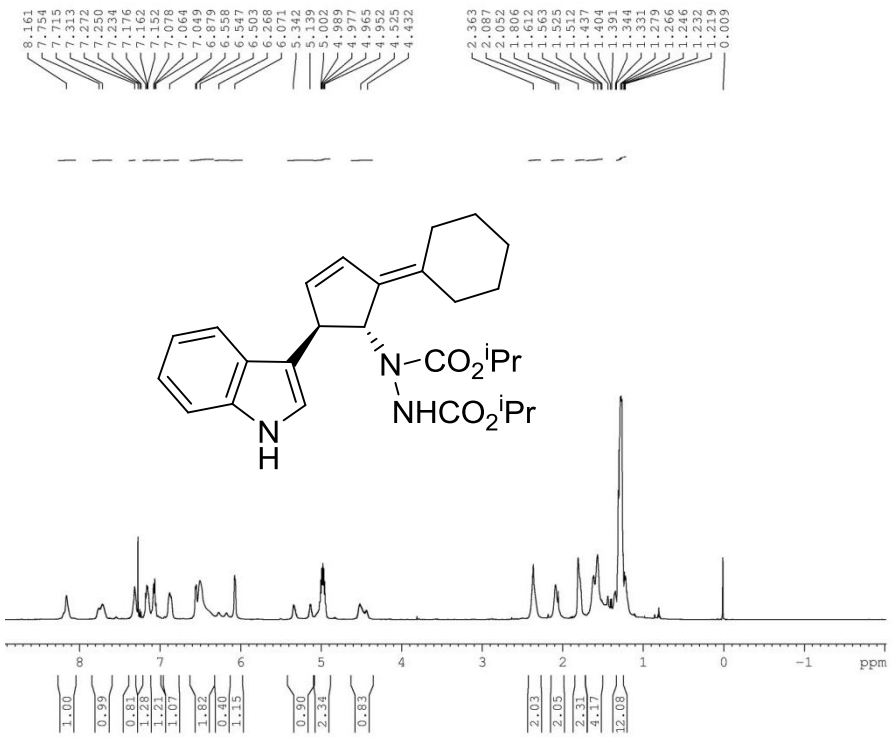
^{13}C NMR of 3ae



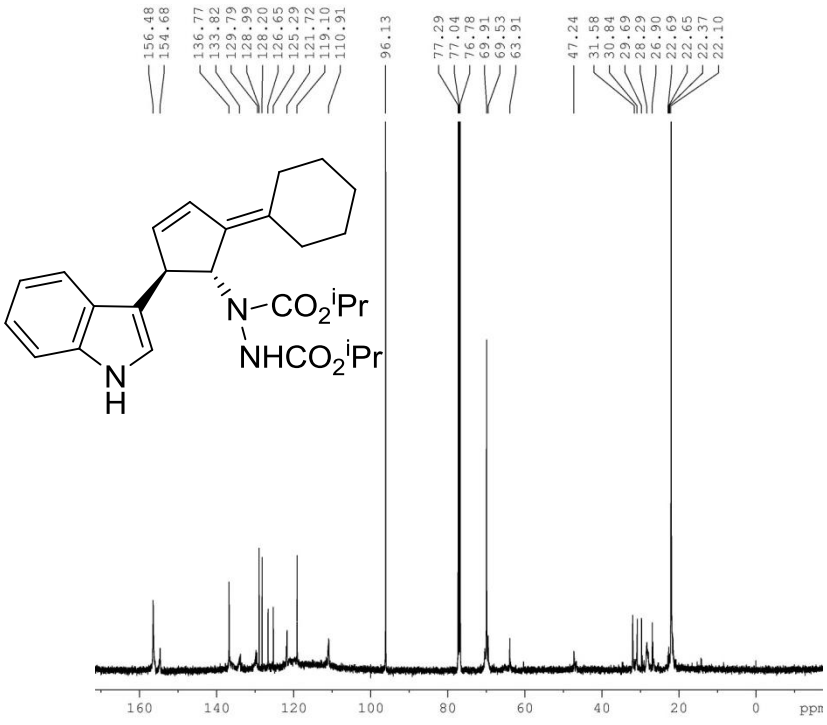
^{1}H NMR of 3af



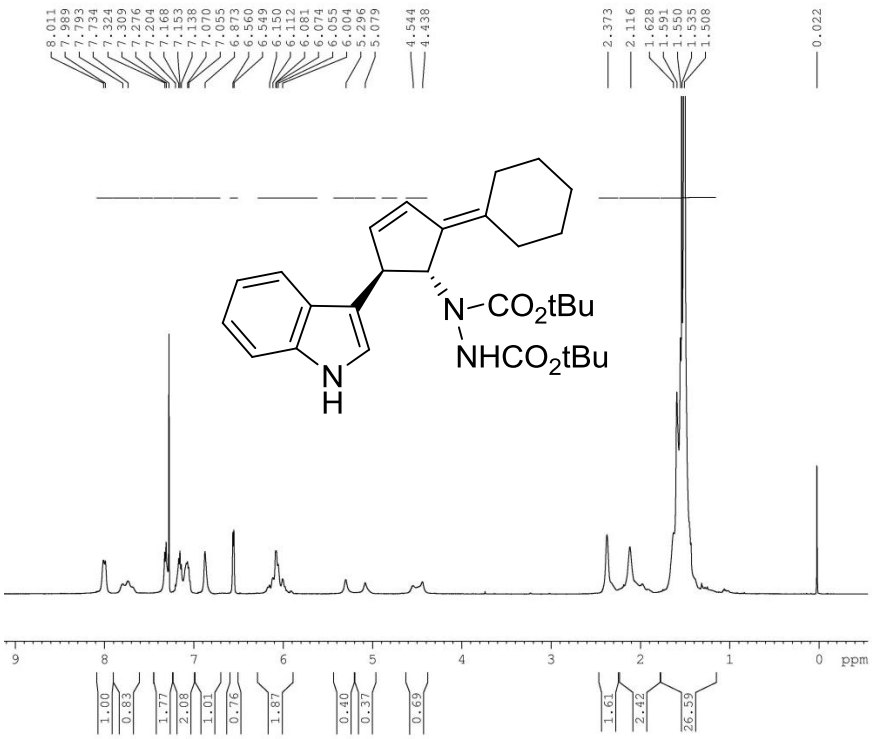
^{13}C NMR of 3af



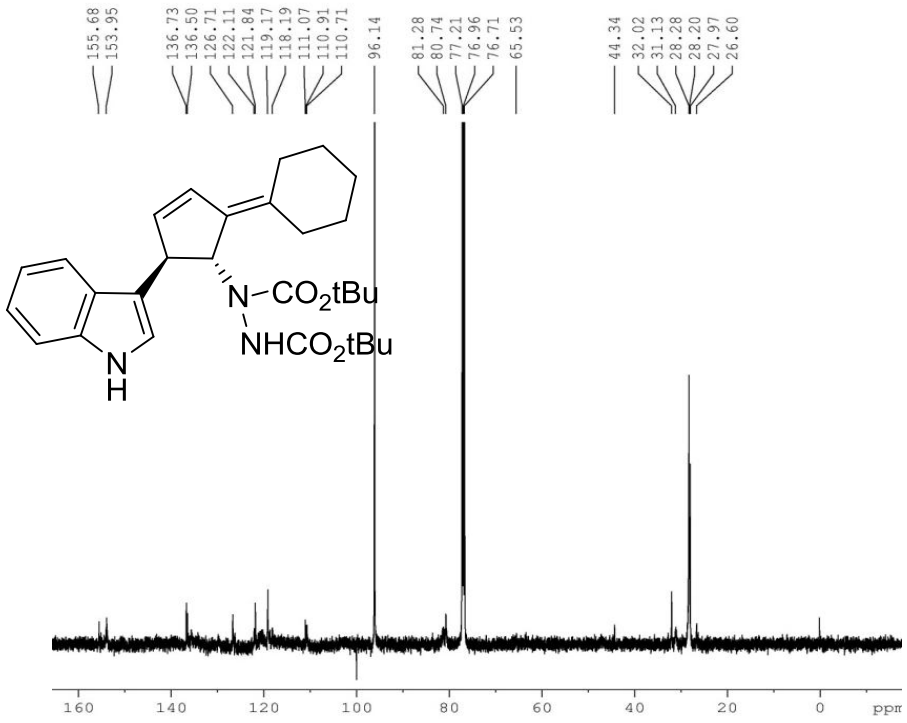
^{1}H NMR of 3ba



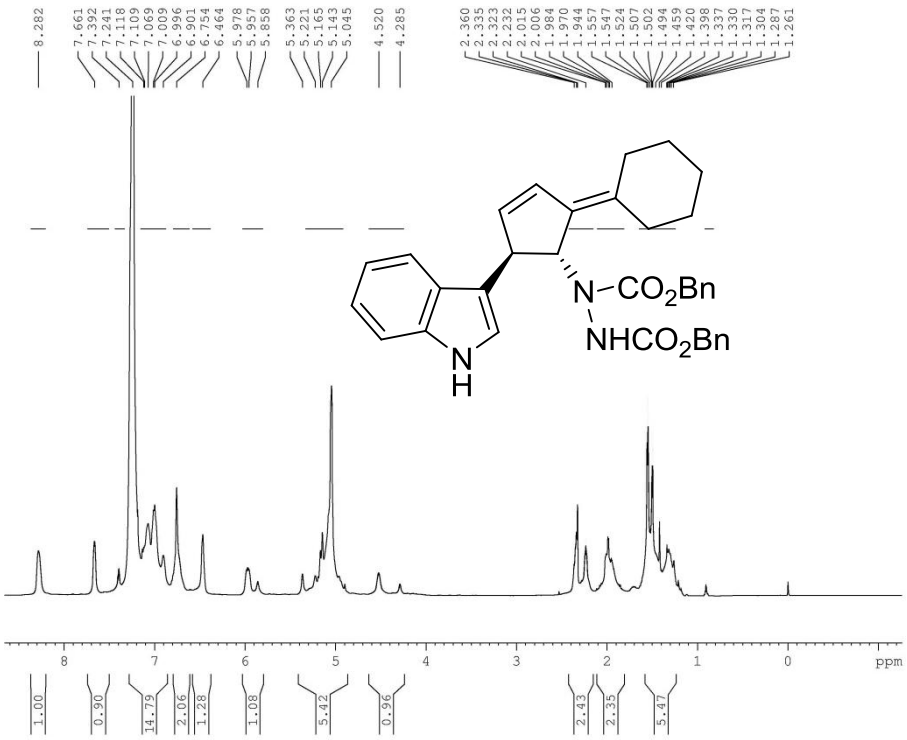
^{13}C NMR of 3ba



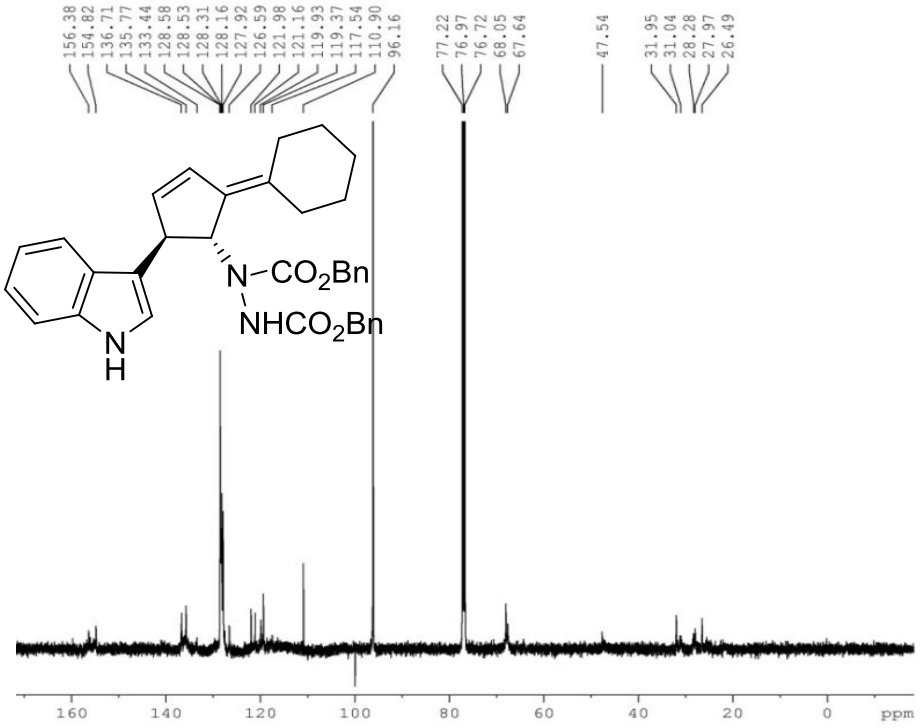
^{1}H NMR of 3ca



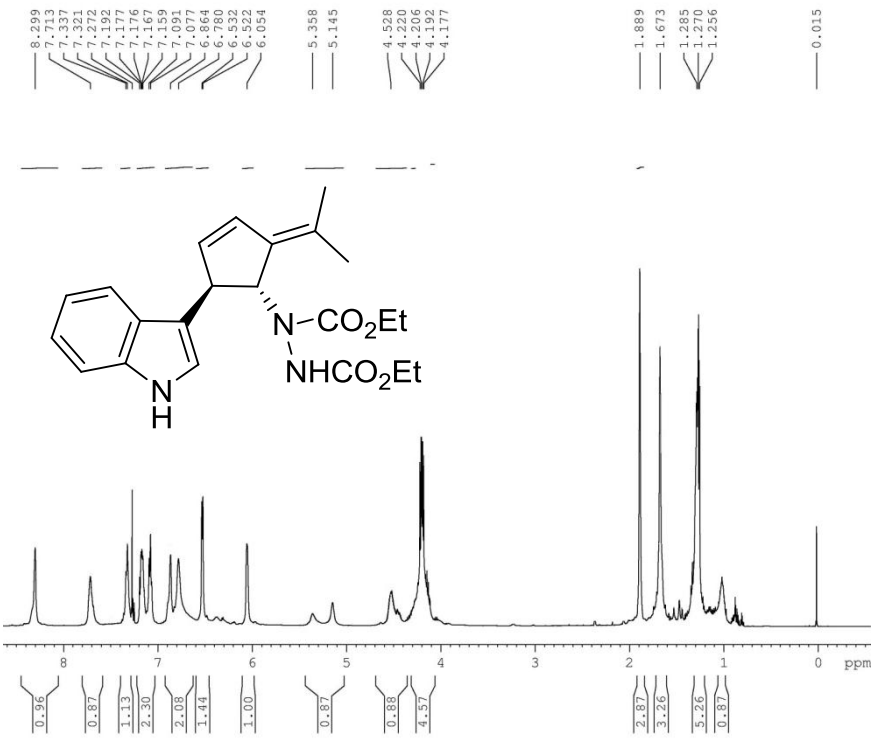
^{13}C NMR of 3ca



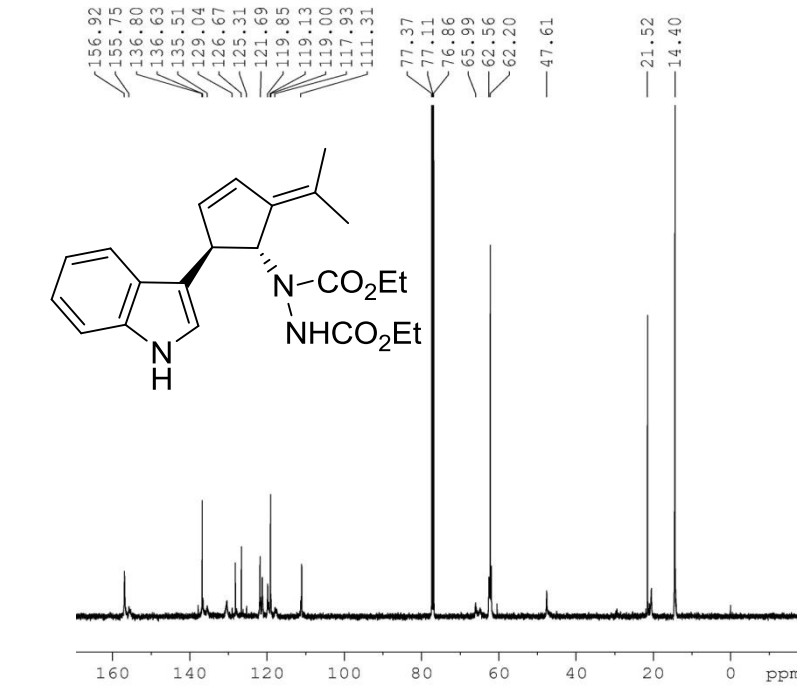
^{1}H NMR of 3da



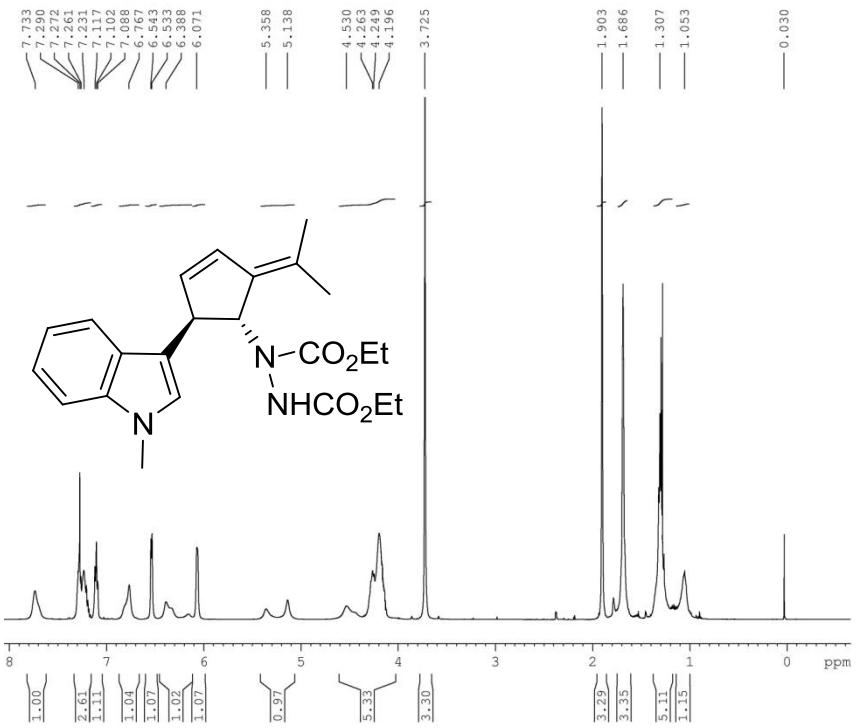
^{13}C NMR of 3da



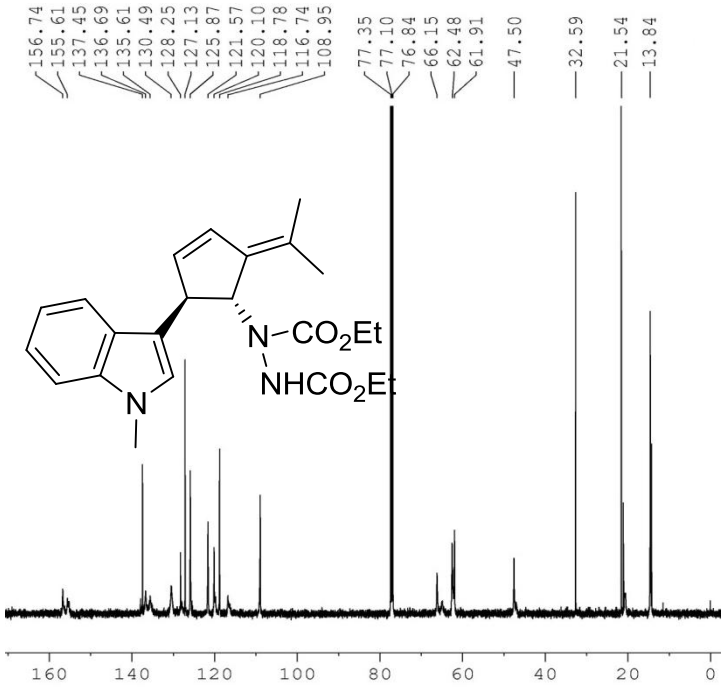
^{1}H NMR of 3ea



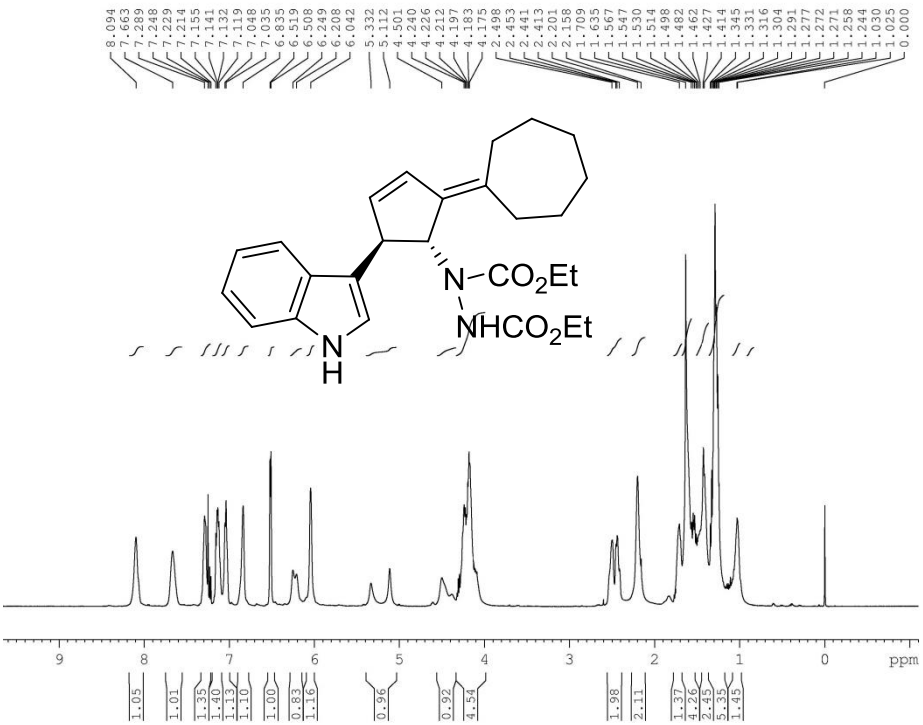
^{13}C NMR of 3ea



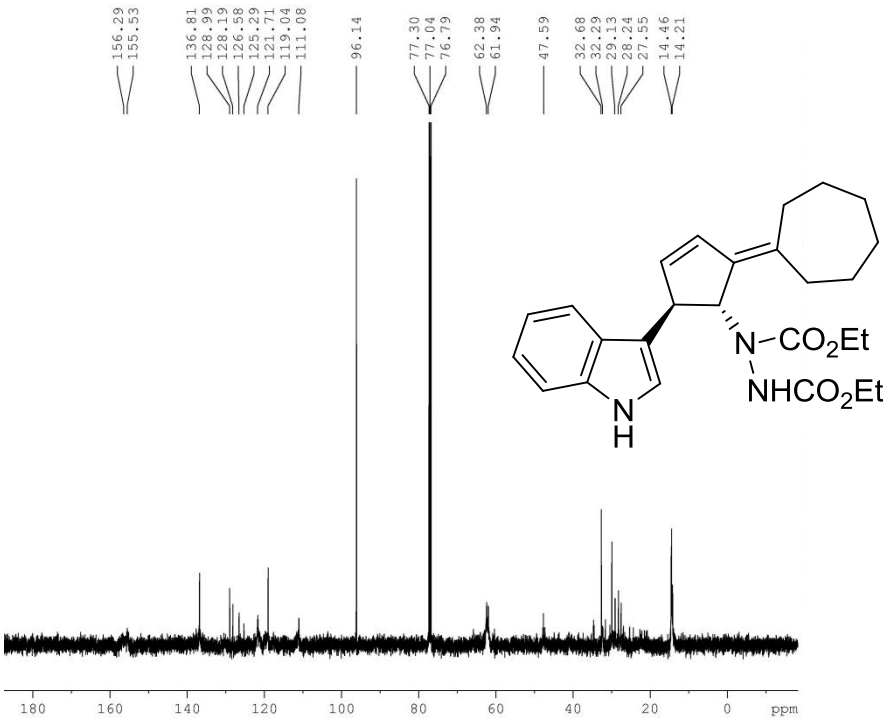
^{1}H NMR of 3eb



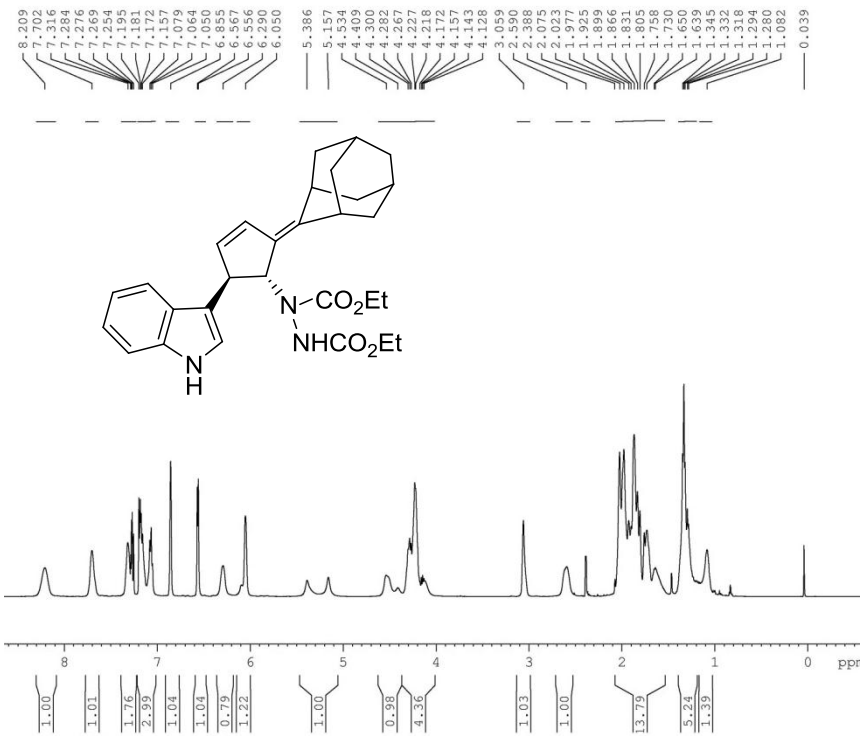
^{13}C NMR of 3eb



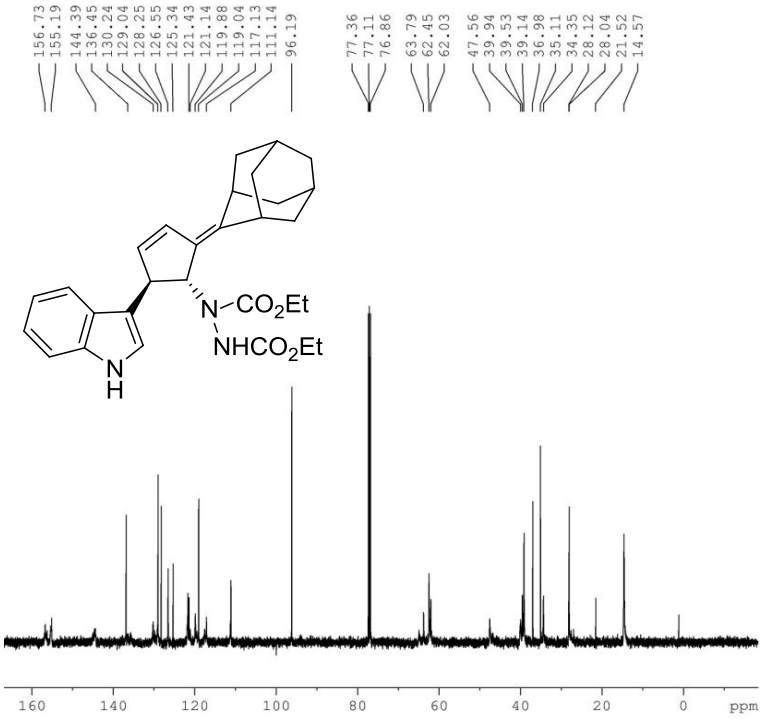
^{1}H NMR of 3fa



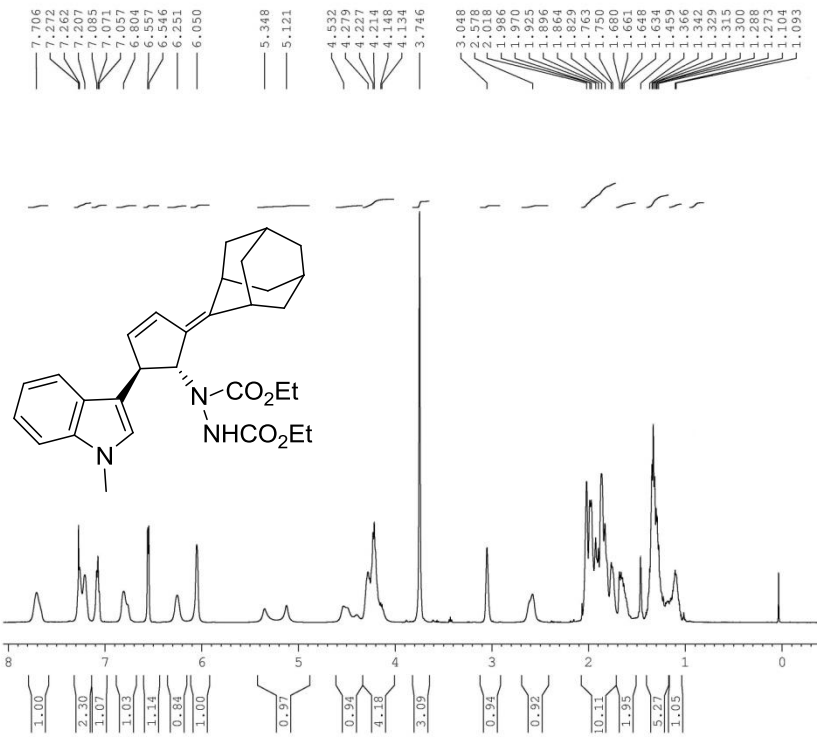
13C NMR of 3fa



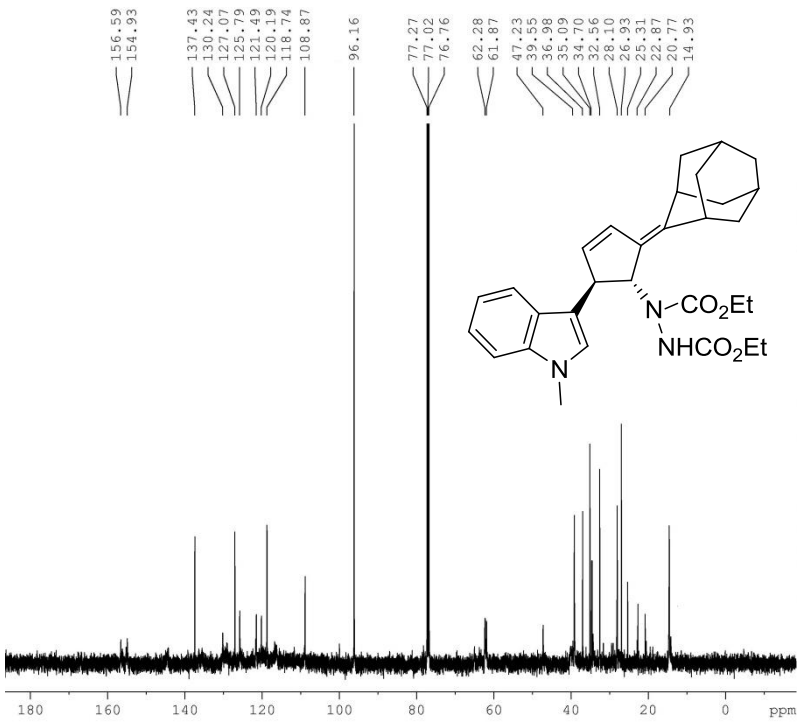
^{1}H NMR of 3ga



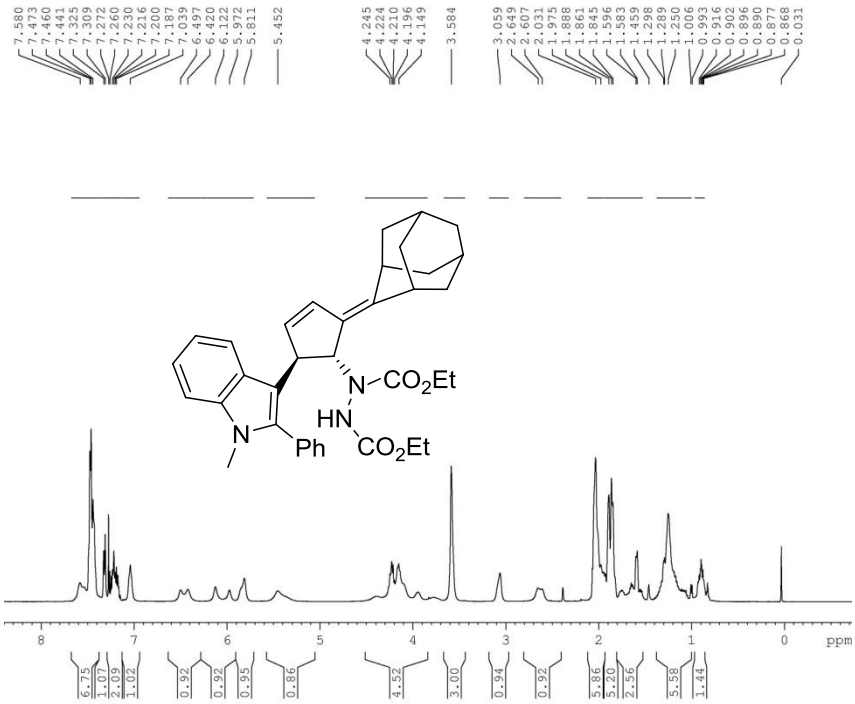
^{13}C NMR of 3ga



^{1}H NMR of 3gb



^{13}C NMR of 3gb



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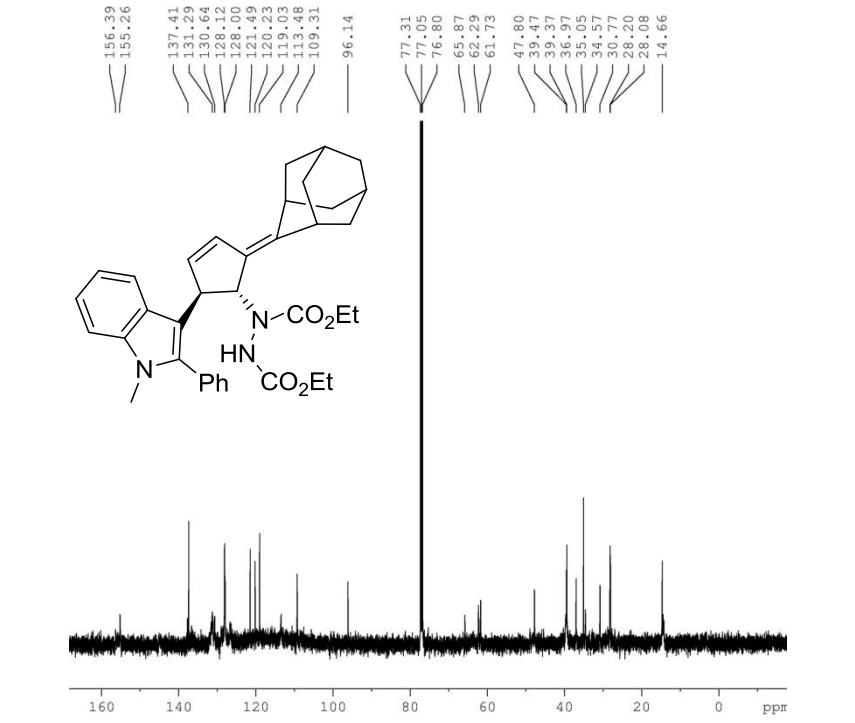
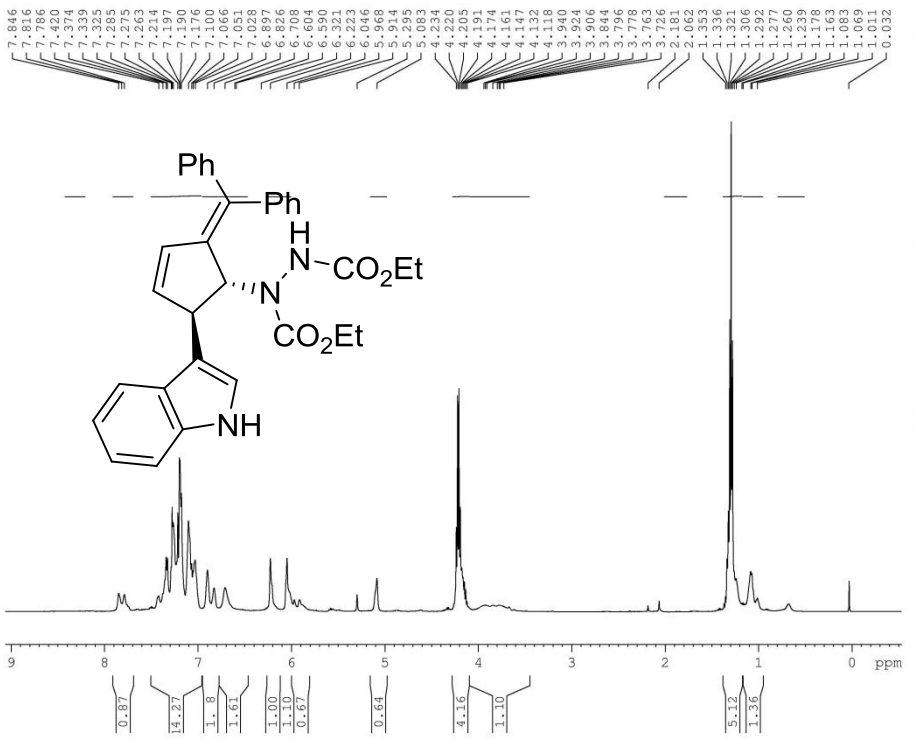
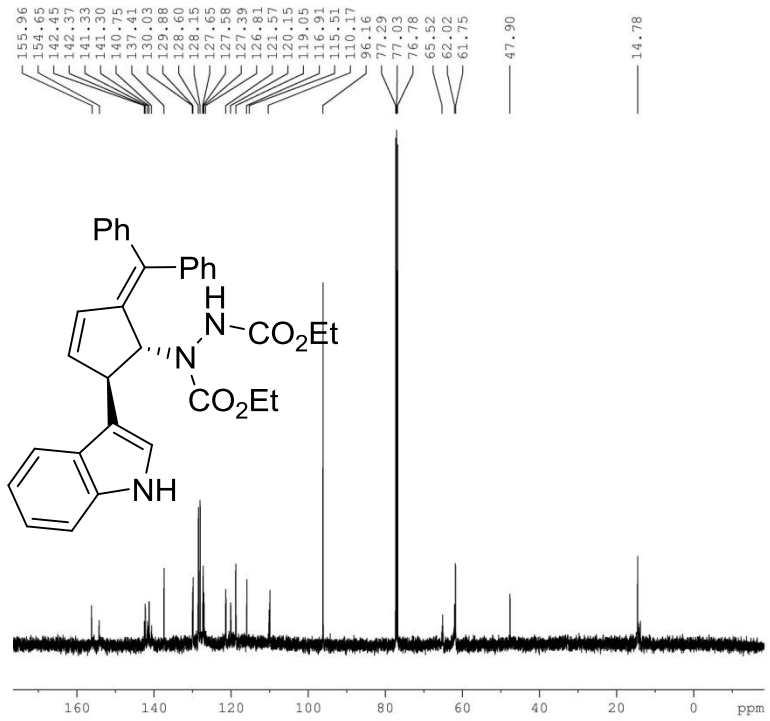


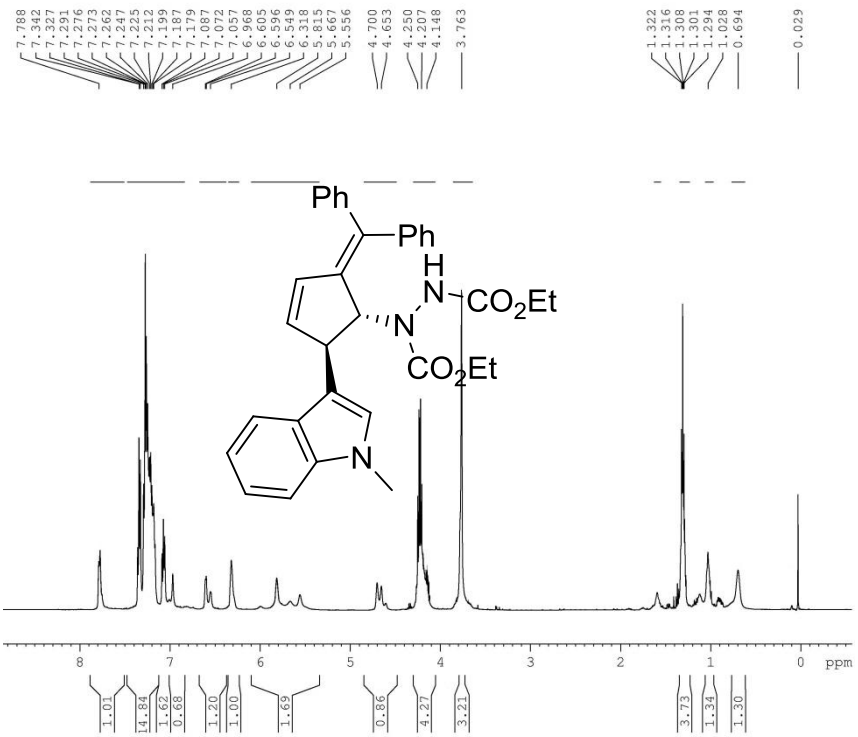
^{13}C NMR of 3gc



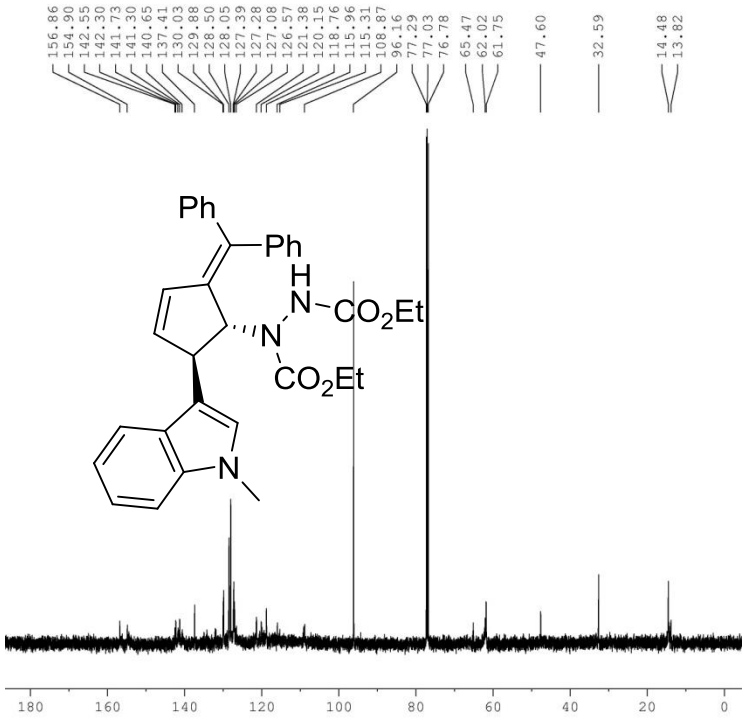
^{1}H NMR of 3ha



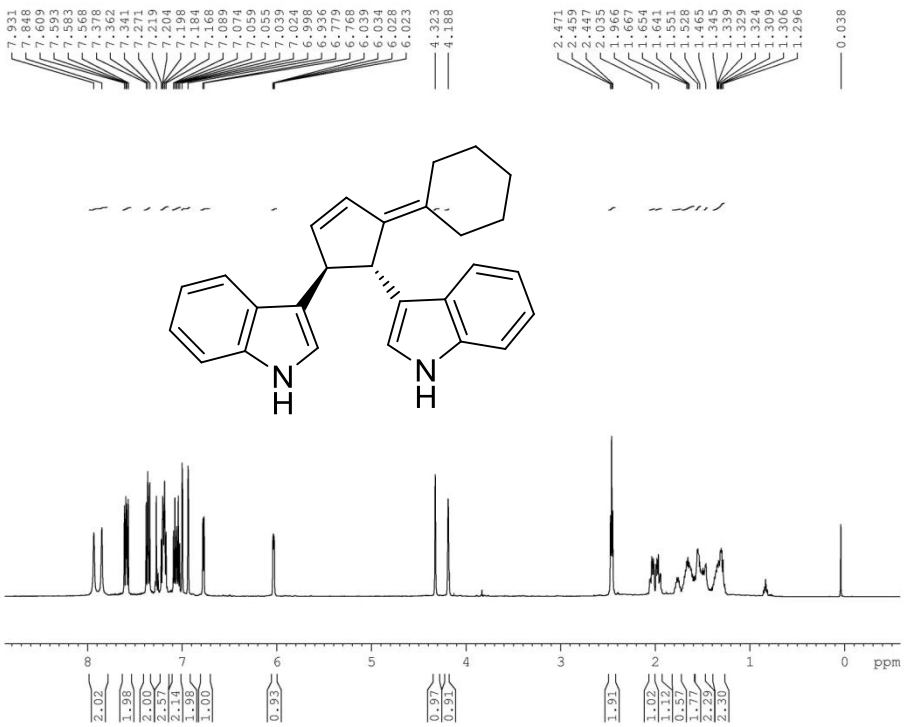
^{13}C NMR of 3ha



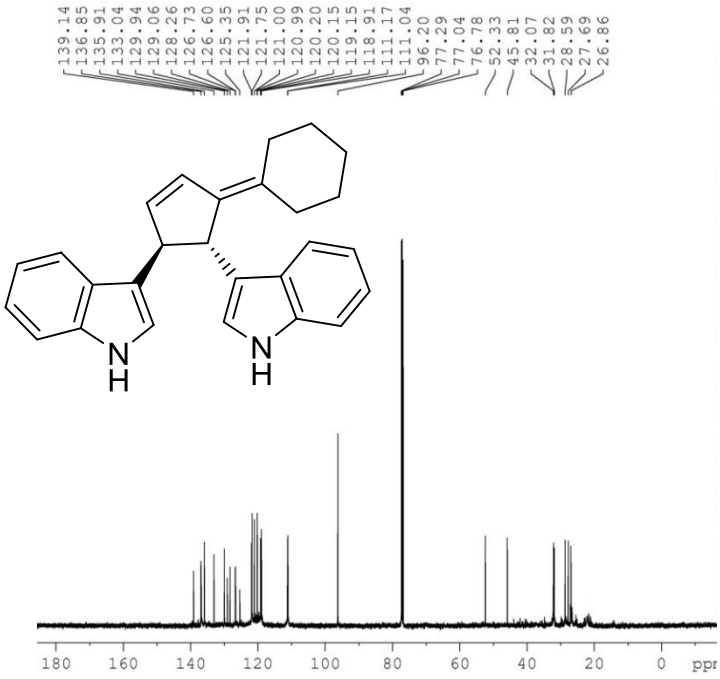
^{1}H NMR of 3hb



^{13}C NMR of 3hb



^{1}H NMR of 4aa



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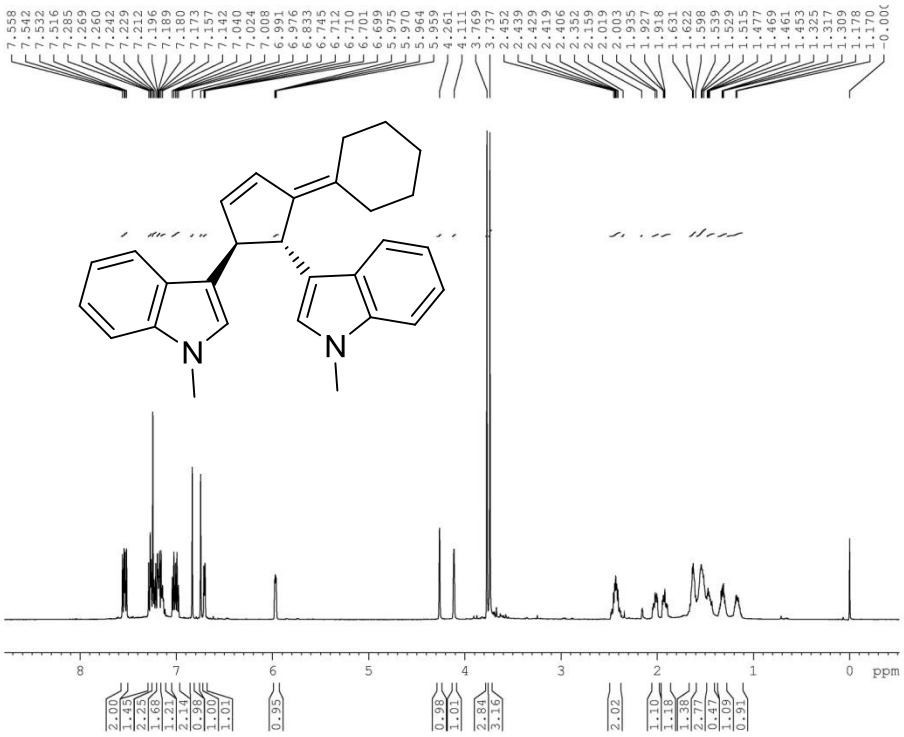

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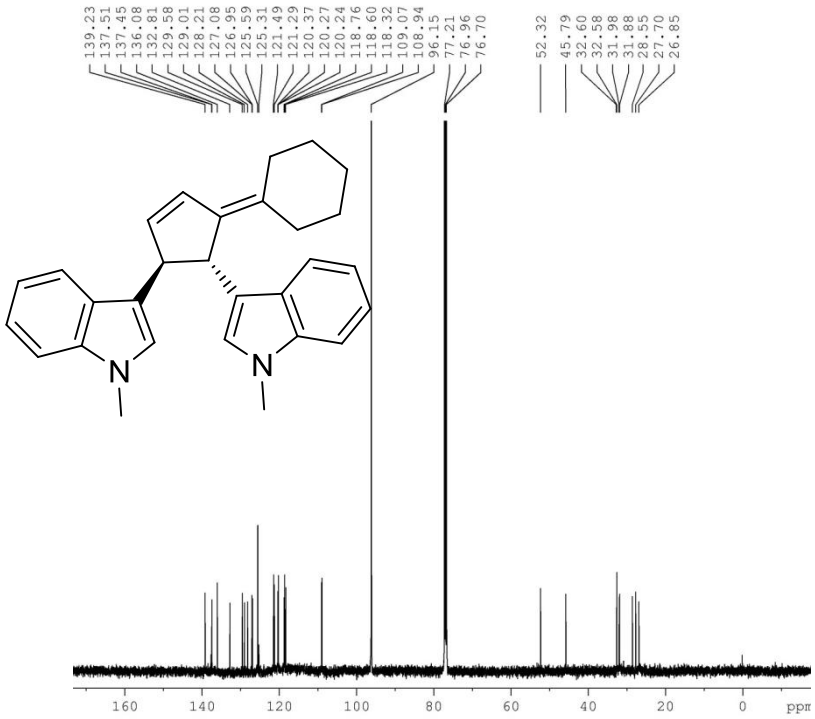
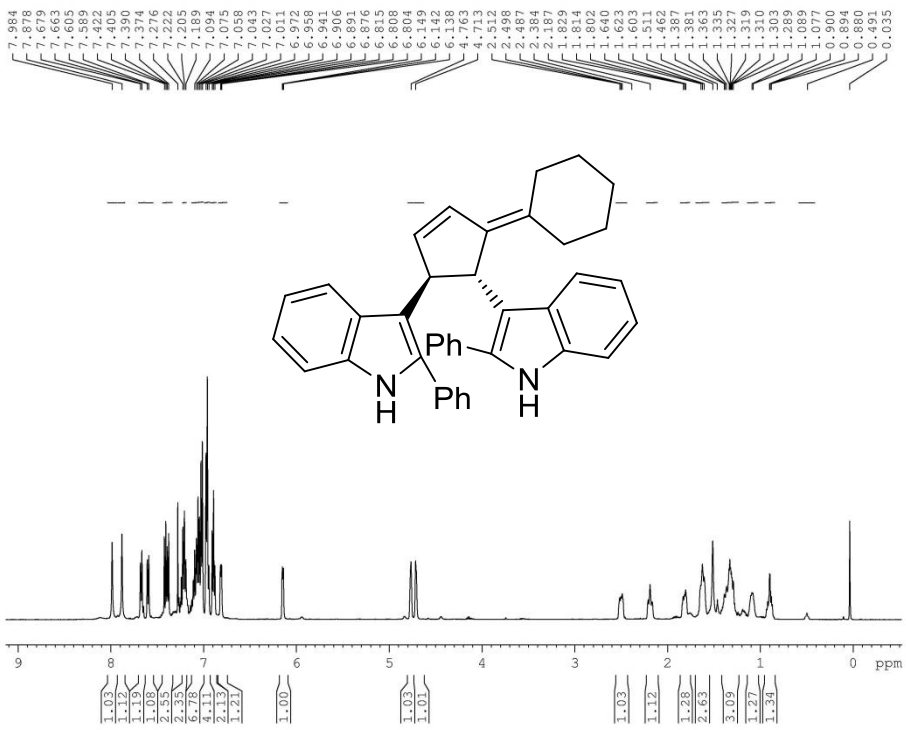
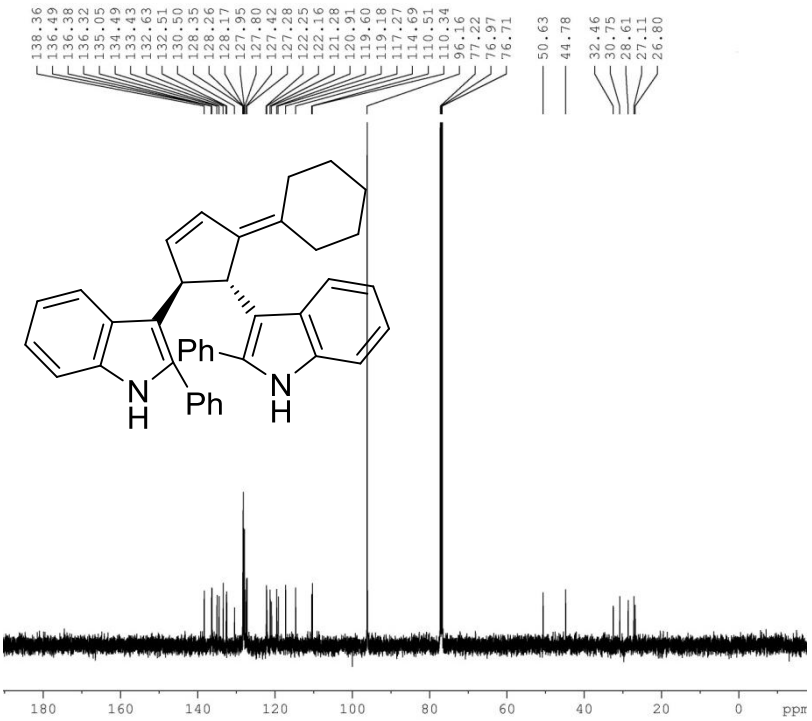


^{13}C NMR of 4ab



^{1}H NMR of 4ac



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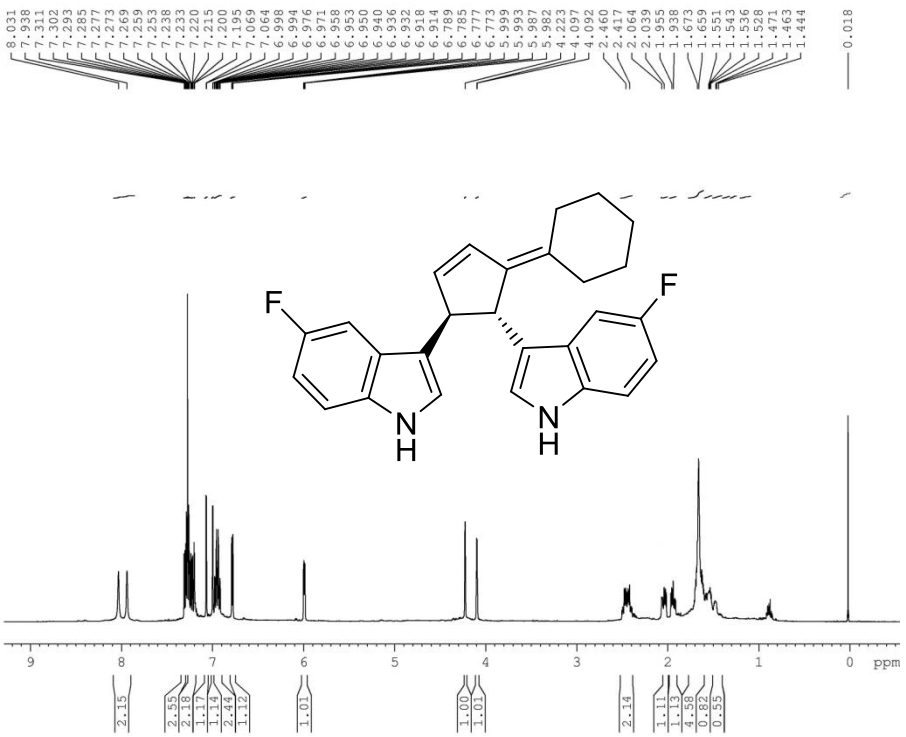
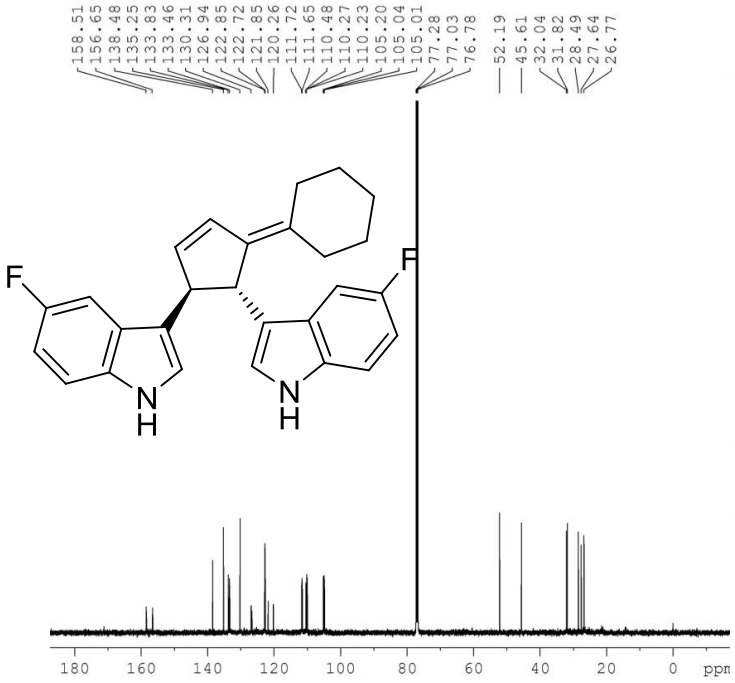
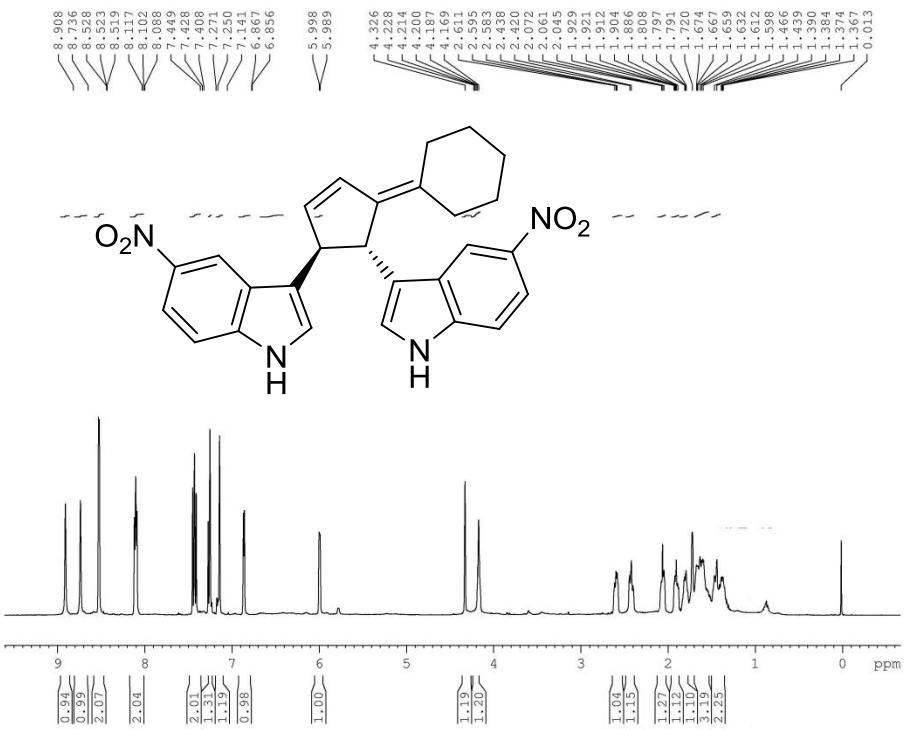


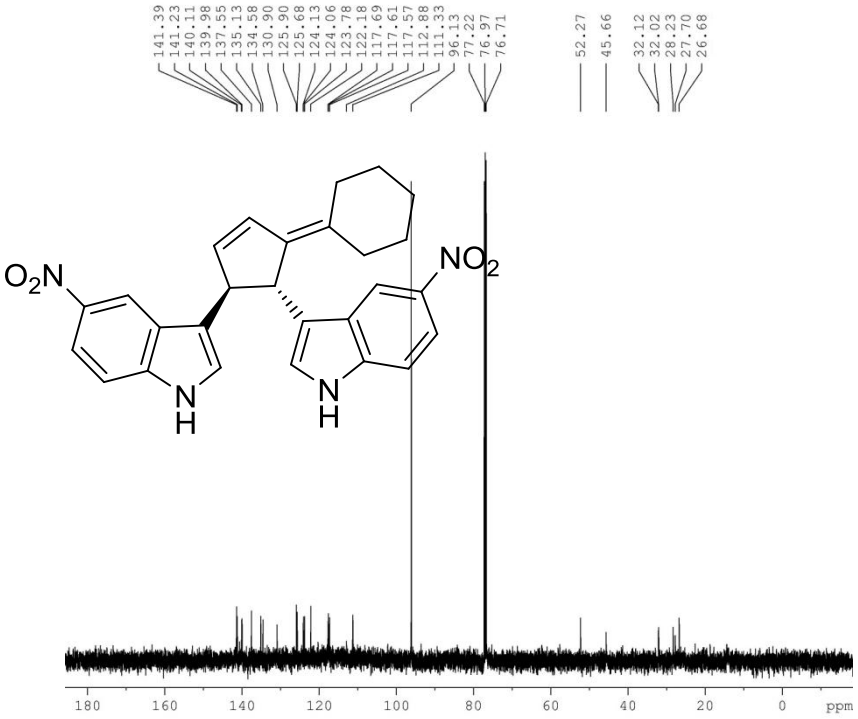
^{1}H NMR of 4ad



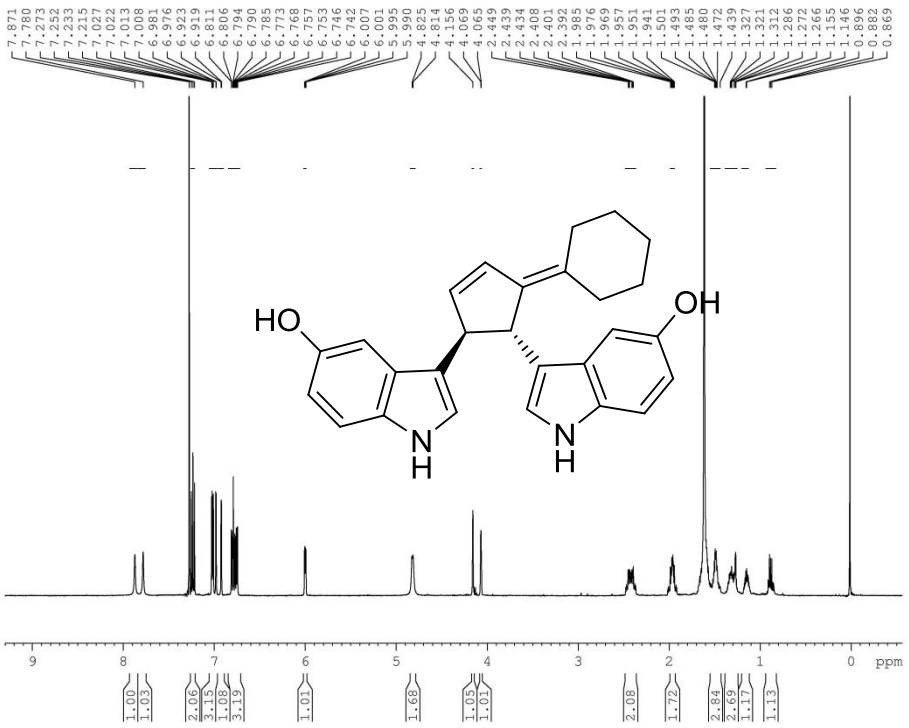
^{13}C NMR of 4ad



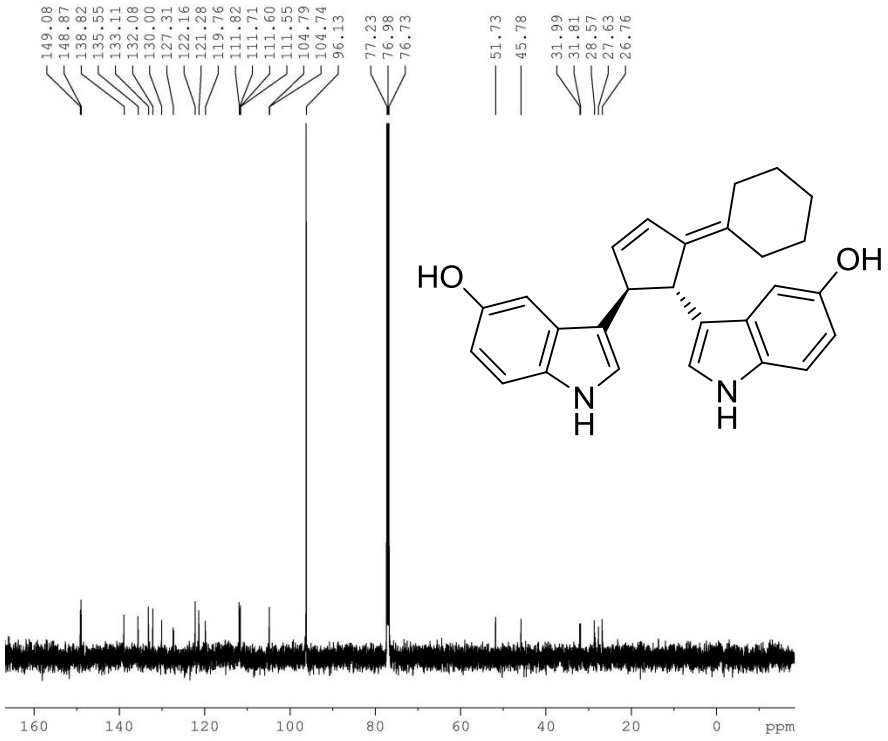
^{1}H NMR of 4ae



^{13}C NMR of 4ae



^{1}H NMR of 4af



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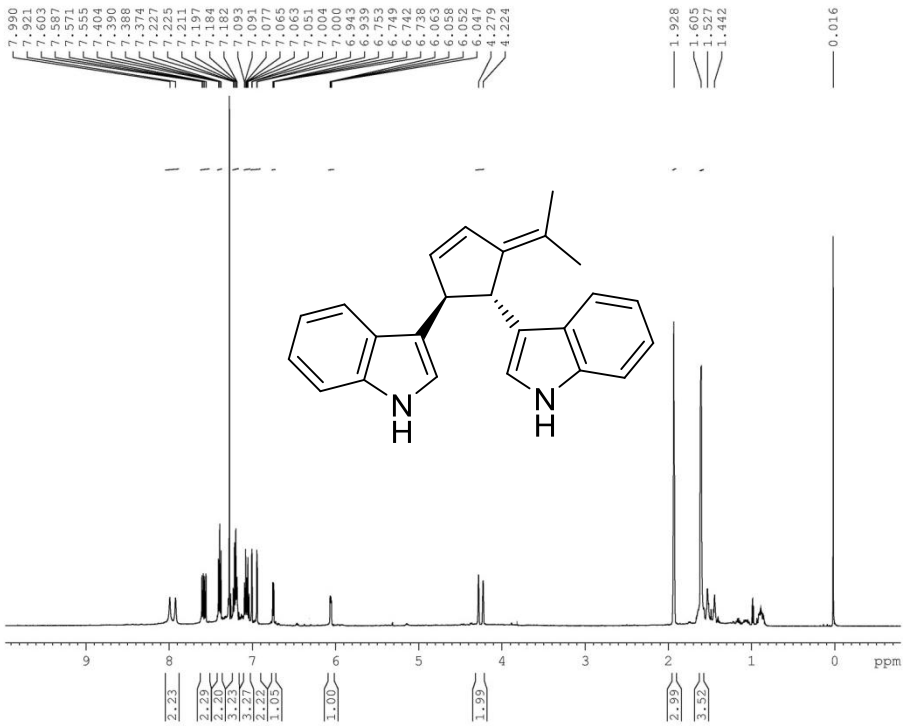

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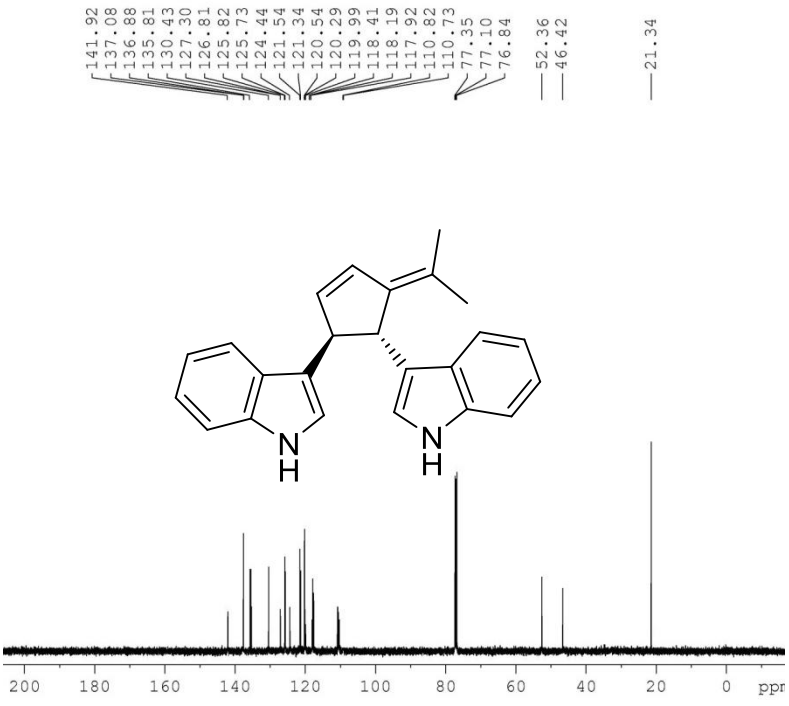

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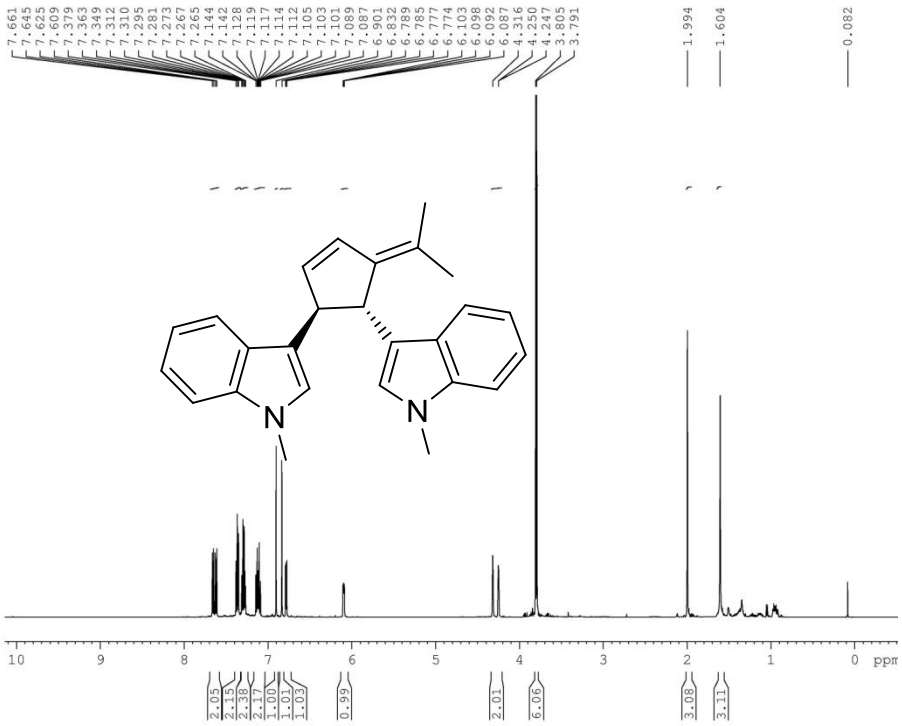
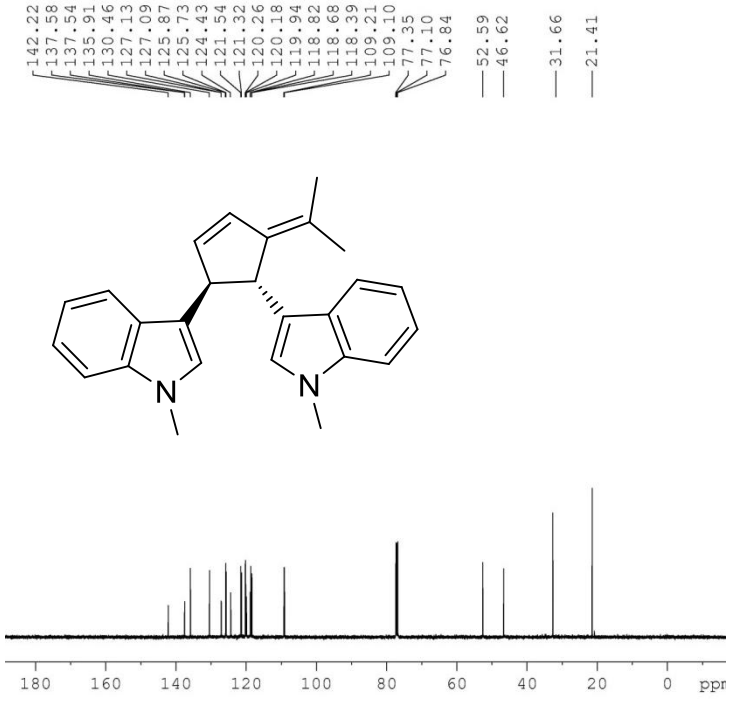
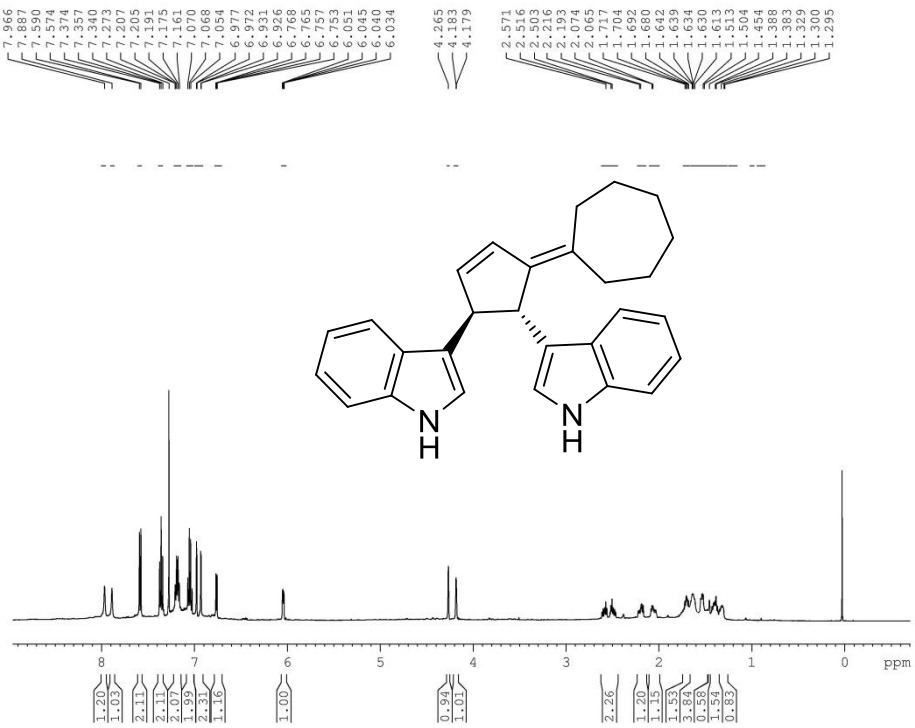


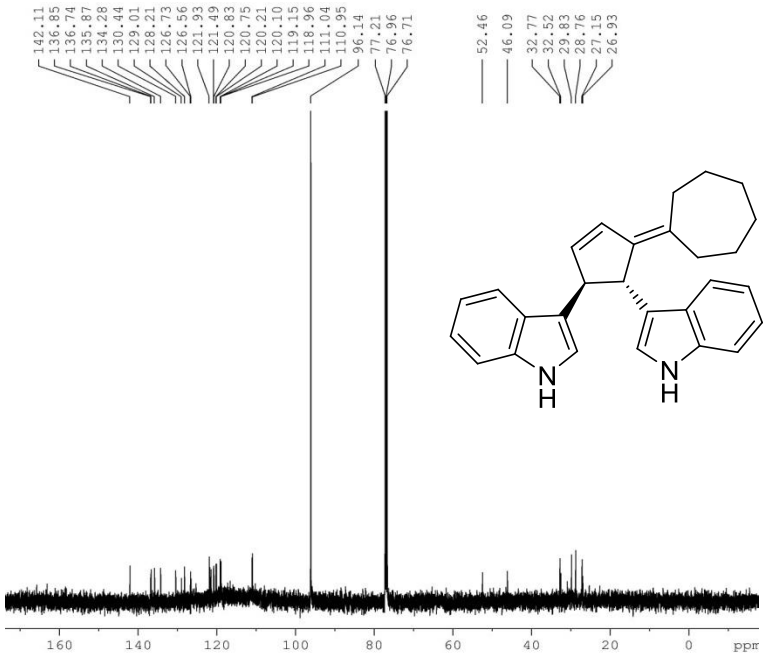
^{1}H NMR of 4eb



^{13}C NMR of 4eb



^{1}H NMR of 4fa



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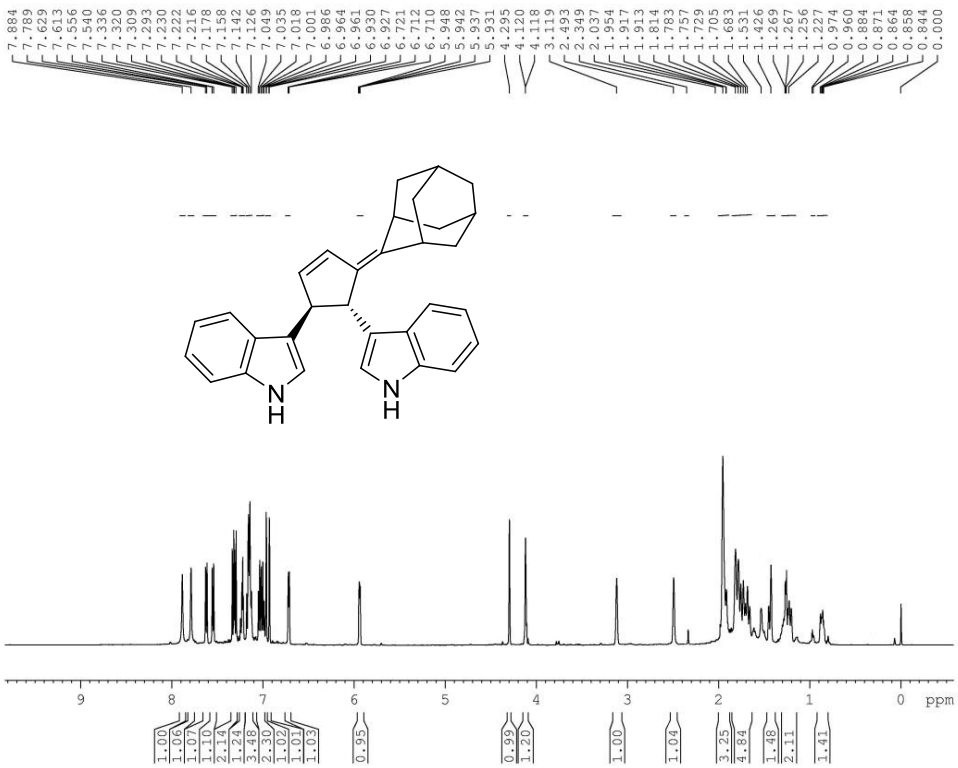
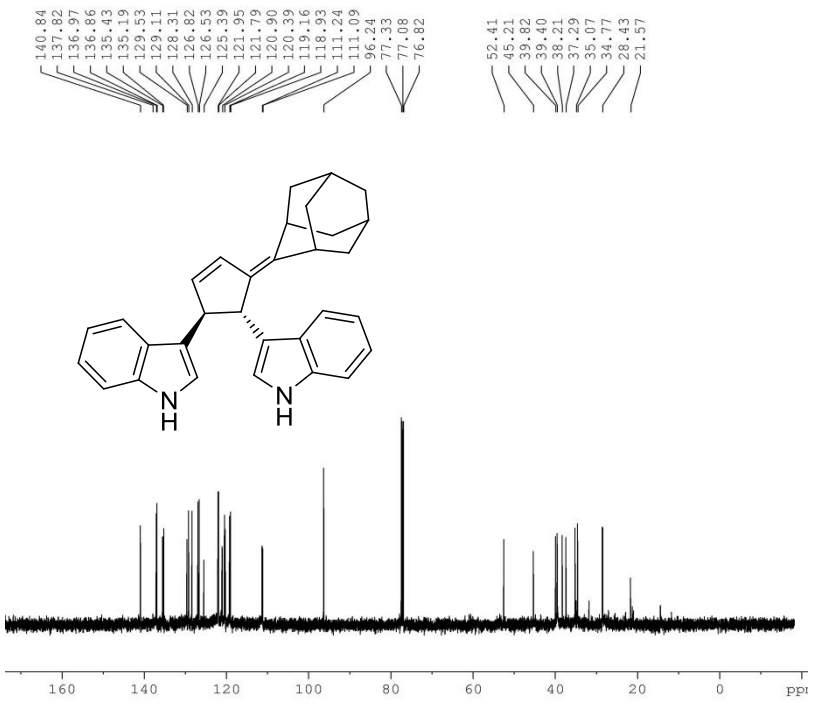
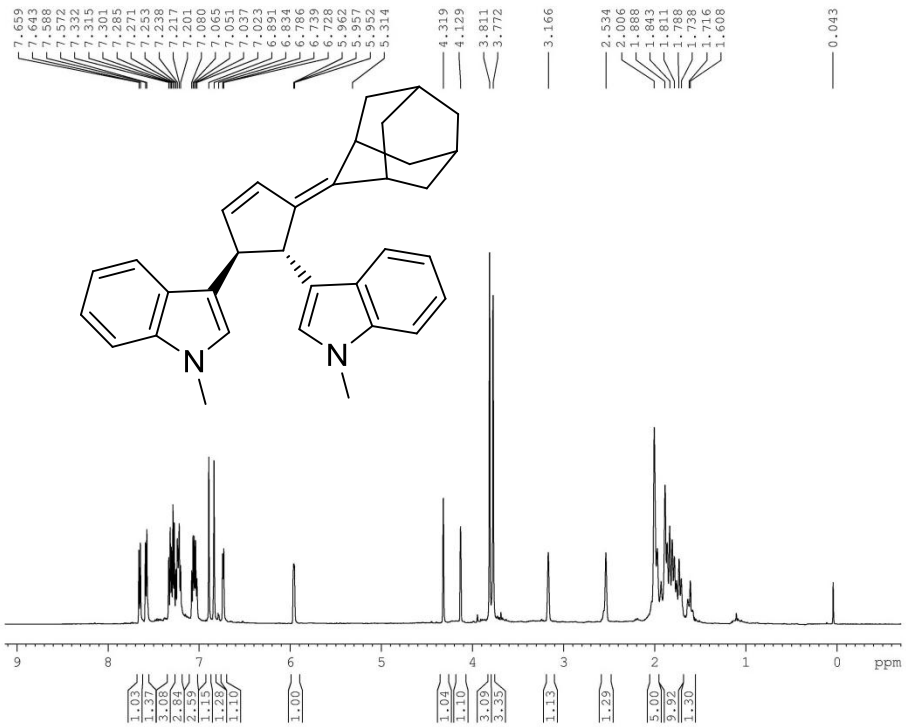


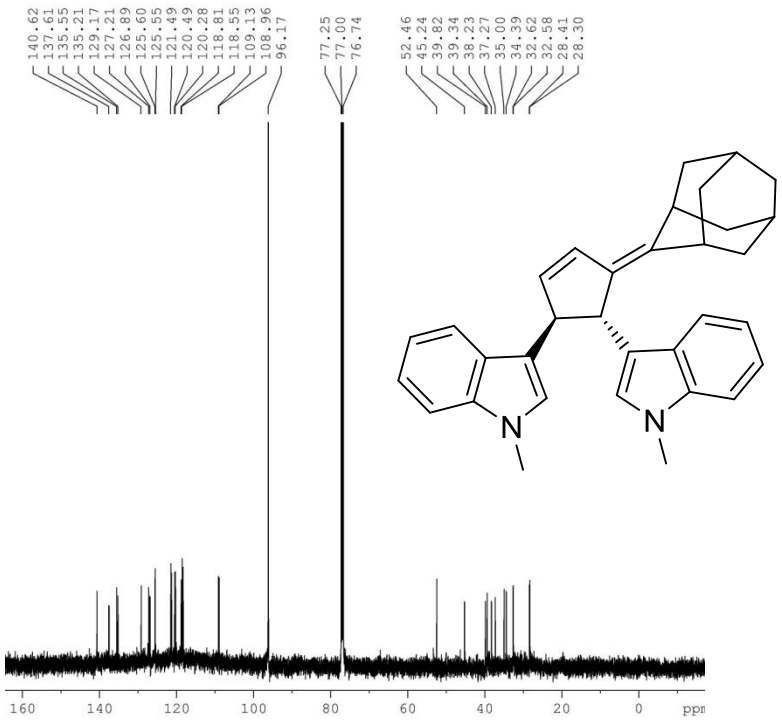
^{1}H NMR of 4ga



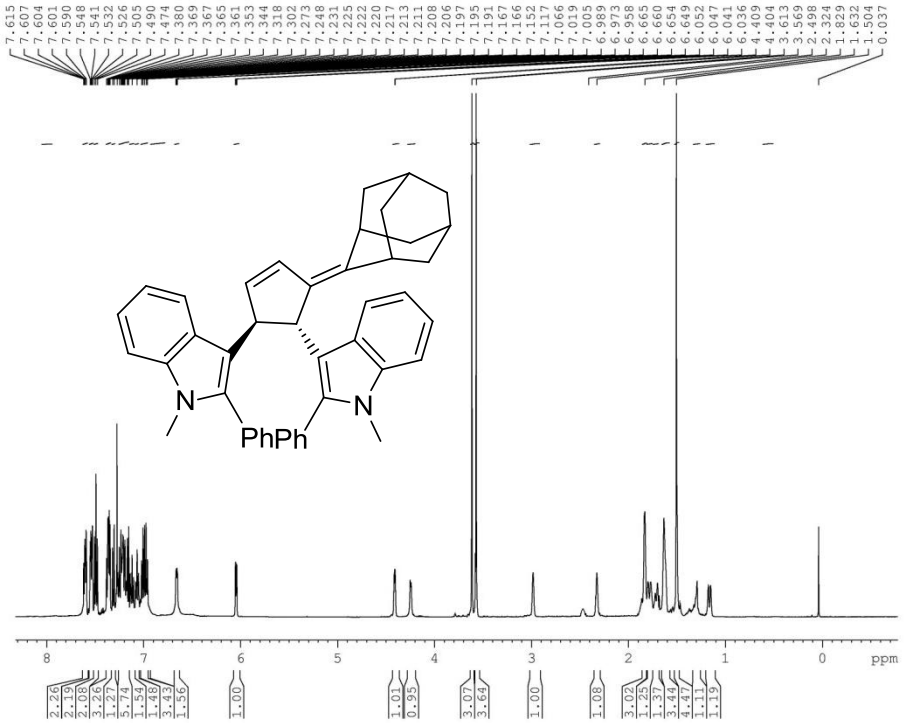
^{13}C NMR of 4ga



^{1}H NMR of 4gb



^{13}C NMR of 4gb



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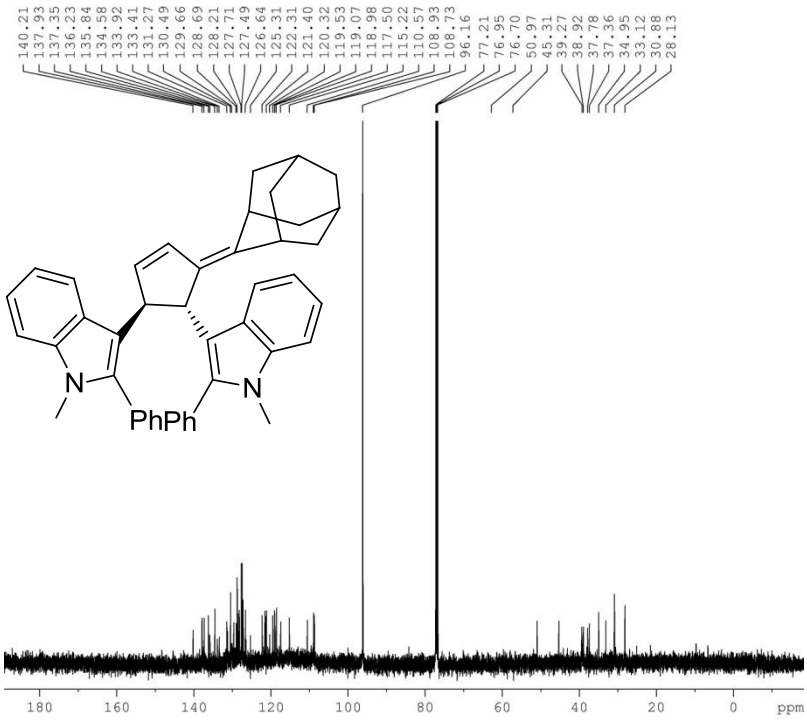

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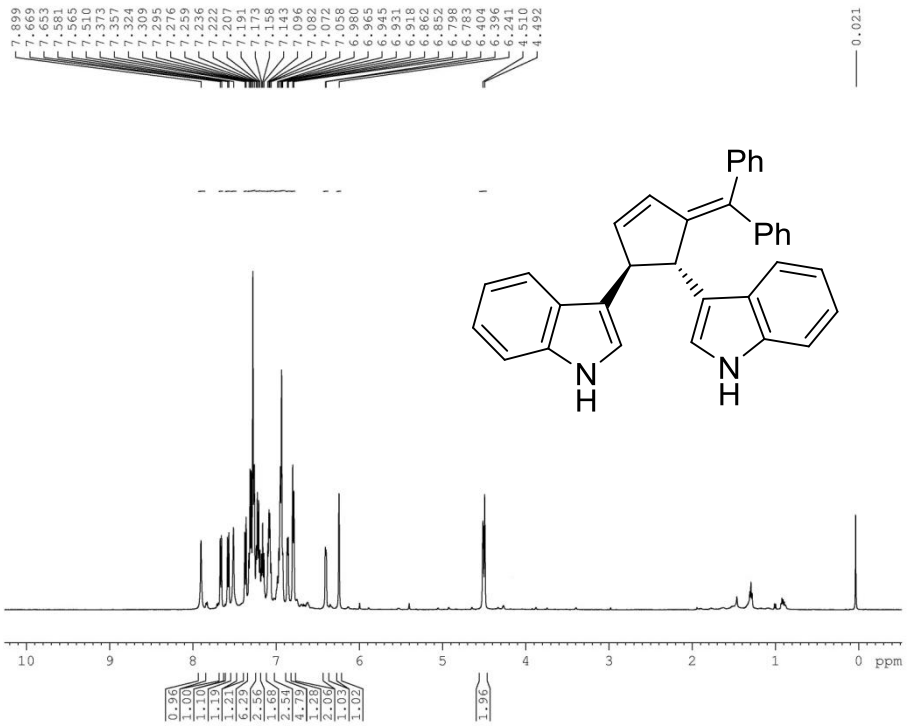
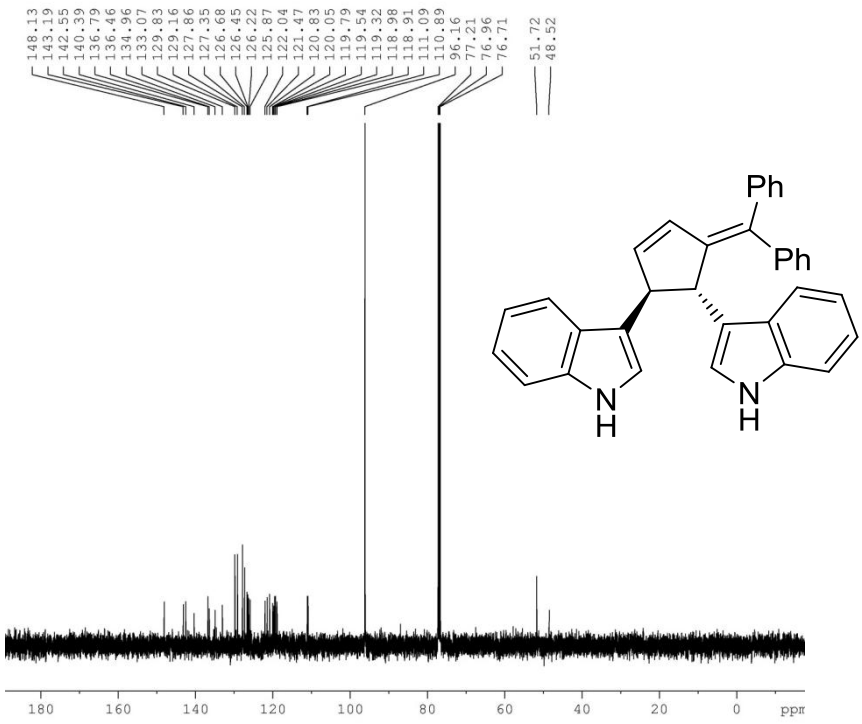


^{1}H NMR of 4ha



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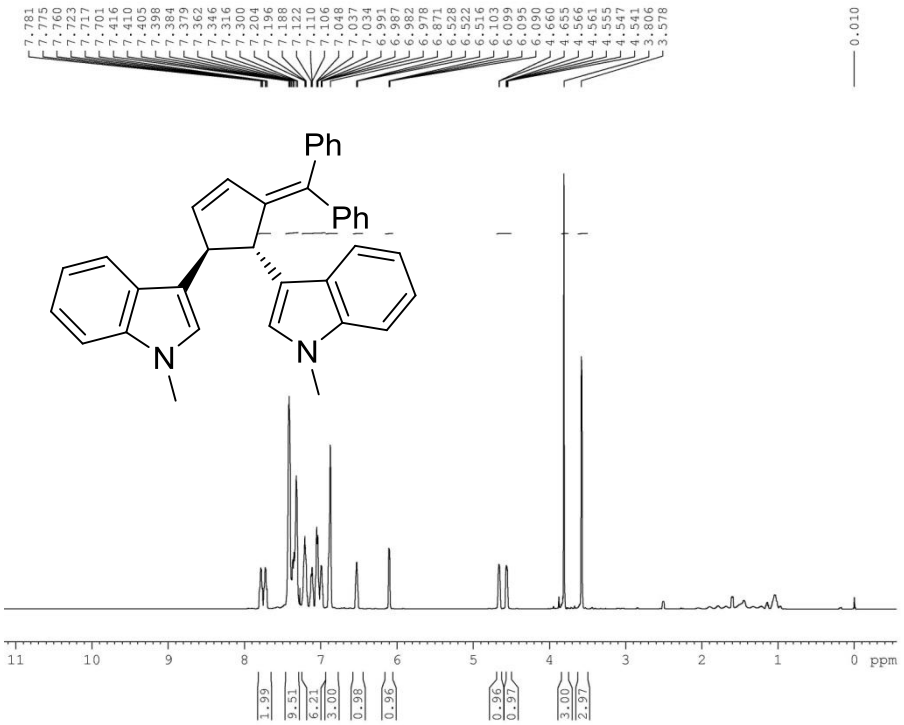

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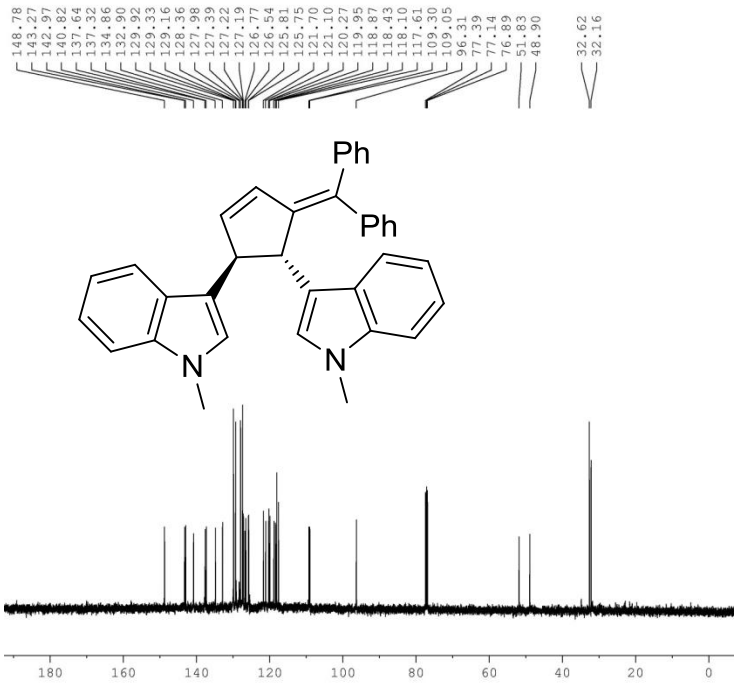
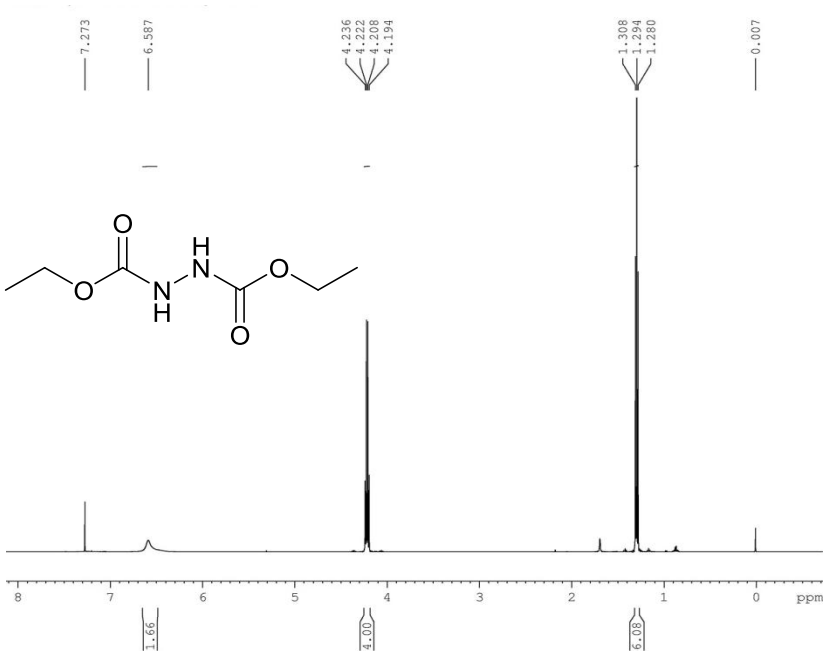
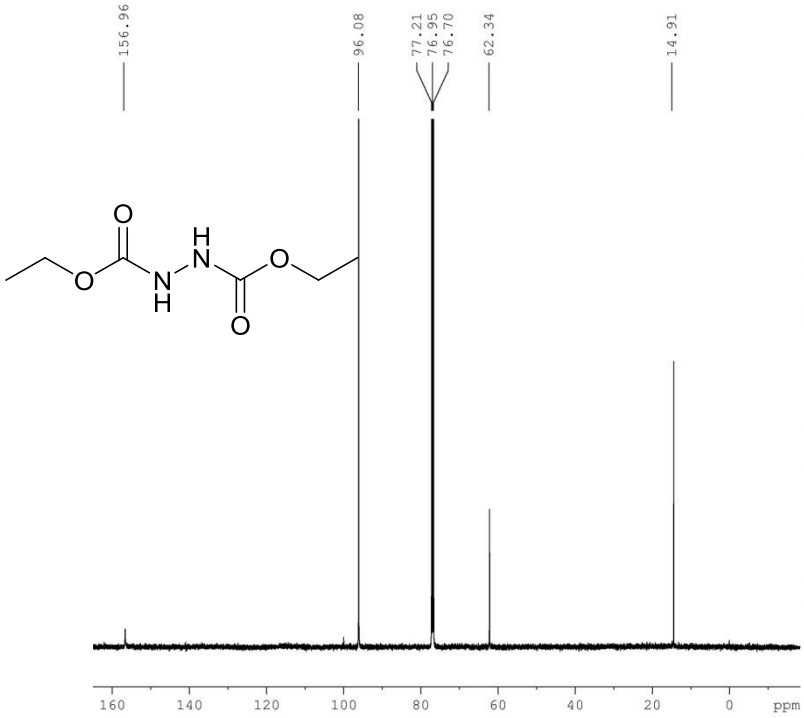


^{13}C NMR of 4hb

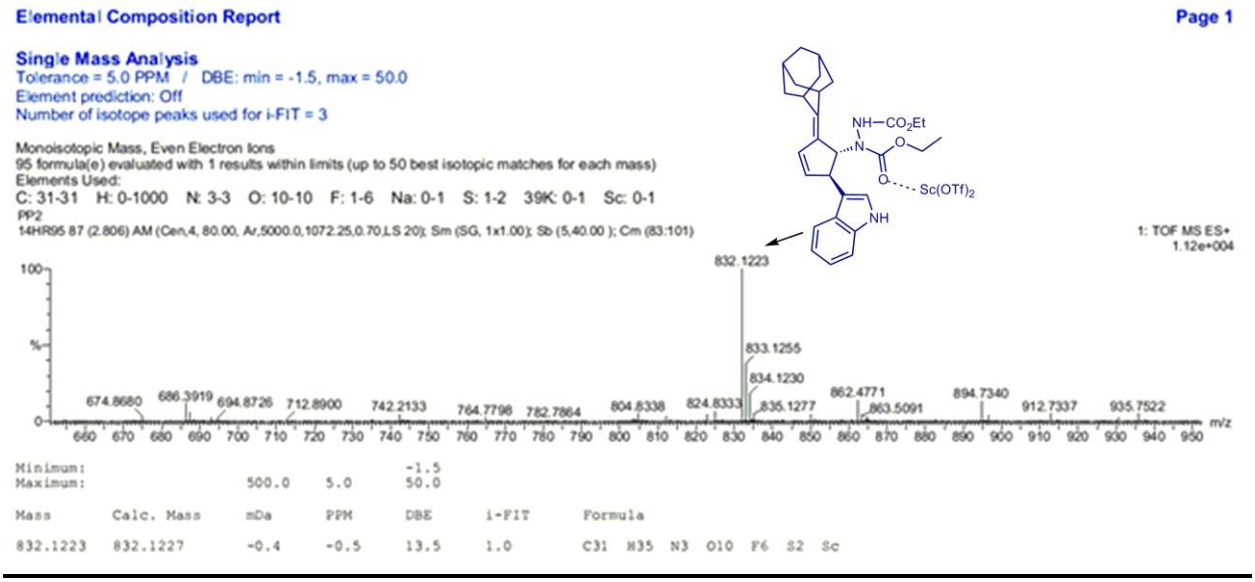


^{1}H NMR of 5

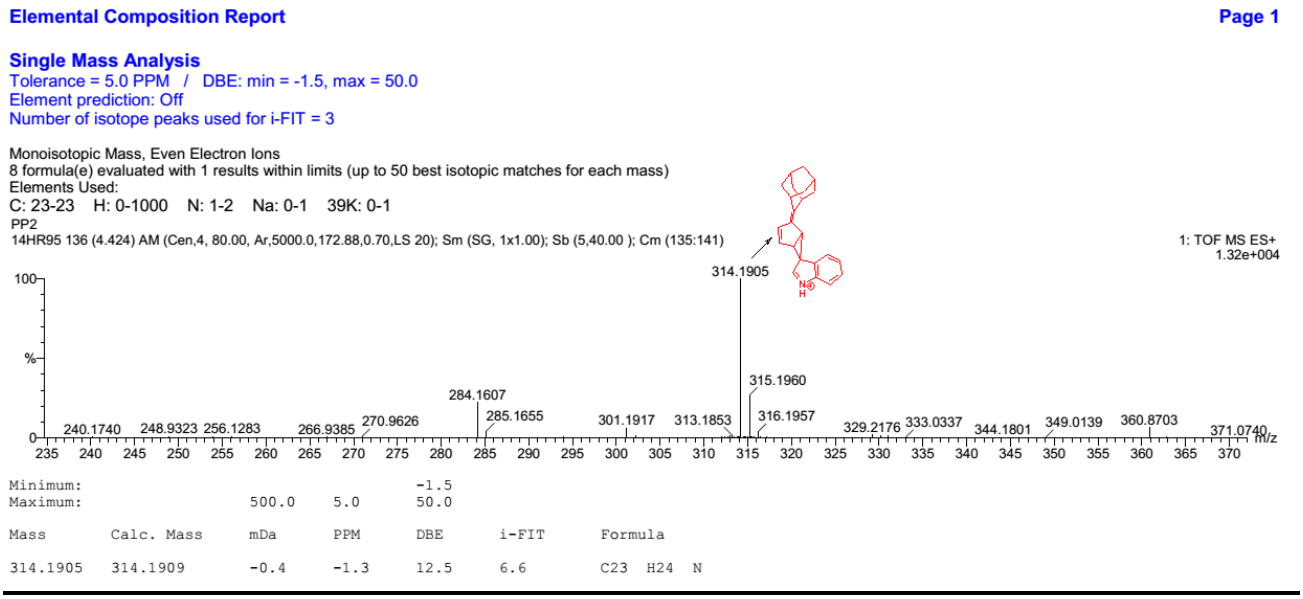


^{13}C NMR of 5

Supporting evidence for the mechanism from ESI-MS studies

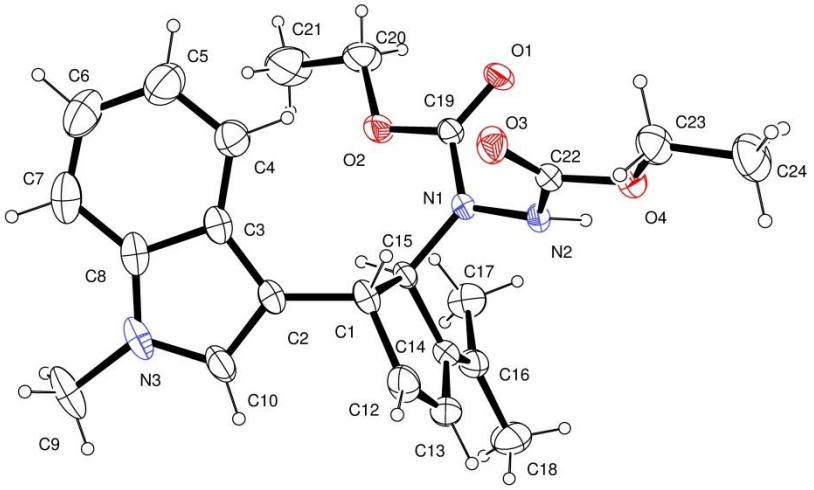


Mass spectrum of intermediate **C**



Mass spectrum of intermediate **D**

Compound **3eb**



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Symmetry_space_group_name_H-M	'P-1 '
Symmetry_space_group_name_Hall	'-P 1 '
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Cell_length_b	9.5191(3)
Cell_length_c	14.2137(4)
Cell_angle_alpha	81.1780(10)
Cell_angle_beta	86.5720(10)
Cell_angle_gamma	87.3920(10)
Cell_volume	1145.87(6)
Cell_formula_units_Z	2
Cell_measurement_temperature	296(2)
Cell_measurement_reflns_used	6522
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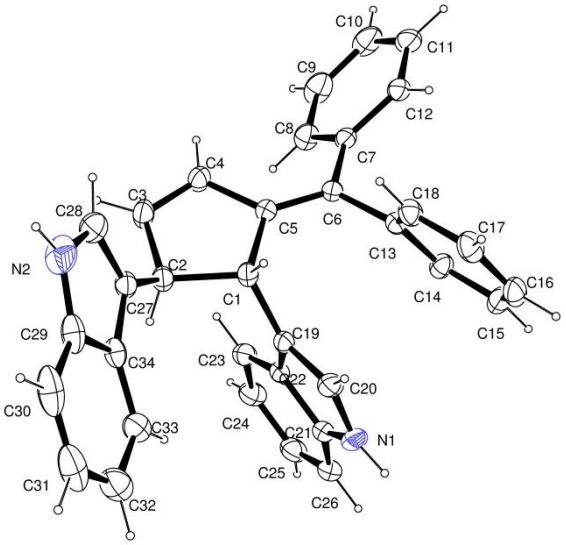
Compound 4ha



CCDC Number: 989506

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Cell_formula_units_Z	4
Cell_measurement_temperature	296(2)
Cell_measurement_reflns_used	7057
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