Rhodium(III)-Catalyzed Indole-Directed Carbenoid Aryl C-H Insertion/Cyclization: Access to 1, 2-Benzocarbazoles

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Supporting Information

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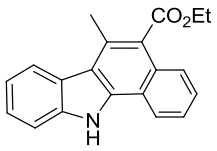
1. General experimental information

All reactions were carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments were performed under argon atmosphere. All reagents were purchased from TCI, Acros or Strem. Solvents were treated with 4 Å molecular sieves or sodium and distilled prior to use. The starting materials (2-arylindoles substrates) **1a-1y**, [1] and diazo compound **2a-2i** [2] were prepared according to the previously reported procedures. Purifications of reaction products were carried out by flash chromatography using Qingdao Haiyang Chemical Co. Ltd silica gel (40-63 mm). Infrared spectra (IR) were recorded on a Brucker TENSOR 27 FTIR spectrophotometer and are reported as wavelength numbers (cm^{-1}). Infrared spectra were recorded by preparing a KBr pellet containing the title compound. ^{1}H NMR and ^{13}C NMR spectra were recorded with tetramethylsilane (TMS) as internal standard at ambient temperature unless otherwise indicated on a Bruker Avance DPX 600 fourier Transform spectrometer operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). Low resolution mass spectra were recorded using a Waters HPLC/ZQ4000 Mass Spectrometer. High resolution mass spectra (HRMS) were recorded on an IF-TOF spectrometer (Micromass). Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS-QP5000 spectrometer. Crystal data were collected on a Bruker D8 Advance employing graphite monochromated Mo - Kα radiation (λ = 0.71073 Å) at 293 (2) K and operating in the φ-ωscan mode. The structure was solved by direct methods SHELXS-97.

UV-vis absorption spectra were recorded on a UV-2450 spectrophotometer. Photoluminescence (PL) spectra were measured using a Jobin-Yvon spectrofluorometer. Photoluminescence quantum yields (PLQYs) were measured on a HAMAMATSU absolute PL quantum yield spectrometer C11347 in solutions or films. Transient PL spectra were measured with an Edinburgh FL920 fluorescence spectrophotometer.

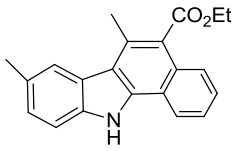
2 General Procedure for the Synthesis of Compounds 3a-3gz

All of the products (**3a-3gz**) were obtained according to the following procedure. To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 2-arylindoles (0.2 mmol), diazo compounds (0.4 mmol), $[RhCp^*Cl_2]_2$ (6.0 mg, 0.01 mmol, 5 mol %), Na_2CO_3 (42.4 mg, 0.4 mmol, 200 mol %), CuCl (9.9 mg, 0.1 mmol, 50 mol %), NaOAc (5 mg, 0.06mmol, 30 mol %), and acetonirtrile (2.0 mL) under an Ar atmosphere. The reaction mixture was stirred at 80 ℃ for 8 h, filtered through a pad of celite and then washed with ethyl acetate (10 mL × 3). Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate/petroleum (v/v = 1/4) as the eluent to give the desired products. All of the yields are isolated yield.



3a

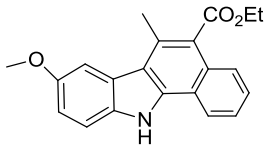
Ethyl 6-methyl-11H-benzo[a]carbazole-5-carboxylate (3a) [3]: Yellow solid. m.p. 193-195 ℃. 50.8 mg, 50.8 % yield. ^{1}HNMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.02 – 7.94 (m, 1H), 7.93 – 7.83 (m, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.48 – 7.37 (m, 3H), 7.28 (t, *J* = 7.5 Hz, 1H), 4.59 (q, *J* = 7.1 Hz, 2H), 2.90 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 170.8, 138.7, 135.3, 130.6, 128.9, 126.1, 125.4, 124.9, 124.6, 124.6, 123.2, 122.2, 120.5, 120.23, 119.3, 117.1, 111.1, 61.3, 18.6, 14.4. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{20}H_{17}NO_2$: 304.1332, found: 304.1339; IR (KBr): 3680, 2804, 2283, 1583, 1506, 1433, 1288, 1201, 1054, 959, 739 cm^{-1}.



3b

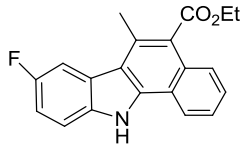
Ethyl 6,8-dimethyl-11H-benzo[a]carbazole-5-carboxylate (**3b**): Yellow solid. m.p. 158-160 ℃. 52 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.03 – 7.84 (m, 3H), 7.51 – 7.37 (m, 3H), 7.25 – 7.20 (m, 1H), 4.59 (q, *J* = 7.1 Hz, 2H), 2.91 (s, 3H), 2.55 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 137.0, 135.6, 130.8, 129.4, 128.8, 126.0, 126.0, 125.3, 124.8, 124.8, 122.9, 122.0, 120.5, 119.3, 116.8, 110.7, 61.3, 21.7, 18.7, 14.4. HR-MS (ESI) calcd for

[M + 1] $^{+}$: $C_{21}H_{20}NO_2$: 318.1489, found: 318.1491; IR (KBr): 3443, 2929, 1551, 1460, 1223, 1123, 788 cm $^{-1}$.



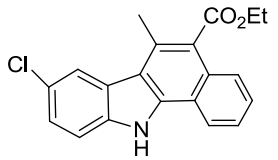
3c

Ethyl 8-methoxy-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3c**): Yellow solid. m.p. 163-165 ℃. 50 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.91 (dd, J = 27.7, 7.2 Hz, 1H), 7.63 (d, J = 2.3 Hz, 3H), 7.42 (ddd, J = 14.9, 6.2, 3.5 Hz, 1H), 7.05 (dd, J = 8.7, 2.4 Hz, 1H), 4.58 (q, J = 7.1 Hz, 1H), 3.92 (s, 2H), 2.87 (d, J = 3.8 Hz, 3H), 1.49 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 154.2, 136.2, 133.8, 130.6, 128.9, 126.1, 125.4, 125.1, 124.9, 122.8, 120.5, 119.4, 117.0, 113.5, 111.6, 105.6, 61.3, 56.1, 29.7, 18.5, 14.4. HR-MS (ESI) calcd for [M + 1] $^{+}$: $C_{21}H_{20}NO_3$: 334.1438, found: 334.1443; IR (KBr): 3430, 2926, 1698, 1554, 1396, 1219, 1039, 761, 531 cm $^{-1}$.



3d

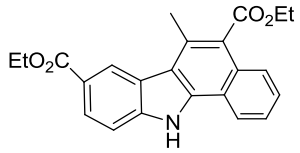
***N*-(3-(Phenylsulfonamido)butyl)picolinamide** (**3d**): Yellow solid. m.p. 166-168 ℃. 43.2 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.95 (s, 1H), 7.80 (dd, J = 23.3, 7.2 Hz, 2H), 7.51 – 7.34 (m, 3H), 7.14 (t, J = 8.1 Hz, 1H), 4.59 (dd, J = 14.0, 6.9 Hz, 2H), 2.82 (s, 3H), 1.50 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.81, 157.7 (d, $^{1}J_{C\text{-}F}$ = 230 Hz), 136.59, 135.09, 130.30, 129.00, 126.34, 125.1, 124.8 (d, $^{2}J_{C\text{-}F}$ = 10 Hz), 123.17, 120.55, 119.29, 116.77, 112.5 (d, $^{3}J_{C\text{-}F}$ = 26 Hz), 107.6 (d, $^{4}J_{C\text{-}F}$ = 25 Hz), 61.48, 18.33, 14.46. HR-MS (ESI) calcd for [M + 1] $^{+}$: $C_{16}H_{20}N_3O_3S$: 322.1238, found: 322.1246; IR (KBr): 3427, 2923, 1551, 1460, 1036, 790 cm $^{-1}$.



3e

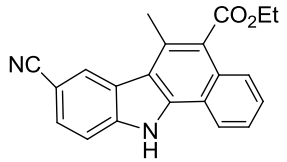
Ethyl 8-chloro-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3e**): Brown solid. m.p. 212-214 ℃. 50.5 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.00 (d, *J* = 1.7 Hz,

1H), 7.88 (dd, *J* = 6.2, 3.2 Hz, 1H), 7.82 – 7.75 (m, 1H), 7.43 – 7.33 (m, 3H), 7.31 (dd, *J* = 8.6, 1.9 Hz, 1H), 4.63 – 4.55 (m, 2H), 2.77 (s, 3H), 1.50 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 136.9, 136.0, 130.2, 129.0, 126.4, 125.5, 125.4, 125.3, 125.0, 124.6, 123.4, 121.5, 120.5, 119.1, 116.2, 112.0, 61.5, 18.4, 14.4. HR-MS (ESI) calcd for [M + 1] $^+$: $C_{20}H_{17}ClNO_2$: 338.0942, found: 338.0947; IR (KBr): 3429, 2924, 1552, 1458, 1393, 1221, 1121, 791 cm $^{-1}$.



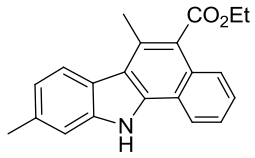
3f

Diethyl 6-methyl-11H-benzo[a]carbazole-5,8-dicarboxylate (**3f**): Yellow solid. m.p. 228-230 ℃. 40.5 mg, 54% yield. ^{1}H NMR (400 MHz, acetone) δ 11.74 (s, 1H), 8.86 (s, 1H), 8.42 – 8.35 (m, 1H), 8.00 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.88 – 7.82 (m, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.51 (dd, *J* = 6.7, 3.0 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.89 (s, 3H), 1.32 (dt, *J* = 21.0, 7.1 Hz, 6H); ^{13}C NMR (100 MHz, acetone) δ 170.4, 167.4, 143.0, 137.6, 130.8, 130.1, 127.4, 126.6, 126.4, 126.3, 125.3, 125.1, 124.8, 123.2, 122.4, 120.7, 117.7, 112.0, 61.8, 61.1, 18.7, 14.7, 14.7. HR-MS (ESI) calcd for [M + 1] $^+$: $C_{23}H_{22}NO_4$: 376.1543, found: 376.1549; IR (KBr): 3429, 2923, 1683, 1550, 1396, 1037, 754 cm $^{-1}$.



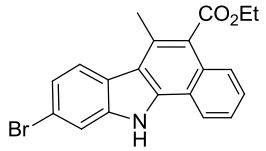
3g

Ethyl 8-cyano-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3g**): Brown solid m.p 178-181 ℃. 24.9 mg, 38% yield. ^{1}H NMR (400 MHz, acetone) δ 11.85 (s, 1H), 8.49 (s, 1H), 8.34 (dd, *J* = 6.1, 3.3 Hz, 1H), 7.82 (dd, *J* = 6.3, 3.3 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.57 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.52 – 7.47 (m, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 2.84 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, acetone) δ 169.4, 141.1, 136.8, 129.8, 129.4, 127.4, 126.9, 126.9, 125.5, 125.5, 124.8, 124.0, 121.6, 120.0, 119.6, 116.0, 112.4, 102.8, 60.9, 17.8, 13.8. HR-MS (ESI) calcd for [M + 1] $^+$: $C_{21}H_{17}N_2O_2$: 329.1285, found: 329.1286; IR (KBr): 3724, 2924, 2217, 1712, 1550, 1394, 1121, 1040 cm $^{-1}$.



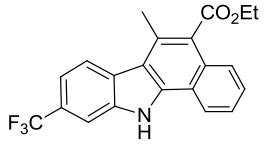
3h

Ethyl 6,9-dimethyl-11H-benzo[a]carbazole-5-carboxylate (**3h**): Brown solid m.p. 219-221℃. 41.2 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.99 (ddd, *J* = 35.9, 12.0, 7.2 Hz, 2H), 7.47 (p, *J* = 6.7 Hz, 1H), 7.29 (s, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 4.59 (q, *J* = 7.1 Hz, 2H), 2.91 (s, 3H), 2.50 (d, *J* = 10.2 Hz, 3H), 1.49 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, acetone) δ 170.7, 140.8, 136.5, 135.4, 130.9, 129.7, 126.6, 126.3, 125.8, 124.2, 123.0, 122.6, 122.4, 122.3, 120.7, 117.6, 112.3, 61.6, 21.9, 18.8, 14.7. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{21}H_{20}NO_2$: 318.1489, found: 318.1494; IR (KBr): 3733, 2925, 2854, 1550, 1396, 1122, 792 cm^{-1}.



3i

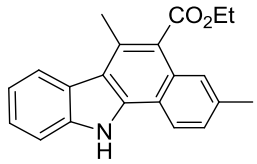
Ethyl 9-bromo-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3i**): Yellow solid. m.p. 189-191 ℃. 46.6 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.05 – 7.96 (m, 2H), 7.89 (dd, *J* = 6.2, 3.4 Hz, 1H), 7.69 (s, 1H), 7.55 – 7.46 (m, 2H), 7.39 (d, *J* = 8.5 Hz, 1H), 4.60 (q, *J* = 7.1 Hz, 2H), 2.87 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 145.2, 141.1, 134.7, 133.6, 131.8, 130.6, 130.2, 128.7, 128.3, 127.8, 127.7, 127.2, 124.5, 122.5, 120.7, 119.2, 66.2, 23.4, 19.4. HR-MS (ESI) calcd for $[M+1]^+$: $C_{20}H_{17}BrNO_2$: 382.0437, found: 382.0439; IR (KBr): 3687, 2980, 1552, 1362, 1024, 783 cm^{-1}.



3j

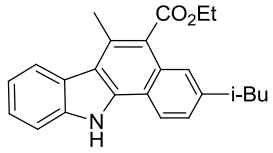
Ethyl 6-methyl-9-(trifluoromethyl)-11H-benzo[a]carbazole-5-carboxylate (**3j**): Yellow solid. m.p 160-162 43.7 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.94 (dd, *J* = 6.0, 3.1 Hz, 1H), 7.85 – 7.75 (m, 2H), 7.52 – 7.42 (m, 3H), 4.61 (q, *J* = 7.1 Hz, 2H), 2.82 (s, 3H), 1.52 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ 169.3, 138.0, 137.2, 129.3 (d, $J_{C\text{-}F}$ = 103 Hz), 127.14, 126.3, 126.1, 125.6, 125.0, 124.3 (d, $J_{C\text{-}F}$ = 33 Hz), 123.3, 122.6, 122.2, 119.3, 115.8 (d, $^{3}J_{C\text{-}F}$ = 4 Hz), 115.1, 108.4 (d, $^{4}J_{C\text{-}F}$ = 5 Hz), 61.1, 18.2, 14.1. HR-MS (ESI) calcd

for [M + 1] $^{+}$: $C_{21}H_{17}F_3NO_2$: 372.1206, found: 372.1205; IR (KBr): 3731, 2920, 2853, 1730, 1549, 1460, 1032, 792 cm $^{-1}$.



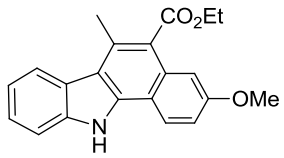
3l

Ethyl 3,6-dimethyl-11H-benzo[a]carbazole-5-carboxylate (**3l**): Red solid. m.p 187-189 38.6 mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.60 (s, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.16 (m, 2H), 4.60 (q, *J* = 7.1 Hz, 2H), 2.89 (s, 3H), 2.41 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 138.7, 135.9, 135.5, 130.5, 129.1, 126.8, 124.7, 124.5, 124.4, 122.7, 122.0, 120.4, 120.1, 117.3, 116.4, 111.1, 61.3, 21.9, 18.6, 14.4. HR-MS (ESI) calcd for [M + 1] $^{+}$: $C_{21}H_{20}NO_2$: 318.1489, found: 318.1490; IR (KBr): 3670, 2979, 1523, 1363, 1042, 892 cm $^{-1}$.



3m

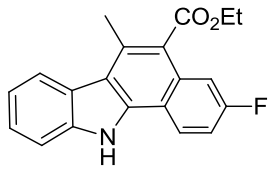
Ethyl 3-isobutyl-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3m**): Yellow solid. m.p. 174-176 ℃. 55.2 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 1H), 7.65 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 2H), 4.60 (q, *J* = 7.1 Hz, 2H), 2.94 (s, 3H), 2.61 (d, *J* = 7.2 Hz, 2H), 1.94 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.50 (t, *J* = 7.1 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 139.7, 138.7, 135.6, 130.6, 129.1, 126.9, 125.0, 124.7, 124.4, 122.9, 122.0, 120.3, 120.1, 117.7, 116.5, 111.1, 61.3, 45.8, 30.2, 22.4, 18.71, 14.5. HR-MS (ESI) calcd for [M + 1] $^{+}$: $C_{24}H_{26}NO_2$: 360.1958, found: 360.1967; IR (KBr): 3347, 2917, 1706, 1583, 1224, 1047, 744 cm $^{-1}$.



3n

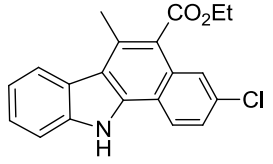
Ethyl 3-methoxy-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3n**): Brown solid. m.p. 158-160 ℃. 49.9 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.10 (d, *J* = 7.9 Hz, 1H), 7.84 – 7.74 (m, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.25 (dd, *J* = 10.2, 4.8 Hz,

1H), 7.07 – 6.93 (m, 1H), 4.58 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 2.86 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 157.8, 138.7, 135.8, 131.5, 130.3, 124.7, 124.1, 122.1, 122.0, 121.8, 120.0, 116.2, 115.6, 114.1, 111.0, 104.9, 61.3, 55.1, 18.7, 14.5. HR-MS (ESI) calcd for [M + 1] $^+$: $C_{21}H_{20}NO_3$: 334.1438, found: 334.1443; IR (KBr): 3346, 2930, 1701, 1575, 1216, 1041, 892 cm^{-1}.



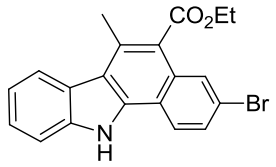
3o

Ethyl 3-fluoro-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3o**): Yellow solid. m.p. 206-208 ℃. 45.5mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.92 (dd, *J* = 9.0, 5.6 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.18 (td, *J* = 8.6, 2.5 Hz, 1H), 4.63 – 4.53 (m, 2H), 2.88 – 2.74 (m, 3H), 1.55 – 1.46 (m, 3H); ^{13}C NMR (100 MHz, acetone) δ 170.2, 163.0, 160., 140., 136.7, 131.1 (d, $^1J_{C\text{-}F}$ = 8 Hz), 125.5, 125.1, (d, $^2J_{C\text{-}F}$ = 9 Hz), 125.0, 123.4, (d, $^3J_{C\text{-}F}$ = 5 Hz), 122.8, 120.9, 117.6, 117.3, 115.3, (d, $^4J_{C\text{-}F}$ = 25 Hz), 112.3, 110.2 (d, $^5J_{C\text{-}F}$ = 23 Hz), 61.8, 19.0, 14.7. HR-MS (ESI) calcd for [M + 1] $^+$: $C_{20}H_{17}FNO_2$: 322.1238, found: 322.1244; IR (KBr): 3763, 2930, 1532, 1374, 1213, 1023, 756 cm^{-1}.



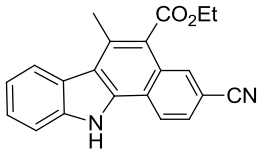
3p

Ethyl 3-chloro-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3p**): Brown solid. m.p. 184-186 ℃. 42.4 mg, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.04 (d, *J* = 7.0 Hz, 1H), 7.87 – 7.72 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.28 (dd, *J* = 17.1, 8.9 Hz, 2H), 4.59 (q, *J* = 7.0 Hz, 2H), 2.72 (d, *J* = 2.4 Hz, 3H), 1.51 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 138.8, 134.9, 132.1, 132.0, 129.5, 125.4, 124.9, 124.4, 124.3, 122.2, 122.0, 120.4, 117.3, 111.2, 61.5, 29.7, 18.5, 14.4. HR-MS (ESI) calcd for [M + 1] $^+$: $C_{20}H_{17}ClNO_2$: 338.0942, found: 338.0947; IR (KBr): 3754, 2922, 1698, 1560, 1370, 1094, 865 cm^{-1}.



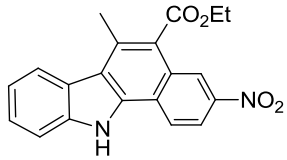
3q

Ethyl 3-bromo-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3q**): Yellow solid. m.p. 201-203 ℃. 46.6 mg, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.07 (dd, *J* = 35.2, 4.7 Hz, 2H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.58 – 7.42 (m, 3H), 7.30 (t, *J* = 7.6 Hz, 1H), 4.60 (q, *J* = 7.1 Hz, 2H), 2.79 (s, 3H), 1.52 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 138.8, 135.0, 132.1, 130.00, 128.0, 127.7, 125.0, 124.3, 122.2, 122.1, 122.1, 120.5, 120.3, 117.6, 117.4, 111.3, 61.5, 18.6, 14.4. HR-MS (ESI) calcd for [M + 1] $^{+}$: $C_{20}H_{17}BrNO_2$: 382.0437, found: 382.0442; IR (KBr): 3361, 2925, 1699, 1552, 1263, 1042, 719 cm $^{-1}$.



3r

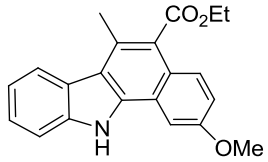
Ethyl 3-cyano-6-methyl-11H-benzo[a]carbazole-5-carboxylate (3r): Brown solid. m.p. 181-183 ℃. 22.9 mg, 35% yield. ^{1}H NMR (400 MHz, DMSO) δ 12.70 (s, 1H), 8.69 (d, *J* = 8.5 Hz, 1H), 8.42 – 8.19 (m, 2H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 2.92 (s, 3H), 1.43 (q, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ 168.6, 139.5, 134.7, 132.5, 130.7, 127.0, 126.0, 125.6, 123.4, 123.0, 122.3, 122.0, 120.8, 120.2, 119.2, 118.1, 111.8, 108.3, 61.4, 18.4, 14.1. HR-MS (ESI) calcd for [M + 1] $^{+}$: $C_{21}H_{17}ClN_2O_2$: 329.1285, found: 329.1281; IR (KBr): 3413, 2917, 2127, 1665, 1261, 1009, 824 cm $^{-1}$.



3s

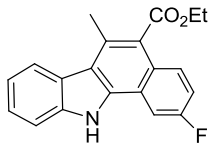
Ethyl 6-methyl-3-nitro-11H-benzo[a]carbazole-5-carboxylate (**3s**): Red solid. m.p. 198-200 ℃. 31.3 mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.10 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 9.2 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.19 (s, 1H), 7.03 (d, *J* = 9.1 Hz, 1H), 4.58 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 2H), 2.79 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 156.8, 138.9, 134.8, 128.0, 126.8, 124.7, 124.5,

123.9, 122.8, 122., 120.2, 120.0, 117.3, 111.1, 100.4, 61.3, 55.3, 18.3, 14.4. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{20}H_{17}ClN_2O_3$: 349.1183, found: 349.1186; IR (KBr): 3437, 2918, 1660, 1553, 1118, 823, 761 cm^{-1}.



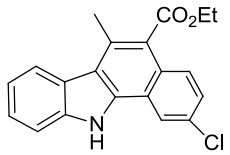
3t

Ethyl 2-methoxy-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3t**): Brown solid. m.p. 190-192 ℃. 44.6 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.5 Hz, 1H), 8.28 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.85 (t, *J* = 7.7 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 2H), 7.47 - 7.41 (m, 1H), 7.25 (d, *J* = 7.9 Hz, 2H), 5.05 (dd, *J* = 8.0, 3.9 Hz, 1H), 3.60 (dq, *J* = 12.8, 6.3 Hz, 1H), 3.41 - 3.27 (m, 2H), 2.39 (s, 3H), 1.90 - 1.79 (m, 1H), 1.60 (td, *J* = 13.8, 6.4 Hz, 1H), 1.44 - 1.28 (m, 2H), 1.24 - 1.02 (m, 2H), 0.71 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 149.9, 148.1, 143.2, 138.1, 137.3, 129.6, 127.0, 126.1, 122.1, 51.7, 37.5, 35.8, 34.9, 21.4, 18.5, 13.6. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{20}H_{19}NO_3$: 334.1438, found: 334.1444; IR (KBr): 3422, 2924, 1696, 1551, 1395, 1121, 784 cm^{-1}.



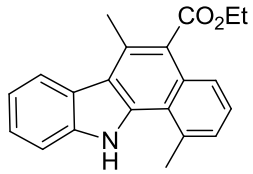
3u

Ethyl 2-fluoro-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3u**): Yellow solid. m.p. 163-165 ℃. 42.3 mg, 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.24 (dt, *J* = 13.1, 7.7 Hz, 2H), 6.88 (dd, *J* = 12.6, 7.7 Hz, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 2.76 (s, 3H), 1.48 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 159.0, 156.5, 139.0, 134.6, 134.5, 130.4, 124.8 (d, $^1J_{C\text{-}F}$= 8Hz), 124.7, 124.2, 122.1, 120.9 (d, $^2J_{C\text{-}F}$= 6Hz), 120.2, 118.4, 118.1 (d, $^3J_{C\text{-}F}$= 13Hz), 117.4, 116.6 (d, $^4J_{C\text{-}F}$= 4Hz), 111.4, 110.5 (d, $^5J_{C\text{-}F}$= 23Hz), 61.7, 17.8, 14.2. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{20}H_{17}FNO_2$: 322.1238, found: 322.1240; IR (KBr): 3433, 2924, 1551, 1395, 1121, 760 cm^{-1}.



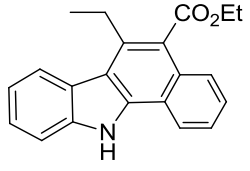
3v

Ethyl 2-chloro-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3v**): Green solid. m.p. 192-194 ℃. 45.2 mg, 67% yield. ^{1}H NMR (400 MHz, DMSO) δ 12.53 (s, 1H), 8.70 (d, *J* = 2.0 Hz, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.61 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 4.51 (q, *J* = 7.1 Hz, 2H), 2.90 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ 169.1, 139.1, 134.6, 130.6, 129.7, 127.1, 126.5, 126.4, 124.9, 123.2, 122.1, 121.9, 121.1, 120.2, 119.8, 116.7, 111.6, 61.0, 18.2, 14.1. HR-MS (ESI) calcd for [M + 1] $^{+}$: $C_{20}H_{17}ClNO_2$: 338.0942, found: 338.0943; IR (KBr): 3444, 2918, 1550, 1451, 1224, 1122, 794 cm $^{-1}$.



3w

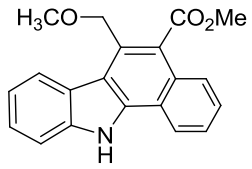
Ethyl 1,6-dimethyl-11H-benzo[a]carbazole-5-carboxylate (**3w**): Yellow solid. m.p. 195-197 ℃. 49.4mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 6.6 Hz, 1H), 4.58 (q, *J* = 7.1 Hz, 2H), 2.99 (s, 3H), 2.77 (d, *J* = 5.1 Hz, 3H), 1.49 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 138.5, 135.7, 131.8, 129.7, 129.6, 127.4, 125.4, 124.4, 124.3, 123.5, 123.4, 122.2, 120.1, 119.6, 117.8, 111.2, 61.3, 23.86, 18.5, 14.4. HR-MS (ESI) calcd for [M + 1] $^{+}$: $C_{21}H_{19}ClNO_2$: 318.1489, found: 318.1491; IR (KBr): 3434, 2918, 1552, 1395, 1221, 1126, 746 cm $^{-1}$.



3x

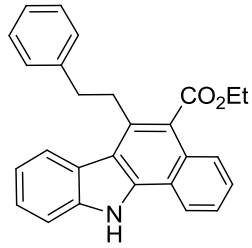
Ethyl 6-ethyl-11H-benzo[a]carbazole-5-carboxylate (3x): Read solide. m.p. 198-221 ℃.45.8 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.05 (dd, *J* = 5.7, 3.7 Hz, 1H), 7.92 (dd, *J* = 6.1, 3.4 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.40 (m, 3H), 7.32 (t, *J* =

7.6 Hz, 1H), 4.59 (q, *J* = 7.1 Hz, 2H), 3.31 (q, *J* = 7.5 Hz, 2H), 1.51 (q, *J* = 7.2 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 138.8, 136.4, 136.0, 129.0, 126.2, 125.5, 125.0, 124.6, 123.6, 122.8, 122.1, 120.6, 120.3, 119.5, 116.1, 111.3, 61.3, 25.6, 14.5, 14.4. HR-MS (ESI) calcd for $[M+1]^+$: $C_{21}H_{20}NO_2$; 318.1489, found : 318.1496; IR (KBr): 3865, 2917, 1584, 1498, 1433, 1286, 1197, 1072, 978, 738 cm^{-1}.



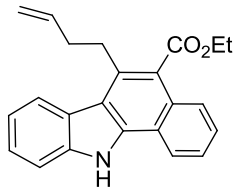
3y

Methyl 6-(methoxymethyl)-11H-benzo[a]carbazole-5-carboxylate (3y): Green solid. m.p. 158-160 ℃. 50.5mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, *J* = 3.3 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.88 (dd, *J* = 22.0, 8.2 Hz, 2H), 7.42 (dd, *J* = 17.3, 8.3 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.25 (t, *J* = 8.2 Hz, 1H), 5.03 (s, 2H), 4.08 (s, 3H), 3.42 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 138.9, 136.0, 129.5, 128.4, 126.2, 125.8, 124.9, 123.8, 123.5, 122.8, 120.7, 120.4, 120.3, 116.2, 111.1, 70.5, 58.0, 52.4. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{20}H_{18}NO_3$: 320.1286, found: 320.1290; IR (KBr): 3475, 2928, 1712, 1585, 1355, 1209, 1068, 743 cm^{-1}.



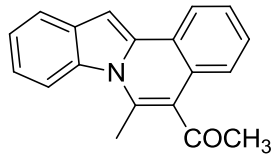
3z

Methyl 6-phenethyl-11H-benzo[a]carbazole-5-carboxylate (3z): Cyan solid. m.p. 183-185 ℃. 46.0 mg, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.16 – 8.07 (m, 1H), 8.00 – 7.90 (m, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.44 – 7.33 (m, 5H), 7.29 (dd, *J* = 5.8, 2.8 Hz, 1H), 4.60 (q, *J* = 7.1 Hz, 2H), 3.68 – 3.56 (m, 2H), 3.27 – 3.15 (m, 2H), 1.49 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 141.8, 138.8, 135.9, 134.1, 129.1, 128.6, 128.2, 126.3, 126.2, 125.8, 125.3, 124.9, 123.8, 123.4, 122.00, 120.6, 120.5, 119.6, 116.3, 111.3, 61.4, 36.1, 34.1, 14.5. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{27}H_{24}NO_2$: 394.1802, found: 394.1805; IR (KBr): 3500, 2945, 1749, 1486, 1361, 1015, 752 cm^{-1}.



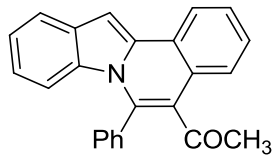
3az

Methyl 6-(but-3-en-1-yl)-11H-benzo[a]carbazole-5-carboxylate (3az): Yellow solid. m.p. 178-180 ℃. 46.9 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.06 (t, *J* = 9.5 Hz, 2H), 7.96 – 7.87 (m, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.40 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 1H), 6.09 (ddt, *J* = 16.7, 10.3, 6.3 Hz, 1H), 5.17 (dd, *J* = 39.7, 13.7 Hz, 2H), 4.58 (q, *J* = 7.1 Hz, 2H), 3.47 – 3.15 (m, 2H), 2.63 (dt, *J* = 20.3, 10.1 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 138.9, 138.0, 136.0, 134.3, 128.9, 126.2, 125.5, 125.1, 124.7, 123.6, 123.0, 121.8, 120.7, 120.4, 119.5, 116.1, 114.8, 111.4, 61.4, 33.8, 31.5, 14.5. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{23}H_{22}NO_2$: 344.1645, found: 344.1646; IR (KBr): 3697, 2985, 1749, 1579, 1485, 1360, 923 cm^{-1}.



3bz

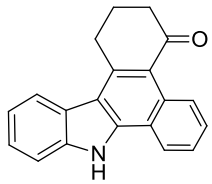
1-(6-methylindolo [2,1-a]isoquinolin-5-yl) ethanone (3bz) [3]**:** Green solide. m.p. 199-201 ℃.45.8 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.04 (m, 2H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.43 (tdd, *J* = 8.6, 7.2, 1.3 Hz, 2H), 7.37 – 7.20 (m, 4H), 2.92 (d, *J* = 16.2 Hz, 3H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.5, 135.4, 133.4, 132.3, 130.1, 127.7, 127.1, 125.5, 124.8, 123.7, 123.3, 122.2, 122.0, 121.1, 120.8, 115.0, 95.2, 33.3, 19.7. HR-MS (ESI) calcd for $[M+1]^+$: $C_{19}H_{15}NO$; 274.1226, found : 274.1230; IR (KBr): 3683, 2915, 1697, 1585, 1491, 1331, 976, 741 cm^{-1}.



3cz

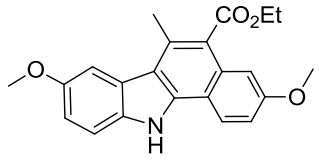
1-(6-phenylindolo[2,1-a]isoquinolin-5-yl)ethanone (3cz): Cyan solid. m.p. 196-198 ℃. 52.2 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.6 Hz, 1H), 8.20 (s, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.86 (dd, *J* = 10.9, 4.4 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.44 (dd, *J* = 7.4, 4.8 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 2H), 5.50 (d, *J* = 5.9 Hz, 1H), 3.55 - 3.45 (m, 2H), 3.40 - 3.32 (m, 1H),

2.26 (s, 3H), 1.19 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 149.2, 148.0, 142.8, 137.7, 137.3, 129.4, 126.9, 126.3, 122.3, 51.3, 44.6, 21.4, 20.0. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{24}H_{18}NO$: 336.1383, found: 336.1387; IR (KBr): 3710, 2913, 1665, 1590, 1377, 1235, 892 cm^{-1}.



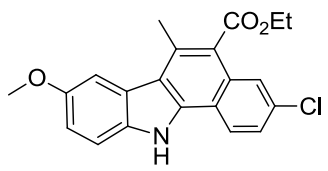
3dz

2,3-Dihydro-1H-dibenzo[a,c]carbazol-4(9H)-one (3dz) [3]**:** Yellow solid. m.p. 183-185 ℃. 35.9 mg, 63% yield. ^{1}H NMR (400 MHz, DMSO) δ 12.68 (s, 1H), 9.59 (dd, *J* = 6.3, 3.6 Hz, 1H), 8.57 (dd, *J* = 6.3, 3.2 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7.75 – 7.62 (m, 3H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 3.70 (t, *J* = 6.0 Hz, 2H), 2.77 (m, 2H), 2.26 (m, 2H); ^{13}C NMR (100 MHz, DMSO) δ 198.7, 145.5, 139.3, 138.4, 130.09, 127.4, 127.2, 125.2, 124.8, 123.7, 122.2, 121.9, 120.4, 120.1, 119.3, 114.8, 111.8, 28.8, 22.1. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{20}H_{16}NO$: 286.1226, found: 286.1230; IR (KBr): 3697, 2985, 1689, 1579, 1425, 1360, 723 cm^{-1}.



3fz

Ethyl 3,8-dimethoxy-6-methyl-11H-benzo[a]carbazole-5-carboxylate (3fz): Brown solid. m.p. 232-234 ℃. 19.2 mg, 4 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.91 – 7.78 (m, 1H), 7.60 (s, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 7.21 (s, 1H), 7.10 – 6.96 (m, 2H), 4.58 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 3.85 (s, 3H), 2.85 (d, *J* = 8.2 Hz, 3H), 1.50 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 157.9, 154.2, 136.7, 133.7, 131.5, 130.4, 125.3, 122.1, 121.9, 116.3, 115.7, 114.3, 112.8, 111.4, 105.6, 105.1, 61.2, 56.1, 55.1, 18.7, 14.5. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{22}H_{22}NO_4$: 364.1385, found: 364.1458; IR (KBr): 3427, 2914, 1631, 1568, 1491, 1252, 1123, 752 cm^{-1}.

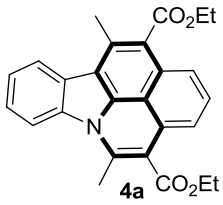


3gz

Ethyl 3-chloro-8-methoxy-6-methyl-11H-benzo[a]carbazole-5-carboxylate (3gz): Brown solid. m.p. 203-205 ℃. 15.3 mg, 7 % yield. ^{1}H NMR (400 MHz, acetone) δ 11.33 (s, 1H), 8.40 (dd, *J* = 8.8, 3.8 Hz, 1H), 7.92 (d, *J* = 1.8 Hz, 1H), 7.70 (d, *J* = 2.4 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.07 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.59 – 4.45 (m, 2H), 3.94 – 3.83 (m, 3H), 2.92 (d, *J* = 2.7 Hz, 3H), 1.44 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, acetone) δ 169.2, 154.5, 136.1, 134.4, 132.5, 131.3, 129.8, 125.2, 124.4, 124.3, 123.5, 121.8, 118.2, 117.0, 114.2, 112.0, 104.9, 60.9, 55.2, 18.1, 13.8.. HR-MS (ESI) calcd for $[M + 1]^{+}$: $C_{21}H_{19}ClNO_3$: 368.0912, found: 368.0881; IR (KBr): 3514, 2934, 1686, 1590, 1375, 1260, 1121, 733 cm^{-1}.

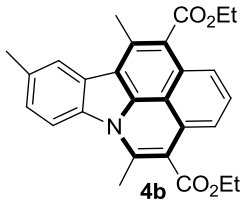
3 General Procedure for the Synthesis of Compounds 4a-4g

All of the products (**4a-4g**) were obtained according to the following procedure. To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 2-arylindoles (0.2 mmol), diazo compounds (0.8 mmol), $[RhCp^*Cl_2]_2$ (6.0 mg, 0.01 mmol, 5 mol %), PivOH (40.8 mg, 0.4 mmol, 200 mol %), and AgOAc (6 mg, 0.06 mmol, 30 mol %), TFE (1.5 mL) under an Ar atmosphere. The reaction mixture was stirred at 120^{o}C for 24 h, filtered through a pad of celite and then washed with ethyl acetate (10 mL × 3). Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel with ethyl acetate/petroleum (v/v = 1/4) as the eluent to give the desired products.

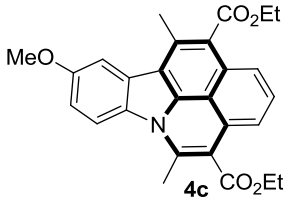


4a

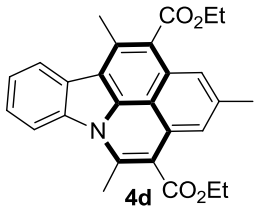
Diethyl 5,11-dimethylisoquinolino[2,1,8-lma]carbazole-4,12-dicarboxylate (4a) [3]: Cyan solid. m.p. 212-214 ℃. 37.2 mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.13 (d, *J* = 2.8 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.48 – 7.36 (m, 3H), 4.58 (dq, *J* = 14.2, 7.1 Hz, 4H), 2.98 (d, *J* = 14.6 Hz, 6H), 1.52 (dt, *J* = 12.8, 6.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 168.1, 136.6, 135.4, 133.4, 131.8, 128.8, 127.4, 126.4, 125.8, 123.5, 122.6, 122.4, 121.9, 119.8, 115.8, 115.2, 114.51, 111.3, 61.58, 6.19, 2.70, 19.4, 18.6, 14.5, 14.4. HR-MS (ESI) calcd for $[M + 1]^{+}$: $C_{26}H_{24}NO_4$: 414.1700, found: 414.1703; IR (KBr): 2922, 1692, 1548, 1443, 1221, 1064, 791 cm^{-1}.



Diethyl 5,9,11-trimethylisoquinolino[2,1,8-lma]carbazole-4,12-dicarboxylate (4b) [3]: Cyan solid. m.p. 216-218 ℃. 35.0 mg, 41% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 21.9, 13.3 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.68 (t, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 4.59 (dq, *J* = 13.9, 7.0 Hz, 4H), 3.00 (d, *J* = 7.2 Hz, 6H), 2.53 (s, *J* = 13.0 Hz, 3H), 1.56 – 1.47 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 168.2, 136.6, 133.6, 133.5, 131.9, 131.7, 128.8, 127.2, 126.4, 125.9, 124.9, 122.3, 121.8, 119.5, 118.8, 115.4, 115.0, 114.0, 111.0, 61.5, 61.1, 21.6, 19.3, 18.6, 14.5, 14.4. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{27}H_{26}NO_4$: 428.1856, found: 428.1859; IR (KBr): 2920, 1714, 1623, 1587, 1444, 1179, 827 cm^{-1}.

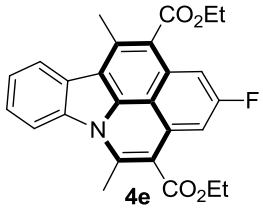


Diethyl 9-methoxy-5,11-dimethylisoquinolino[2,1,8-lma]carbazole-4,12-dicarboxylate (4c) [3]: Cyan solid. m.p. 201-203 ℃. 60.3 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.49 (s, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 1H), 4.58 (dq, *J* = 14.0, 7.1 Hz, 4H), 3.88 (d, *J* = 17.3 Hz, 3H), 2.93 (d, *J* = 10.4 Hz, 6H), 1.51 (dd, *J* = 11.8, 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 168.2, 156.5, 136.3, 136.2, 133.1, 131.0, 128.2, 126.8, 126.0, 122.3, 122.1, 119.7, 119.6, 118.7, 115.7, 114.9, 111.3, 110.4, 99.4, 61.5, 61.1, 55.5, 19.1, 18.4, 14.5, 14.4. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{27}H_{26}NO_4$: 444.1805, found: 444.1808; IR (KBr): 2921, 1716, 1456, 1280, 1083, 845, 617 cm^{-1}.



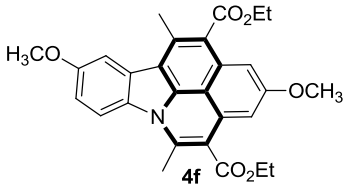
Diethyl 2,5,11-trimethylisoquinolino[2,1,8-lma]carbazole-4,12-dicarboxylate (4d): Cyan solid. m.p. 188-190 ℃. 55.5 mg, 65% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.37 (m, 1H), 8.28

(dd, *J* = 6.1, 3.1 Hz, 1H), 7.67 (s, 1H), 7.58 – 7.48 (m, 2H), 7.32 (s, 1H), 4.59 (dq, *J* = 10.4, 7.1 Hz, 4H), 3.10 (d, *J* = 7.1 Hz, 3H), 3.03 (s, 3H), 2.62 (d, *J* = 8.2 Hz, 3H), 1.52 (td, *J* = 7.1, 3.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 168.2, 137.6, 136.6, 135.6, 133.7, 131.8, 129.1, 126.3, 126.1, 123.3, 122.4, 122.1, 121.9, 119.7, 117.29, 116.7, 115.6, 114.5, 110.8, 61.5, 61.1, 23.0, 19.5, 18.6, 14.5, 14.3. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{27}H_{26}NO_4$: 428.1856, found: 428.1857; IR (KBr): 2930, 1720, 1545, 1393, 1222, 1025, 749 cm^{-1}.



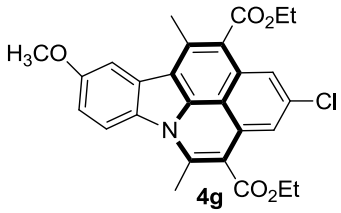
4e

Diethyl 2-fluoro-5,11-dimethylisoquinolino[2,1,8-lma]carbazole-4,12-dicarboxylate (4e) [3]: Cyan solid. m.p. 197-199 ℃. 28.5 mg, 33% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 48.2 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 3H), 7.20 (d, *J* = 9.5 Hz, 1H), 4.58 (p, *J* = 7.2 Hz, 4H), 2.98 (dd, *J* = 33.0, 5.9 Hz, 6H), 1.52 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 167.6, 163.6, 161.2, 138.5, 135.5, 133.6, 133.1, 130.2, (d, $^1J_{C\text{-}F}$ = 11Hz) , 128.5, (d, $^2J_{C\text{-}F}$ = 11Hz), 125.9, 123.7, 122.8, 122.0, 115.8, 115.0, 114.7, 111.0, 105.2, (d, $^3J_{C\text{-}F}$ = 25Hz), 104.3,(d, $^4J_{C\text{-}F}$ = 28Hz), 61.7, 61.3, 29.7, 19.5, 18.7, 14.4, 14.3. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{26}H_{23}FNO_4$: 432.1606, found: 432.1608; IR (KBr): 2927, 1708, 1551, 1396, 1216, 1124, 746, 577 cm^{-1}.



4f

Diethyl 2,9-dimethoxy-5,11-dimethylisoquinolino[2,1,8-lma]carbazole-4,12-dicarboxylate (4f): Cyan solid. m.p. 223-225 ℃. 35.0 mg, 37% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 9.2 Hz, 1H), 7.69 (s, 1H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.09 (s, 1H), 7.01 (d, *J* = 9.2 Hz, 1H), 4.75 – 4.39 (m, 4H), 3.96 (s, 6H), 2.99 (d, *J* = 19.9 Hz, 6H), 1.52 (dd, *J* = 13.5, 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 167.0, 158.5, 154.5, 136.4, 133.3, 131.8, 129.5, 129.4, 127.0, 126.2, 120.3, 114.1, 113.6, 113.5, 110.5, 109.00, 103.8, 100.9, 60.5, 60.0, 54.6, 54.4, 28.6, 18.3, 17.6, 13.5, 13.3. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{28}H_{28}NO_6$: 474.1911, found: 474.1908; IR (KBr): 2927, 1710, 1555, 1464, 1363, 1120, 742 cm^{-1}.

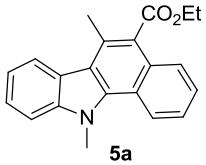


4g

Diethyl2-chloro-9-methoxy-5, 11- dimethylisoquinolino [2, 1, 8- lma] carbazole-4, 12-dicarboxylate (4g): Cyan solid. m.p. 227-229 ℃. 49.6 mg, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 1H), 7.67 (s, 1H), 7.51 (s, 1H), 7.33 (s, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 4.59 (s, 4H), 3.93 (s, 3H), 2.90 (d, *J* = 21.5 Hz, 6H), 1.53 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 167.5, 155.3, 138.0, 133.5, 132.9, 132.7, 129.7, 129.3, 127.5, 126.2, 121.0, 118.4, 116.4, 115.0, 113.6, 112.0, 110.8, 104.3, 61.6, 61.2, 55.3, 19.0, 18.3, 14.4, 14.3. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{27}H_{26}ClNO_5$: 478.1416, found: 478.1411; IR (KBr): 2925, 1706, 1551, 1459, 1260, 1124, 746, 577 cm^{-1}.

4 General Procedure for the Synthesis of Compound 5a

To a stirred solution of **3a** (60.6 mg, 0.2 mmol) in dry DMF (3.0 mL), NaH (12.0 mg, 60% suspension in mineral oil, 0.3 mmol) was added portionwise under nitrogen atmosphere at 0 ^{o}C. The reaction mixture was then warmed to room temperature and stirred for 30 min. After cooling to 0 ^{o}C, MeI (0.018 mL, 0.3 mmol) was added dropwise to the reaction mixture. The reaction mixture was warmed to room temperature and stirredovernight. Water was added and the aqueous layer was extracted with ether. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 10/1) to give compound **5a** as yellow solid.



5a

Ethyl 6,11-dimethyl-11H-benzo[a]carbazole-5-carboxylate (5a) [4]**:** Yellow solid. m.p. 195-197 ℃. R_f = 0.54 (petroleum ether / ethyl acetate = 4:1). 54.2 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 – 8.46 (m, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.86 (dd, *J* = 7.3, 2.2 Hz, 1H), 7.48 – 7.35 (m, 4H), 7.21 (ddd, *J* = 8.0, 5.9, 2.1 Hz, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 4.15 (s, 3H), 2.83 (s,

3H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 141.0, 135.9, 130.1, 129.9, 125.7, 125.5, 124.5, 124.5, 123.9, 123.4, 122.3, 122.3, 120.9, 119.9, 117.5, 109.1, 61.3, 34.1, 18.9, 14.4. HR-MS (ESI) calcd for $[M + 1]^+$: $C_{21}H_{20}NO_2$: 318.1489, found: 318.1490; IR (KBr): 2918, 1687, 1541, 1443, 1254, 1023, 763, 689 cm^{-1}.

5. Preliminary mechanistic studies

(1): H/D Exchange of 2-phenlindole (*d1*-1a)

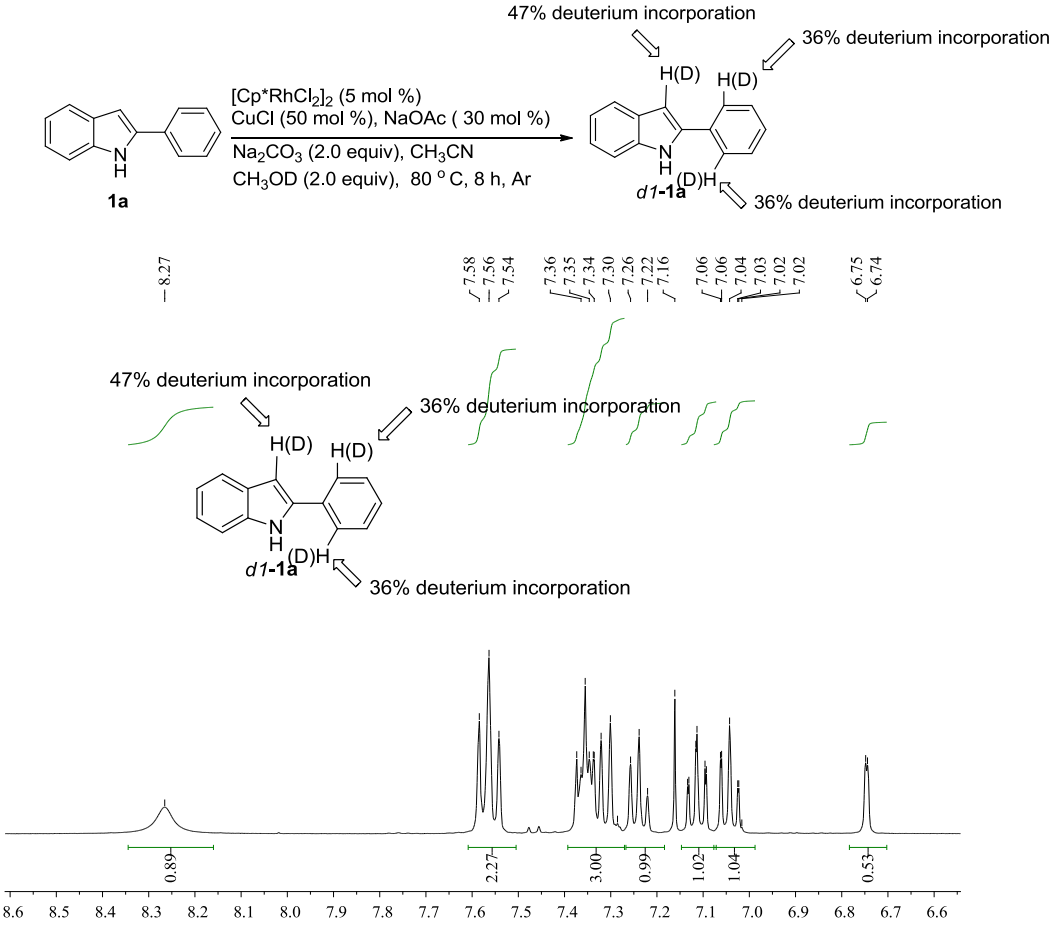


Figure S1. The conversion of *d1*-**1a** was monitored by ^{1}H NMR method

H/D exchange of 2-phenlindole (*d1*-**1a**): To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 2-phenlindole **1a** (19.3 mg, 0.1 mmol), [RhCp*Cl_2]$_2$ (3.0 mg, 0.005 mmol, 5 mol %), NaOAc (2.5 mg, 0.03 mmol, 30 mol %), CuCl (5mg, 0.05 mmol, 50 mol %), Na_2CO_3(21.2 mg, 0.2 mmol, 200 mol %), CH_3OD (6.6 mg, 0.2 mmol, 200 mol %)and CH_3CN (1.0 mL) under an Ar atmosphere. The corresponding reaction mixture was filtered through a pad of Celite, washed with EtOAc and concentrated under reduced pressure. The residue was purified by flash chromatography on silical gel to afford the desired compound *d1*-**1a** (97% yield) as gray solid. The deuterium incorporation was determined to be 47% and 36% by ^{1}H NMR method (Support information, Figure S1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.56 (t, *J* = 8.5 Hz, 2.27H), 7.39 – 7.27 (m, 3H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.15 – 7.07 (m, 1H), 7.08 – 6.99 (m, 1H), 6.75 (d, *J* = 1.6 Hz, 0.53H).

(2): H/D Exchange of 2-phenlindole (*d2*-1a)

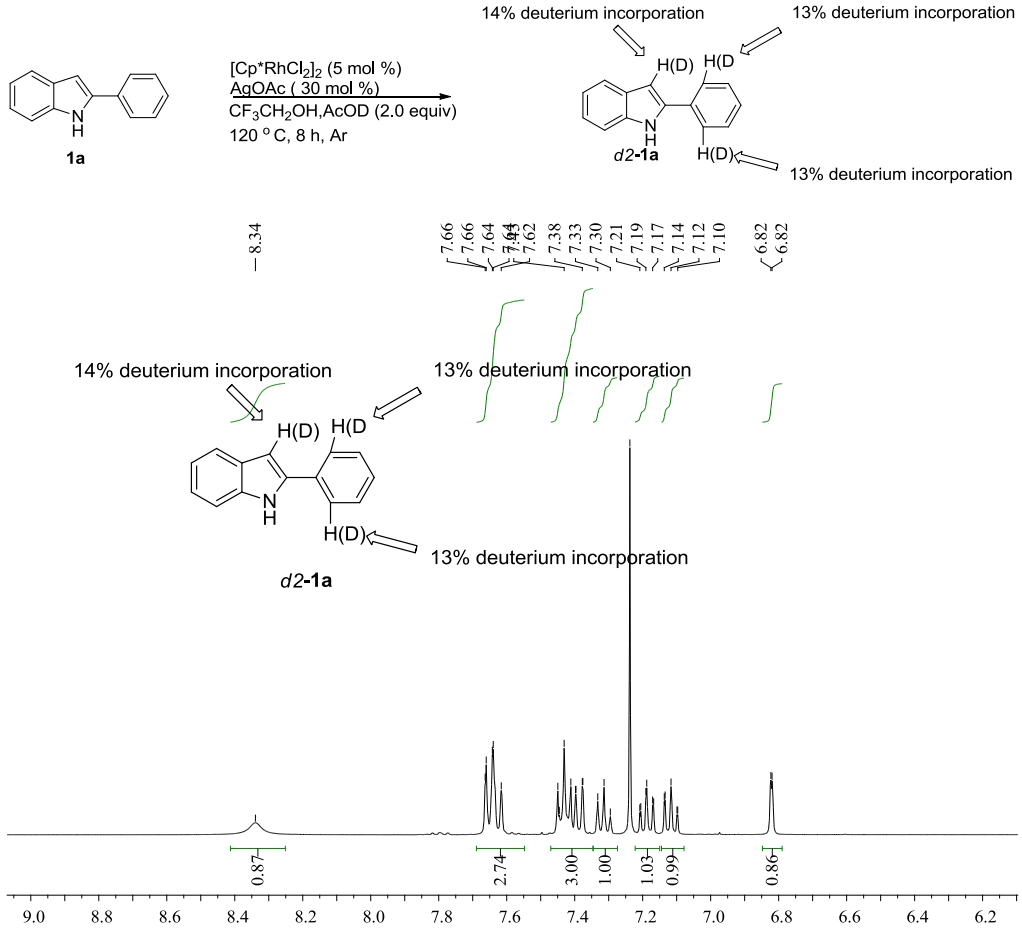


Figure S2. The conversion of *d2*-**1a** was monitored by ^{1}H NMR method

H/D exchange of 2-phenlindole (*d2*-**1a**): To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 2-phenlindole **1a** (19.3 mg, 0.1 mmol), $[RhCp^*Cl_2]_2$ (3.0 mg, 0.005 mmol, 5 mol %), AgOAc (3 mg, 0.03 mmol, 30 mol %), PivOH (20.4 mg, 0.2 mmol, 200 mol %), CH_3CO_2D (20.4 mg, 0.2 mmol, 200 mol %) and CF_3CH_2OH (1.0 mL) under an Ar atmosphere. The corresponding reaction mixture was filtered through a pad of celite, washed with EtOAc and concentrated under reduced pressure. The residue was purified by flash chromatography on silical gel to afford the desired compound *d2*-**1a** (68% yield) as gray solid. The deuterium incorporation was determined to be 14% and 13% by ^{1}H NMR method (Support information, Figure S2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.64 (dt, *J* = 10.5, 5.4 Hz, 2.74H), 7.41 (ddd, *J* = 14.1, 7.7, 1.2 Hz, 3H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.22 – 7.15 (m, 1H), 7.14 – 7.08 (m, 1H), 6.82 (d, *J* = 1.4 Hz, 0.86H).

(3): H/D Exchange of 1-methyl-2-phenyl-1H-indole (1y*)*

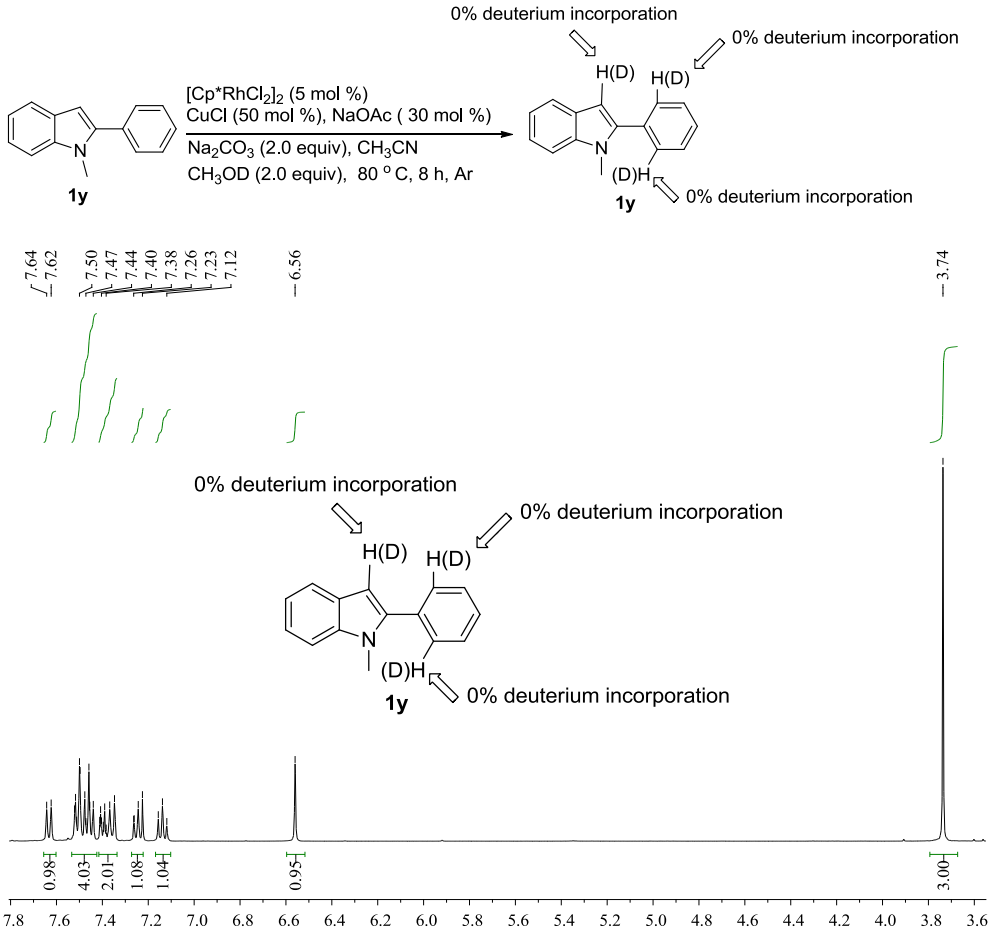
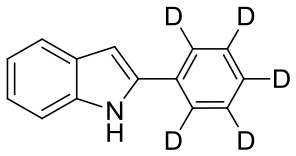


Figure S3. The conversion of **1y** was monitored by ^{1}H NMR method

H/D exchange of 1-methyl-2-phenyl-1H-indole (**1y**): To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 3-methyl-2-phenyl-1H-indole **1y** (20.7 mg, 0.1 mmol), $[RhCp^*Cl_2]_2$ (3.0 mg, 0.005 mmol, 5 mol %), NaOAc (2.5 mg, 0.03 mmol, 30 mol %), CuCl (5mg, 0.05 mmol, 50 mol %), Na_2CO_3 (21.2 mg, 0.2 mmol, 200 mol %), CH_3OD (6.6 mg, 0.2 mmol, 200 mol %) and CH_3CN (1.0 mL) under an Ar atmosphere. The corresponding reaction mixture was filtered through a pad of Celite, washed with EtOAc and concentrated under reduced pressure. The residue was purified by flash chromatography on silical gel to afford the desired compound1y (97% yield) as gray solid. The deuterium incorporation was determined to be 0% by ^{1}H NMR method (SI, Figure S3).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.42 (m, 4H), 7.42 – 7.34 (m, 2H), 7.25 (dd, *J* = 11.2, 4.1 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.56 (s, 1H), 3.74 (s, 3H).

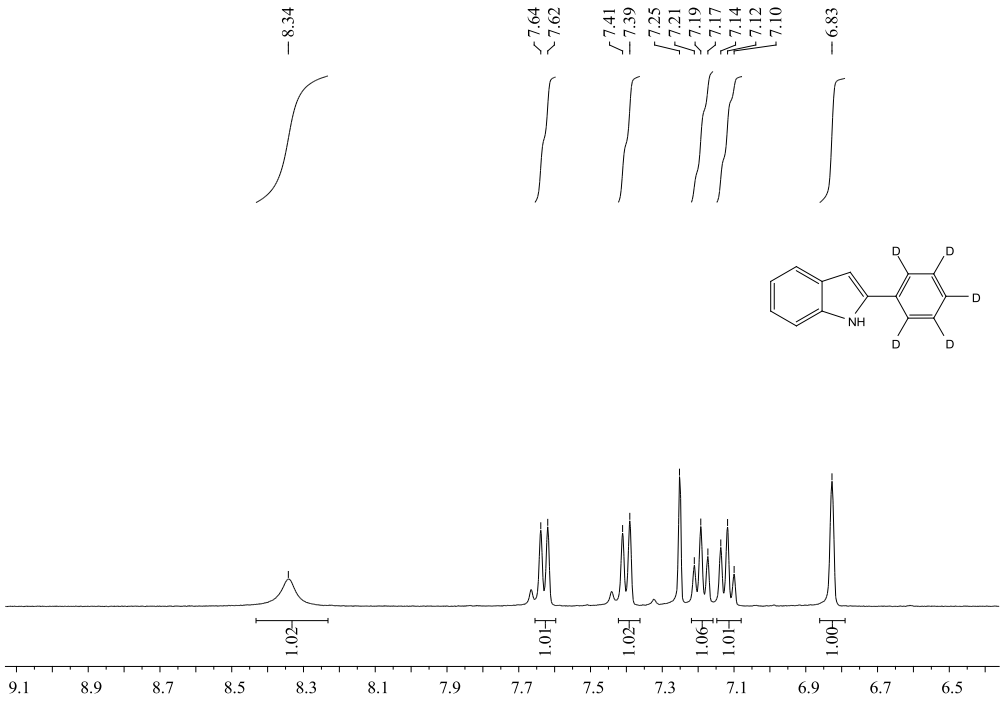
(4) Competitive experiment

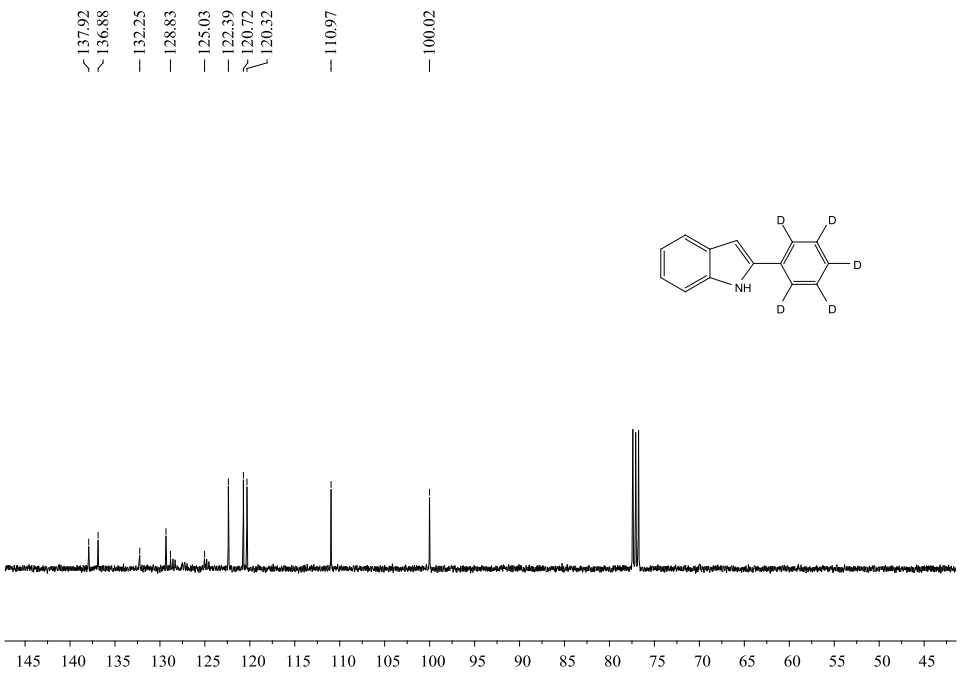


***d3*-1a**

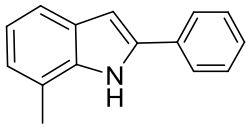
Procedure for the synthesis deuterated-2-phenylindole (*d3*-**1a**): A Schlenk tube equipped with a stirrer bar was charged with *N*-aryl imine (0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol %) and $Cu(OAc)_2$ (109 mg, 0.6 mmol, 3 equiv). The Schlenk tube was evacuated and refilled with N_2 for three times, followed by addition of DMSO (1 mL). The Schlenk tube was sealed with a Teflon screwcap and then the reaction mixture was stirred at 40 ℃ for 12 h. Upon cooling to room temperature, the reaction mixture was diluted with 5 mL of ethyl acetate, followed by filtration through a pad of silica gel. The filtrate was washed with water (10 mL), dried over Na_2SO_4, and then concentrated under reduced pressure.Purification of the residue by flash chromatography on silica gel was purified afforded the indole product.[1]

a) ^{1}H NMR and ^{13}C NMR of ***d3*-1a:**





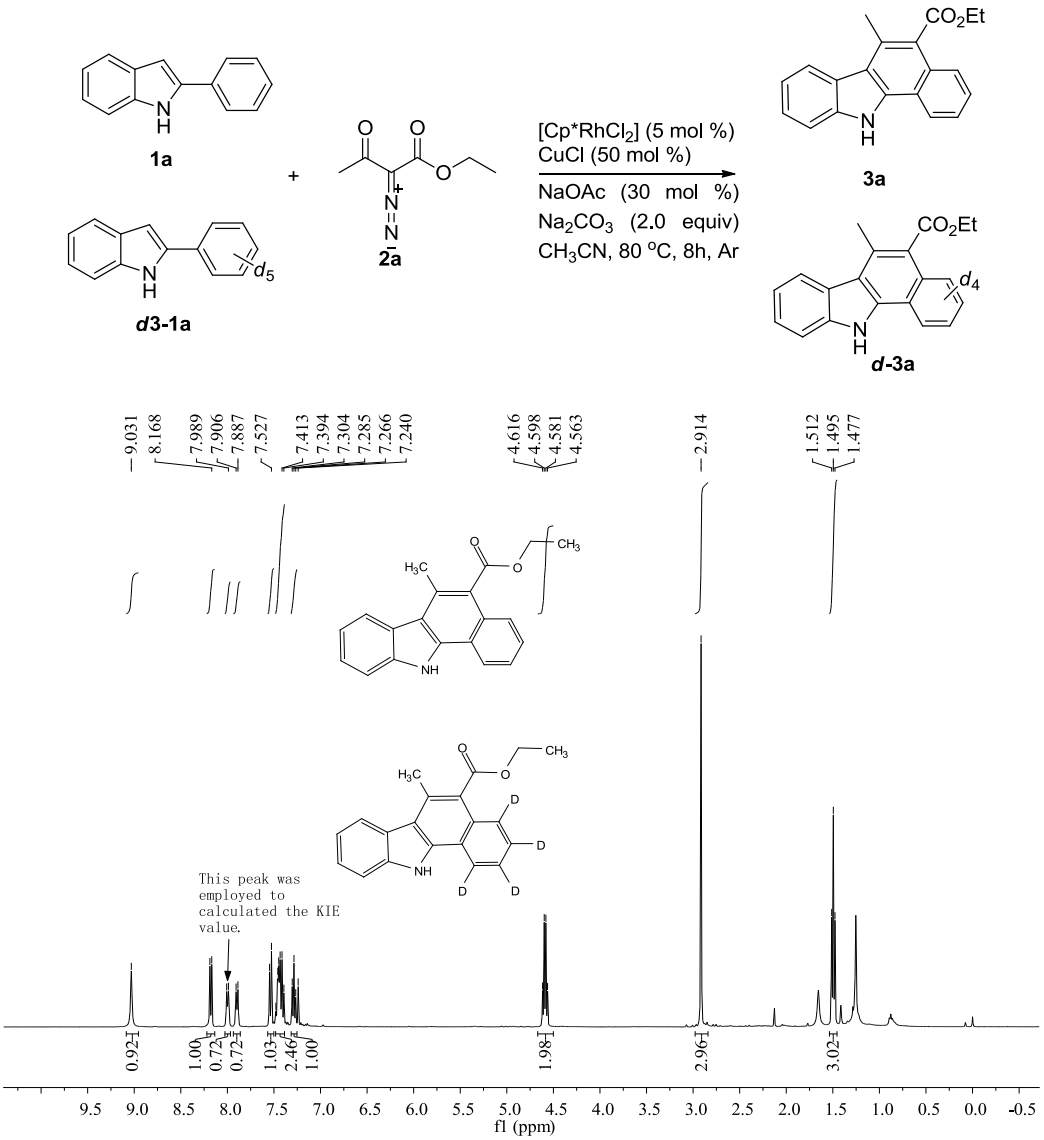
Deuterated-2-phenylindole(*d3*-**1a**): [1]Gray solid; 29.3 mg, 74 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 136.8, 132.2, 129.3, 128.8, 125.0, 122.3, 120.7, 120.3, 110.9, 100.0.



2k

The compound (**2k**) was prepared according to the above-mentioned procedure. [1] The product was obtained as yellow oil in 74 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.66 (d, *J* = 7.7 Hz, 2H), 7.51 – 7.37 (m, 3H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.08 – 6.94 (m, 2H), 6.82 (s, 1H), 2.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 136.4, 132.5, 129.0, 128.8, 127.7, 125.2, 123.0, 120.5, 120.1, 118.4, 100.6, 16.7.

b) The procedure of the competitive experiment



Competitive experiment: To a screw capped vial with a spinvane triangular-shaped Teflon stir bar were added 2-phenylindol 1a (19.3mg mg, 0.1 mmol and *d3*-**1a** (94% D): 19.8 mg, 0.1 mmol), diazocompound **2a** (62.4 mg, 0.4 mmol), $[RhCp^*Cl_2]_2$ (6.0 mg, 0.01 mmol, 5 mol %), NaOAc (5 mg, 0.06 mmol, 30 mol %), Na_2CO_3 (42.4mg, 0.4 mmol, 200 mol %), and dry CH_3CN (2.0 mL) under Ar atmosphere conditions. The reaction mixture was stirred at 80 °C for 8 h, and then was cooled to room temperature. Organic solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel (*n*-hexane/EtOAc) to give the desired product. Yellow solid; 47.2 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.44 (dq, *J* = 16.1, 8.1 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 4.59 (q, *J* = 7.1 Hz, 2H), 2.91 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H). The reaction progress in the early stage (8 hours) indicated a kinetic isotope

effect (KIE) of 2.7.

6. Photophysical data of the representative derivatives

UV-vis absorption spectra were recorded on a UV-2450 spectrophotometer. Photoluminescence (PL) spectra were measured using a Jobin-Yvon spectrofluorometer. Photoluminescence quantum yields (PLQYs) were measured on a HAMAMATSU absolute PL quantum yield spectrometer C11347 in solutions or films. Transient PL spectra were measured with an Edinburgh FL920 fluorescence spectrophotometer.

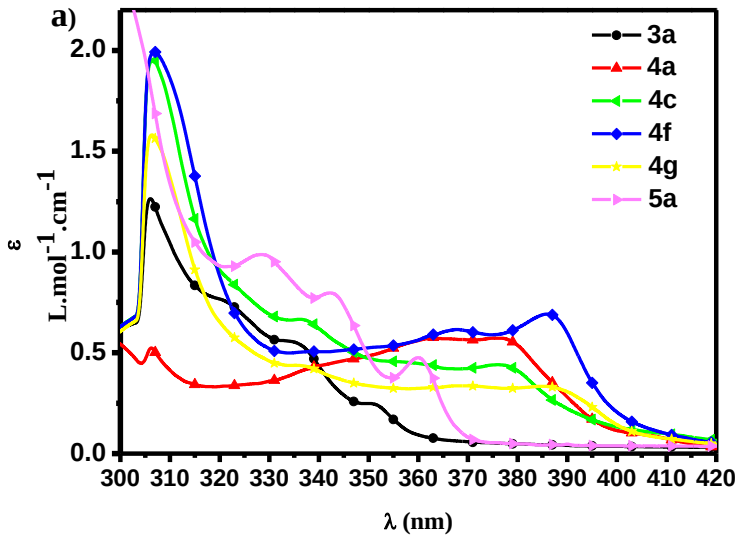


Figure S4. UV-vis absorption spectra of the compounds **3a, 4a, 4c, 4f, 4g,** and **5a** in dichloromethane solutions (10^{-5} M).

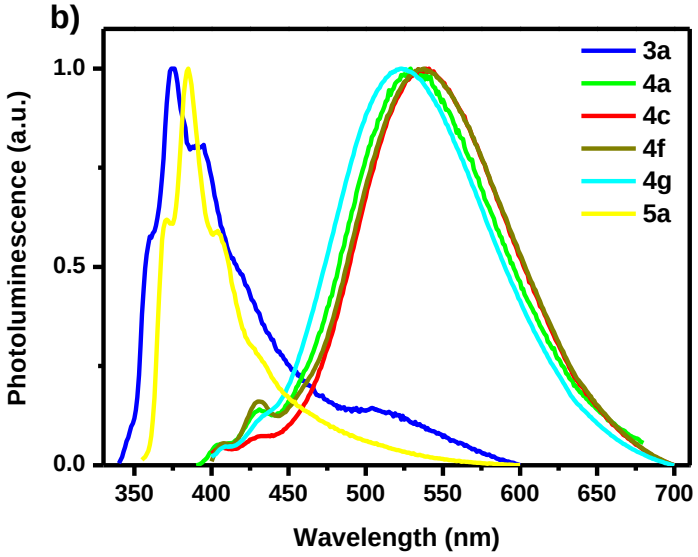


Figure S5. Photoluminescence spectra of the compounds **3a**, **4a**, **4c**, **4f, 4g,** and **5a** in

dichloromethane solutions (10^{-5} M).

c)

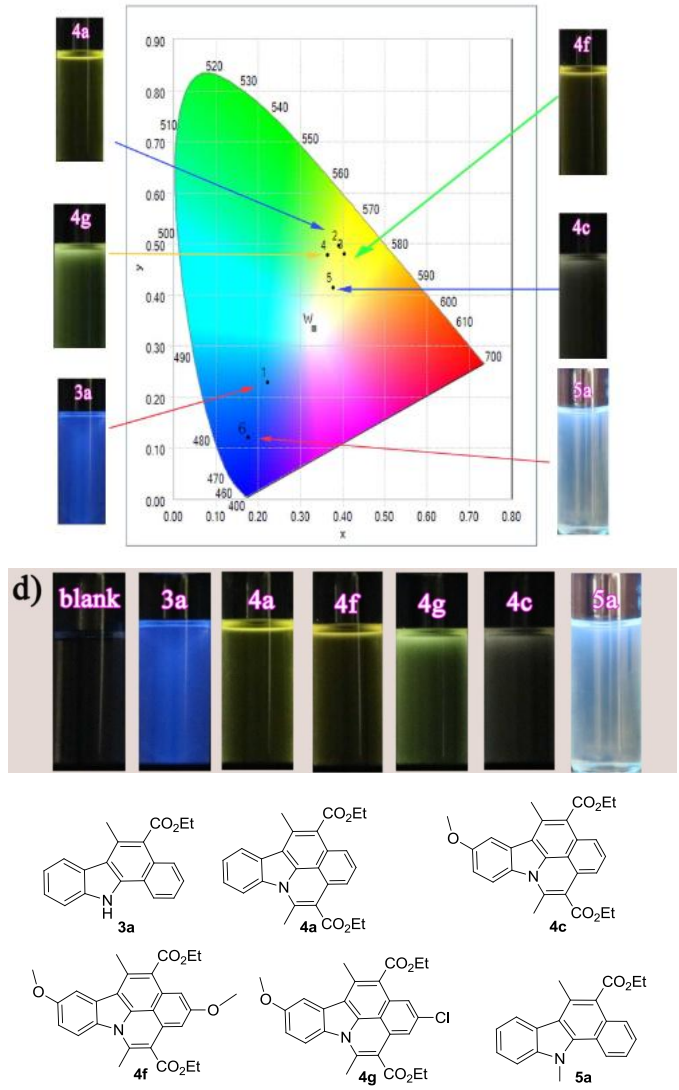


Figure S6 CIE diagrams for emission color change of **3a**, **4a**, **4c**, **4f, 4g** and **5a** in dichloromethane upon excitation at 365 nm (10^{-5} M). (c) Observed fluorescence under UV excitation (365 nm) (d).

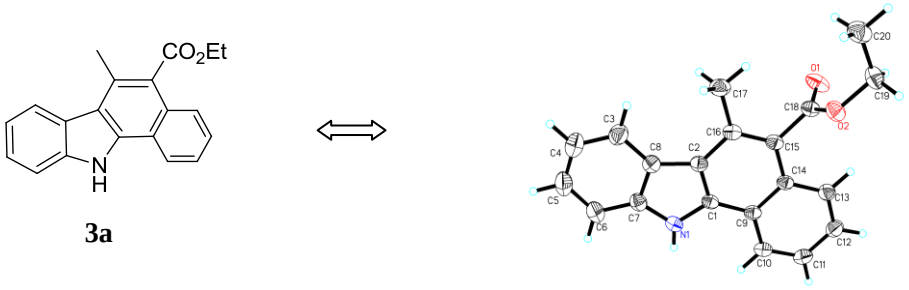
Table S1 Spectral properties of representative derivatives in DCM

Comp.	**λ_{abs} (nm)**	**λ_{em} (nm)**	**ε ($M^{-1}.cm^{-1}$)**	**τ (ns)**	**Φ**	**k_r ($10^5 s^{-1}$)**	**k_{nr} ($10^7 s^{-1}$)**
3a	351	374	24842	1.600	0.012	75	61.75
4a	378	530	57224	2.794	0.058	207	33.72
4c	375	539	44274	2.423	0.048	198	39.29

4f	387	536	70573	3.647	0.096	263	24.79
4g	389	521	32505	2.411	0.066	273	38.74
5a	361	386	46472	-[a]	0.081	-	-

RT measurements in DCM (10^{-5} M). [a] The lifetime of **5a** is shorter than the instrument.

7. Single crystal data about 3a



3a

Figure S7. The single crystal structure of **3a** (The ellipsoid contour probability level is 30%)

Table S2. Crystal data and structure refinement for 3a

Identification code	3a
Empirical formula	$C_{20}H_{17}NO_2$
Formula weight	303.35
Temperature	293(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a = 10.3910(4) A alpha = 90 deg.
	b = 17.2188(6) A beta = 98.489(4) deg.
	c = 8.7009(3) A gamma = 90 deg.
Volume	1539.71(10) A^3
Z, Calculated density	4, 1.309 Mg/m^3
Absorption coefficient	0.673 mm^-1
F(000)	640
Crystal size	0.2 x 0.18 x 0.11 mm

Theta range for data collection	6.71 to 62.79 deg.
Limiting indices	-11<=h<=11, -19<=k<=19, -6<=l<=9
Reflections collected / unique	5497 / 2438 [R(int) = 0.0195]
Completeness to theta = 62.79	98.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2438 / 0 / 272
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.1190
R indices (all data)	R1 = 0.0450, wR2 = 0.1278
Largest diff. peak and hole	0.121 and -0.150 e.A^-3

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 3a. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	8390(1)	4918(1)	7530(1)	48(1)
O(1)	9024(1)	5716(1)	634(1)	70(1)
O(2)	7721(1)	6686(1)	1102(1)	57(1)
C(1)	8477(1)	5289(1)	6158(1)	41(1)
C(2)	7502(1)	5016(1)	5006(2)	44(1)
C(3)	5722(2)	3958(1)	5259(2)	65(1)
C(4)	5327(2)	3439(1)	6299(3)	80(1)
C(5)	5951(2)	3395(1)	7823(3)	78(1)
C(6)	6982(2)	3871(1)	8354(2)	65(1)
C(7)	7381(1)	4394(1)	7304(2)	50(1)
C(8)	6781(1)	4444(1)	5749(2)	49(1)
C(9)	9400(1)	5858(1)	5876(2)	42(1)
C(10)	10360(1)	6160(1)	7036(2)	50(1)

C(11)	11222(2)	6699(1)	6669(2)	56(1)
C(12)	11174(2)	6955(1)	5144(2)	56(1)
C(13)	10248(1)	6675(1)	3995(2)	50(1)
C(14)	9333(1)	6118(1)	4319(1)	42(1)
C(15)	8357(1)	5809(1)	3138(2)	44(1)
C(16)	7440(1)	5279(1)	3451(2)	46(1)
C(17)	6423(2)	4964(1)	2207(2)	60(1)
C(18)	8410(1)	6050(1)	1500(2)	47(1)
C(19)	7702(2)	6978(1)	-485(2)	65(1)
C(20)	6632(2)	6614(1)	-1562(2)	75(1)

Table S4. Bond lengths [A] and angles [deg] for 3a.

Bond	Lengths [A]
N(1)-C(1)	1.3683(17)
N(1)-C(7)	1.3751(18)
N(1)-H(3A)	0.8600
O(1)-C(18)	1.2040(17)
O(2)-C(18)	1.3255(16)
O(2)-C(19)	1.4672(19)
C(1)-C(2)	1.3975(18)
C(1)-C(9)	1.4176(19)
C(2)-C(16)	1.4197(19)
C(2)-C(8)	1.447(2)
C(3)-C(4)	1.376(3)
C(3)-C(8)	1.398(2)
C(3)-H(21)	1.00(2)
C(4)-C(5)	1.390(3)
C(4)-H(23)	0.99(2)
C(5)-C(6)	1.373(3)

C(5)-H(22)	0.98(2)
C(6)-C(7)	1.389(2)
C(6)-H(15)	1.003(18)
C(7)-C(8)	1.405(2)
C(9)-C(10)	1.4103(19)
C(9)-C(14)	1.4192(19)
C(10)-C(11)	1.360(2)
C(10)-H(13)	1.002(17)
C(11)-C(12)	1.392(2)
C(11)-H(18)	1.014(16)
C(12)-C(13)	1.369(2)
C(12)-H(17)	0.98(2)
C(13)-C(14)	1.407(2)
C(13)-H(9)	0.976(16)
C(14)-C(15)	1.4359(18)
C(15)-C(16)	1.374(2)
C(15)-C(18)	1.492(2)
C(16)-C(17)	1.498(2)
C(17)-H(19A)	0.96(2)
C(17)-H(19B)	0.96(2)
C(17)-H(19C)	0.97(2)
C(19)-C(20)	1.483(3)
C(19)-H(20A)	0.984(19)
C(19)-H(20B)	1.05(2)
C(20)-H(16A)	0.97(2)
C(20)-H(16B)	1.02(2)
C(20)-H(16C)	1.00(2)
C(1)-N(1)-C(7)	109.18(11)
C(1)-N(1)-H(3A)	125.4

C(7)-N(1)-H(3A)	125.4
C(18)-O(2)-C(19)	117.50(12)
N(1)-C(1)-C(2)	109.54(12)
N(1)-C(1)-C(9)	127.39(11)
C(2)-C(1)-C(9)	123.06(12)
C(1)-C(2)-C(16)	120.16(12)
C(1)-C(2)-C(8)	106.05(12)
C(16)-C(2)-C(8)	133.66(13)
C(4)-C(3)-C(8)	119.06(19)
C(4)-C(3)-H(21)	120.7(11)
C(8)-C(3)-H(21)	120.3(11)
C(3)-C(4)-C(5)	121.34(19)
C(3)-C(4)-H(23)	117.6(12)
C(5)-C(4)-H(23)	121.0(11)
C(6)-C(5)-C(4)	121.27(17)
C(6)-C(5)-H(22)	117.3(12)
C(4)-C(5)-H(22)	121.3(12)
C(5)-C(6)-C(7)	117.35(18)
C(5)-C(6)-H(15)	122.0(10)
C(7)-C(6)-H(15)	120.6(10)
N(1)-C(7)-C(6)	128.78(15)
N(1)-C(7)-C(8)	108.55(12)
C(6)-C(7)-C(8)	122.65(15)
C(3)-C(8)-C(7)	118.31(14)
C(3)-C(8)-C(2)	135.01(15)
C(7)-C(8)-C(2)	106.66(12)
C(10)-C(9)-C(1)	123.81(12)
C(10)-C(9)-C(14)	119.78(13)
C(1)-C(9)-C(14)	116.41(11)

C(11)-C(10)-C(9)	120.30(14)
C(11)-C(10)-H(13)	120.4(9)
C(9)-C(10)-H(13)	119.3(9)
C(10)-C(11)-C(12)	120.54(14)
C(10)-C(11)-H(18)	118.5(9)
C(12)-C(11)-H(18)	120.9(9)
C(13)-C(12)-C(11)	120.44(15)
C(13)-C(12)-H(17)	119.4(11)
C(11)-C(12)-H(17)	120.2(11)
C(12)-C(13)-C(14)	121.11(14)
C(12)-C(13)-H(9)	118.6(9)
C(14)-C(13)-H(9)	120.3(9)
C(13)-C(14)-C(9)	117.83(12)
C(13)-C(14)-C(15)	122.43(12)
C(9)-C(14)-C(15)	119.74(12)
C(16)-C(15)-C(14)	122.77(12)
C(16)-C(15)-C(18)	119.86(12)
C(14)-C(15)-C(18)	117.27(12)
C(15)-C(16)-C(2)	117.76(12)
C(15)-C(16)-C(17)	122.20(13)
C(2)-C(16)-C(17)	120.02(13)
C(16)-C(17)-H(19A)	115.6(12)
C(16)-C(17)-H(19B)	112.6(13)
H(19A)-C(17)-H(19B)	107.6(18)
C(16)-C(17)-H(19C)	110.9(13)
H(19A)-C(17)-H(19C)	105.7(17)
H(19B)-C(17)-H(19C)	104(2)
O(1)-C(18)-O(2)	123.16(13)
O(1)-C(18)-C(15)	124.23(12)

O(2)-C(18)-C(15)	112.60(11)
O(2)-C(19)-C(20)	110.75(15)
O(2)-C(19)-H(20A)	107.8(11)
C(20)-C(19)-H(20A)	111.8(11)
O(2)-C(19)-H(20B)	100.2(11)
C(20)-C(19)-H(20B)	112.2(11)
H(20A)-C(19)-H(20B)	113.4(16)
C(19)-C(20)-H(16A)	111.7(14)
C(19)-C(20)-H(16B)	109.3(13)
H(16A)-C(20)-H(16B)	109(2)
C(19)-C(20)-H(16C)	111.5(13)
H(16A)-C(20)-H(16C)	106(2)
H(16B)-C(20)-H(16C)	108.9(17)

Table S5. Anisotropic displacement parameters for shelxl.

	U11	U22	U33	U23	U13	U12
N(1)	53(1)	56(1)	36(1)	-1(1)	6(1)	3(1)
O(1)	81(1)	88(1)	41(1)	0(1)	12(1)	31(1)
O(2)	63(1)	58(1)	50(1)	9(1)	9(1)	11(1)
C(1)	43(1)	45(1)	36(1)	-4(1)	7(1)	6(1)
C(2)	42(1)	48(1)	42(1)	-5(1)	7(1)	5(1)
C(3)	56(1)	66(1)	74(1)	-3(1)	10(1)	-10(1)
C(4)	72(1)	74(1)	97(2)	4(1)	18(1)	-19(1)
C(5)	83(1)	66(1)	90(1)	16(1)	32(1)	-7(1)
C(6)	70(1)	65(1)	64(1)	10(1)	22(1)	6(1)
C(7)	51(1)	50(1)	51(1)	1(1)	15(1)	7(1)
C(8)	46(1)	49(1)	53(1)	-2(1)	10(1)	5(1)
C(9)	44(1)	44(1)	39(1)	-7(1)	6(1)	8(1)

C(10)	52(1)	56(1)	40(1)	-9(1)	4(1)	2(1)
C(11)	54(1)	58(1)	54(1)	-15(1)	2(1)	-3(1)
C(12)	57(1)	52(1)	61(1)	-8(1)	10(1)	-6(1)
C(13)	55(1)	48(1)	48(1)	-1(1)	10(1)	2(1)
C(14)	45(1)	41(1)	39(1)	-4(1)	7(1)	7(1)
C(15)	47(1)	46(1)	38(1)	-3(1)	5(1)	8(1)
C(16)	44(1)	50(1)	42(1)	-6(1)	2(1)	6(1)
C(17)	57(1)	73(1)	48(1)	-6(1)	-3(1)	-6(1)
C(18)	47(1)	53(1)	40(1)	-3(1)	2(1)	6(1)
C(19)	65(1)	70(1)	59(1)	19(1)	8(1)	4(1)
C(20)	82(1)	78(1)	60(1)	5(1)	-3(1)	16(1)

Table S6. Hydrogen coordinates and isotropic displacement parameters for shelxl.

	x	y	z	U(eq)
H(3A)	8888	4999	8395	58
H(21)	5270(19)	3983(10)	4170(20)	73(5)
H(23)	4560(20)	3114(12)	5930(20)	84(6)
H(22)	5646(19)	3041(12)	8580(20)	82(5)
H(15)	7420(16)	3858(9)	9460(20)	63(4)
H(13)	10400(15)	5974(9)	8130(20)	57(4)
H(18)	11923(16)	6891(9)	7520(18)	60(4)
H(17)	11820(19)	7329(11)	4880(20)	74(5)
H(9)	10248(14)	6858(9)	2933(19)	55(4)
H(19A)	6443(19)	5166(12)	1180(30)	90(6)
H(19B)	5560(20)	5035(13)	2440(20)	96(7)
H(19C)	6500(20)	4403(13)	2120(20)	86(6)
H(20A)	8557(19)	6872(10)	-790(20)	75(5)
H(20B)	7534(19)	7572(12)	-310(20)	83(6)
H(16A)	5790(20)	6678(14)	-1200(30)	102(7)

H(16B)	6820(20)	6037(14)	-1660(30)	100(7)
H(16C)	6540(20)	6855(13)	-2620(30)	102(7)

Table S7. Bond angles [deg] for shelxl.

Bond	Bond angles [deg]
C(7)-N(1)-C(1)-C(2)	0.67(14)
C(7)-N(1)-C(1)-C(9)	-178.50(12)
N(1)-C(1)-C(2)-C(16)	-176.10(11)
C(9)-C(1)-C(2)-C(16)	3.12(19)
N(1)-C(1)-C(2)-C(8)	0.32(14)
C(9)-C(1)-C(2)-C(8)	179.54(11)
C(8)-C(3)-C(4)-C(5)	0.6(3)
C(3)-C(4)-C(5)-C(6)	0.4(3)
C(4)-C(5)-C(6)-C(7)	-0.5(3)
C(1)-N(1)-C(7)-C(6)	176.90(14)
C(1)-N(1)-C(7)-C(8)	-1.42(14)
C(5)-C(6)-C(7)-N(1)	-178.61(14)
C(5)-C(6)-C(7)-C(8)	-0.5(2)
C(4)-C(3)-C(8)-C(7)	-1.5(2)
C(4)-C(3)-C(8)-C(2)	176.28(16)
N(1)-C(7)-C(8)-C(3)	179.93(13)
C(6)-C(7)-C(8)-C(3)	1.5(2)
N(1)-C(7)-C(8)-C(2)	1.59(14)
C(6)-C(7)-C(8)-C(2)	-176.86(13)
C(1)-C(2)-C(8)-C(3)	-179.10(16)
C(16)-C(2)-C(8)-C(3)	-3.4(3)
C(1)-C(2)-C(8)-C(7)	-1.16(14)
C(16)-C(2)-C(8)-C(7)	174.56(14)
N(1)-C(1)-C(9)-C(10)	-3.2(2)

C(2)-C(1)-C(9)-C(10)	177.68(12)
N(1)-C(1)-C(9)-C(14)	175.96(11)
C(2)-C(1)-C(9)-C(14)	-3.11(18)
C(1)-C(9)-C(10)-C(11)	179.16(12)
C(14)-C(9)-C(10)-C(11)	0.0(2)
C(9)-C(10)-C(11)-C(12)	-0.4(2)
C(10)-C(11)-C(12)-C(13)	0.7(2)
C(11)-C(12)-C(13)-C(14)	-0.6(2)
C(12)-C(13)-C(14)-C(9)	0.11(19)
C(12)-C(13)-C(14)-C(15)	-179.57(13)
C(10)-C(9)-C(14)-C(13)	0.19(18)
C(1)-C(9)-C(14)-C(13)	-179.06(11)
C(10)-C(9)-C(14)-C(15)	179.87(11)
C(1)-C(9)-C(14)-C(15)	0.62(17)
C(13)-C(14)-C(15)-C(16)	-178.42(12)
C(9)-C(14)-C(15)-C(16)	1.91(19)
C(13)-C(14)-C(15)-C(18)	5.08(18)
C(9)-C(14)-C(15)-C(18)	-174.59(11)
C(14)-C(15)-C(16)-C(2)	-1.97(19)
C(18)-C(15)-C(16)-C(2)	174.44(11)
C(14)-C(15)-C(16)-C(17)	179.71(13)
C(18)-C(15)-C(16)-C(17)	-3.9(2)
C(1)-C(2)-C(16)-C(15)	-0.48(19)
C(8)-C(2)-C(16)-C(15)	-175.72(13)
C(1)-C(2)-C(16)-C(17)	177.87(12)
C(8)-C(2)-C(16)-C(17)	2.6(2)
C(19)-O(2)-C(18)-O(1)	1.1(2)
C(19)-O(2)-C(18)-C(15)	179.96(12)
C(16)-C(15)-C(18)-O(1)	-87.88(19)

C(14)-C(15)-C(18)-O(1)	88.72(17)
C(16)-C(15)-C(18)-O(2)	93.24(15)
C(14)-C(15)-C(18)-O(2)	-90.15(15)
C(18)-O(2)-C(19)-C(20)	88.46(18)

8. Single crystal data about 4e

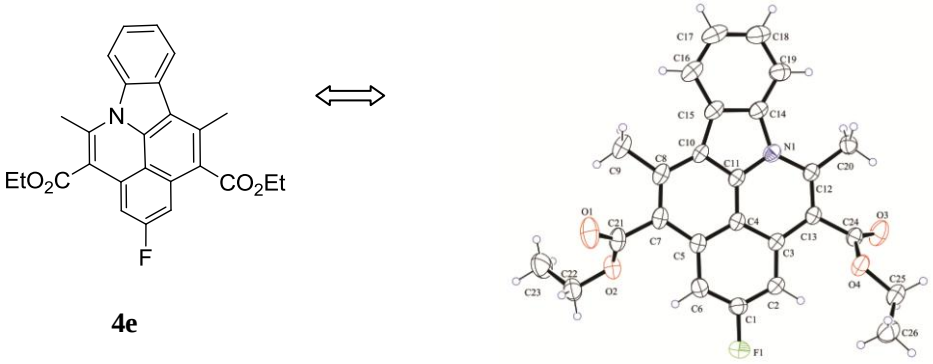


Figure S8. The single crystal structure of **4e** (The ellipsoid contour probability level is 30%)

Table S8. Crystal data and structure refinement for 4e

Identification code	4e
Empirical formula	$C_{26}H_{22}FNO_4$
Formula weight	431.45
Temperature	571(2) K
Wavelength	1.54184 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 12.2335(5) A alpha = 95.978(3) deg.
	b = 13.0790(6) A beta = 106.554(4) deg.
	c = 14.4423(5) A gamma = 105.092(4) deg.
Volume	2098.56(15) A^3
Z, Calculated density	4, 1.366 Mg/m^3
Absorption coefficient	0.808 mm^-1
F(000)	904
Crystal size	0.30 x 0.25 x 0.20 mm

Theta range for data collection	3.25 to 62.84 deg.
Limiting indices	-14<=h<=14, -15<=k<=14, -10<=l<=16
Reflections collected / unique	18225 / 6724 [R(int) = 0.0211]
Completeness to theta = 62.84	99.5 %
Max. and min. transmission	0.8551 and 0.7936
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6724 / 0 / 577
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0631, wR2 = 0.1835
R indices (all data)	R1 = 0.0720, wR2 = 0.1957
Largest diff. peak and hole	0.778 and -0.325 e.A^-3

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 3a. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	6816(3)	-2841(2)	-139(2)	96(1)
O(2)	6337(2)	-2077(2)	1073(2)	72(1)
O(3)	10647(2)	4637(2)	2321(2)	89(1)
O(4)	9362(2)	3974(1)	817(1)	67(1)
O(5)	14479(2)	3344(2)	4324(2)	86(1)
O(6)	14699(2)	2631(2)	5659(2)	88(1)
O(7)	6832(2)	1706(2)	4225(2)	77(1)
O(8)	7398(2)	2739(2)	3213(1)	62(1)
F(1)	5825(1)	1419(1)	729(2)	81(1)
F(2)	11403(2)	5176(1)	4636(1)	77(1)
N(1)	11196(2)	1449(2)	1673(2)	53(1)
N(2)	11304(2)	295(2)	3975(2)	60(1)

C(1)	6894(2)	1213(2)	904(2)	56(1)
C(2)	7898(2)	2095(2)	1185(2)	53(1)
C(3)	9010(2)	1924(2)	1346(2)	45(1)
C(4)	9015(2)	837(2)	1228(2)	45(1)
C(5)	7968(2)	-62(2)	943(2)	49(1)
C(6)	6876(2)	160(2)	772(2)	58(1)
C(7)	8115(3)	-1128(2)	822(2)	54(1)
C(8)	9222(3)	-1279(2)	972(2)	55(1)
C(9)	9411(3)	-2368(2)	900(2)	73(1)
C(10)	10244(2)	-371(2)	1250(2)	46(1)
C(11)	10109(2)	646(2)	1382(2)	46(1)
C(12)	11224(2)	2535(2)	1811(2)	47(1)
C(13)	10153(2)	2760(2)	1630(2)	47(1)
C(14)	12088(2)	915(2)	1726(2)	52(1)
C(15)	11498(3)	-209(2)	1462(2)	55(1)
C(16)	12167(3)	-927(3)	1423(2)	70(1)
C(17)	13374(3)	-515(3)	1646(2)	81(1)
C(18)	13951(3)	585(3)	1917(2)	79(1)
C(19)	13317(3)	1306(3)	1956(2)	67(1)
C(20)	12412(2)	3384(2)	2116(2)	61(1)
C(21)	7042(3)	-2100(2)	520(2)	64(1)
C(22)	5272(3)	-2983(3)	838(3)	81(1)
C(23)	5512(4)	-3854(3)	1355(4)	113(2)
C(24)	10133(2)	3895(2)	1669(2)	52(1)
C(25)	9058(3)	4965(2)	779(3)	79(1)
C(26)	7972(4)	4727(3)	-100(4)	115(2)
C(27)	11165(2)	4085(2)	4464(2)	56(1)
C(28)	12123(2)	3694(2)	4571(2)	56(1)
C(29)	11888(2)	2573(2)	4382(2)	50(1)

C(30)	10680(2)	1928(2)	4099(2)	47(1)
C(31)	9708(2)	2352(2)	4010(2)	47(1)
C(32)	9988(2)	3475(2)	4205(2)	55(1)
C(33)	8527(2)	1583(2)	3764(2)	49(1)
C(34)	8322(2)	485(2)	3585(2)	50(1)
C(35)	7104(3)	-324(2)	3278(2)	64(1)
C(36)	9309(2)	94(2)	3660(1)	42(1)
C(37)	10439(2)	812(2)	3918(2)	48(1)
C(38)	12527(2)	930(2)	4256(2)	54(1)
C(39)	13462(3)	375(3)	4297(2)	69(1)
C(40)	12791(2)	2032(2)	4463(2)	54(1)
C(41)	10677(3)	-832(2)	3738(2)	54(1)
C(42)	9454(3)	-960(2)	3551(2)	54(1)
C(43)	8636(3)	-1991(2)	3329(2)	69(1)
C(44)	9050(4)	-2869(3)	3293(2)	79(1)
C(45)	10247(4)	-2749(3)	3478(2)	79(1)
C(46)	11074(3)	-1745(2)	3698(2)	68(1)
C(47)	14061(2)	2734(2)	4783(2)	62(1)
C(48)	15971(3)	3256(5)	6026(3)	115(2)
C(49)	16539(5)	3032(6)	6945(4)	145(2)
C(50)	7499(2)	1994(2)	3768(2)	53(1)
C(51)	6496(3)	3261(3)	3259(3)	74(1)
C(52)	6410(5)	3947(4)	2545(5)	138(2)

Table S10. Bond lengths [A] and angles [deg] for 3a.

Bond	Lengths [A]
O(1)-C(21)	1.200(3)
O(2)-C(21)	1.335(4)
O(2)-C(22)	1.441(4)

O(3)-C(24)	1.175(3)
O(4)-C(24)	1.353(3)
O(4)-C(25)	1.441(3)
O(5)-C(47)	1.194(3)
O(6)-C(47)	1.326(3)
O(6)-C(48)	1.465(4)
O(7)-C(50)	1.201(3)
O(8)-C(50)	1.333(3)
O(8)-C(51)	1.453(3)
F(1)-C(1)	1.362(3)
F(2)-C(27)	1.360(3)
N(1)-C(11)	1.382(3)
N(1)-C(12)	1.404(3)
N(1)-C(14)	1.430(3)
N(2)-C(37)	1.385(3)
N(2)-C(38)	1.425(4)
N(2)-C(41)	1.426(4)
C(1)-C(6)	1.365(4)
C(1)-C(2)	1.373(4)
C(2)-C(3)	1.394(3)
C(2)-H(2A)	0.9300
C(3)-C(4)	1.415(3)
C(3)-C(13)	1.450(3)
C(4)-C(11)	1.385(3)
C(4)-C(5)	1.417(3)
C(5)-C(6)	1.399(4)
C(5)-C(7)	1.451(3)
C(6)-H(6A)	0.9300
C(7)-C(8)	1.378(4)

C(7)-C(21)	1.490(4)
C(8)-C(10)	1.405(4)
C(8)-C(9)	1.499(4)
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-C(11)	1.384(3)
C(10)-C(15)	1.429(4)
C(12)-C(13)	1.376(3)
C(12)-C(20)	1.495(4)
C(13)-C(24)	1.486(3)
C(14)-C(19)	1.384(4)
C(14)-C(15)	1.415(4)
C(15)-C(16)	1.404(4)
C(16)-C(17)	1.361(5)
C(16)-H(16A)	0.9300
C(17)-C(18)	1.385(5)
C(17)-H(17A)	0.9300
C(18)-C(19)	1.374(4)
C(18)-H(18A)	0.9300
C(19)-H(19A)	0.9300
C(20)-H(20A)	0.9600
C(20)-H(20B)	0.9600
C(20)-H(20C)	0.9600
C(22)-C(23)	1.473(5)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600

C(23)-H(23C)	0.9600
C(25)-C(26)	1.489(5)
C(25)-H(25A)	0.9700
C(25)-H(25B)	0.9700
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
C(27)-C(28)	1.372(4)
C(27)-C(32)	1.372(4)
C(28)-C(29)	1.400(4)
C(28)-H(28A)	0.9300
C(29)-C(30)	1.414(4)
C(29)-C(40)	1.443(3)
C(30)-C(37)	1.391(3)
C(30)-C(31)	1.418(3)
C(31)-C(32)	1.396(4)
C(31)-C(33)	1.450(4)
C(32)-H(32A)	0.9300
C(33)-C(34)	1.375(4)
C(33)-C(50)	1.492(3)
C(34)-C(36)	1.411(3)
C(34)-C(35)	1.497(4)
C(35)-H(35A)	0.9600
C(35)-H(35B)	0.9600
C(35)-H(35C)	0.9600
C(36)-C(37)	1.375(3)
C(36)-C(42)	1.433(3)
C(38)-C(40)	1.373(4)
C(38)-C(39)	1.497(4)

C(39)-H(39A)	0.9600
C(39)-H(39B)	0.9600
C(39)-H(39C)	0.9600
C(40)-C(47)	1.494(4)
C(41)-C(46)	1.402(4)
C(41)-C(42)	1.404(4)
C(42)-C(43)	1.395(4)
C(43)-C(44)	1.372(5)
C(43)-H(43A)	0.9300
C(44)-C(45)	1.374(5)
C(44)-H(44A)	0.9300
C(45)-C(46)	1.375(5)
C(45)-H(45A)	0.9300
C(46)-H(46A)	0.9300
C(48)-C(49)	1.411(6)
C(48)-H(48A)	0.9700
C(48)-H(48B)	0.9700
C(49)-H(49A)	0.9600
C(49)-H(49B)	0.9600
C(49)-H(49C)	0.9600
C(51)-C(52)	1.436(5)
C(51)-H(51A)	0.9700
C(51)-H(51B)	0.9700
C(52)-H(52A)	0.9600
C(52)-H(52B)	0.9600
C(52)-H(52C)	0.9600
C(21)-O(2)-C(22)	117.0(2)
C(24)-O(4)-C(25)	117.6(2)
C(47)-O(6)-C(48)	117.1(3)

C(50)-O(8)-C(51)	116.0(2)
C(11)-N(1)-C(12)	119.5(2)
C(11)-N(1)-C(14)	106.4(2)
C(12)-N(1)-C(14)	134.0(2)
C(37)-N(2)-C(38)	118.9(2)
C(37)-N(2)-C(41)	105.8(2)
C(38)-N(2)-C(41)	135.3(2)
F(1)-C(1)-C(6)	117.7(2)
F(1)-C(1)-C(2)	116.4(2)
C(6)-C(1)-C(2)	125.8(2)
C(1)-C(2)-C(3)	118.4(2)
C(1)-C(2)-H(2A)	120.8
C(3)-C(2)-H(2A)	120.8
C(2)-C(3)-C(4)	116.7(2)
C(2)-C(3)-C(13)	125.6(2)
C(4)-C(3)-C(13)	117.6(2)
C(11)-C(4)-C(3)	117.8(2)
C(11)-C(4)-C(5)	118.3(2)
C(3)-C(4)-C(5)	123.9(2)
C(6)-C(5)-C(4)	116.8(2)
C(6)-C(5)-C(7)	125.7(2)
C(4)-C(5)-C(7)	117.4(2)
C(1)-C(6)-C(5)	118.3(2)
C(1)-C(6)-H(6A)	120.9
C(5)-C(6)-H(6A)	120.9
C(8)-C(7)-C(5)	122.2(2)
C(8)-C(7)-C(21)	118.3(2)
C(5)-C(7)-C(21)	119.5(3)
C(7)-C(8)-C(10)	119.0(2)

C(7)-C(8)-C(9)	123.5(3)
C(10)-C(8)-C(9)	117.4(3)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-C(8)	118.9(2)
C(11)-C(10)-C(15)	106.2(2)
C(8)-C(10)-C(15)	134.9(2)
N(1)-C(11)-C(10)	111.8(2)
N(1)-C(11)-C(4)	124.1(2)
C(10)-C(11)-C(4)	124.1(2)
C(13)-C(12)-N(1)	118.2(2)
C(13)-C(12)-C(20)	123.5(2)
N(1)-C(12)-C(20)	118.3(2)
C(12)-C(13)-C(3)	122.7(2)
C(12)-C(13)-C(24)	119.9(2)
C(3)-C(13)-C(24)	117.3(2)
C(19)-C(14)-C(15)	120.4(2)
C(19)-C(14)-N(1)	132.0(3)
C(15)-C(14)-N(1)	107.7(2)
C(16)-C(15)-C(14)	119.5(3)
C(16)-C(15)-C(10)	132.5(3)
C(14)-C(15)-C(10)	108.0(2)
C(17)-C(16)-C(15)	118.6(3)
C(17)-C(16)-H(16A)	120.7
C(15)-C(16)-H(16A)	120.7

C(16)-C(17)-C(18)	121.7(3)
C(16)-C(17)-H(17A)	119.1
C(18)-C(17)-H(17A)	119.1
C(19)-C(18)-C(17)	120.9(3)
C(19)-C(18)-H(18A)	119.6
C(17)-C(18)-H(18A)	119.6
C(18)-C(19)-C(14)	118.9(3)
C(18)-C(19)-H(19A)	120.6
C(14)-C(19)-H(19A)	120.6
C(12)-C(20)-H(20A)	109.5
C(12)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(12)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(1)-C(21)-O(2)	122.2(3)
O(1)-C(21)-C(7)	125.1(3)
O(2)-C(21)-C(7)	112.8(2)
O(2)-C(22)-C(23)	111.5(3)
O(2)-C(22)-H(22A)	109.3
C(23)-C(22)-H(22A)	109.3
O(2)-C(22)-H(22B)	109.3
C(23)-C(22)-H(22B)	109.3
H(22A)-C(22)-H(22B)	108.0
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5

H(23B)-C(23)-H(23C)	109.5
O(3)-C(24)-O(4)	122.0(2)
O(3)-C(24)-C(13)	128.5(2)
O(4)-C(24)-C(13)	109.4(2)
O(4)-C(25)-C(26)	106.0(3)
O(4)-C(25)-H(25A)	110.5
C(26)-C(25)-H(25A)	110.5
O(4)-C(25)-H(25B)	110.5
C(26)-C(25)-H(25B)	110.5
H(25A)-C(25)-H(25B)	108.7
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
F(2)-C(27)-C(28)	117.2(2)
F(2)-C(27)-C(32)	117.0(2)
C(28)-C(27)-C(32)	125.9(2)
C(27)-C(28)-C(29)	117.7(2)
C(27)-C(28)-H(28A)	121.1
C(29)-C(28)-H(28A)	121.1
C(28)-C(29)-C(30)	117.4(2)
C(28)-C(29)-C(40)	124.7(2)
C(30)-C(29)-C(40)	117.9(2)
C(37)-C(30)-C(29)	117.8(2)
C(37)-C(30)-C(31)	118.4(2)
C(29)-C(30)-C(31)	123.7(2)
C(32)-C(31)-C(30)	116.7(2)

C(32)-C(31)-C(33)	126.2(2)
C(30)-C(31)-C(33)	117.1(2)
C(27)-C(32)-C(31)	118.6(2)
C(27)-C(32)-H(32A)	120.7
C(31)-C(32)-H(32A)	120.7
C(34)-C(33)-C(31)	122.9(2)
C(34)-C(33)-C(50)	118.2(2)
C(31)-C(33)-C(50)	118.8(2)
C(33)-C(34)-C(36)	118.3(2)
C(33)-C(34)-C(35)	123.8(2)
C(36)-C(34)-C(35)	117.8(2)
C(34)-C(35)-H(35A)	109.5
C(34)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(34)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(37)-C(36)-C(34)	119.5(2)
C(37)-C(36)-C(42)	106.1(2)
C(34)-C(36)-C(42)	134.4(2)
C(36)-C(37)-N(2)	112.0(2)
C(36)-C(37)-C(30)	123.7(2)
N(2)-C(37)-C(30)	124.2(2)
C(40)-C(38)-N(2)	118.0(2)
C(40)-C(38)-C(39)	122.9(3)
N(2)-C(38)-C(39)	119.1(2)
C(38)-C(39)-H(39A)	109.5
C(38)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5

C(38)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(38)-C(40)-C(29)	123.2(2)
C(38)-C(40)-C(47)	120.1(2)
C(29)-C(40)-C(47)	116.7(2)
C(46)-C(41)-C(42)	119.7(3)
C(46)-C(41)-N(2)	132.0(3)
C(42)-C(41)-N(2)	108.2(2)
C(43)-C(42)-C(41)	120.2(3)
C(43)-C(42)-C(36)	132.0(3)
C(41)-C(42)-C(36)	107.8(2)
C(44)-C(43)-C(42)	118.8(3)
C(44)-C(43)-H(43A)	120.6
C(42)-C(43)-H(43A)	120.6
C(43)-C(44)-C(45)	121.4(3)
C(43)-C(44)-H(44A)	119.3
C(45)-C(44)-H(44A)	119.3
C(44)-C(45)-C(46)	121.2(3)
C(44)-C(45)-H(45A)	119.4
C(46)-C(45)-H(45A)	119.4
C(45)-C(46)-C(41)	118.7(3)
C(45)-C(46)-H(46A)	120.6
C(41)-C(46)-H(46A)	120.6
O(5)-C(47)-O(6)	122.2(3)
O(5)-C(47)-C(40)	125.1(2)
O(6)-C(47)-C(40)	112.7(2)
C(49)-C(48)-O(6)	110.6(4)
C(49)-C(48)-H(48A)	109.5

O(6)-C(48)-H(48A)	109.5
C(49)-C(48)-H(48B)	109.5
O(6)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	108.1
C(48)-C(49)-H(49A)	109.5
C(48)-C(49)-H(49B)	109.5
H(49A)-C(49)-H(49B)	109.5
C(48)-C(49)-H(49C)	109.5
H(49A)-C(49)-H(49C)	109.5
H(49B)-C(49)-H(49C)	109.5
O(7)-C(50)-O(8)	122.6(2)
O(7)-C(50)-C(33)	124.7(2)
O(8)-C(50)-C(33)	112.8(2)
C(52)-C(51)-O(8)	109.0(3)
C(52)-C(51)-H(51A)	109.9
O(8)-C(51)-H(51A)	109.9
C(52)-C(51)-H(51B)	109.9
O(8)-C(51)-H(51B)	109.9
H(51A)-C(51)-H(51B)	108.3
C(51)-C(52)-H(52A)	109.5
C(51)-C(52)-H(52B)	109.5
H(52A)-C(52)-H(52B)	109.5
C(51)-C(52)-H(52C)	109.5
H(52A)-C(52)-H(52C)	109.5
H(52B)-C(52)-H(52C)	109.5
C(6)-C(5)-C(4)	121.27(17)
C(6)-C(5)-H(22)	117.3(12)
C(4)-C(5)-H(22)	121.3(12)
C(5)-C(6)-C(7)	117.35(18)

C(5)-C(6)-H(15)	122.0(10)
C(7)-C(6)-H(15)	120.6(10)
N(1)-C(7)-C(6)	128.78(15)
N(1)-C(7)-C(8)	108.55(12)
C(6)-C(7)-C(8)	122.65(15)
C(3)-C(8)-C(7)	118.31(14)
C(3)-C(8)-C(2)	135.01(15)
C(7)-C(8)-C(2)	106.66(12)
C(10)-C(9)-C(1)	123.81(12)
C(10)-C(9)-C(14)	119.78(13)
C(1)-C(9)-C(14)	116.41(11)
C(11)-C(10)-C(9)	120.30(14)
C(11)-C(10)-H(13)	120.4(9)
C(9)-C(10)-H(13)	119.3(9)
C(10)-C(11)-C(12)	120.54(14)
C(10)-C(11)-H(18)	118.5(9)
C(12)-C(11)-H(18)	120.9(9)
C(13)-C(12)-C(11)	120.44(15)
C(13)-C(12)-H(17)	119.4(11)
C(11)-C(12)-H(17)	120.2(11)
C(12)-C(13)-C(14)	121.11(14)
C(12)-C(13)-H(9)	118.6(9)
C(14)-C(13)-H(9)	120.3(9)
C(13)-C(14)-C(9)	117.83(12)
C(13)-C(14)-C(15)	122.43(12)
C(9)-C(14)-C(15)	119.74(12)
C(16)-C(15)-C(14)	122.77(12)
C(16)-C(15)-C(18)	119.86(12)
C(14)-C(15)-C(18)	117.27(12)

C(15)-C(16)-C(2)	117.76(12)
C(15)-C(16)-C(17)	122.20(13)
C(2)-C(16)-C(17)	120.02(13)
C(16)-C(17)-H(19A)	115.6(12)
C(16)-C(17)-H(19B)	112.6(13)
H(19A)-C(17)-H(19B)	107.6(18)
C(16)-C(17)-H(19C)	110.9(13)
H(19A)-C(17)-H(19C)	105.7(17)
H(19B)-C(17)-H(19C)	104(2)
O(1)-C(18)-O(2)	123.16(13)
O(1)-C(18)-C(15)	124.23(12)
O(2)-C(18)-C(15)	112.60(11)
O(2)-C(19)-C(20)	110.75(15)
O(2)-C(19)-H(20A)	107.8(11)
C(20)-C(19)-H(20A)	111.8(11)
O(2)-C(19)-H(20B)	100.2(11)
C(20)-C(19)-H(20B)	112.2(11)
H(20A)-C(19)-H(20B)	113.4(16)
C(19)-C(20)-H(16A)	111.7(14)
C(19)-C(20)-H(16B)	109.3(13)
H(16A)-C(20)-H(16B)	109(2)
C(19)-C(20)-H(16C)	111.5(13)
H(16A)-C(20)-H(16C)	106(2)
H(16B)-C(20)-H(16C)	108.9(17)

Table S11. Anisotropic displacement parameters for shelxl.

	U11	U22	U33	U23	U13	U12
O(1)	133(2)	61(1)	72(1)	-15(1)	40(1)	-5(1)
O(2)	82(1)	54(1)	68(1)	6(1)	27(1)	3(1)

O(3)	124(2)	53(1)	75(1)	-1(1)	11(1)	28(1)
O(4)	82(1)	48(1)	71(1)	15(1)	17(1)	26(1)
O(5)	62(1)	123(2)	87(1)	47(1)	31(1)	30(1)
O(6)	65(1)	122(2)	67(1)	30(1)	11(1)	16(1)
O(7)	71(1)	102(2)	86(1)	39(1)	45(1)	43(1)
O(8)	62(1)	72(1)	65(1)	21(1)	25(1)	36(1)
F(1)	55(1)	77(1)	114(1)	22(1)	26(1)	25(1)
F(2)	76(1)	50(1)	101(1)	-2(1)	28(1)	21(1)
N(1)	64(1)	53(1)	49(1)	15(1)	20(1)	25(1)
N(2)	78(2)	65(1)	49(1)	14(1)	22(1)	37(1)
C(1)	53(1)	61(2)	59(1)	16(1)	18(1)	21(1)
C(2)	62(2)	49(1)	55(1)	12(1)	22(1)	23(1)
C(3)	57(1)	44(1)	39(1)	10(1)	18(1)	20(1)
C(4)	58(1)	43(1)	36(1)	10(1)	16(1)	17(1)
C(5)	63(1)	46(1)	37(1)	10(1)	15(1)	16(1)
C(6)	58(2)	54(2)	53(1)	12(1)	13(1)	9(1)
C(7)	79(2)	42(1)	40(1)	9(1)	18(1)	14(1)
C(8)	84(2)	45(1)	39(1)	11(1)	20(1)	25(1)
C(9)	110(2)	50(2)	68(2)	14(1)	28(2)	36(2)
C(10)	67(2)	40(1)	38(1)	11(1)	19(1)	25(1)
C(11)	60(1)	44(1)	37(1)	12(1)	17(1)	21(1)
C(12)	58(1)	47(1)	40(1)	13(1)	18(1)	19(1)
C(13)	59(1)	43(1)	40(1)	10(1)	17(1)	18(1)
C(14)	66(2)	59(2)	44(1)	19(1)	23(1)	32(1)
C(15)	77(2)	59(2)	44(1)	17(1)	25(1)	37(1)
C(16)	101(2)	71(2)	64(2)	22(1)	35(2)	53(2)
C(17)	100(3)	104(3)	75(2)	33(2)	43(2)	71(2)
C(18)	79(2)	104(3)	80(2)	33(2)	39(2)	51(2)
C(19)	64(2)	84(2)	68(2)	27(1)	26(1)	34(2)

C(20)	60(2)	58(2)	64(2)	16(1)	21(1)	16(1)
C(21)	89(2)	46(1)	46(1)	9(1)	17(1)	12(1)
C(22)	77(2)	60(2)	93(2)	15(2)	22(2)	7(2)
C(23)	94(3)	90(3)	142(4)	58(3)	23(2)	8(2)
C(24)	62(1)	46(1)	47(1)	7(1)	17(1)	17(1)
C(25)	87(2)	54(2)	99(2)	22(2)	26(2)	30(2)
C(26)	87(3)	82(2)	154(4)	40(3)	-3(3)	30(2)
C(27)	66(2)	47(1)	59(1)	4(1)	23(1)	22(1)
C(28)	55(1)	59(2)	54(1)	5(1)	20(1)	18(1)
C(29)	55(1)	59(1)	41(1)	11(1)	19(1)	25(1)
C(30)	56(1)	55(1)	37(1)	8(1)	17(1)	24(1)
C(31)	55(1)	55(1)	38(1)	9(1)	18(1)	24(1)
C(32)	58(2)	58(2)	54(1)	7(1)	21(1)	27(1)
C(33)	54(1)	60(1)	39(1)	10(1)	16(1)	23(1)
C(34)	62(1)	56(1)	36(1)	12(1)	17(1)	22(1)
C(35)	67(2)	64(2)	56(2)	7(1)	18(1)	14(1)
C(36)	52(1)	45(1)	32(1)	8(1)	14(1)	20(1)
C(37)	61(1)	54(1)	36(1)	11(1)	18(1)	26(1)
C(38)	61(2)	69(2)	44(1)	16(1)	21(1)	34(1)
C(39)	80(2)	83(2)	66(2)	22(1)	31(1)	49(2)
C(40)	58(1)	68(2)	44(1)	13(1)	20(1)	29(1)
C(41)	76(2)	56(2)	38(1)	11(1)	17(1)	30(1)
C(42)	77(2)	54(1)	35(1)	9(1)	17(1)	26(1)
C(43)	88(2)	60(2)	53(1)	11(1)	19(1)	17(2)
C(44)	117(3)	53(2)	61(2)	10(1)	23(2)	21(2)
C(45)	127(3)	59(2)	60(2)	14(1)	25(2)	47(2)
C(46)	97(2)	64(2)	53(1)	14(1)	21(1)	44(2)
C(47)	58(2)	80(2)	58(2)	18(1)	23(1)	34(1)
C(48)	67(2)	167(4)	91(3)	40(3)	12(2)	9(2)

C(49)	94(3)	196(6)	121(4)	27(4)	8(3)	36(3)
C(50)	52(1)	62(2)	48(1)	10(1)	16(1)	21(1)
C(51)	63(2)	77(2)	89(2)	11(2)	20(2)	37(2)
C(52)	171(5)	132(4)	198(5)	98(4)	103(4)	114(4)

Table S12. Hydrogen coordinates and isotropic displacement parameters for shelxl.

	x	y	z	U(eq)
H(2A)	7838	2791	1265	64
H(6A)	6157	-397	572	69
H(9A)	8651	-2918	705	110
H(9B)	9901	-2431	1529	110
H(9C)	9801	-2453	420	110
H(16A)	11794	-1668	1248	85
H(17A)	13823	-985	1617	97
H(18A)	14779	839	2075	94
H(19A)	13708	2044	2133	80
H(20A)	12300	4085	2183	92
H(20B)	12792	3310	1627	92
H(20C)	12908	3304	2735	92
H(22A)	4970	-3256	133	97
H(22B)	4661	-2747	1022	97
H(23A)	4787	-4444	1185	170
H(23B)	5799	-3589	2053	170
H(23C)	6106	-4097	1165	170
H(25A)	9710	5532	717	94
H(25B)	8892	5196	1372	94
H(26A)	7728	5364	-159	172
H(26B)	7337	4162	-29	172
H(26C)	8150	4500	-679	172

H(28A)	12901	4158	4762	67
H(32A)	9390	3802	4161	66
H(35A)	6516	45	3254	97
H(35B)	7078	-794	3744	97
H(35C)	6936	-741	2638	97
H(39A)	14237	904	4497	104
H(39B)	13305	-38	3658	104
H(39C)	13444	-98	4762	104
H(43A)	7825	-2082	3208	83
H(44A)	8510	-3559	3141	95
H(45A)	10501	-3359	3453	95
H(46A)	11882	-1671	3818	82
H(48A)	16355	3077	5557	139
H(48B)	16052	4020	6095	139
H(49A)	17370	3446	7174	217
H(49B)	16467	2277	6875	217
H(49C)	16166	3220	7412	217
H(51A)	5729	2720	3124	89
H(51B)	6715	3685	3913	89
H(52A)	5815	4294	2571	208
H(52B)	6189	3522	1899	208
H(52C)	7170	4485	2687	208

Table S13. Bond angles [deg] for shelxl.

Bond	Bond angles [deg]
F(1)-C(1)-C(2)-C(3)	-178.3(2)
C(6)-C(1)-C(2)-C(3)	0.5(4)
C(1)-C(2)-C(3)-C(4)	-1.5(3)

C(1)-C(2)-C(3)-C(13)	179.1(2)
C(2)-C(3)-C(4)-C(11)	179.86(19)
C(13)-C(3)-C(4)-C(11)	-0.6(3)
C(2)-C(3)-C(4)-C(5)	1.2(3)
C(13)-C(3)-C(4)-C(5)	-179.32(19)
C(11)-C(4)-C(5)-C(6)	-178.6(2)
C(3)-C(4)-C(5)-C(6)	0.1(3)
C(11)-C(4)-C(5)-C(7)	-0.7(3)
C(3)-C(4)-C(5)-C(7)	178.0(2)
F(1)-C(1)-C(6)-C(5)	179.6(2)
C(2)-C(1)-C(6)-C(5)	0.8(4)
C(4)-C(5)-C(6)-C(1)	-1.1(3)
C(7)-C(5)-C(6)-C(1)	-178.8(2)
C(6)-C(5)-C(7)-C(8)	177.6(2)
C(4)-C(5)-C(7)-C(8)	-0.1(3)
C(6)-C(5)-C(7)-C(21)	-2.2(4)
C(4)-C(5)-C(7)-C(21)	-179.8(2)
C(5)-C(7)-C(8)-C(10)	-0.1(3)
C(21)-C(7)-C(8)-C(10)	179.6(2)
C(5)-C(7)-C(8)-C(9)	176.9(2)
C(21)-C(7)-C(8)-C(9)	-3.3(4)
C(7)-C(8)-C(10)-C(11)	1.1(3)
C(9)-C(8)-C(10)-C(11)	-176.1(2)
C(7)-C(8)-C(10)-C(15)	-179.7(2)
C(9)-C(8)-C(10)-C(15)	3.0(4)
C(12)-N(1)-C(11)-C(10)	177.98(18)
C(14)-N(1)-C(11)-C(10)	0.4(2)
C(12)-N(1)-C(11)-C(4)	-1.2(3)
C(14)-N(1)-C(11)-C(4)	-178.8(2)

C(8)-C(10)-C(11)-N(1)	178.79(18)
C(15)-C(10)-C(11)-N(1)	-0.6(2)
C(8)-C(10)-C(11)-C(4)	-2.0(3)
C(15)-C(10)-C(11)-C(4)	178.6(2)
C(3)-C(4)-C(11)-N(1)	2.1(3)
C(5)-C(4)-C(11)-N(1)	-179.11(19)
C(3)-C(4)-C(11)-C(10)	-176.98(19)
C(5)-C(4)-C(11)-C(10)	1.8(3)
C(11)-N(1)-C(12)-C(13)	-1.2(3)
C(14)-N(1)-C(12)-C(13)	175.5(2)
C(11)-N(1)-C(12)-C(20)	-179.4(2)
C(14)-N(1)-C(12)-C(20)	-2.7(4)
N(1)-C(12)-C(13)-C(3)	2.7(3)
C(20)-C(12)-C(13)-C(3)	-179.2(2)
N(1)-C(12)-C(13)-C(24)	-173.89(19)
C(20)-C(12)-C(13)-C(24)	4.2(3)
C(2)-C(3)-C(13)-C(12)	177.7(2)
C(4)-C(3)-C(13)-C(12)	-1.8(3)
C(2)-C(3)-C(13)-C(24)	-5.6(3)
C(4)-C(3)-C(13)-C(24)	174.89(19)
C(11)-N(1)-C(14)-C(19)	178.5(3)
C(12)-N(1)-C(14)-C(19)	1.4(4)
C(11)-N(1)-C(14)-C(15)	-0.1(2)
C(12)-N(1)-C(14)-C(15)	-177.1(2)
C(19)-C(14)-C(15)-C(16)	-0.7(4)
N(1)-C(14)-C(15)-C(16)	178.0(2)
C(19)-C(14)-C(15)-C(10)	-179.0(2)
N(1)-C(14)-C(15)-C(10)	-0.3(2)
C(11)-C(10)-C(15)-C(16)	-177.5(3)

C(8)-C(10)-C(15)-C(16)	3.3(5)
C(11)-C(10)-C(15)-C(14)	0.6(2)
C(8)-C(10)-C(15)-C(14)	-178.7(2)
C(14)-C(15)-C(16)-C(17)	0.3(4)
C(10)-C(15)-C(16)-C(17)	178.1(3)
C(15)-C(16)-C(17)-C(18)	0.6(4)
C(16)-C(17)-C(18)-C(19)	-1.0(5)
C(17)-C(18)-C(19)-C(14)	0.5(4)
C(15)-C(14)-C(19)-C(18)	0.3(4)
N(1)-C(14)-C(19)-C(18)	-178.0(3)
C(22)-O(2)-C(21)-O(1)	-0.7(4)
C(22)-O(2)-C(21)-C(7)	179.9(2)
C(8)-C(7)-C(21)-O(1)	-49.5(4)
C(5)-C(7)-C(21)-O(1)	130.2(3)
C(8)-C(7)-C(21)-O(2)	129.8(3)
C(5)-C(7)-C(21)-O(2)	-50.4(3)
C(21)-O(2)-C(22)-C(23)	87.6(4)
C(25)-O(4)-C(24)-O(3)	-8.5(4)
C(25)-O(4)-C(24)-C(13)	169.2(2)
C(12)-C(13)-C(24)-O(3)	-56.3(4)
C(3)-C(13)-C(24)-O(3)	126.9(3)
C(12)-C(13)-C(24)-O(4)	126.1(2)
C(3)-C(13)-C(24)-O(4)	-50.6(3)
C(24)-O(4)-C(25)-C(26)	-164.3(3)
F(2)-C(27)-C(28)-C(29)	-179.1(2)
C(32)-C(27)-C(28)-C(29)	1.3(4)
C(27)-C(28)-C(29)-C(30)	-0.2(3)
C(27)-C(28)-C(29)-C(40)	-179.8(2)
C(28)-C(29)-C(30)-C(37)	-179.5(2)

C(40)-C(29)-C(30)-C(37)	0.1(3)
C(28)-C(29)-C(30)-C(31)	-0.8(3)
C(40)-C(29)-C(30)-C(31)	178.7(2)
C(37)-C(30)-C(31)-C(32)	179.5(2)
C(29)-C(30)-C(31)-C(32)	0.9(3)
C(37)-C(30)-C(31)-C(33)	1.9(3)
C(29)-C(30)-C(31)-C(33)	-176.8(2)
F(2)-C(27)-C(32)-C(31)	179.1(2)
C(28)-C(27)-C(32)-C(31)	-1.3(4)
C(30)-C(31)-C(32)-C(27)	0.1(3)
C(33)-C(31)-C(32)-C(27)	177.5(2)
C(32)-C(31)-C(33)-C(34)	-179.7(2)
C(30)-C(31)-C(33)-C(34)	-2.3(3)
C(32)-C(31)-C(33)-C(50)	-3.8(3)
C(30)-C(31)-C(33)-C(50)	173.62(19)
C(31)-C(33)-C(34)-C(36)	1.0(3)
C(50)-C(33)-C(34)-C(36)	-174.92(19)
C(31)-C(33)-C(34)-C(35)	-176.6(2)
C(50)-C(33)-C(34)-C(35)	7.4(3)
C(33)-C(34)-C(36)-C(37)	0.7(3)
C(35)-C(34)-C(36)-C(37)	178.5(2)
C(33)-C(34)-C(36)-C(42)	178.6(2)
C(35)-C(34)-C(36)-C(42)	-3.6(4)
C(34)-C(36)-C(37)-N(2)	178.90(19)
C(42)-C(36)-C(37)-N(2)	0.4(2)
C(34)-C(36)-C(37)-C(30)	-1.1(3)
C(42)-C(36)-C(37)-C(30)	-179.5(2)
C(38)-N(2)-C(37)-C(36)	-178.65(19)
C(41)-N(2)-C(37)-C(36)	-0.1(2)

C(38)-N(2)-C(37)-C(30)	1.3(3)
C(41)-N(2)-C(37)-C(30)	179.9(2)
C(29)-C(30)-C(37)-C(36)	178.44(19)
C(31)-C(30)-C(37)-C(36)	-0.3(3)
C(29)-C(30)-C(37)-N(2)	-1.5(3)
C(31)-C(30)-C(37)-N(2)	179.8(2)
C(37)-N(2)-C(38)-C(40)	0.4(3)
C(41)-N(2)-C(38)-C(40)	-177.7(2)
C(37)-N(2)-C(38)-C(39)	-178.6(2)
C(41)-N(2)-C(38)-C(39)	3.3(4)
N(2)-C(38)-C(40)-C(29)	-1.8(3)
C(39)-C(38)-C(40)-C(29)	177.1(2)
N(2)-C(38)-C(40)-C(47)	178.6(2)
C(39)-C(38)-C(40)-C(47)	-2.4(4)
C(28)-C(29)-C(40)-C(38)	-178.9(2)
C(30)-C(29)-C(40)-C(38)	1.6(3)
C(28)-C(29)-C(40)-C(47)	0.7(3)
C(30)-C(29)-C(40)-C(47)	-178.8(2)
C(37)-N(2)-C(41)-C(46)	-178.3(3)
C(38)-N(2)-C(41)-C(46)	-0.1(5)
C(37)-N(2)-C(41)-C(42)	-0.3(2)
C(38)-N(2)-C(41)-C(42)	177.9(2)
C(46)-C(41)-C(42)-C(43)	0.3(3)
N(2)-C(41)-C(42)-C(43)	-178.0(2)
C(46)-C(41)-C(42)-C(36)	178.9(2)
N(2)-C(41)-C(42)-C(36)	0.6(2)
C(37)-C(36)-C(42)-C(43)	177.7(2)
C(34)-C(36)-C(42)-C(43)	-0.4(4)
C(37)-C(36)-C(42)-C(41)	-0.6(2)

C(34)-C(36)-C(42)-C(41)	-178.8(2)
C(41)-C(42)-C(43)-C(44)	-0.4(4)
C(36)-C(42)-C(43)-C(44)	-178.6(2)
C(42)-C(43)-C(44)-C(45)	0.5(4)
C(43)-C(44)-C(45)-C(46)	-0.5(5)
C(44)-C(45)-C(46)-C(41)	0.4(4)
C(42)-C(41)-C(46)-C(45)	-0.2(4)
N(2)-C(41)-C(46)-C(45)	177.5(2)
C(48)-O(6)-C(47)-O(5)	-3.4(5)
C(48)-O(6)-C(47)-C(40)	177.8(3)
C(38)-C(40)-C(47)-O(5)	114.3(3)
C(29)-C(40)-C(47)-O(5)	-65.3(4)
C(38)-C(40)-C(47)-O(6)	-67.0(3)
C(29)-C(40)-C(47)-O(6)	113.4(3)
C(47)-O(6)-C(48)-C(49)	-177.8(4)
C(51)-O(8)-C(50)-O(7)	5.4(4)
C(51)-O(8)-C(50)-C(33)	-173.8(2)
C(34)-C(33)-C(50)-O(7)	50.2(4)
C(31)-C(33)-C(50)-O(7)	-125.9(3)
C(34)-C(33)-C(50)-O(8)	-130.6(2)
C(31)-C(33)-C(50)-O(8)	53.3(3)
C(50)-O(8)-C(51)-C(52)	-173.7(4)
C(8)-C(2)-C(16)-C(17)	2.6(2)
C(19)-O(2)-C(18)-O(1)	1.1(2)
C(19)-O(2)-C(18)-C(15)	179.96(12)
C(16)-C(15)-C(18)-O(1)	-87.88(19)
C(14)-C(15)-C(18)-O(1)	88.72(17)
C(16)-C(15)-C(18)-O(2)	93.24(15)
C(14)-C(15)-C(18)-O(2)	-90.15(15)

C(18)-O(2)-C(19)-C(20)	88.46(18)

9. References

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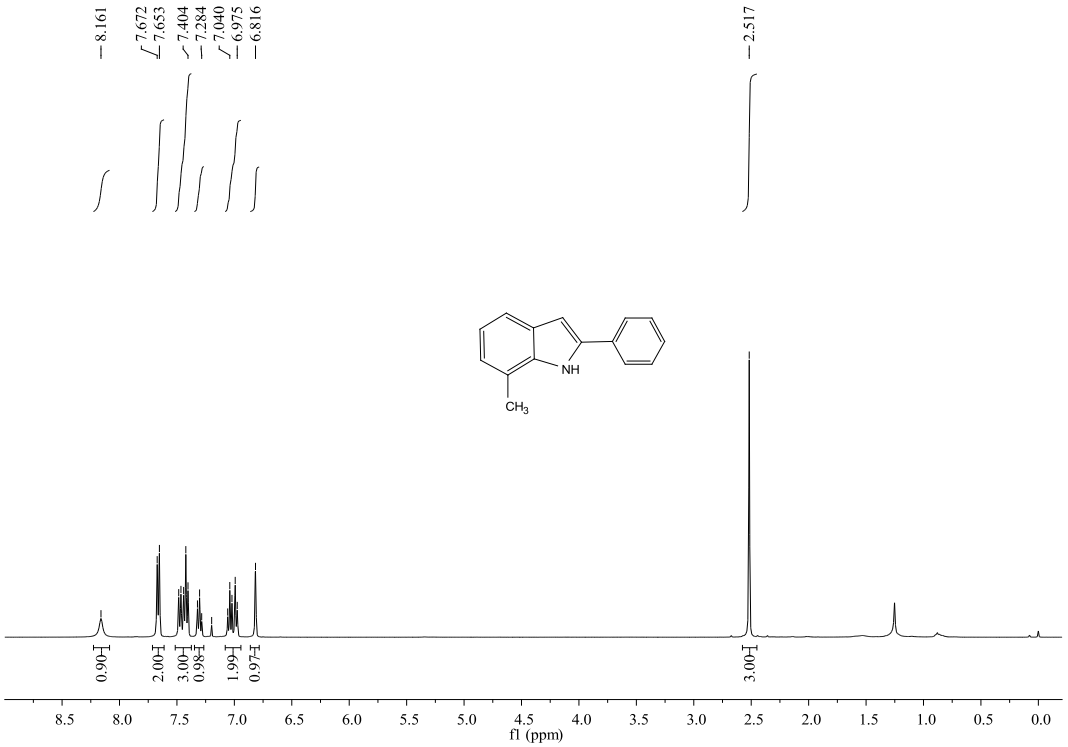
2 a) X. Chen, Y. Xie, X. Xiao, G. Li, Y. Deng, H. Jiang and W. Zeng, *Chem. Commun.*, 2015, **51**, 15328; b) R. Pasceri, H. E. Bartrum, C. J. Hayes and C. J. Moody, *Chem. Commun.*, 2012, **48**, 12077.

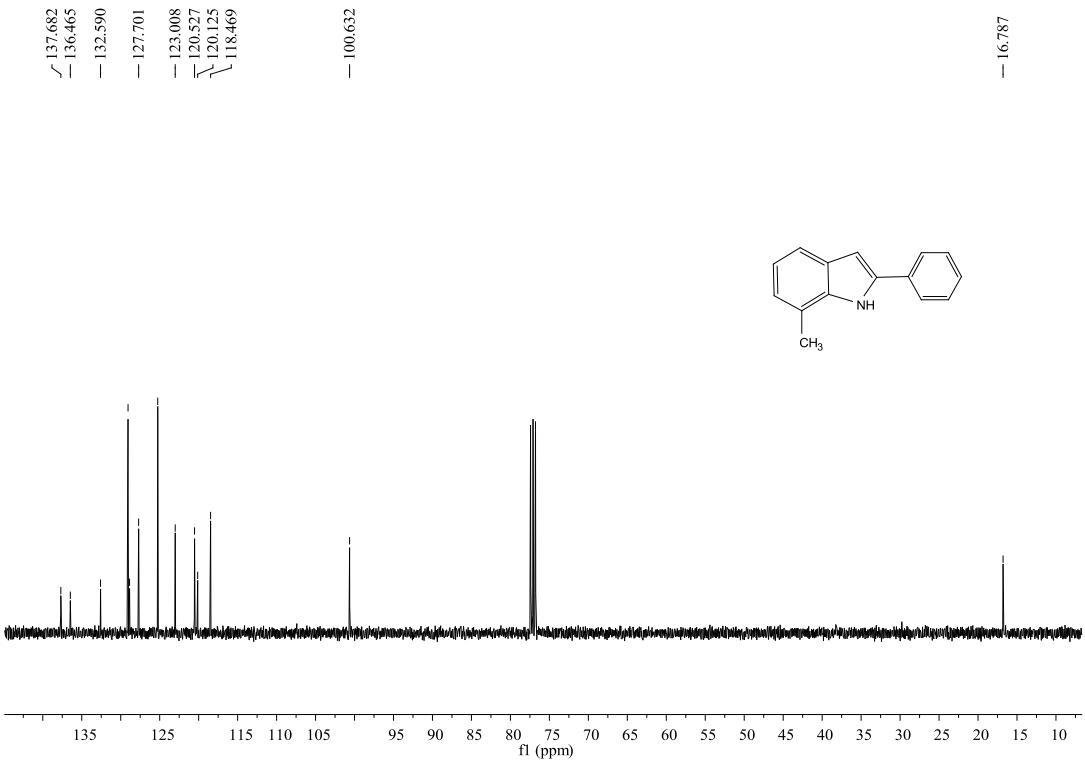
3 a) S. S. Li, Y. Q. Xia, F. Z. Hu, C. F. Liu, F. Su and L. Dong, *Chem. Asian J.*, 2016, **11**, 3165; b) B. Li, B. Zhang, X. Zhang, X. Fan, *Chem. Commun*. 2017, **53**, 1297.

4 V. Pirovano, D. Facoetti, M. Dell'Acqua, E. Della Fontana, G. Abbiati and E. Rossi, *Org. Lett.*, 2013, **15**, 3812.

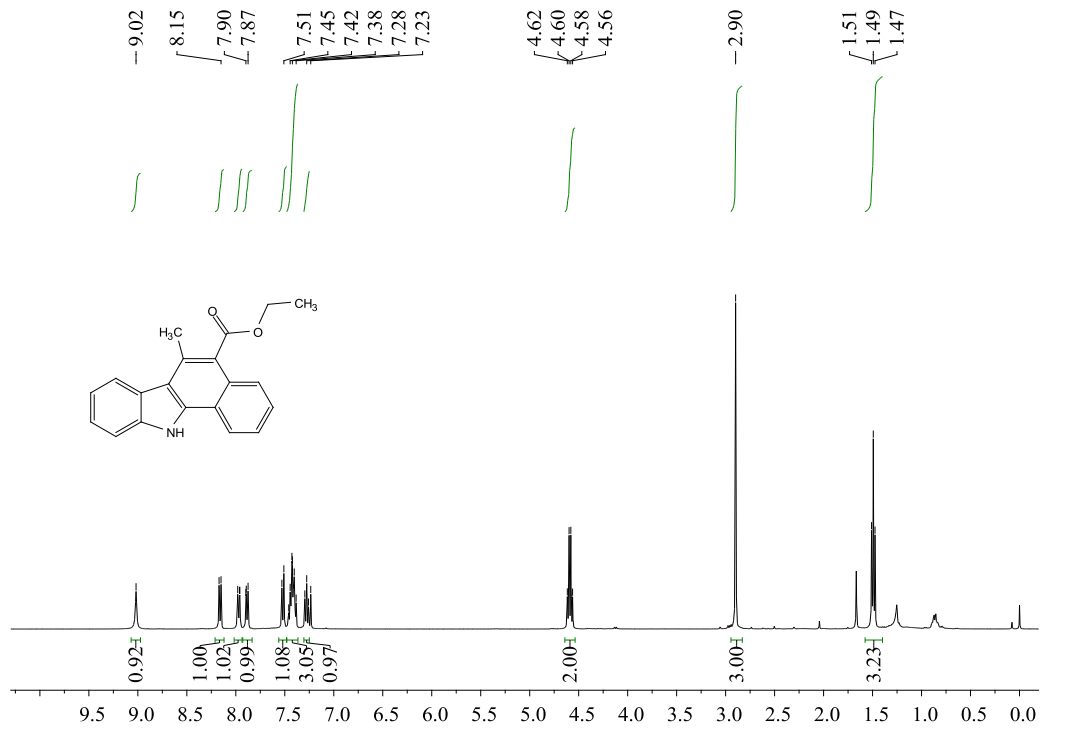
10. ^{1}H NMR and ^{13}C NMR spectrum for all isolated products.

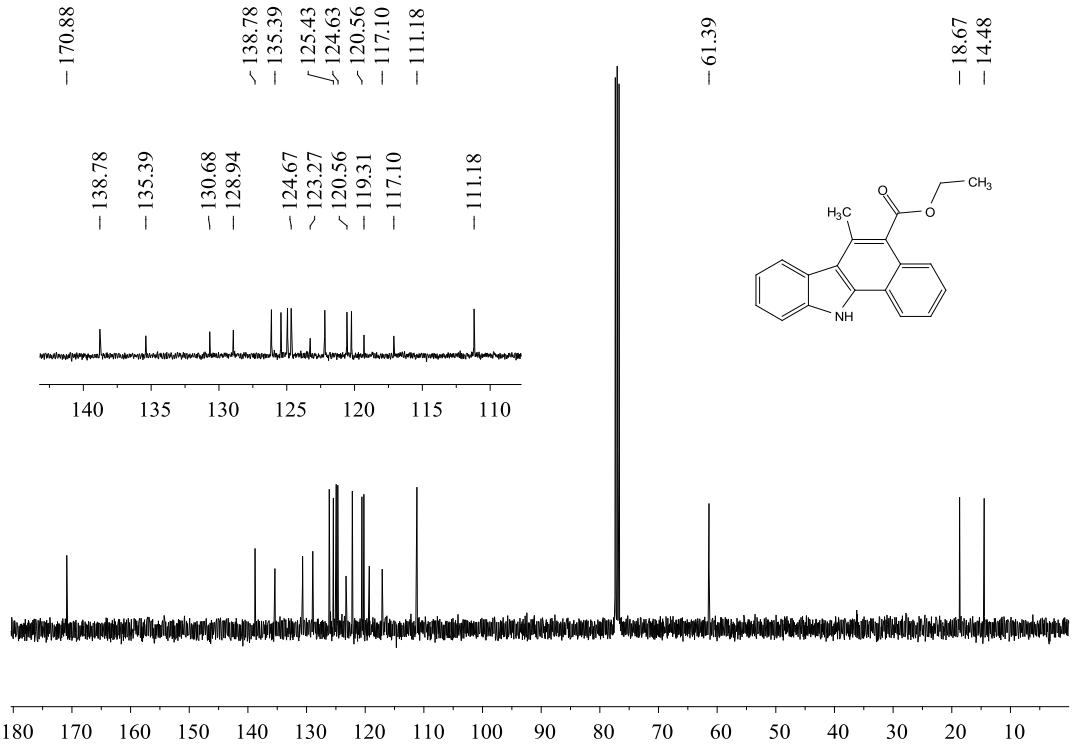
1) 7-Methyl-2-phenyl-1H-indole (**2k**) (Using $CDCl_3$ as solvent)



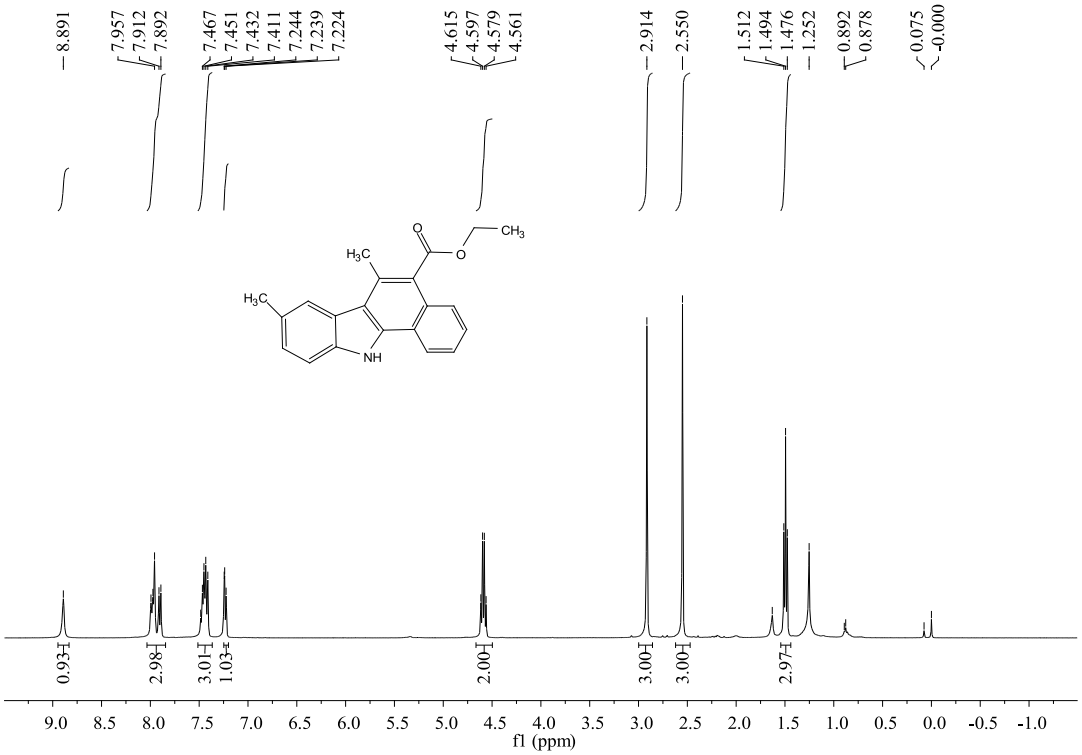


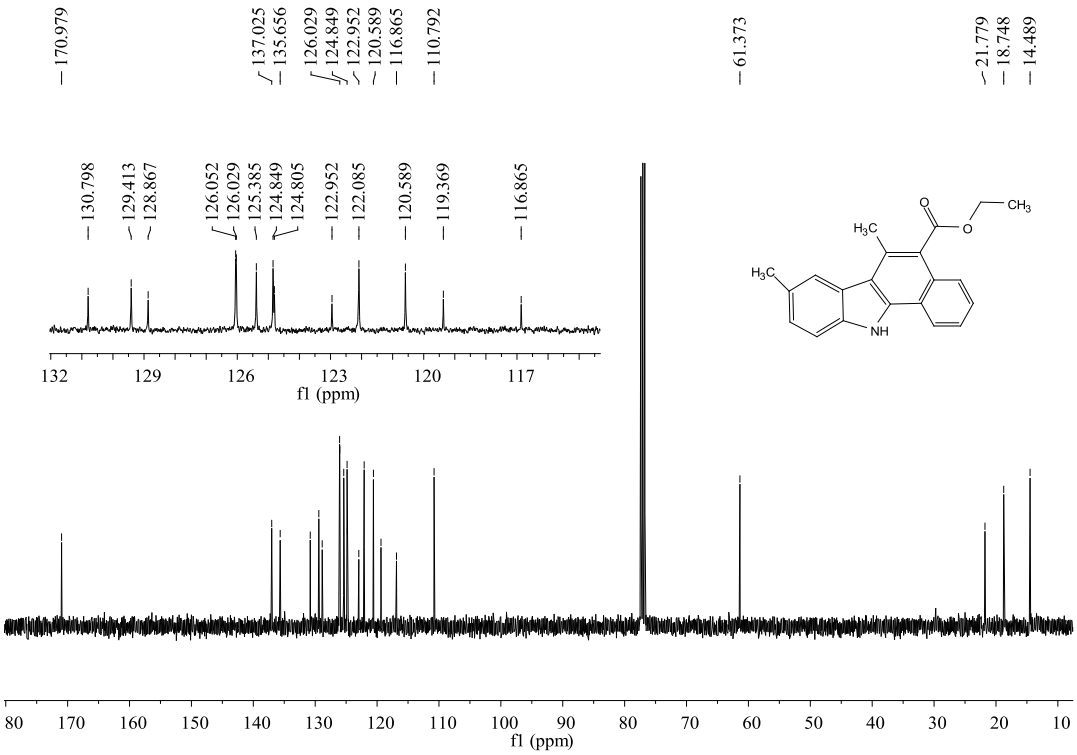
2) Ethyl 6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3a**) (Using $CDCl_3$ as solvent)



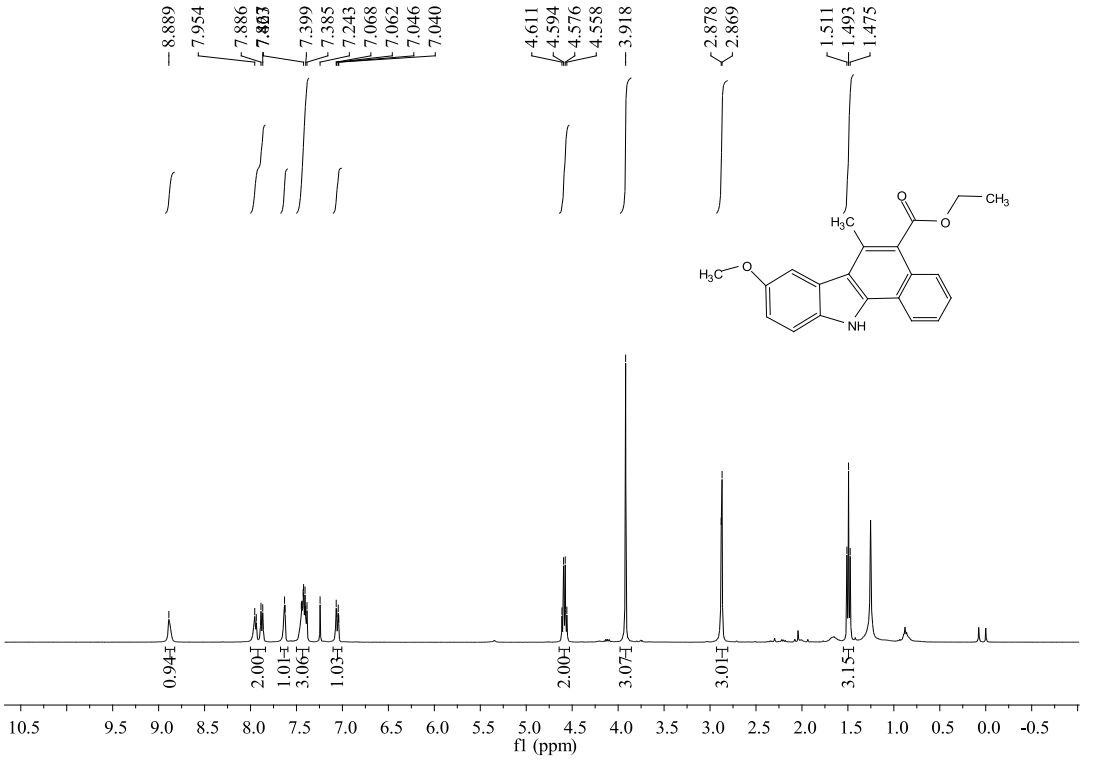


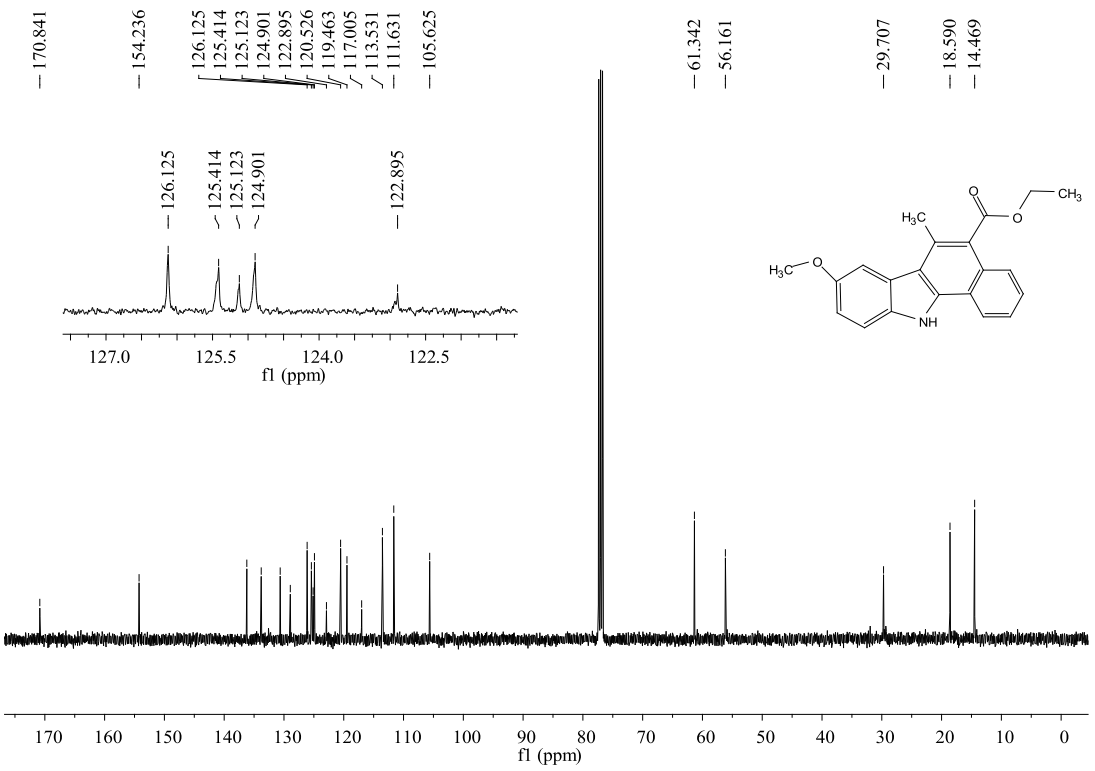
3) Ethyl 6,8-dimethyl-11H-benzo[a]carbazole-5-carboxylate (**3b**) (Using $CDCl_3$ as solvent)



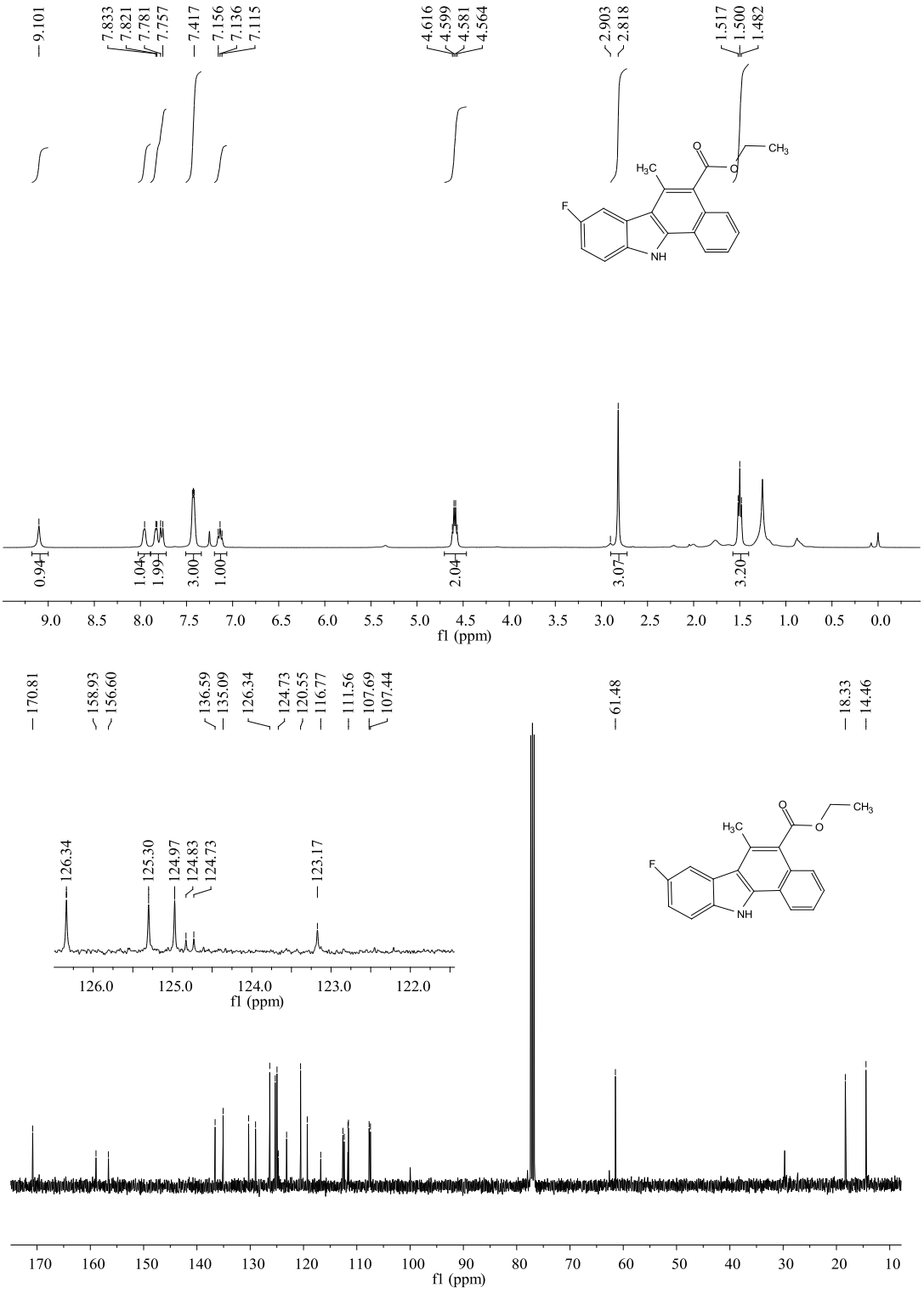


4) Ethyl 8-methoxy-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3c**) (Using $CDCl_3$ as solvent)



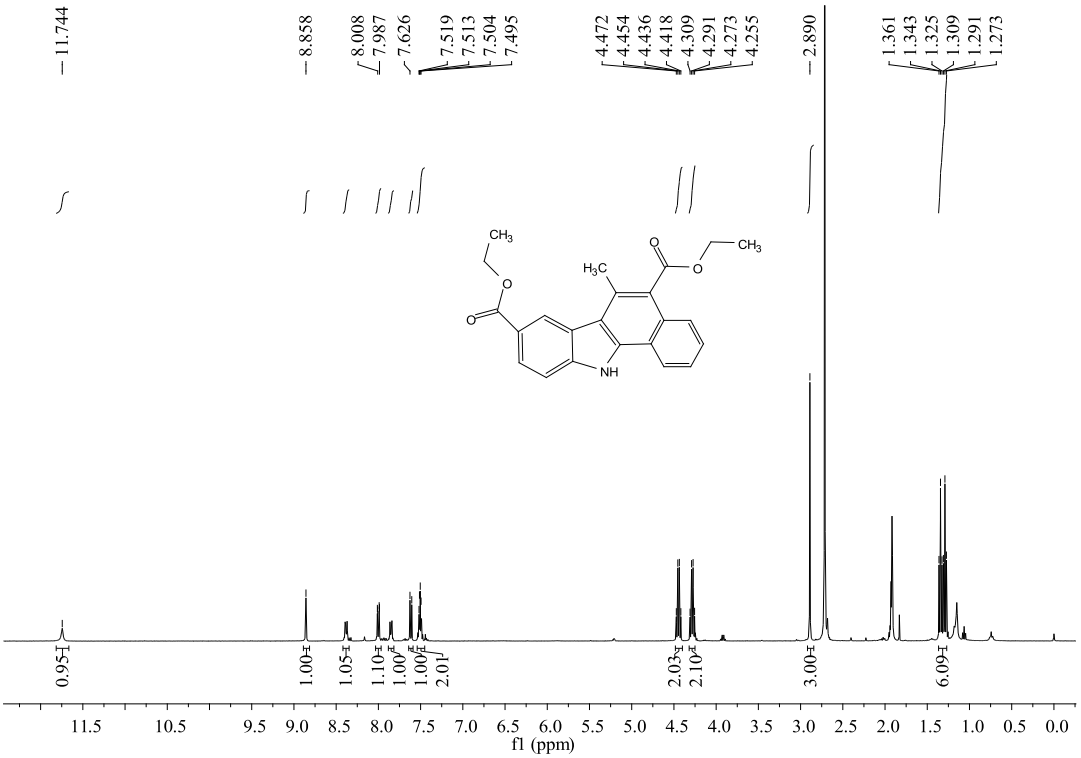


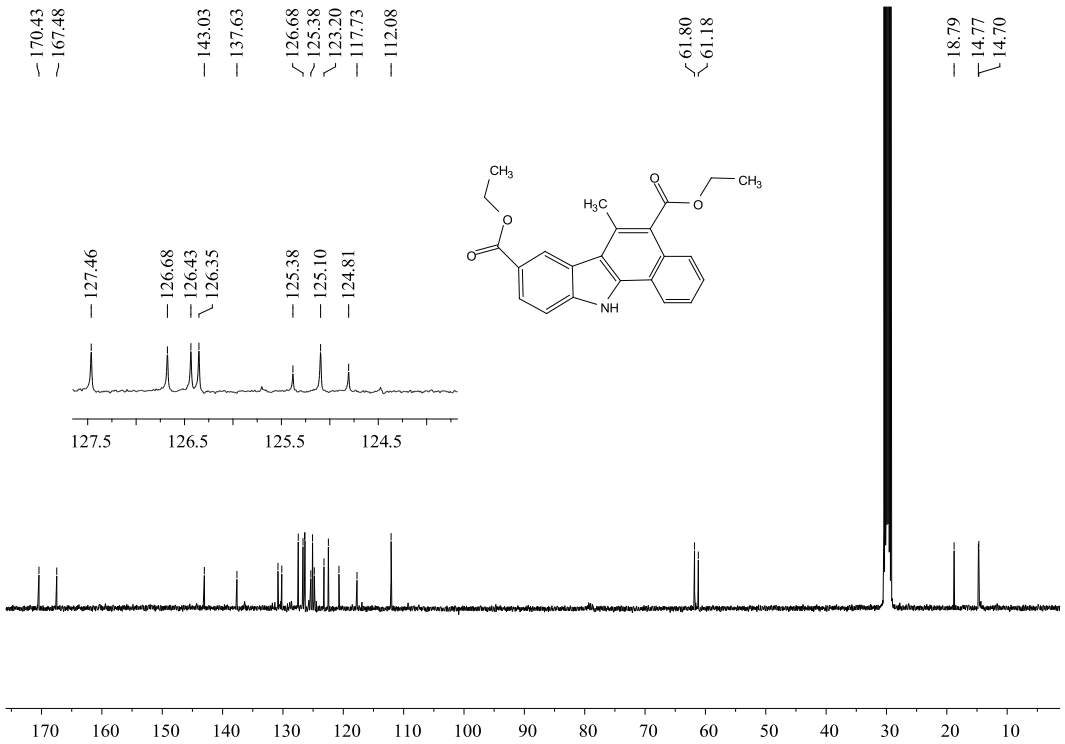
5) Ethyl 8-fluoro-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3d**) (Using $CDCl_3$ as solvent)



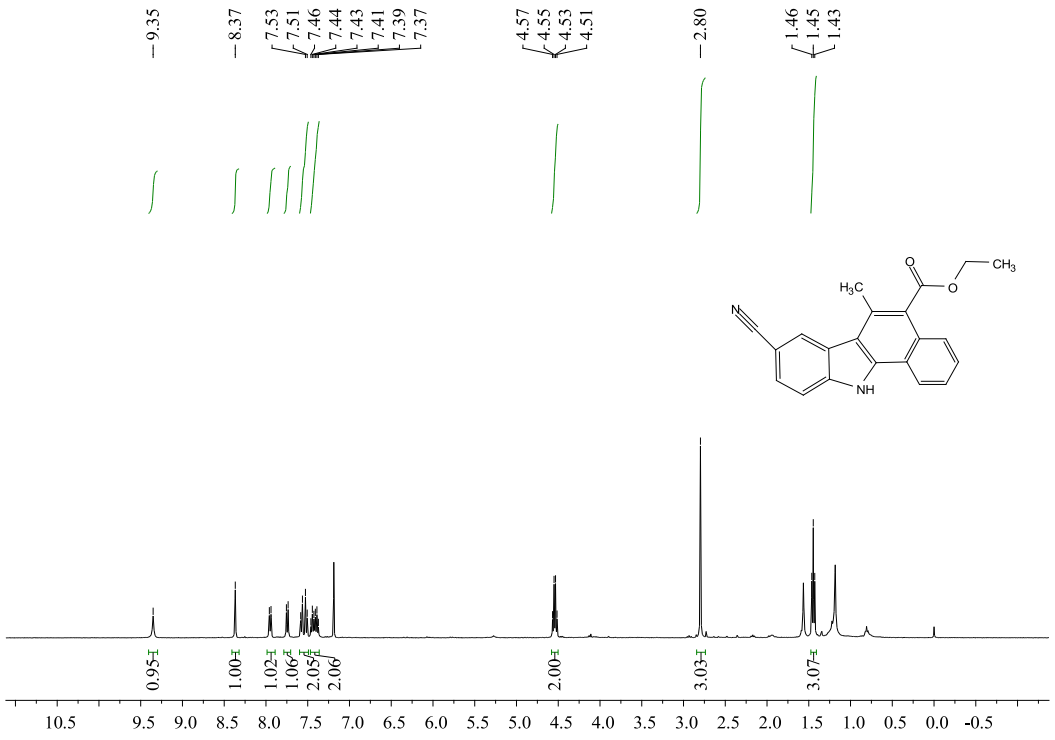
6) Ethyl 8-chloro-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3e**) (Using $CDCl_3$ as solvent)

7) Diethyl 6-methyl-11H-benzo[a]carbazole-5,8-dicarboxylate (**3f**) (Using $(CD_3)_2CO$ as solvent)

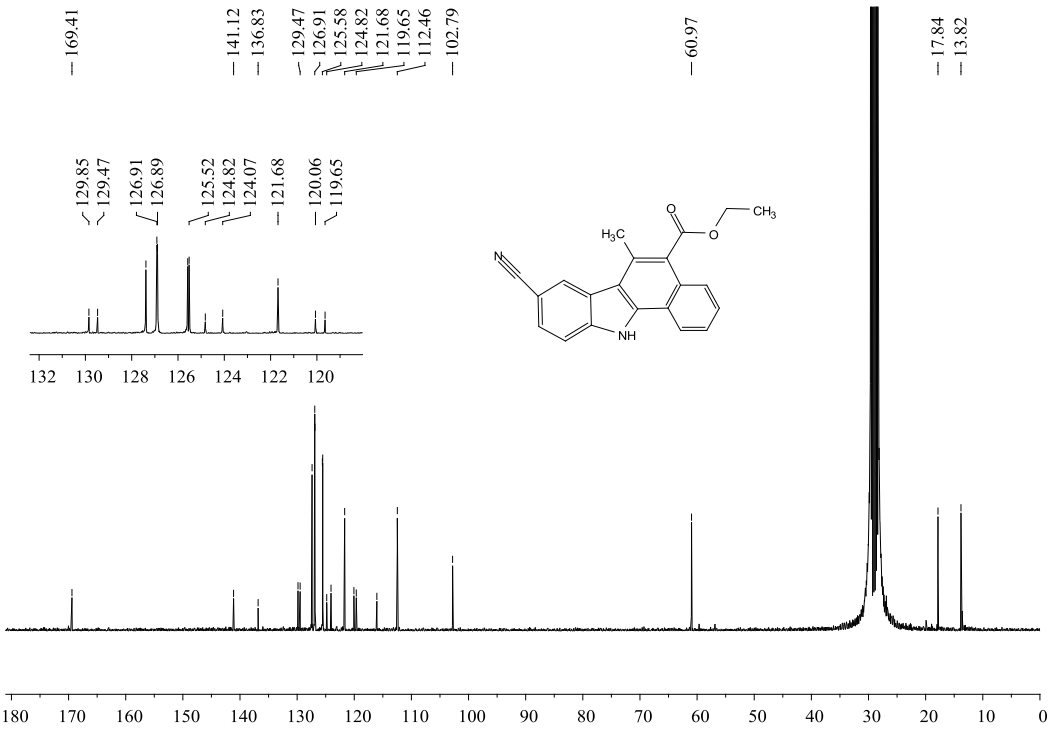




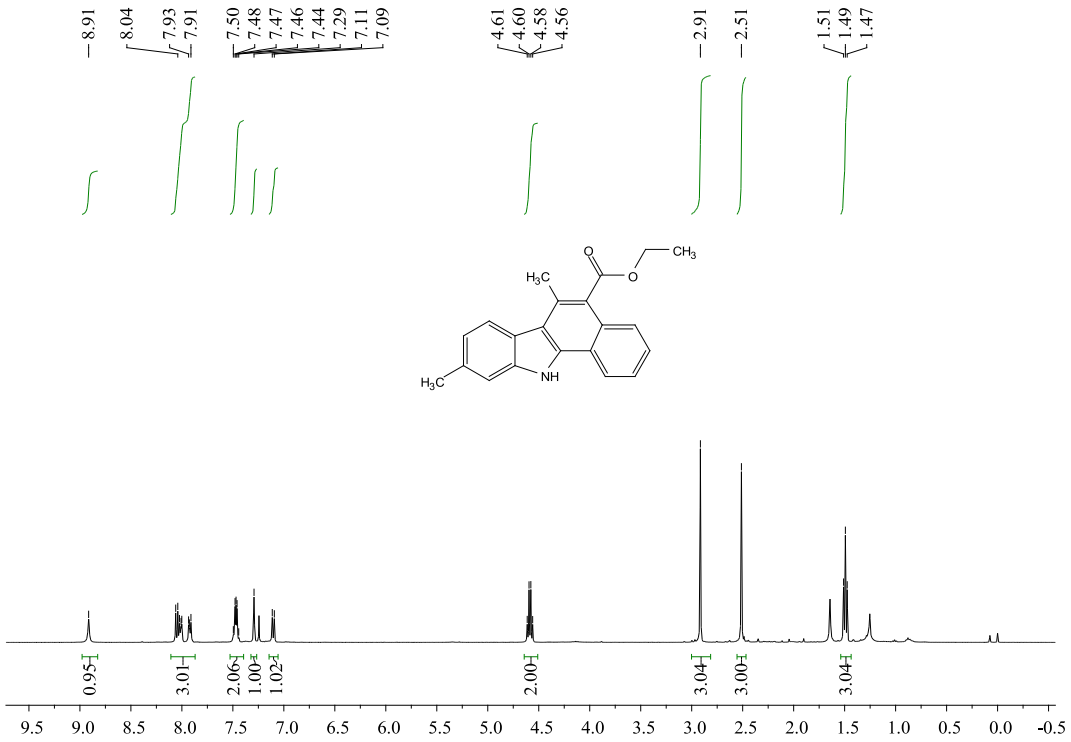
8) Ethyl 8-cyano-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3g**) (Using $CDCl_3$ as solvent)



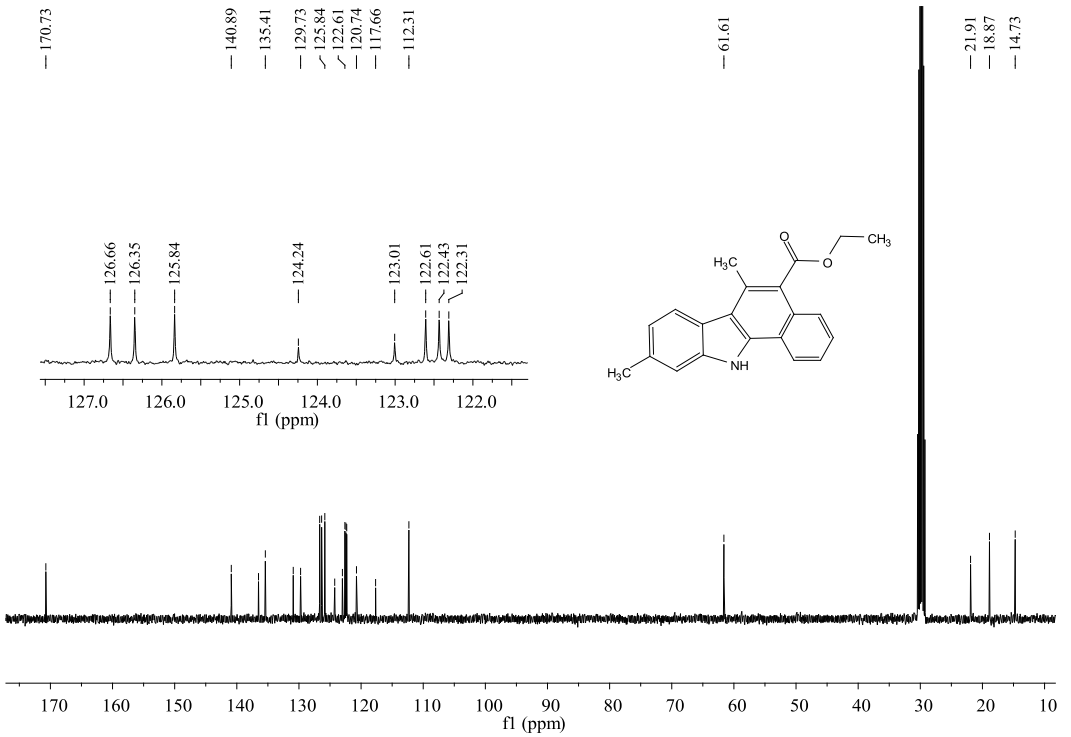
Ethyl 8-cyano-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3g**) (Using $(CD_3)_2CO$ as solvent)



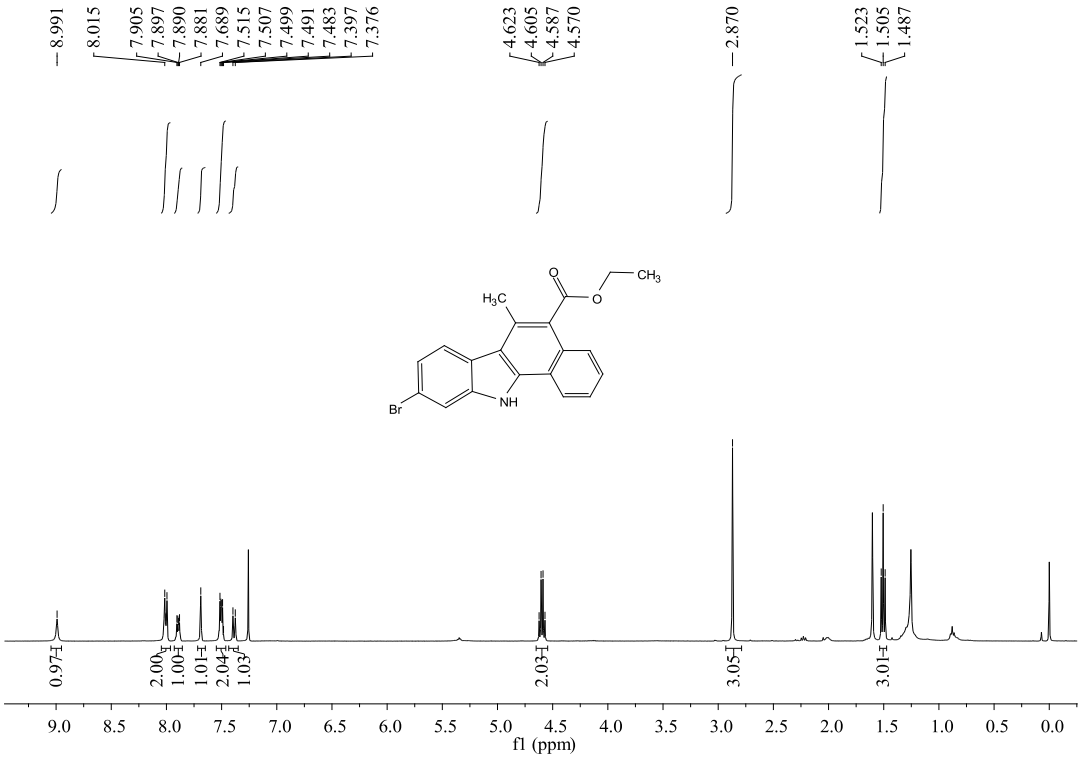
9) Ethyl 6,9-dimethyl-11H-benzo[a]carbazole-5-carboxylate (**3h**) (Using $CDCl_3$ as solvent)



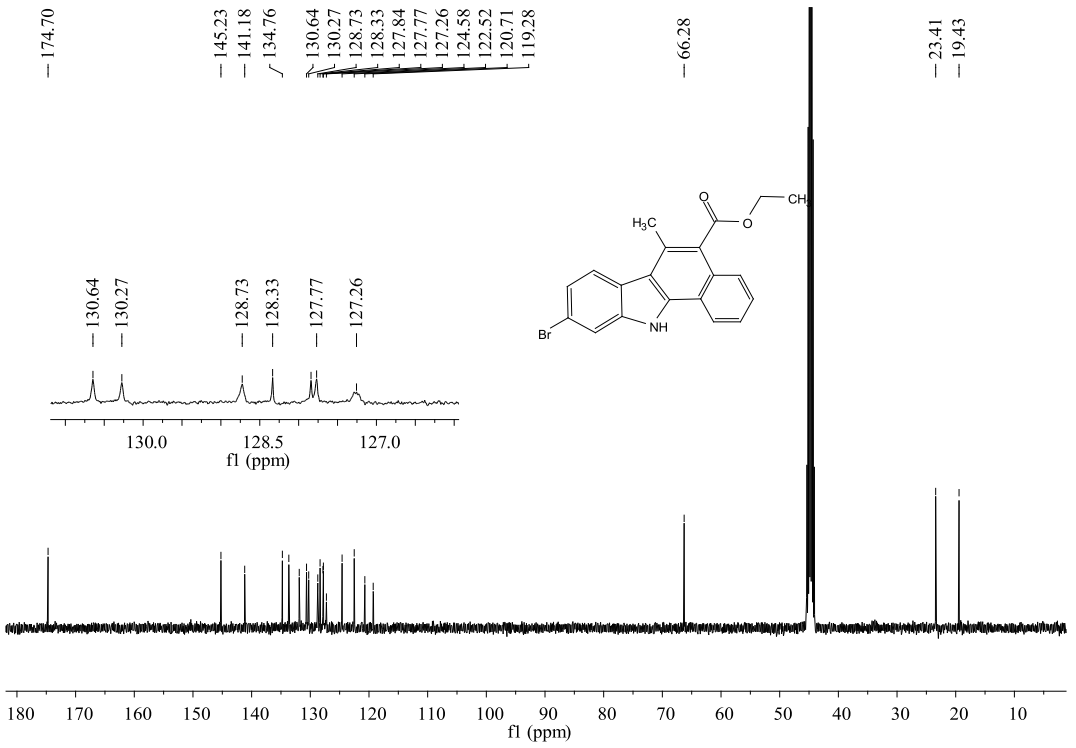
Ethyl 6,9-dimethyl-11H-benzo[a]carbazole-5-carboxylate (**3h**) (Using CD_3COCD_3 as solvent)



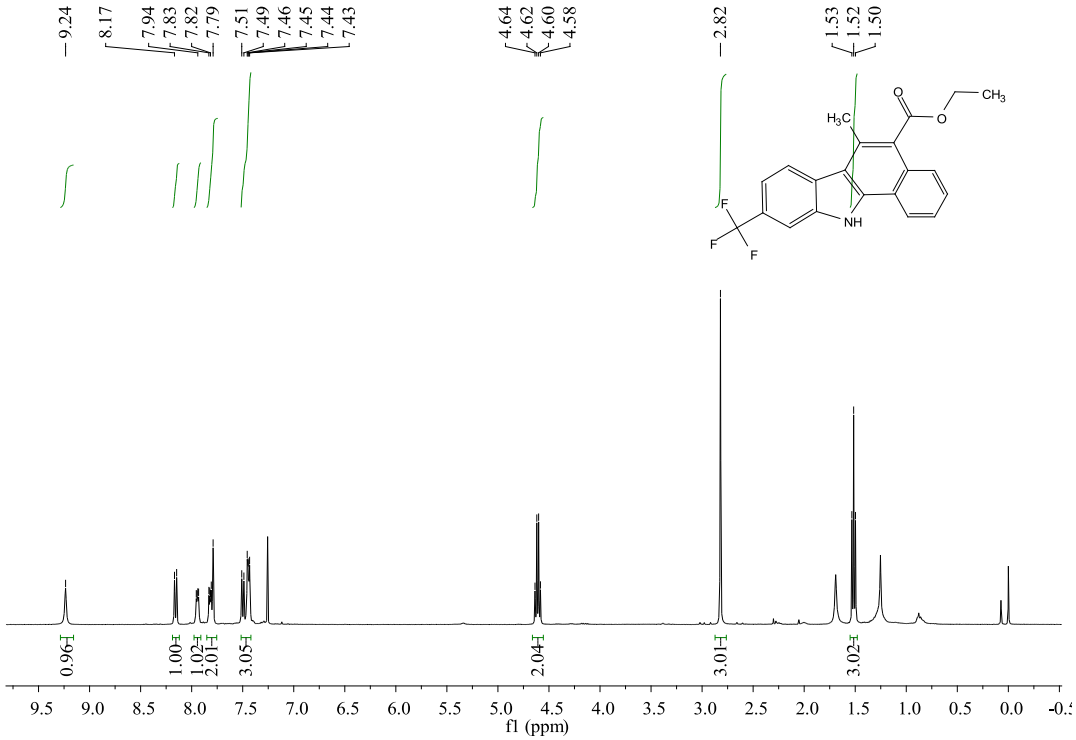
10) Ethyl 9-bromo-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3i**) (Using $CDCl_3$ as solvent)



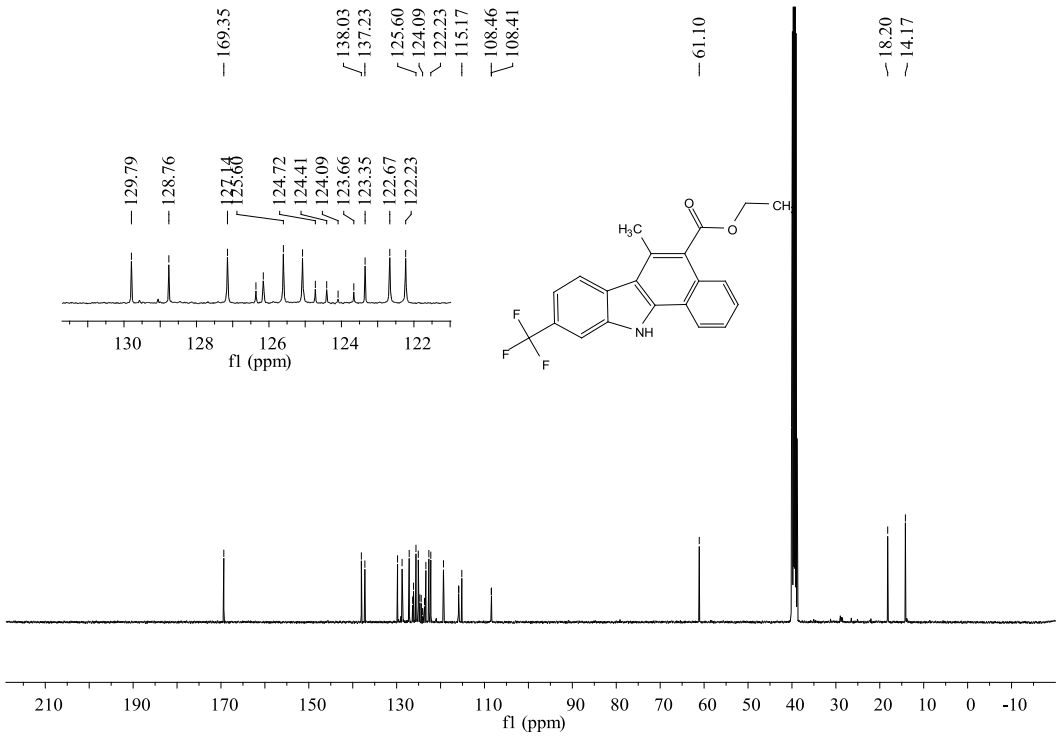
Ethyl 9-bromo-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3i**) (Using $(CD_3)_2SO$ as solvent)



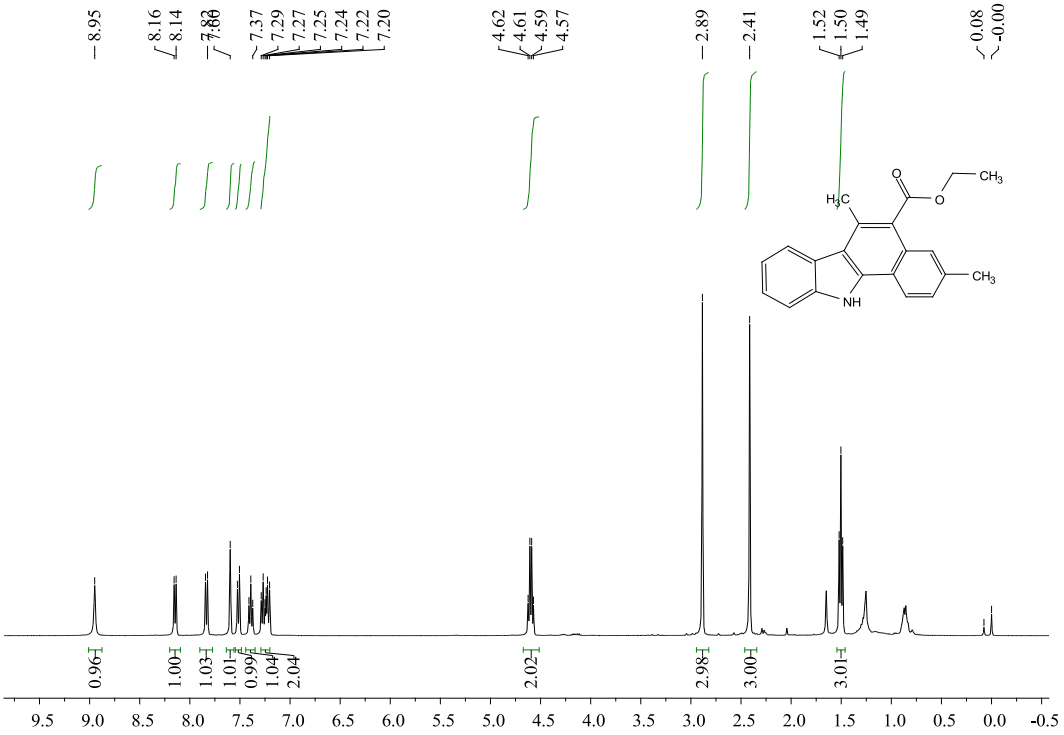
11) Ethyl 6-methyl-9-(trifluoromethyl)-11H-benzo[a]carbazole-5-carboxylate (**3j**) (Using $CDCl_3$ as solvent)

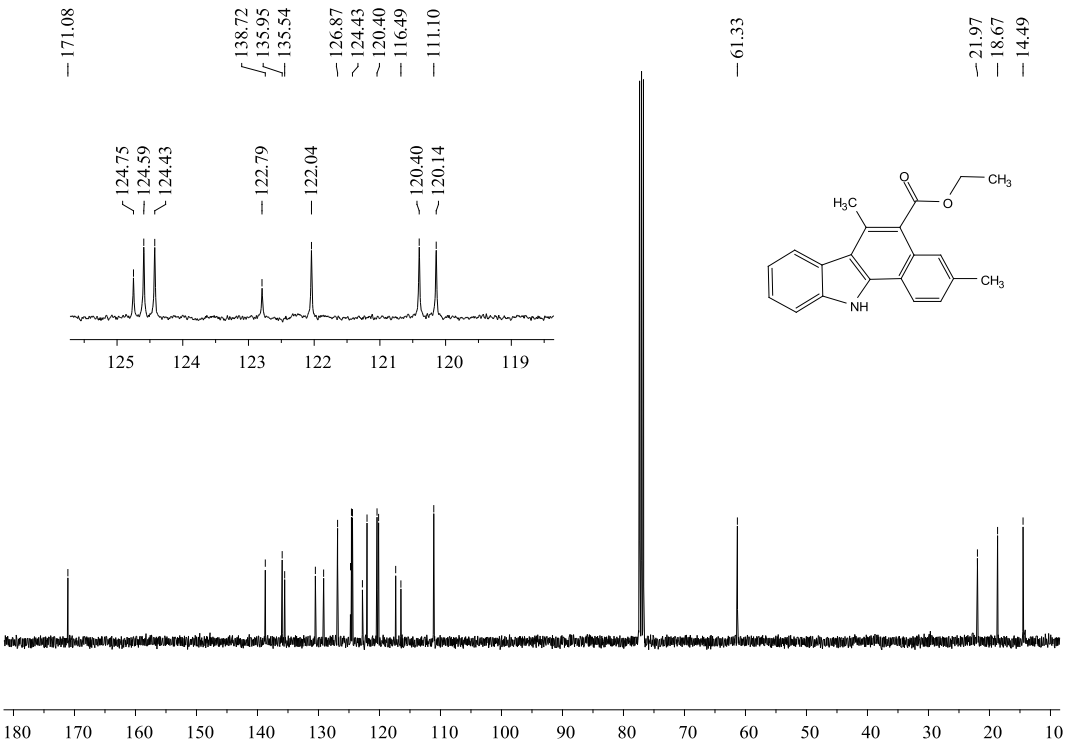


Ethyl 6-methyl-9-(trifluoromethyl)-11H-benzo[a]carbazole-5-carboxylate (**3j**) (Using $(CD_3)_2SO$ as solvent)

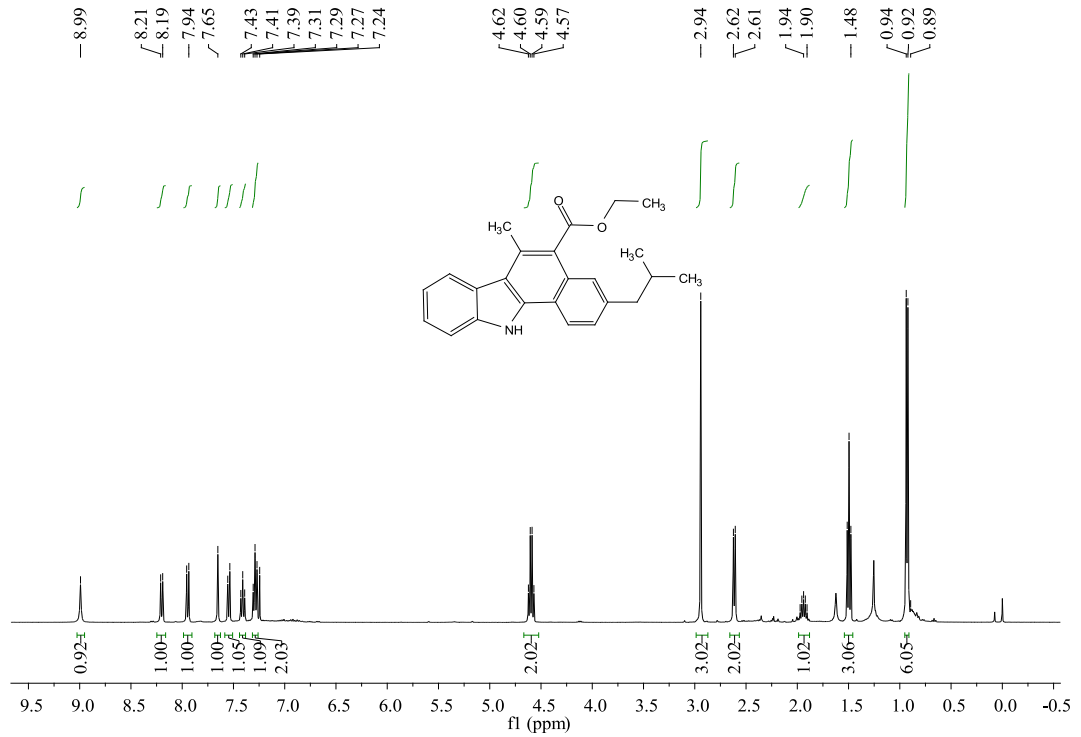


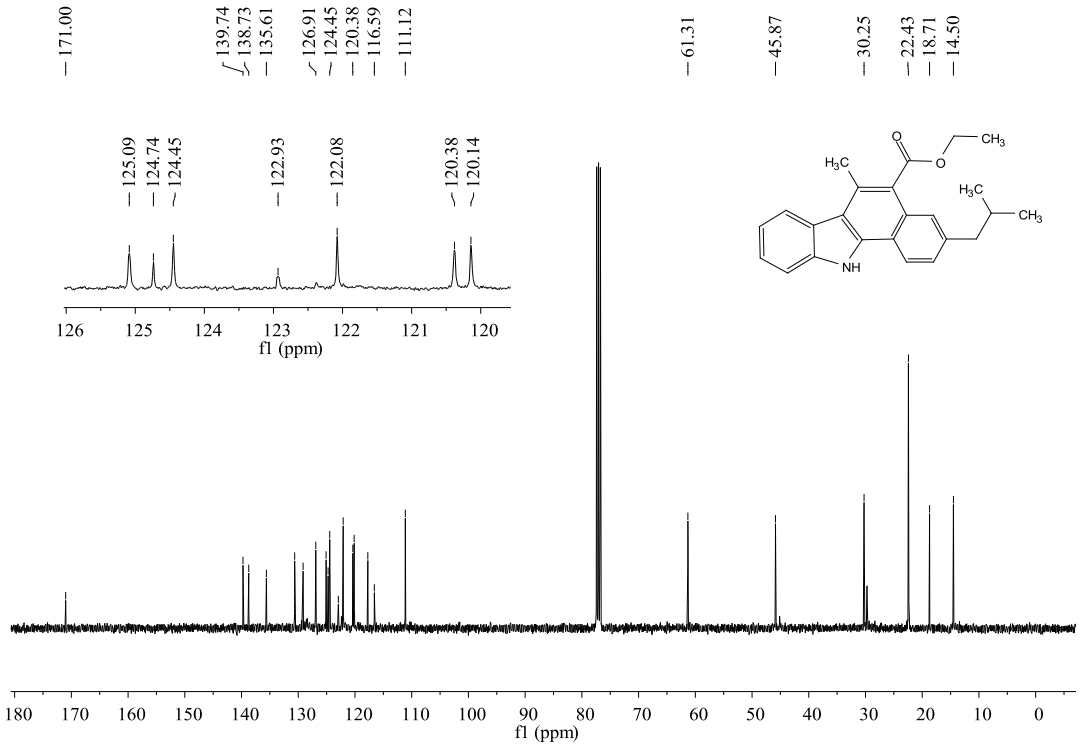
12) Ethyl 3,6-dimethyl-11H-benzo[a]carbazole-5-carboxylate (**3l**) (Using $CDCl_3$ as solvent)



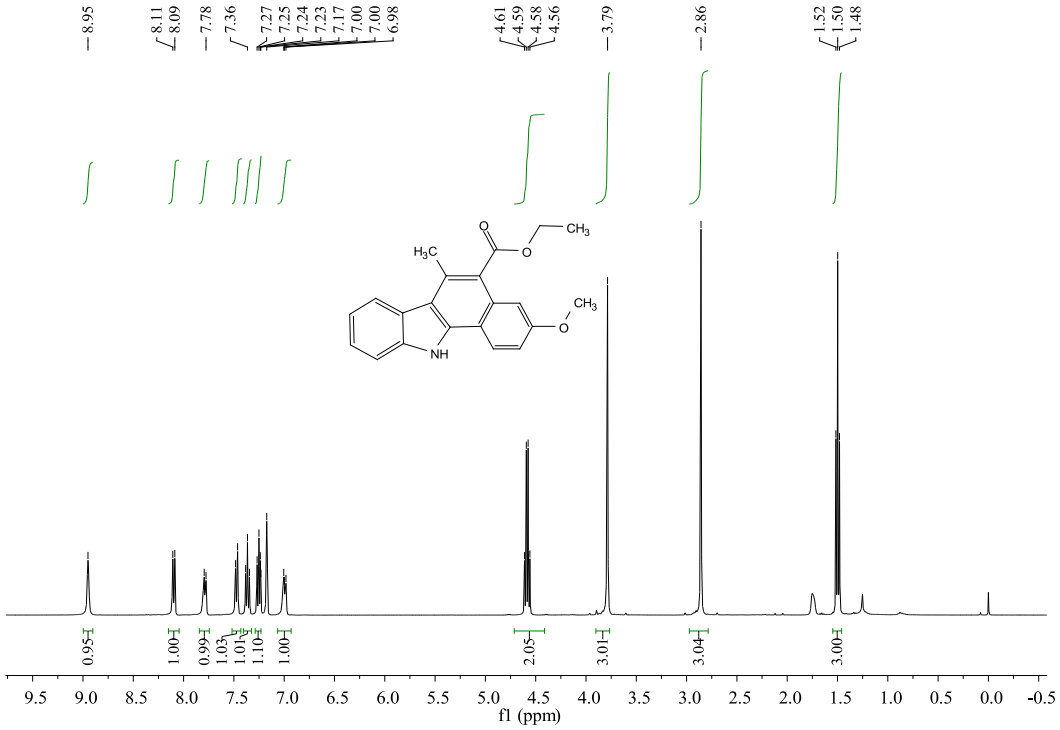


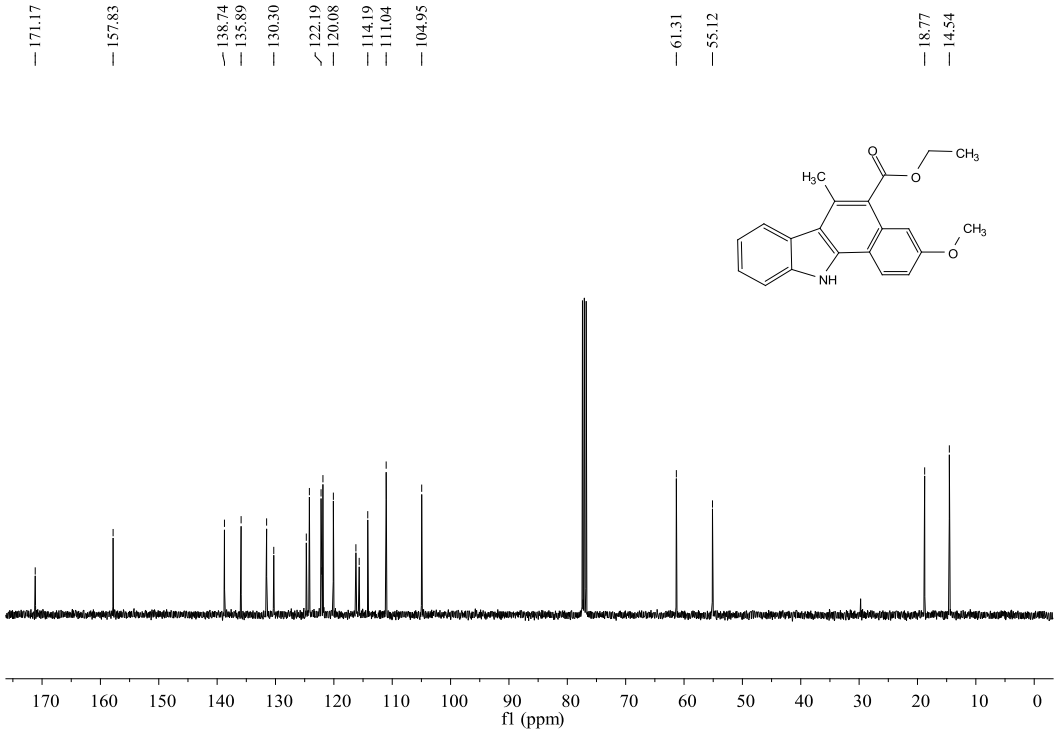
13) Ethyl 3-isobutyl-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3m**) (Using $CDCl_3$ as solvent)



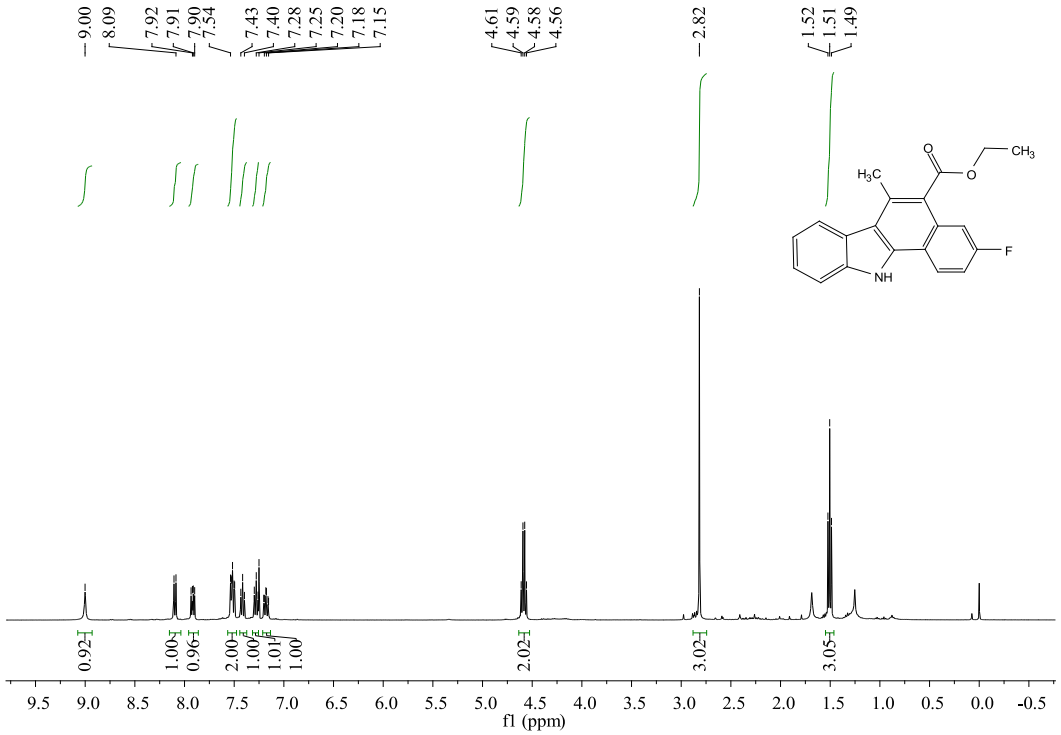


14) Ethyl 3-methoxy-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3n**) (Using $CDCl_3$ as solvent)

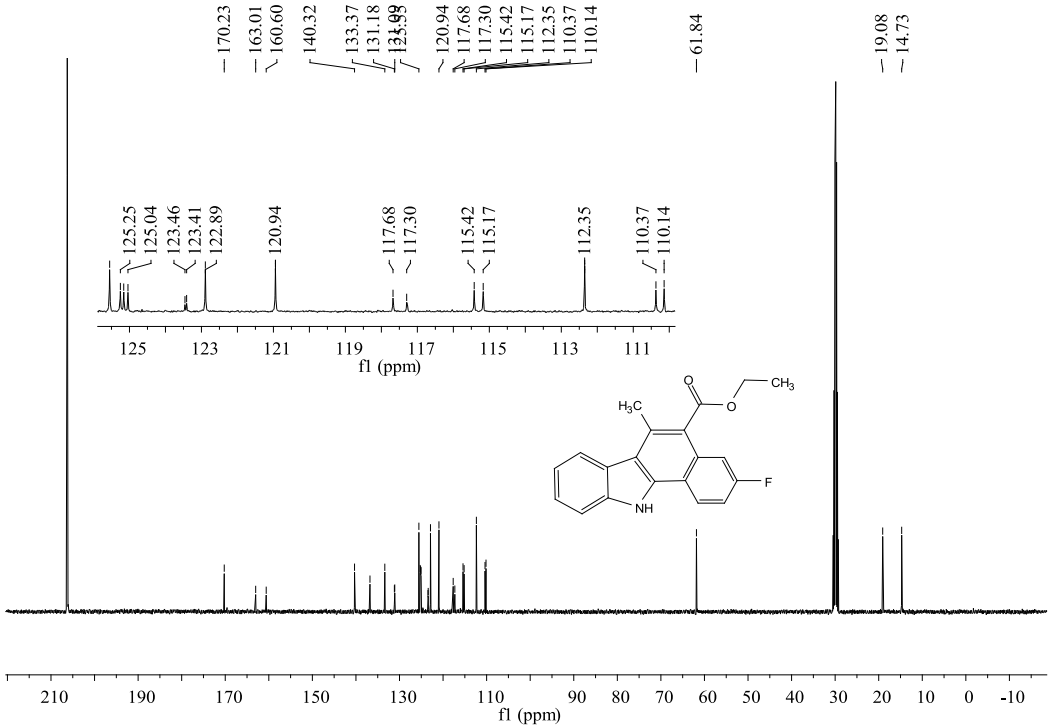




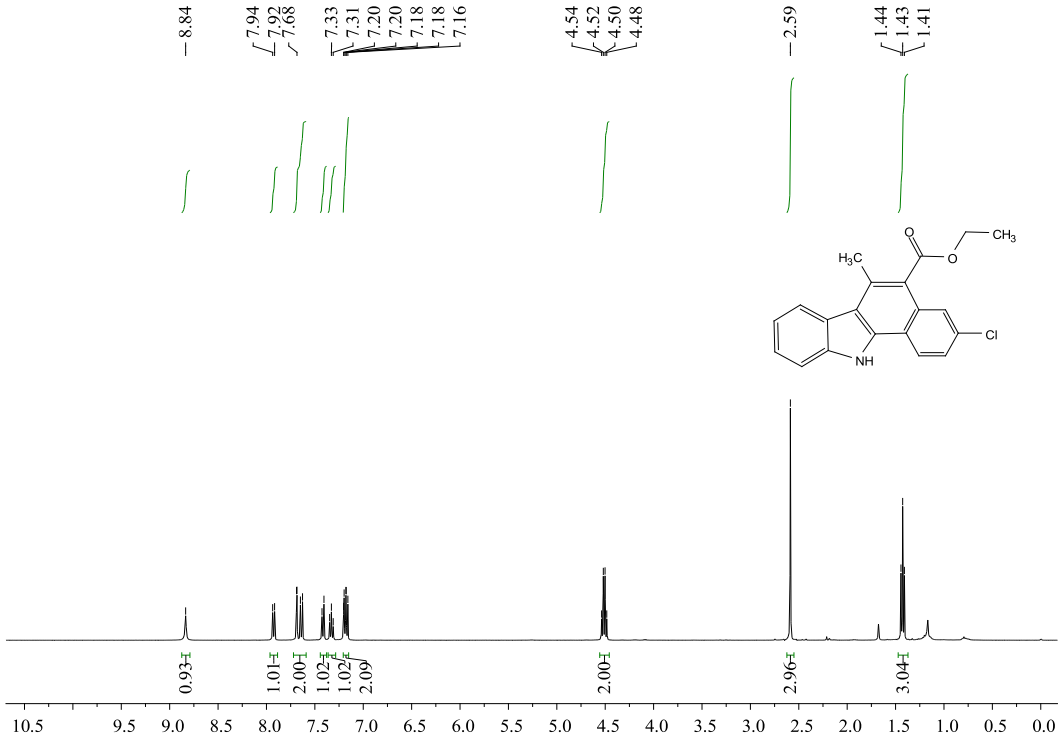
15) Ethyl 3-fluoro-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3o**) (Using $CDCl_3$ as solvent)

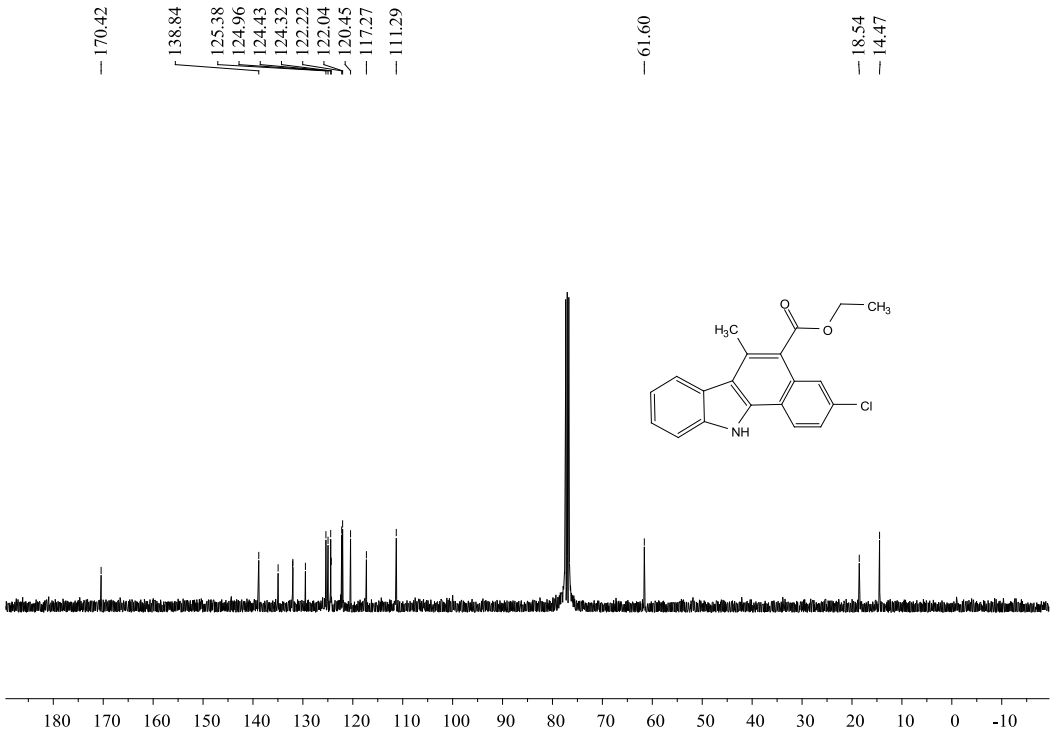


ethyl 3-fluoro-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3o**) (Using $(CD_3)_2CO$ as solvent)

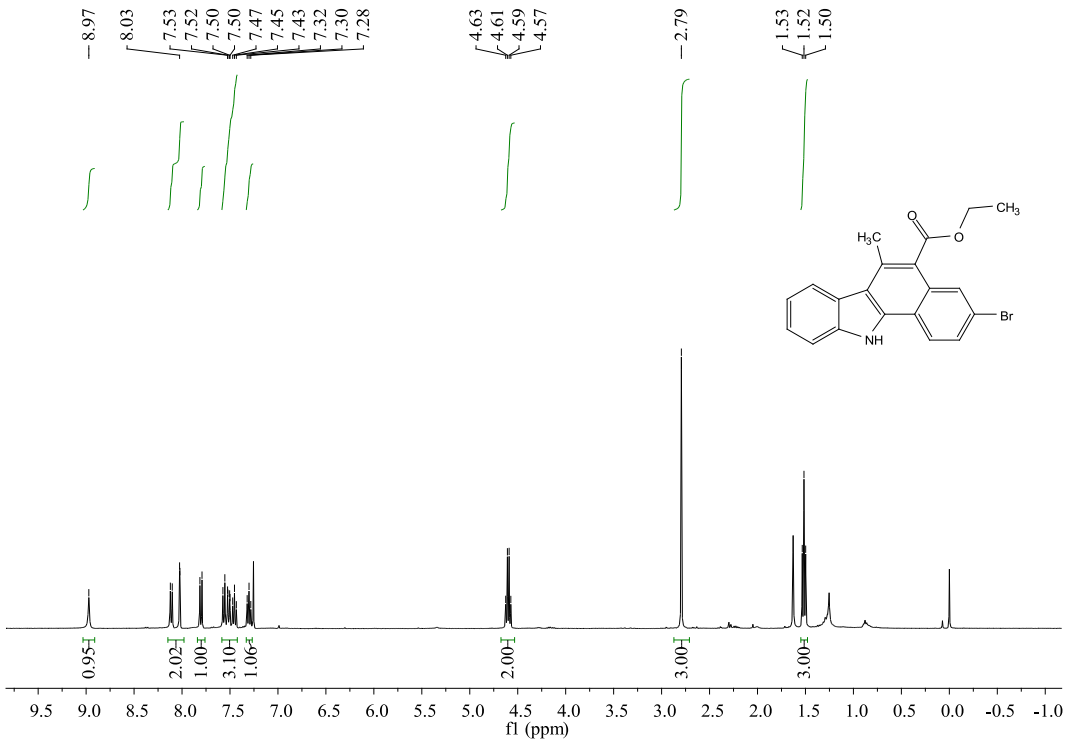


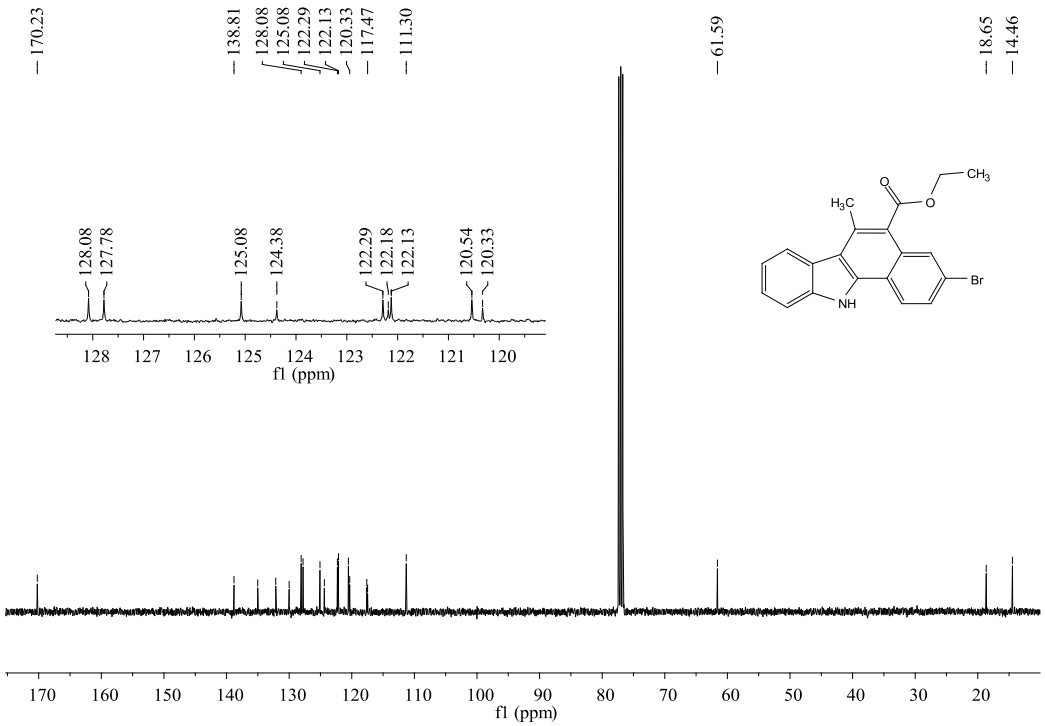
16) Ethyl 3-chloro-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3p**) (Using $CDCl_3$ as solvent)



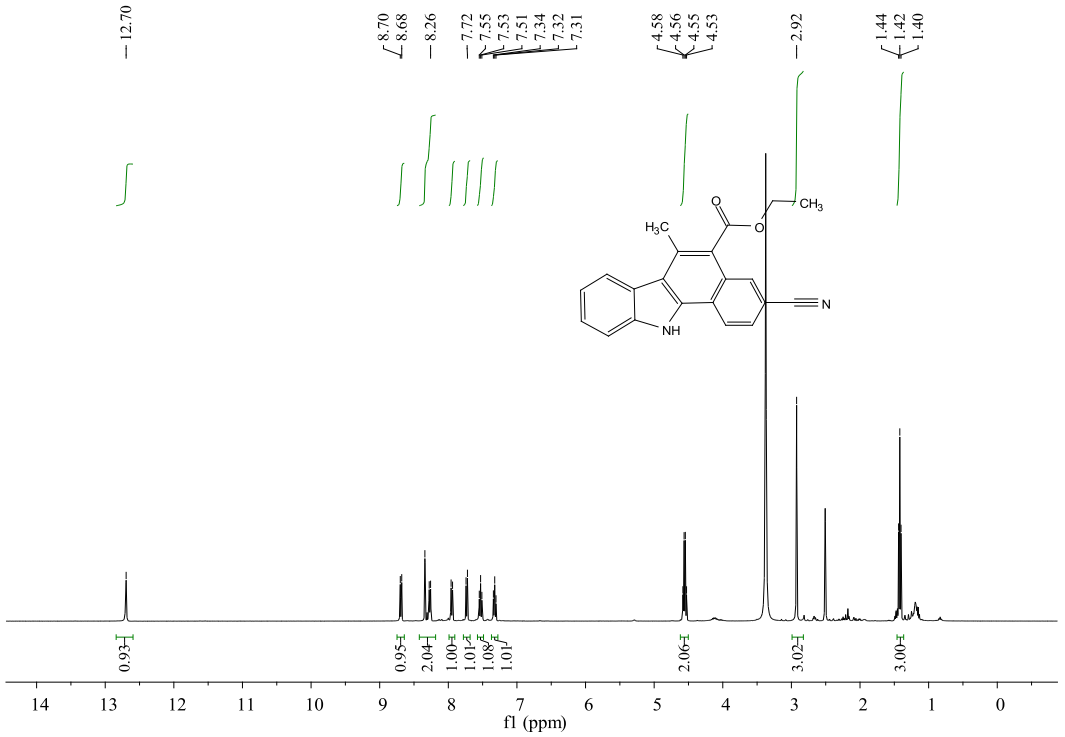


17) Ethyl 3-bromo-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3q**) (Using $CDCl_3$ as solvent)

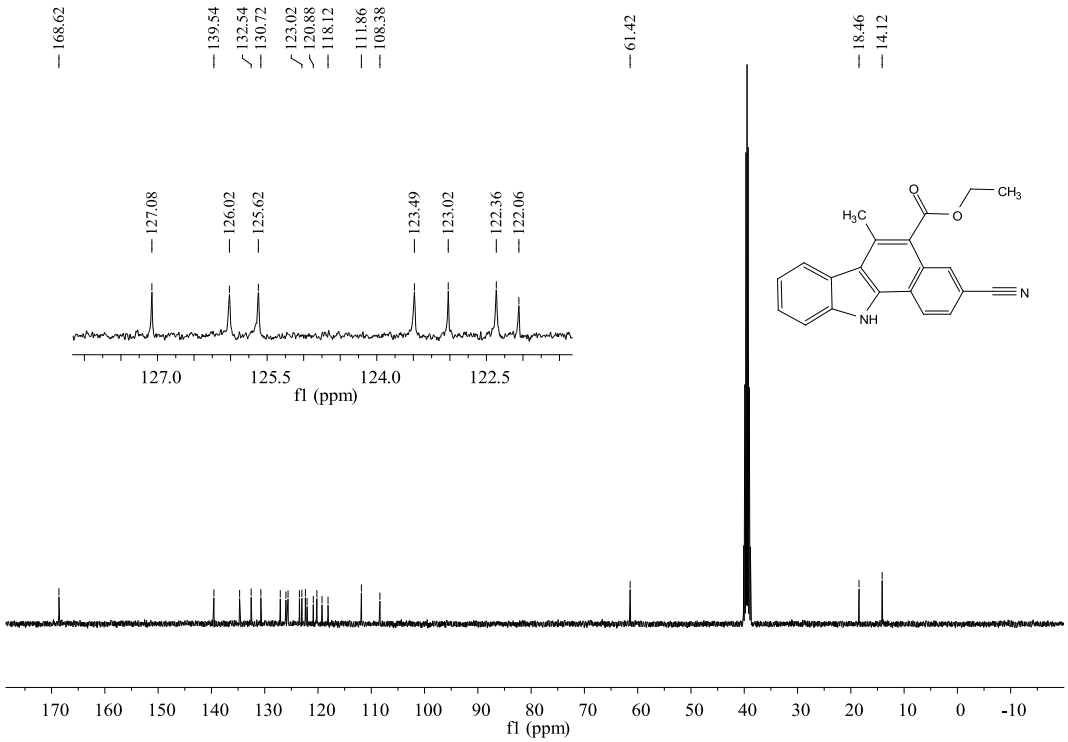




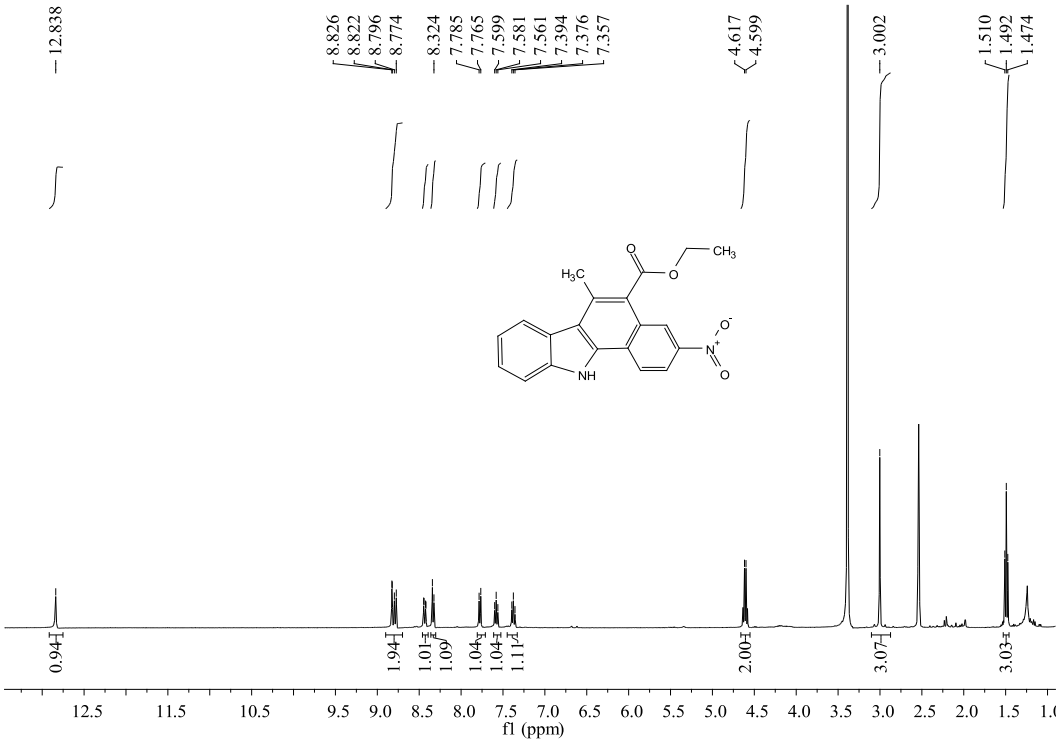
18) Ethyl 3-cyano-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3r**) (Using $CDCl_3$ as solvent)

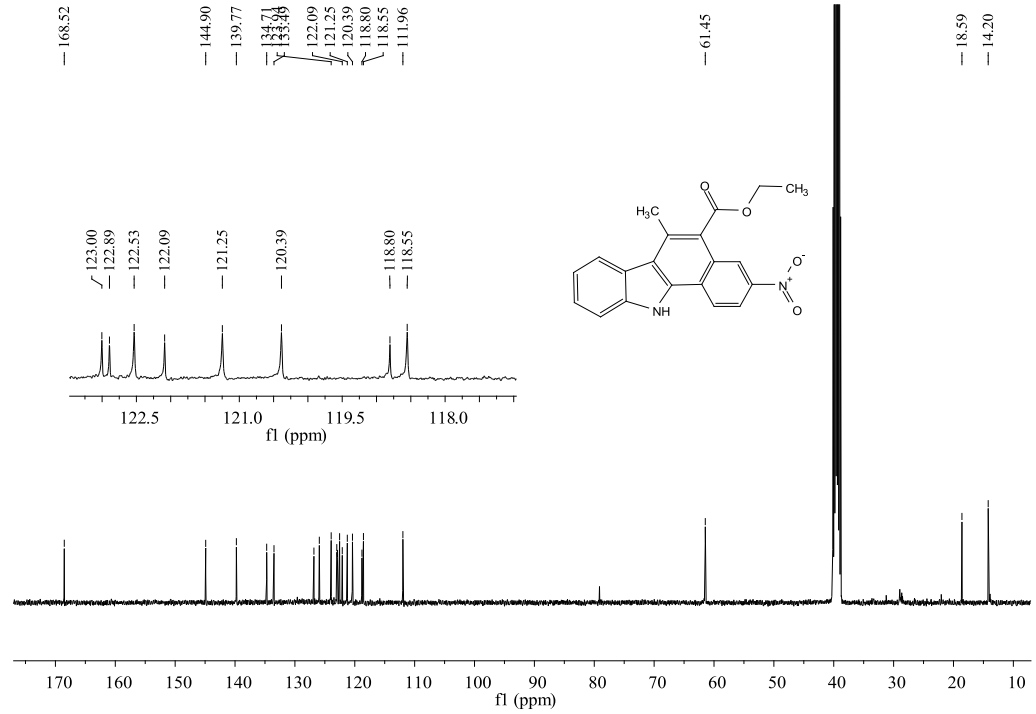


Ethyl 3-cyano-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3r**) (Using $(CD_3)_2SO$ as solvent)

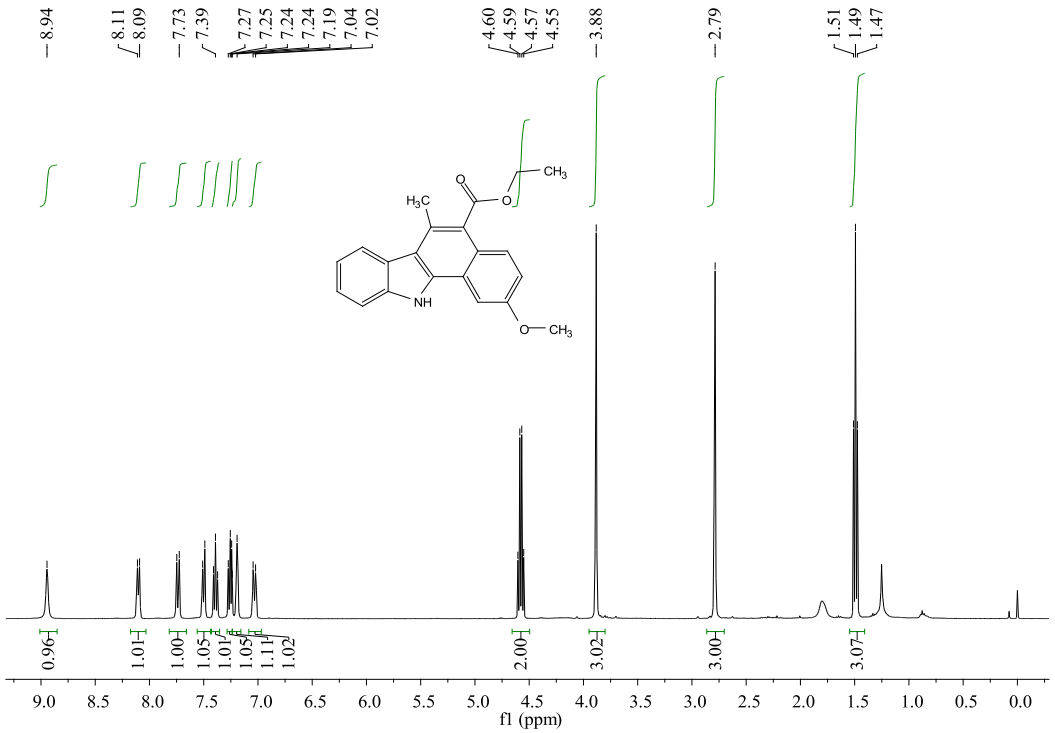


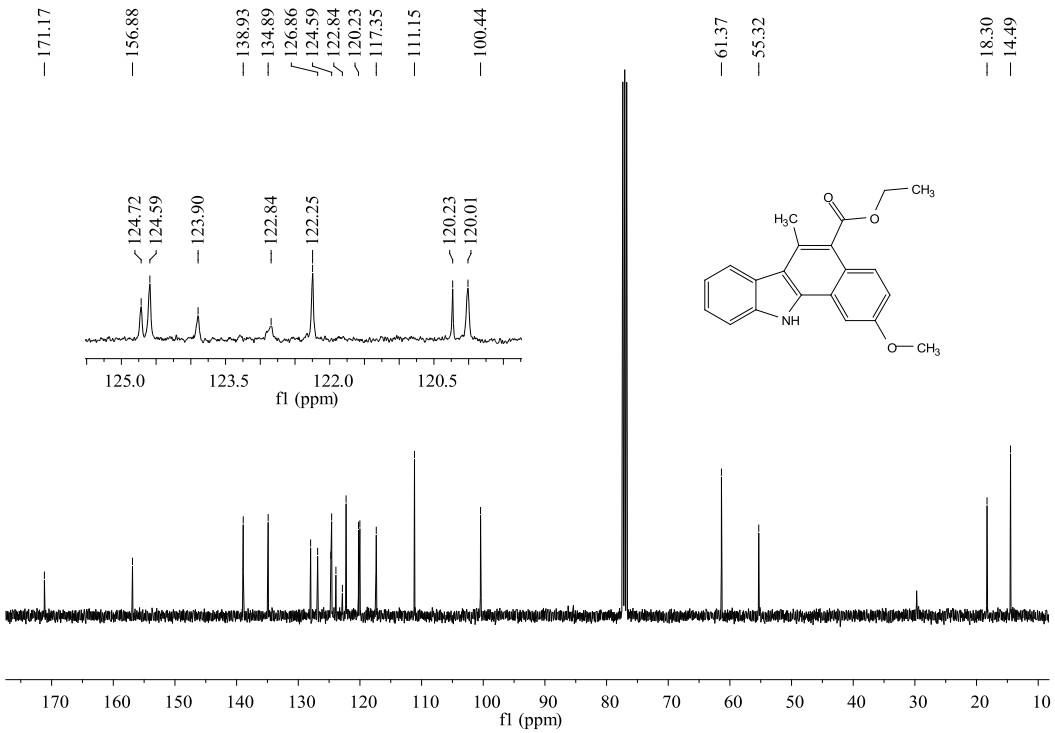
19) Ethyl 6-methyl-3-nitro-11H-benzo[a]carbazole-5-carboxylate (**3s**) (Using $(CD_3)_2SO$ as solvent)



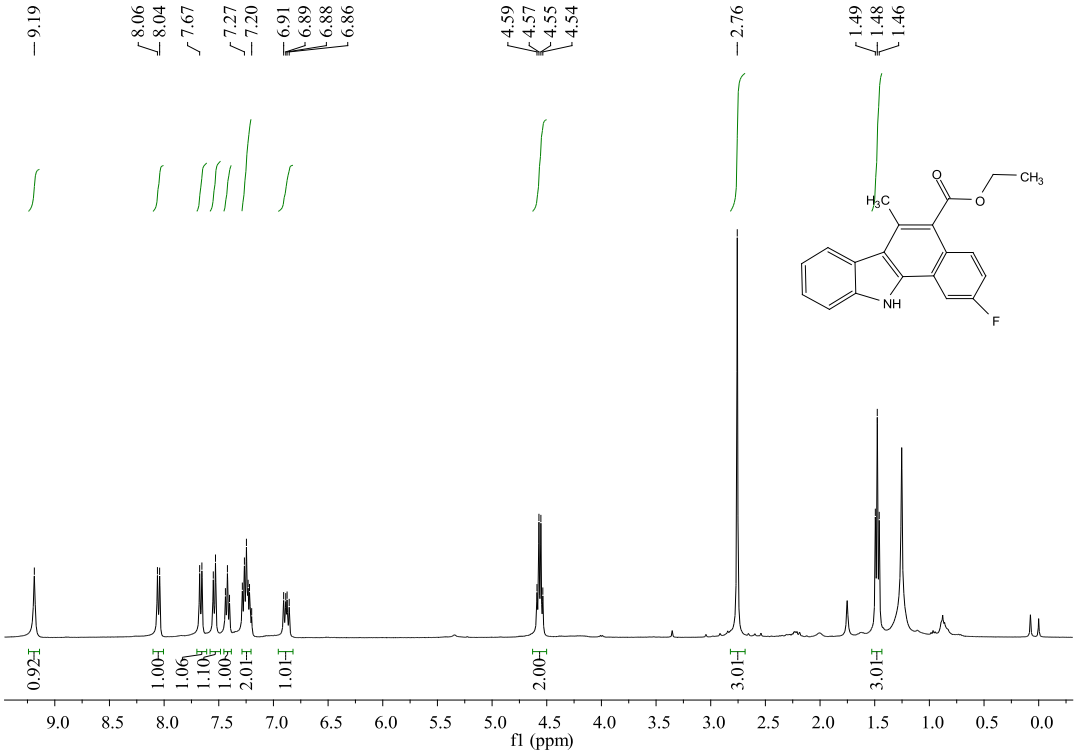


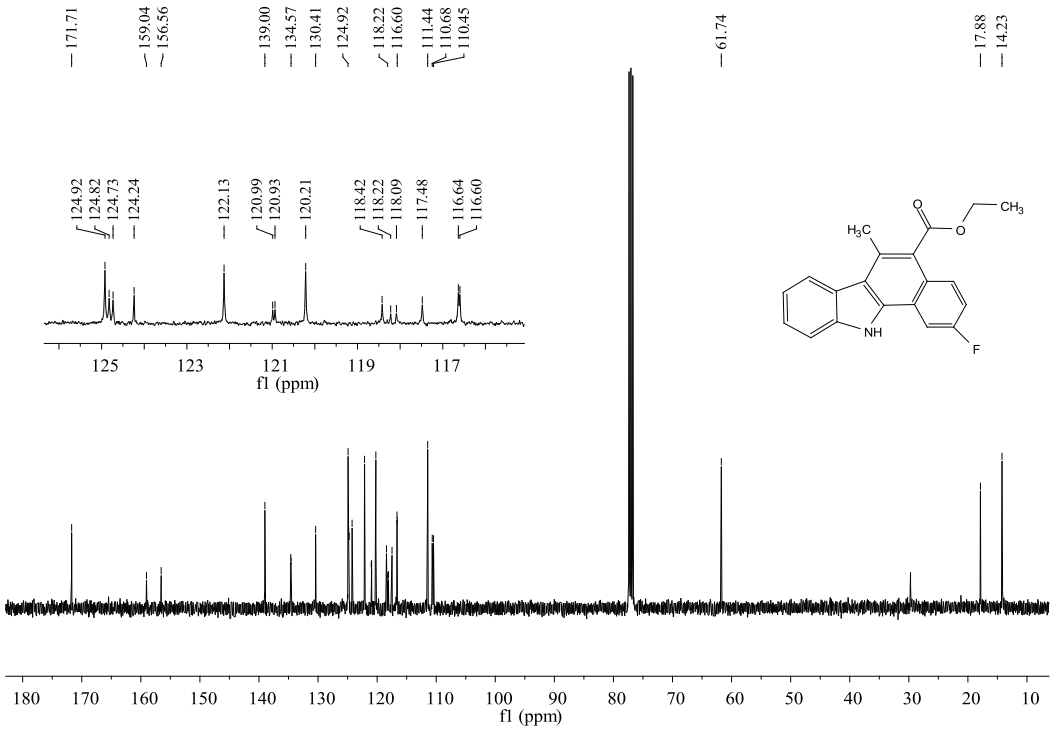
20) Ethyl 2-methoxy-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3t**) (Using $CDCl_3$ as solvent)



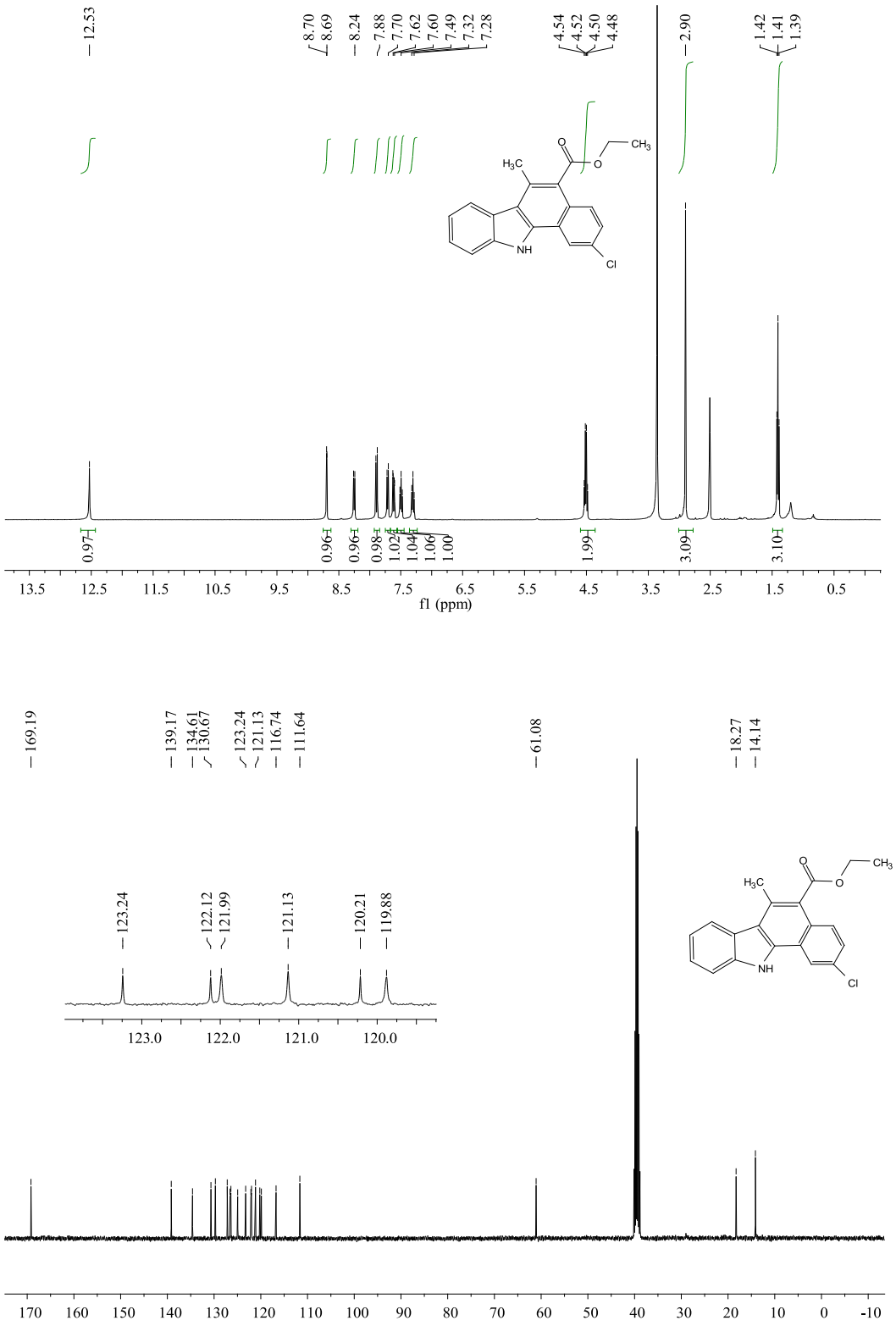


21) Ethyl 2-fluoro-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3u**) (Using $CDCl_3$ as solvent)

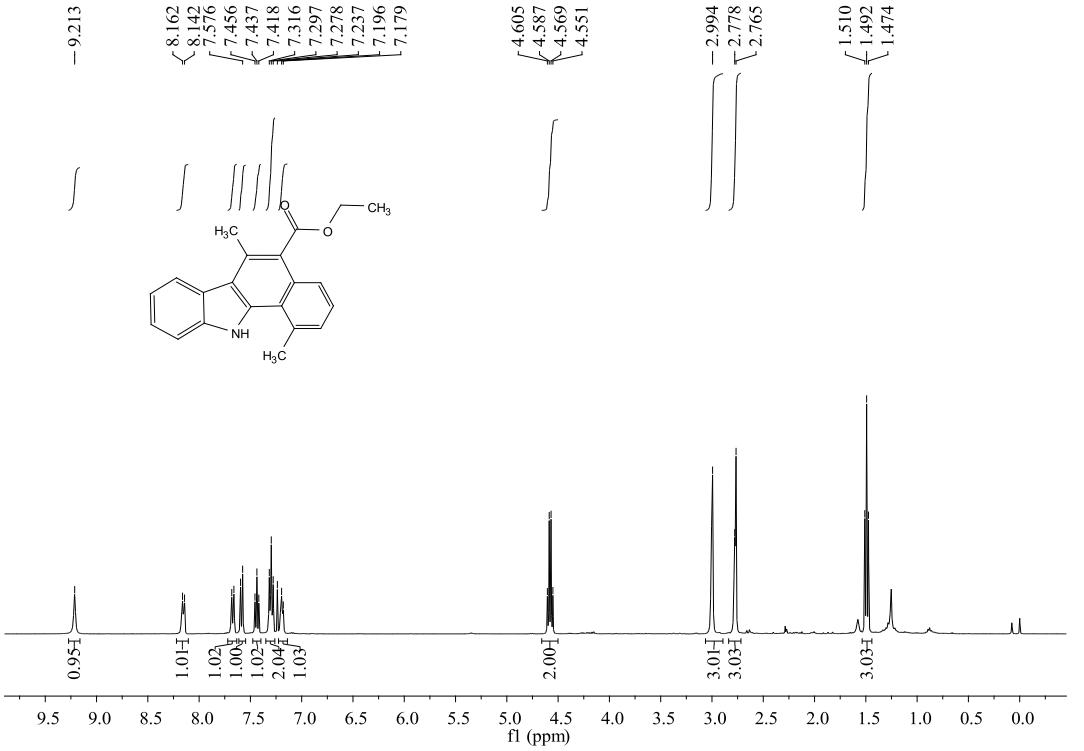


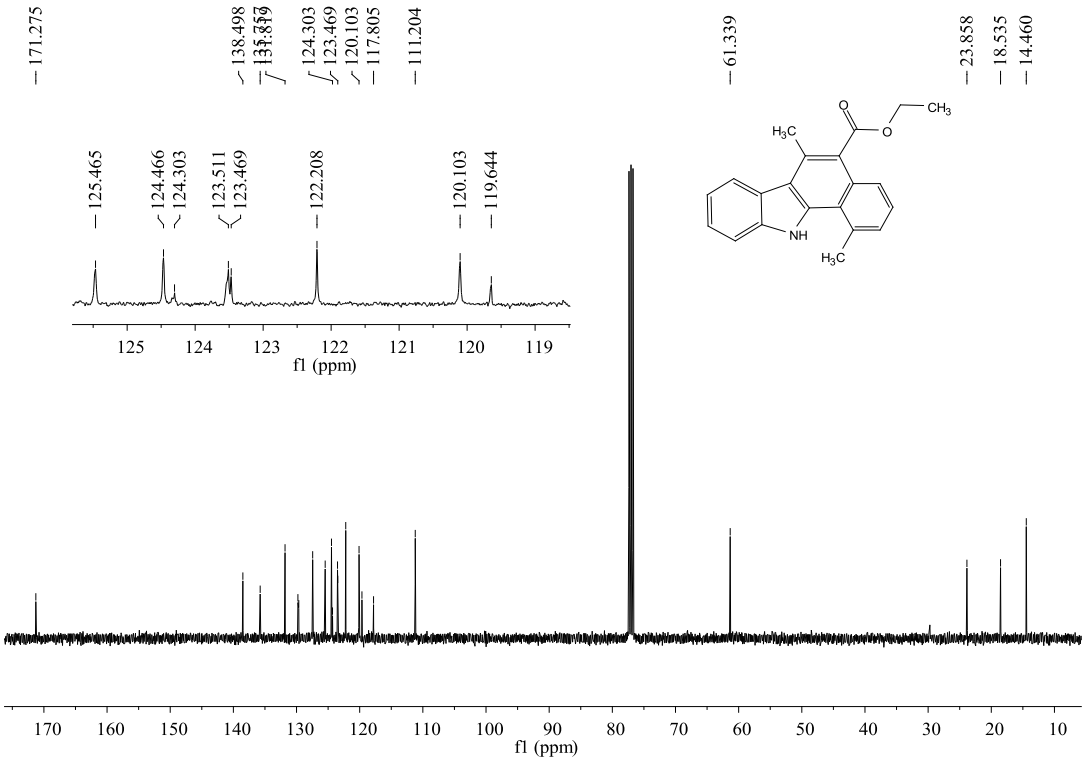


22) Ethyl 2-chloro-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3v**) (Using $(CD_3)_2SO$ as solvent)

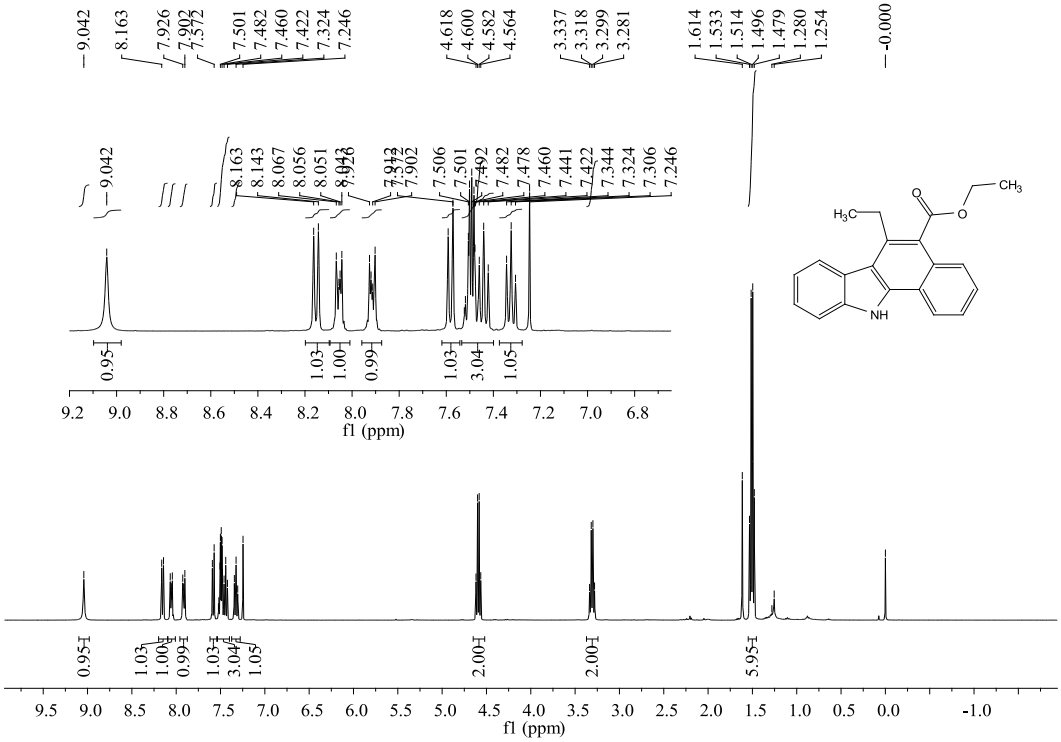


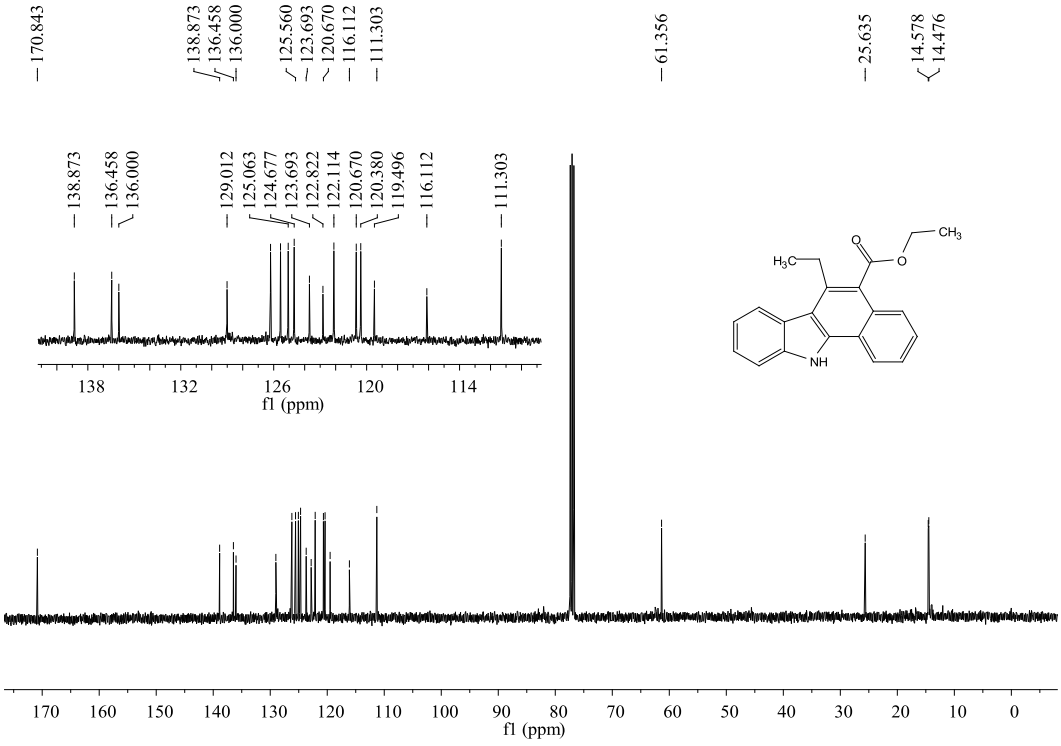
23) Ethyl 1,6-dimethyl-11H-benzo[a]carbazole-5-carboxylate (**3w**) (Using $CDCl_3$ as solvent)



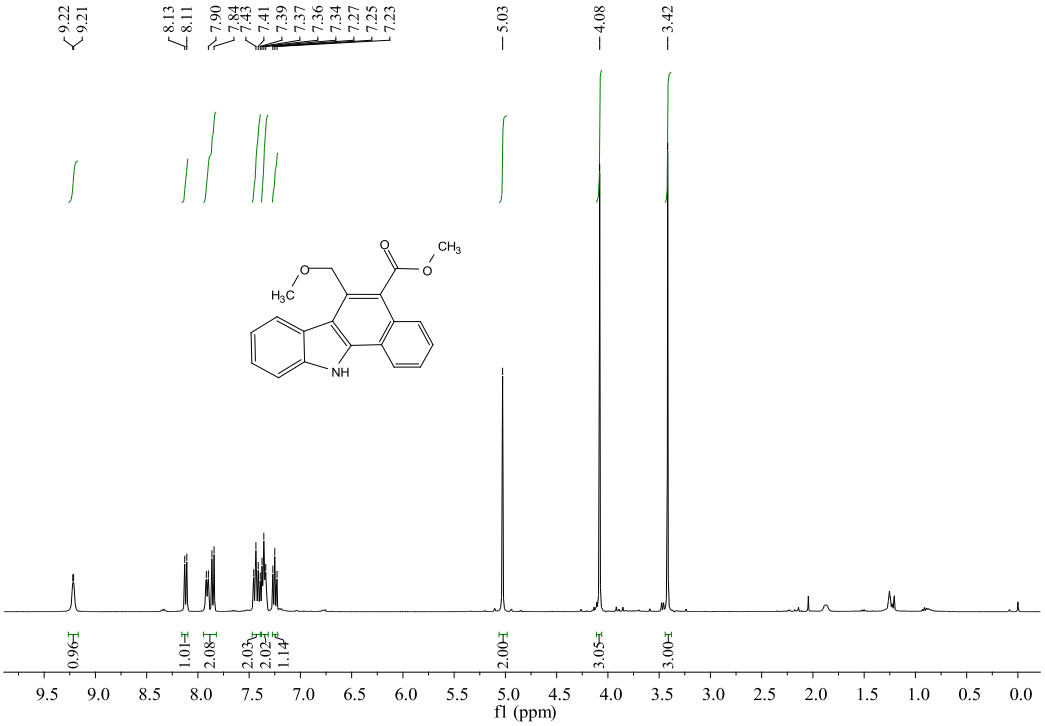


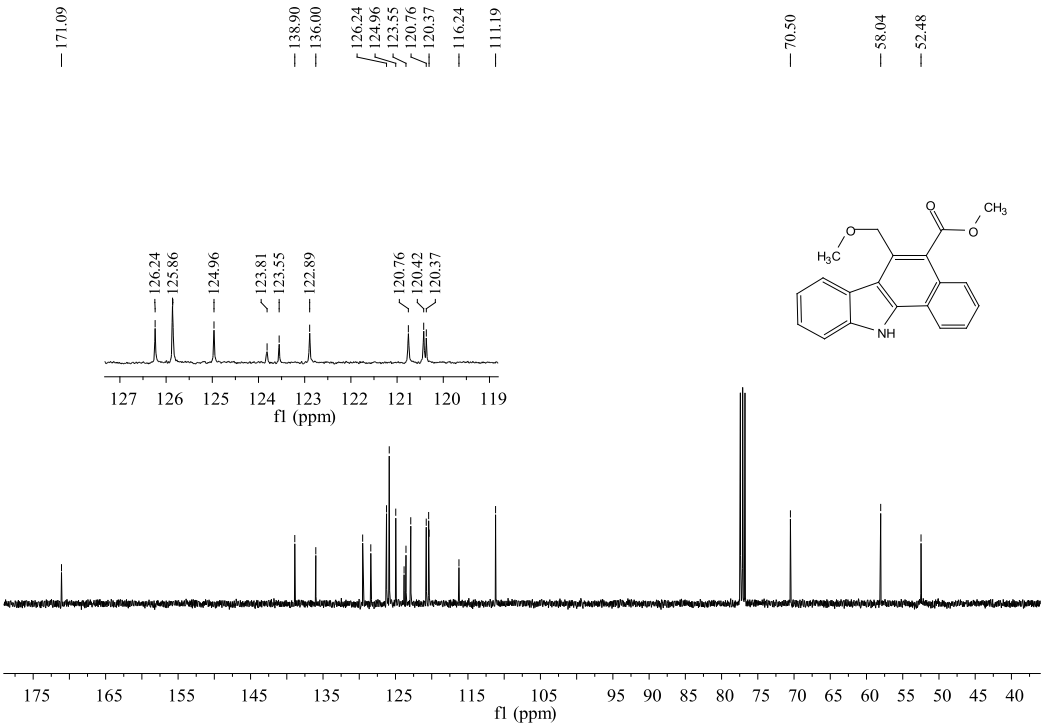
24) Ethyl 6-ethyl-11H-benzo[a]carbazole-5-carboxylate (**3x**) (Using $CDCl_3$ as solvent)



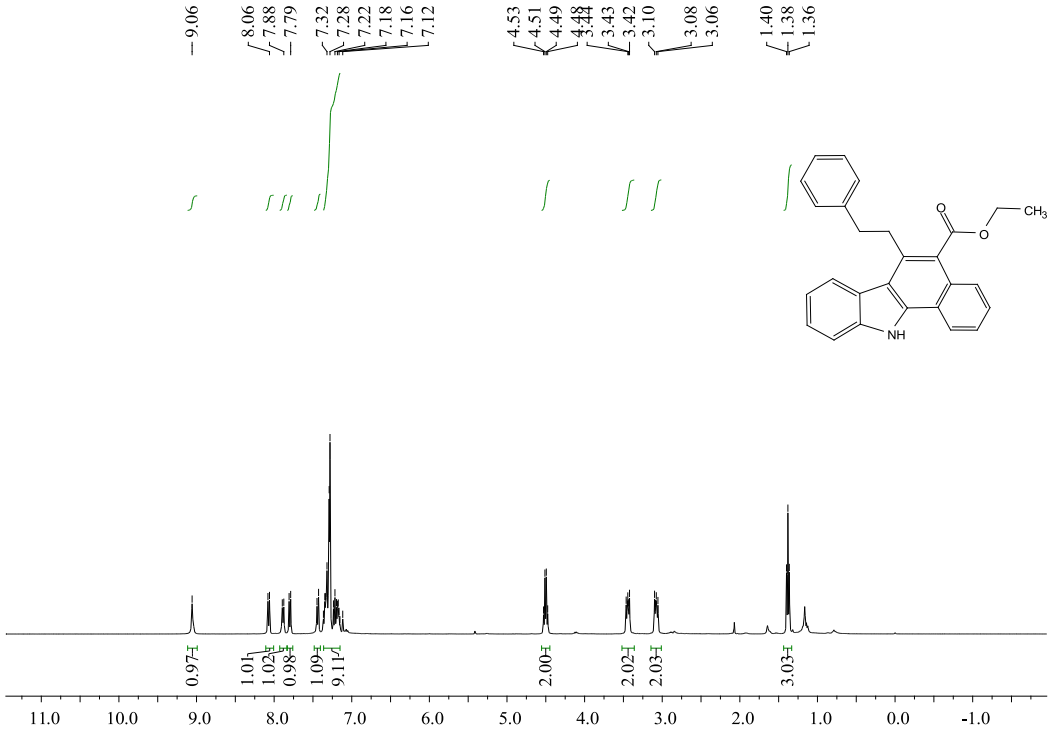


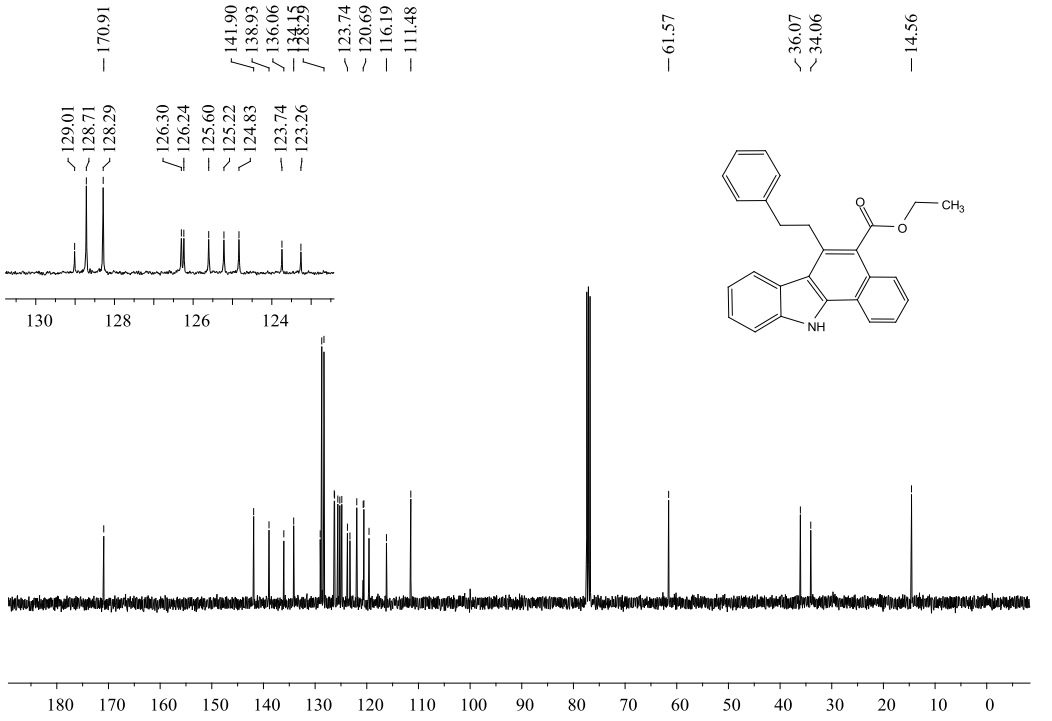
25) Methyl 6-(methoxymethyl)-11H-benzo[a]carbazole-5-carboxylate (**3y**) (Using $CDCl_3$ as solvent)



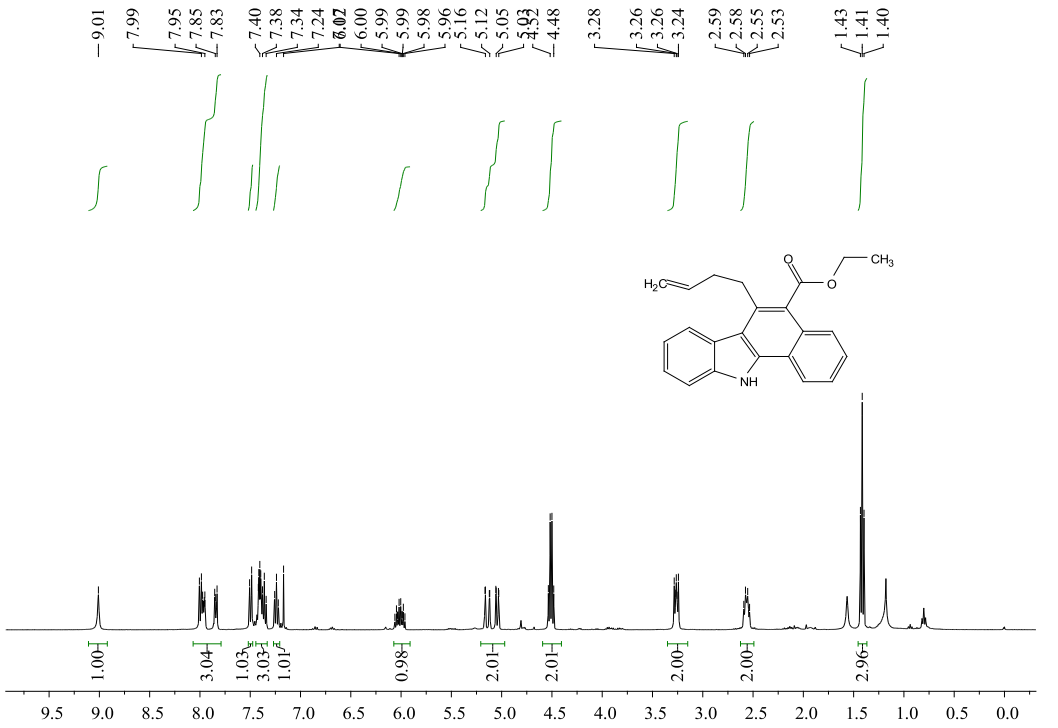


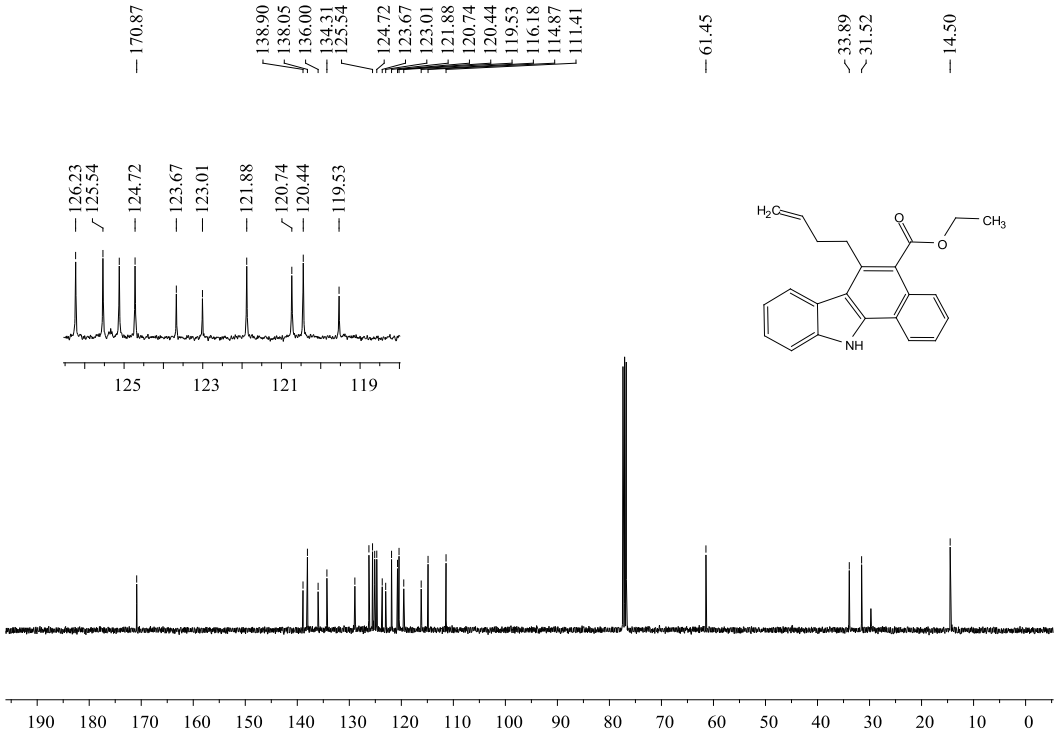
26) Methyl 6-phenethyl-11H-benzo[a]carbazole-5-carboxylate (**3z**) (Using $CDCl_3$ as solvent)



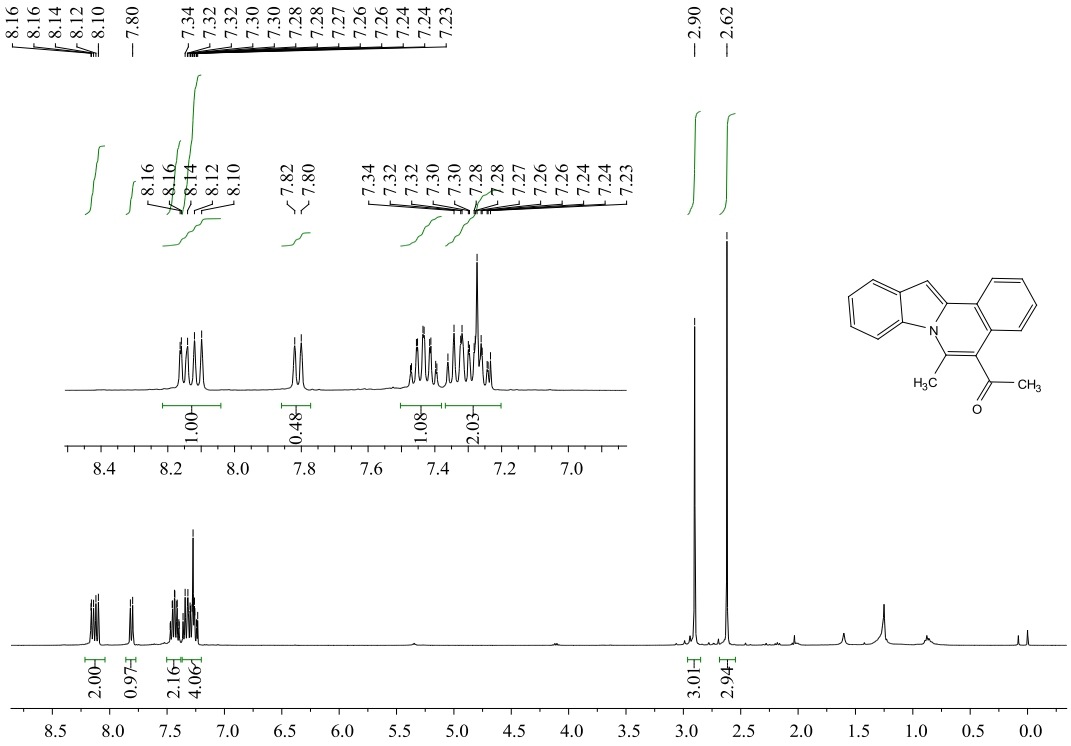


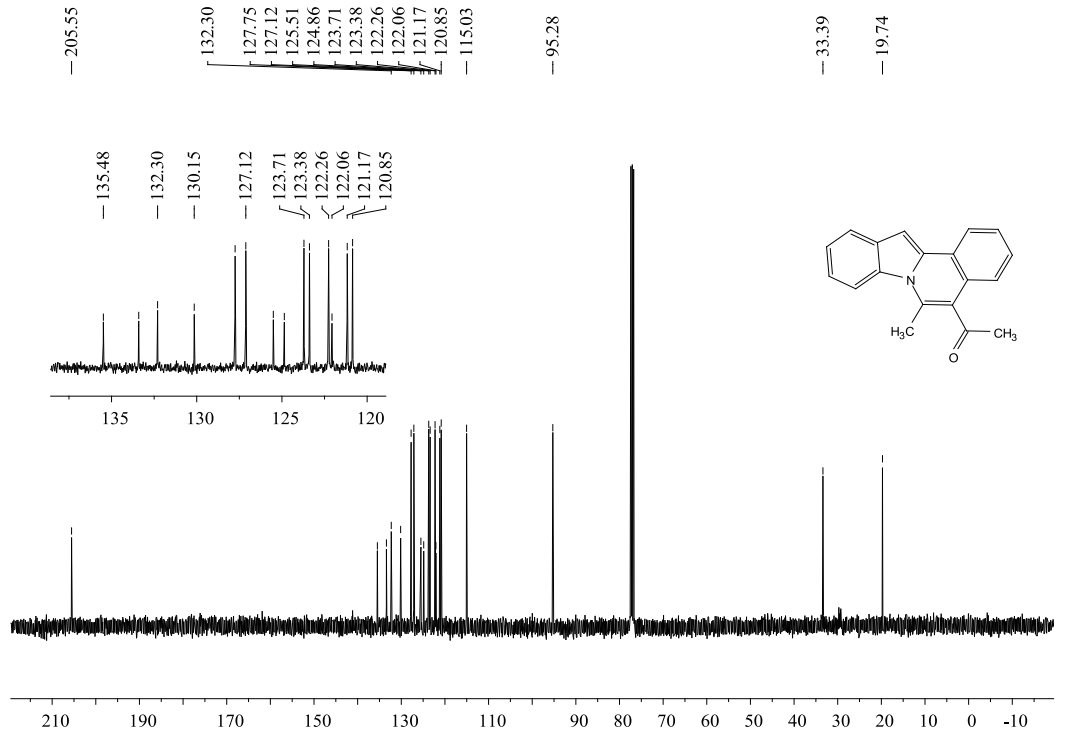
27) Methyl 6-(but-3-en-1-yl)-11H-benzo[a]carbazole-5-carboxylate (**3az**) (Using $CDCl_3$ as solvent)



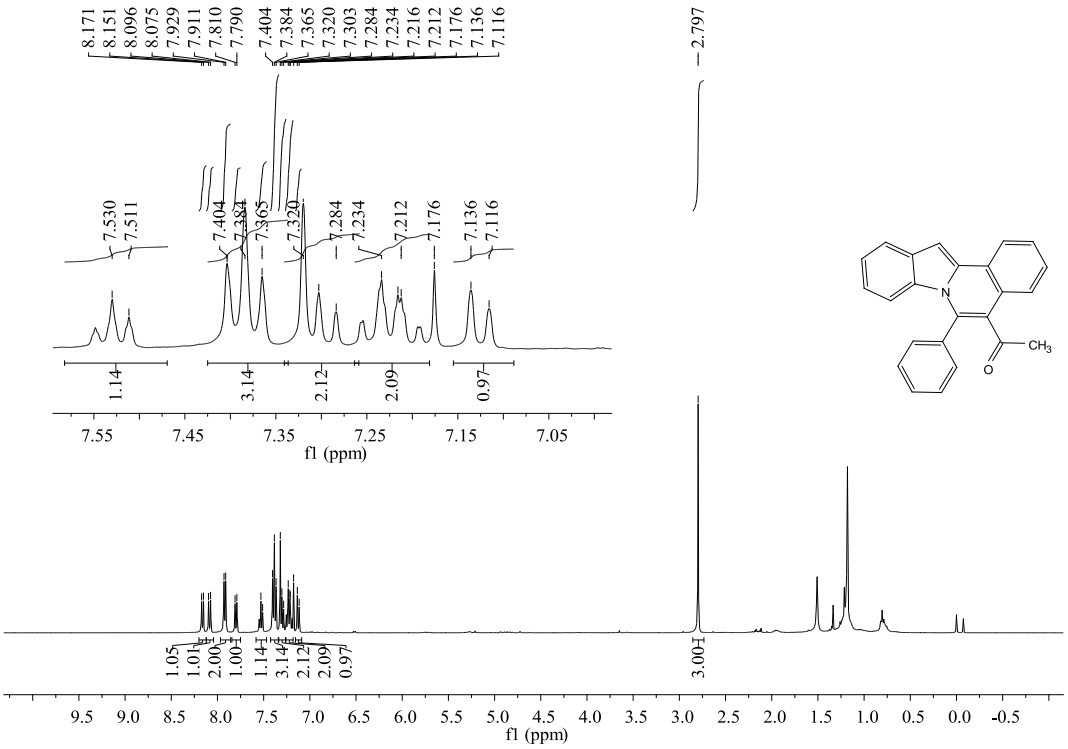


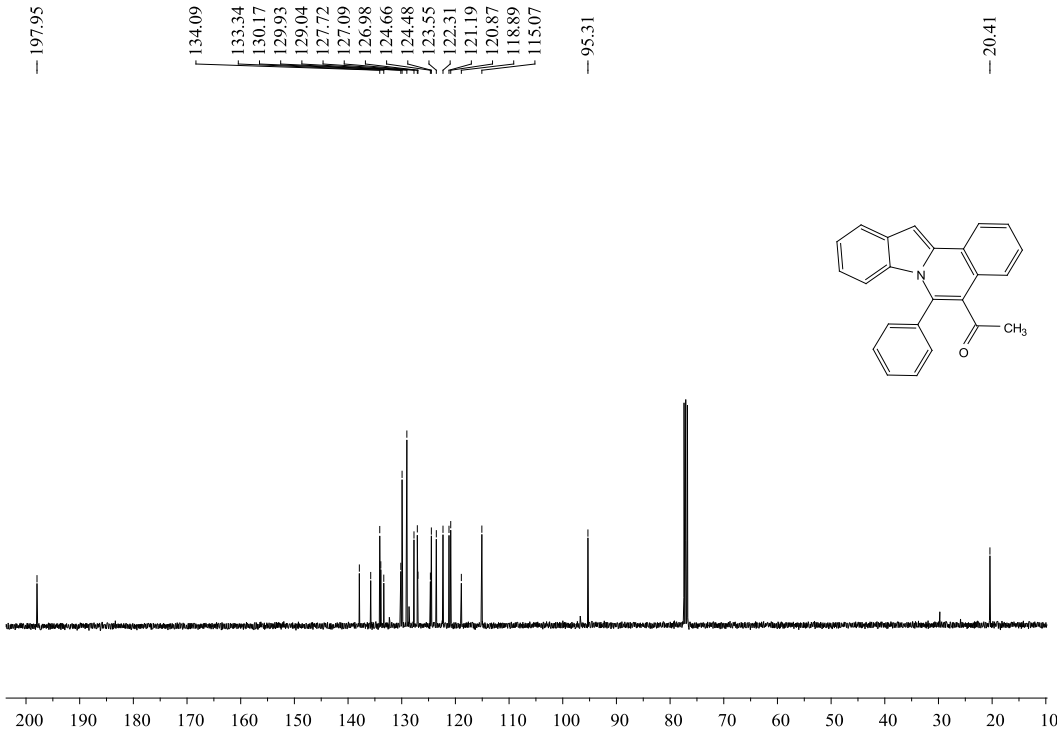
28) 1-(6-Methylindolo[2,1-a]isoquinolin-5-yl)ethanone (**3bz**) (Using $CDCl_3$ as solvent)



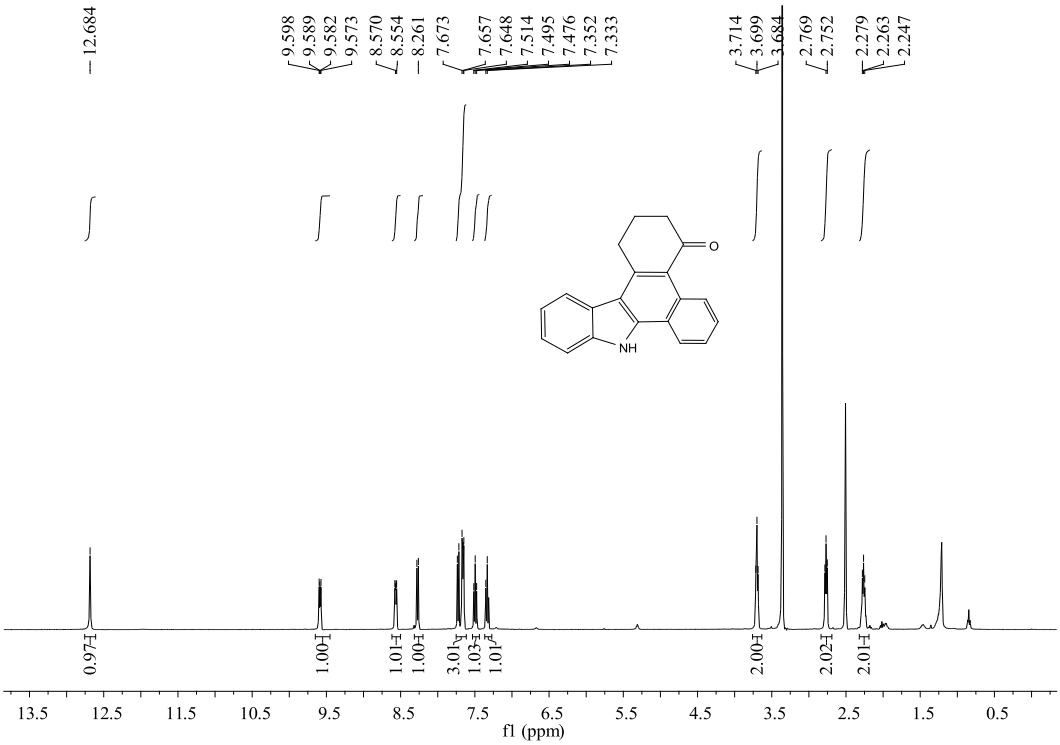


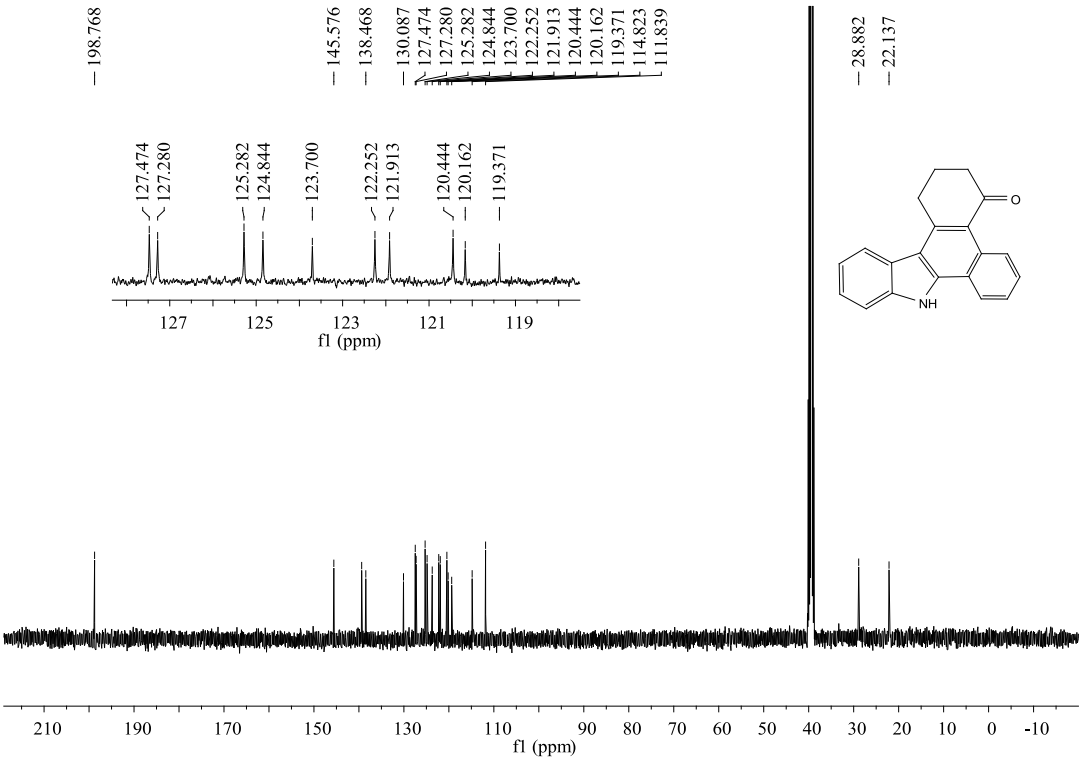
29) 1-(6-Phenylindolo[2,1-a]isoquinolin-5-yl)ethanone (**3cz**) (Using $CDCl_3$ as solvent)



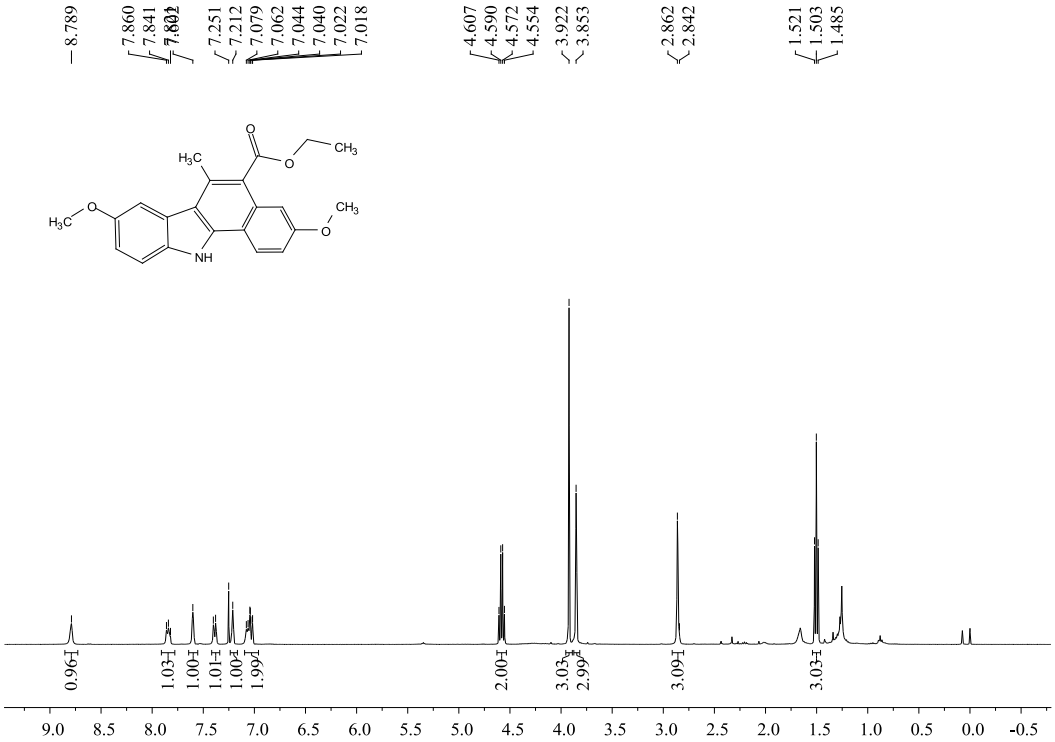


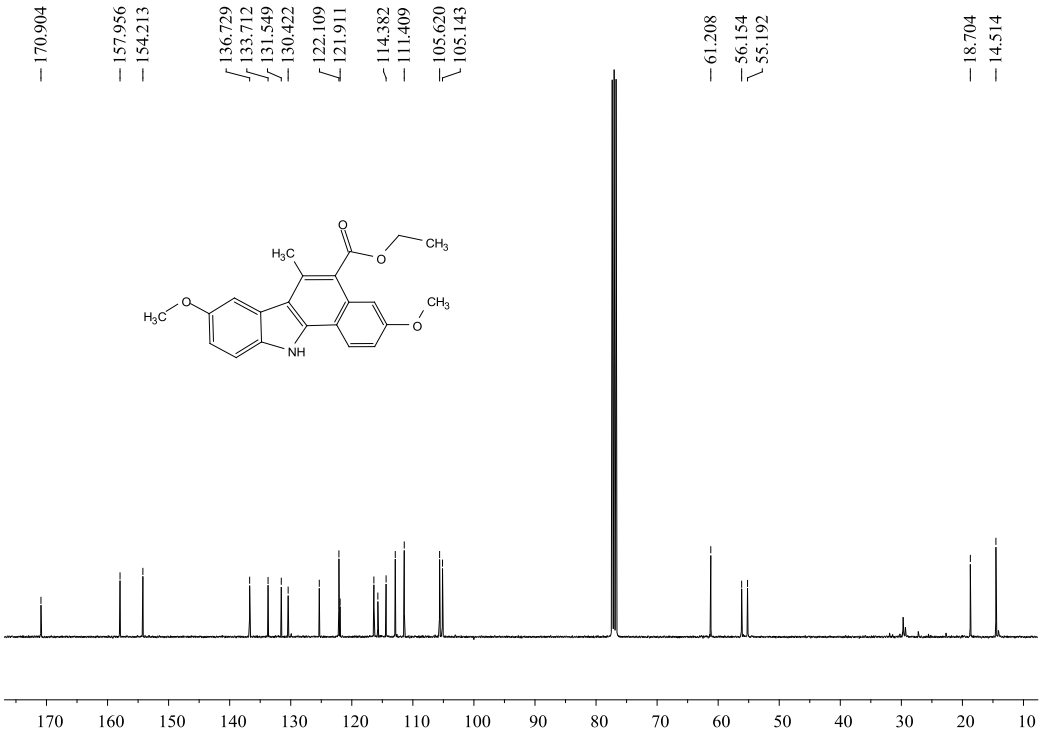
30) 2,3-Dihydro-1H-dibenzo[a,c]carbazol-4(9H)-one (**3dz**) (Using DMSO-d_6 as solvent)



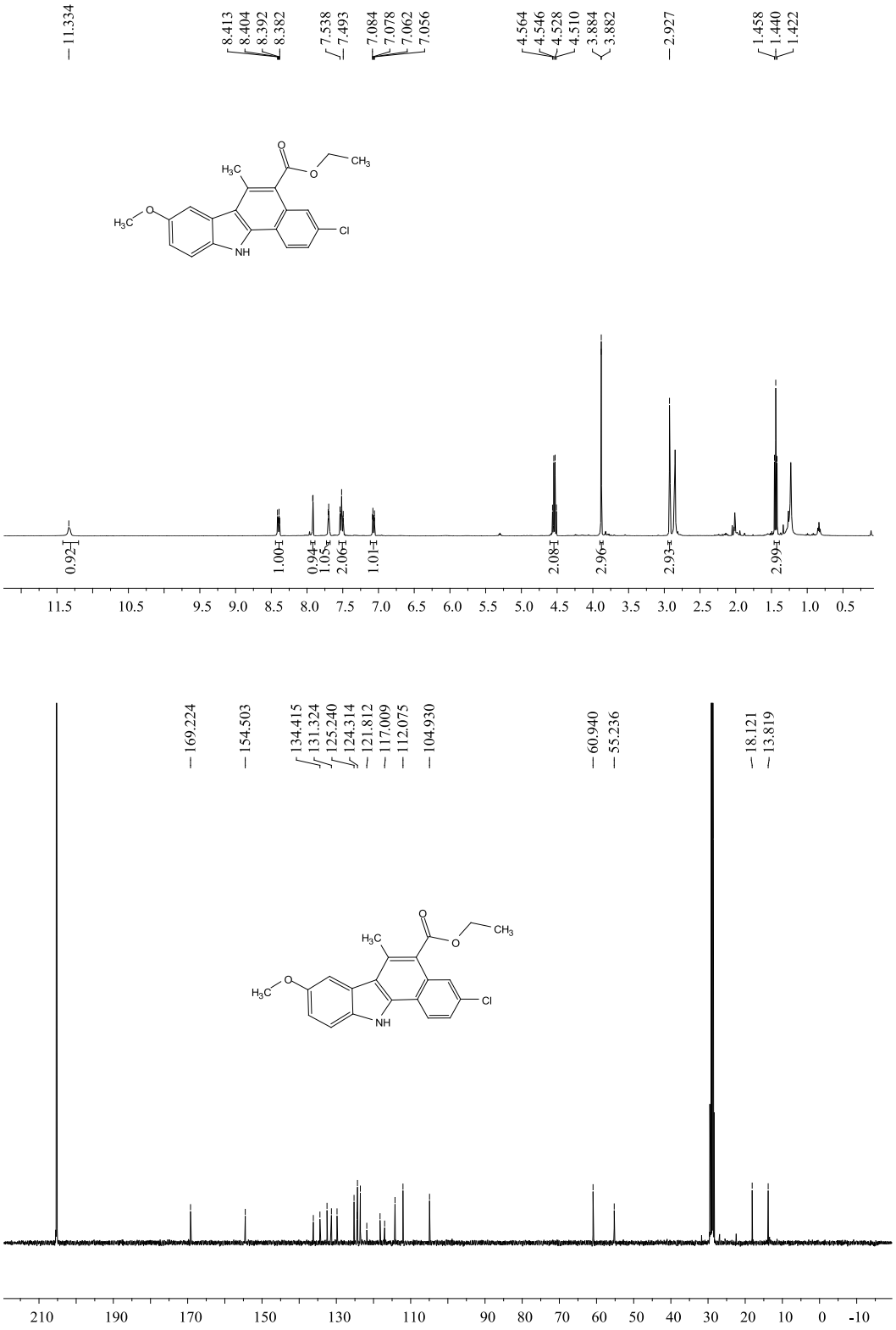


31) Ethyl 3,8-dimethoxy-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3fz**) (Using $CDCl_3$ as solvent)

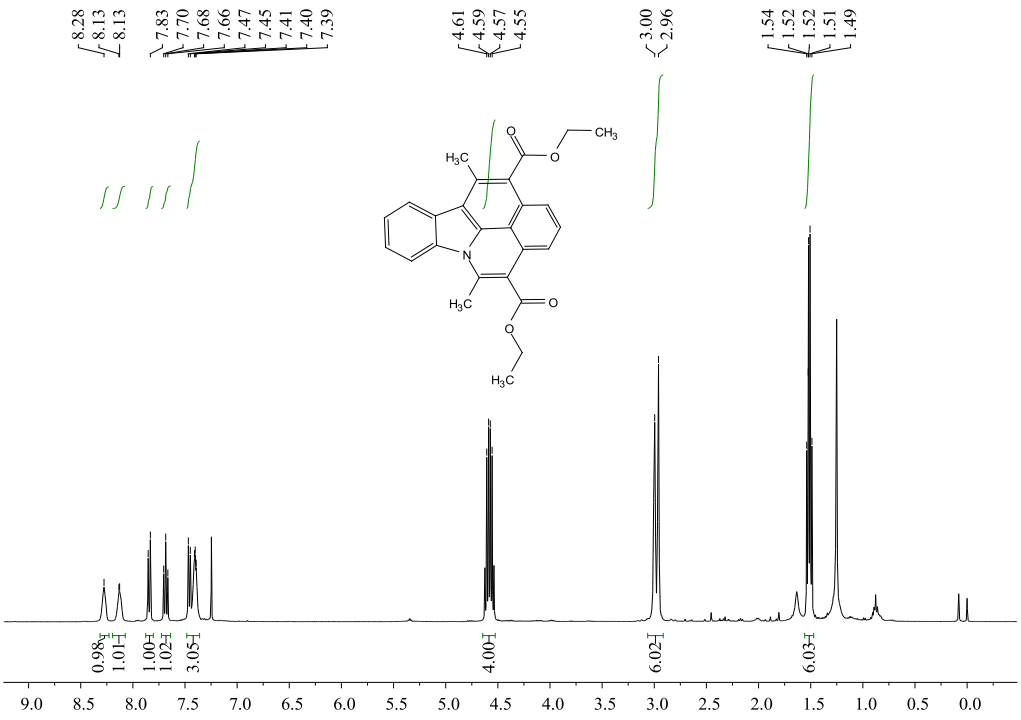


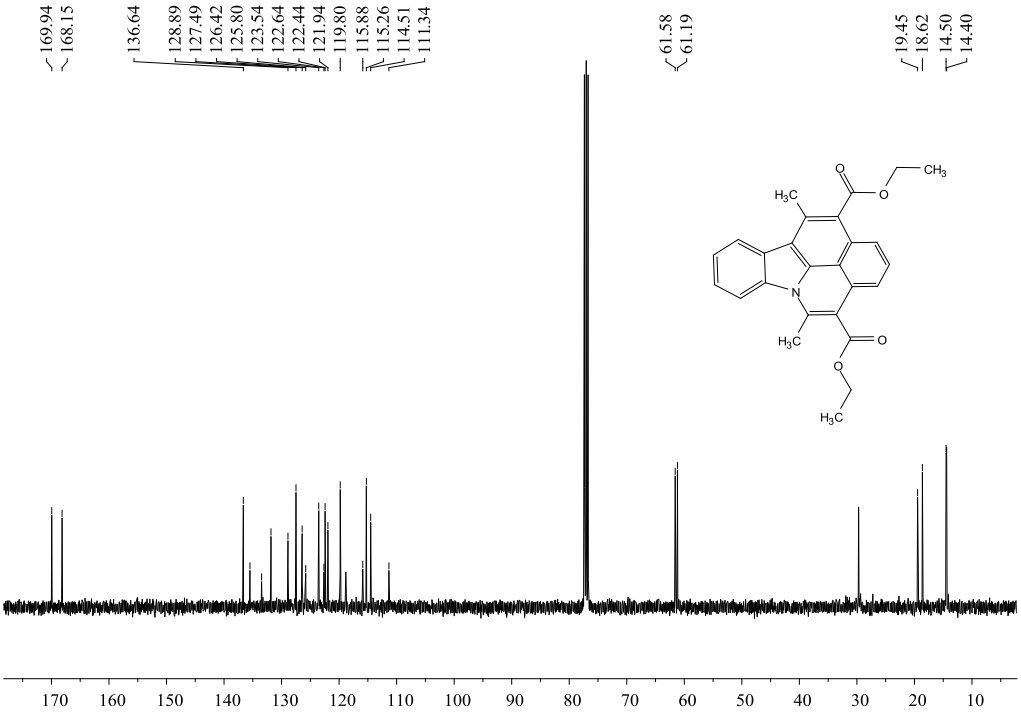


32) Ethyl 3-chloro-8-methoxy-6-methyl-11H-benzo[a]carbazole-5-carboxylate (**3gz**) (Using CD_3COCD_3 as solvent)

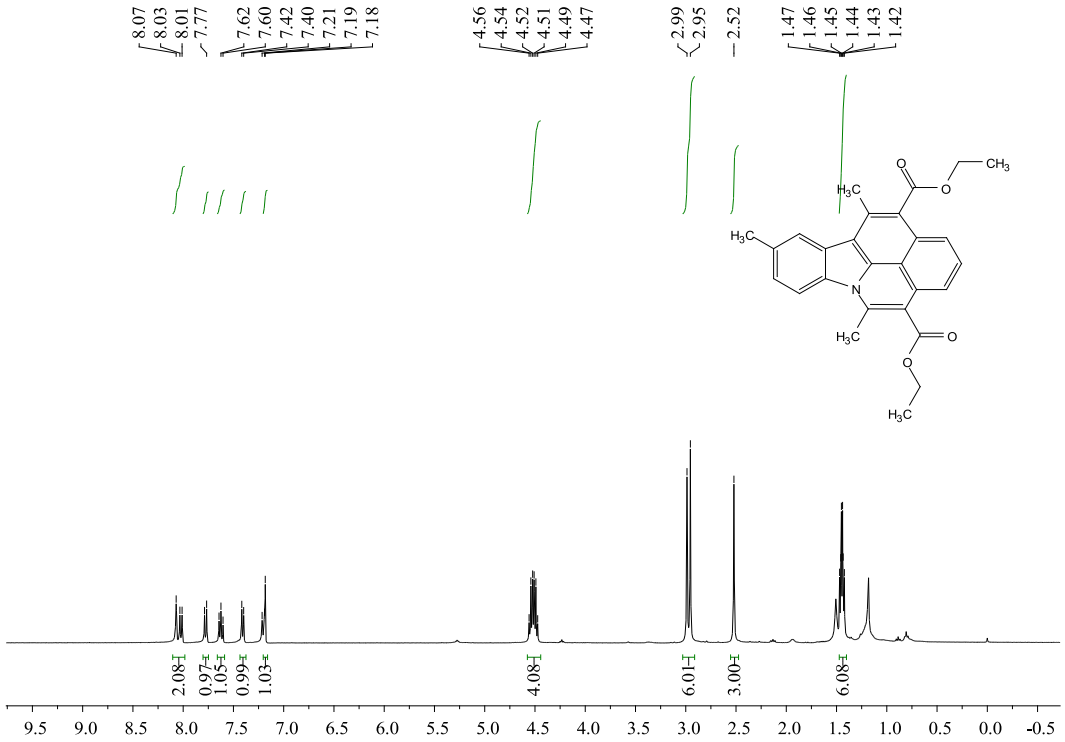


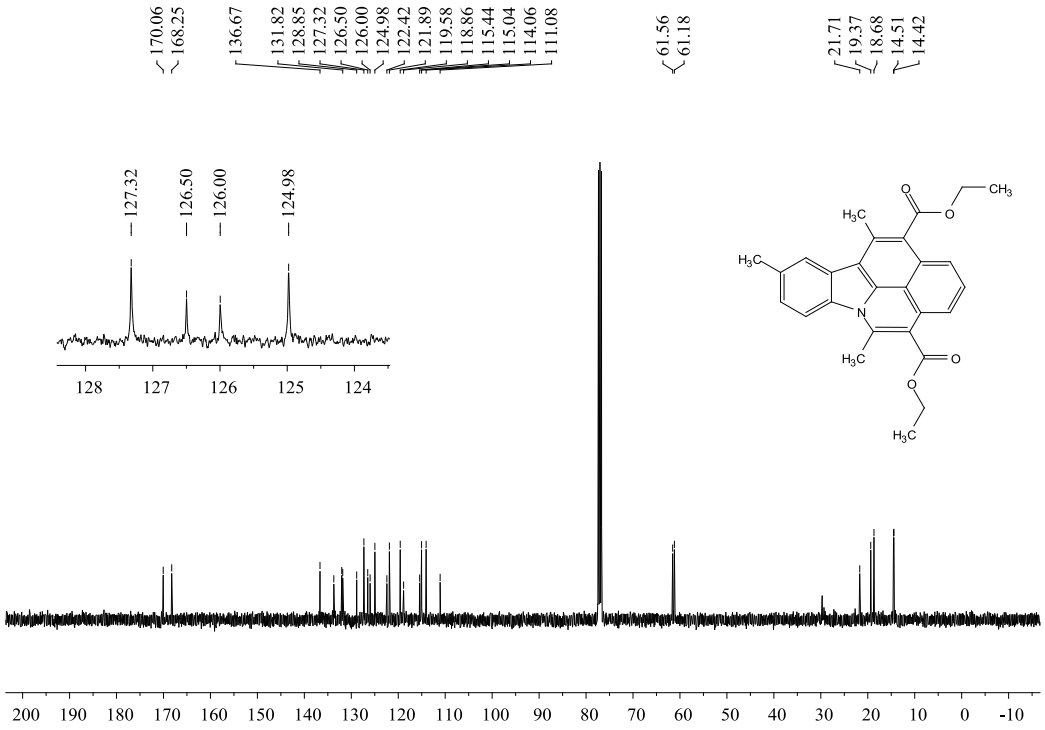
33) Diethyl 5,11-dimethylisoquinolino[2,1,8-lma]carbazole-4,12-dicarboxylate (**4a**) (Using $CDCl_3$ as solvent)



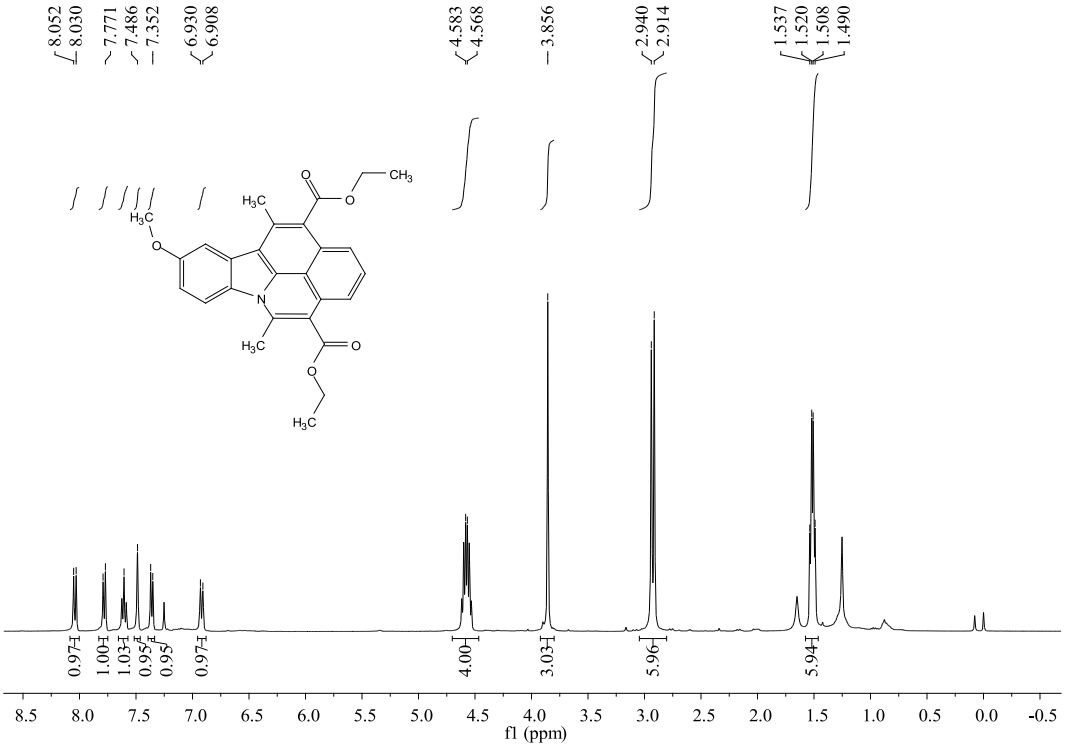


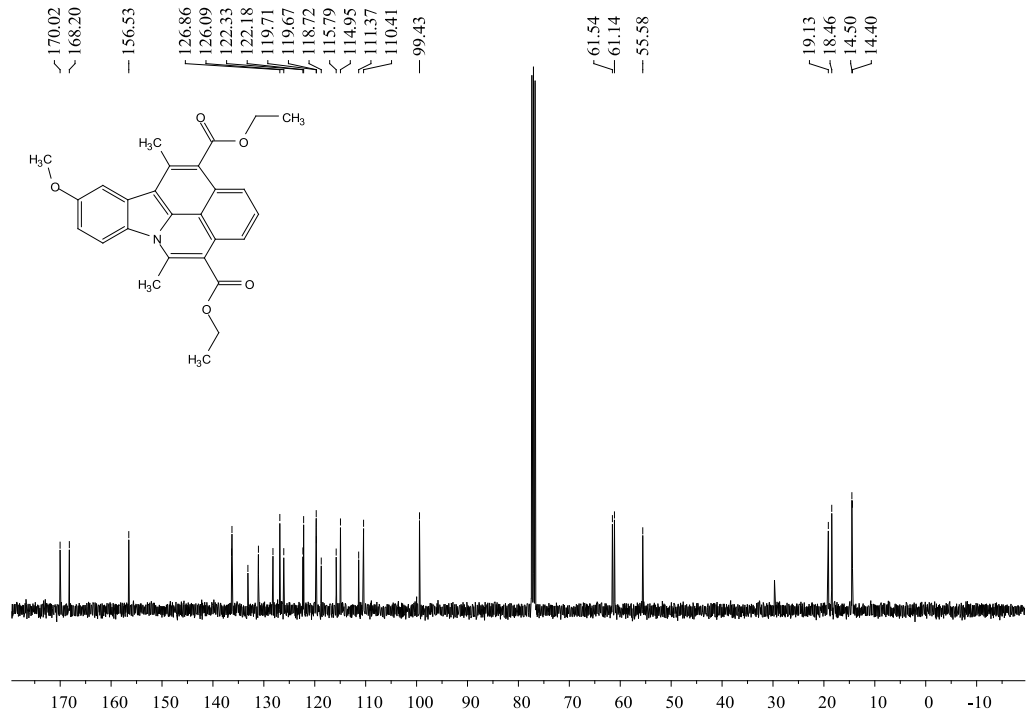
34) Diethyl 5,9,11-trimethylisoquinolino[2,1,8-lma]carbazole-4,12-dicarboxylate (**4b**) (Using $CDCl_3$ as solvent)



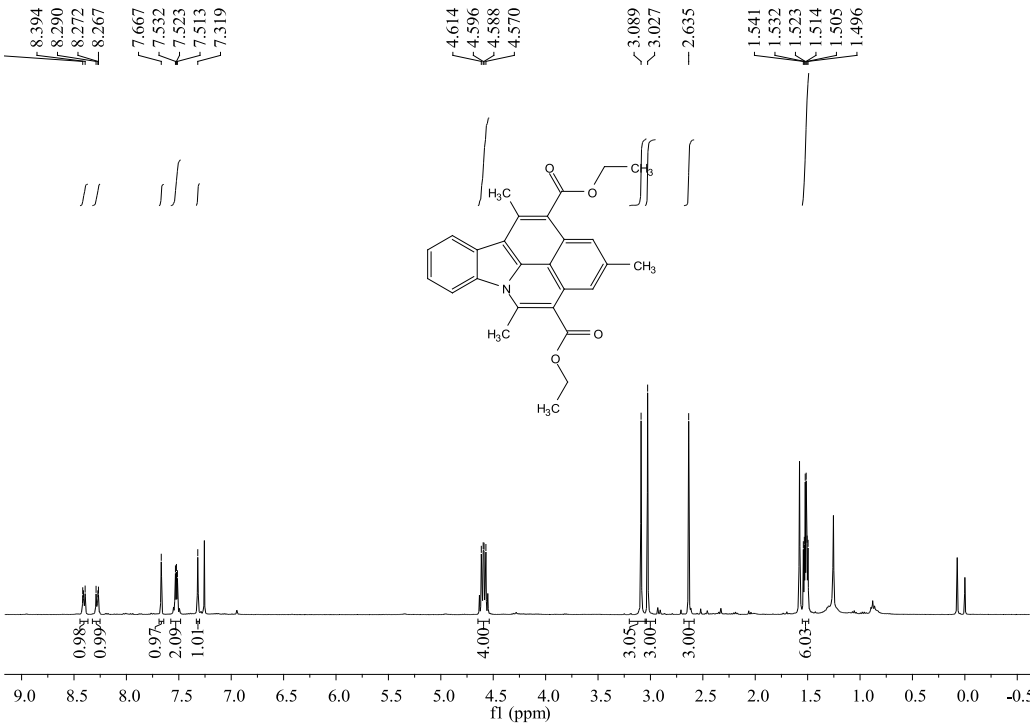


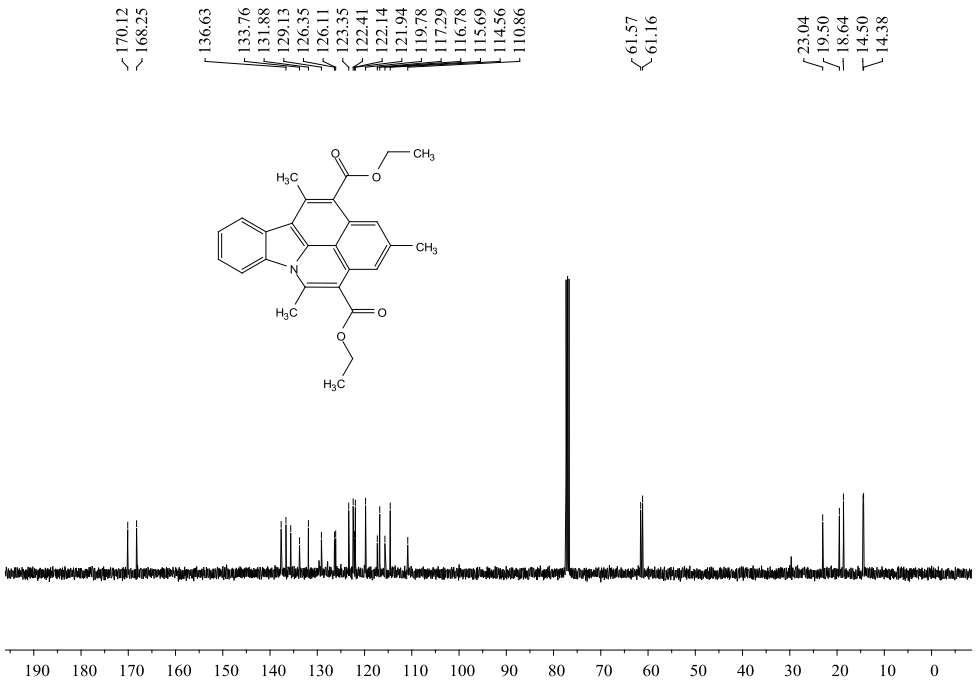
35) Diethyl 9-methoxy-5,11-dimethylisoquinolino[2,1,8-lma]carbazole-4,12-dicarboxylate (**4c**) (Using $CDCl_3$ as solvent)



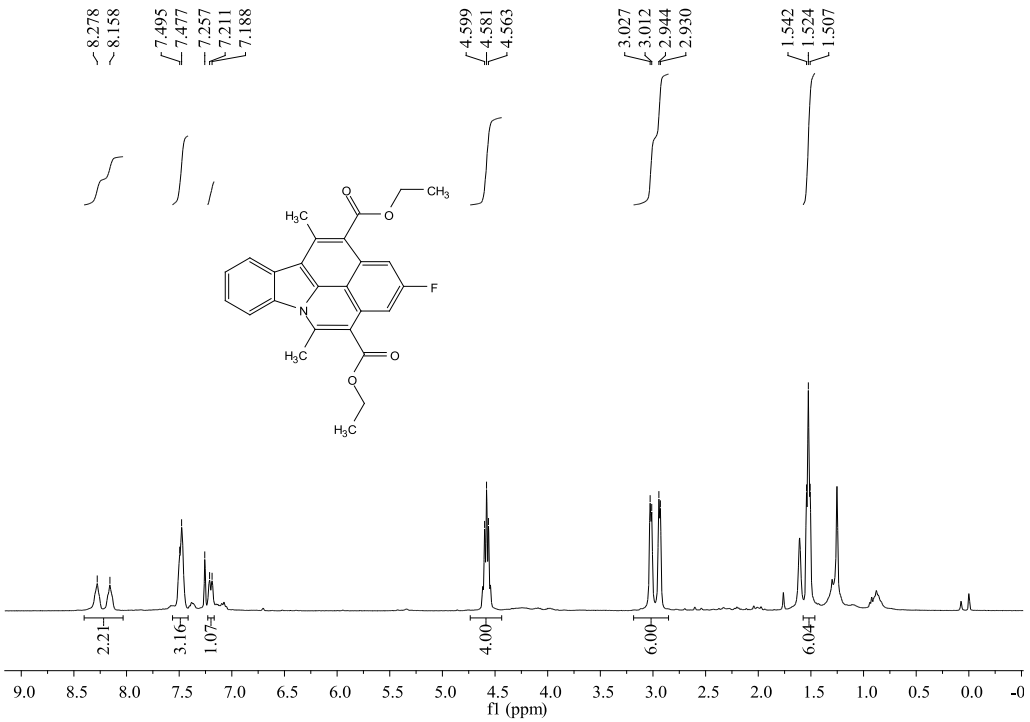


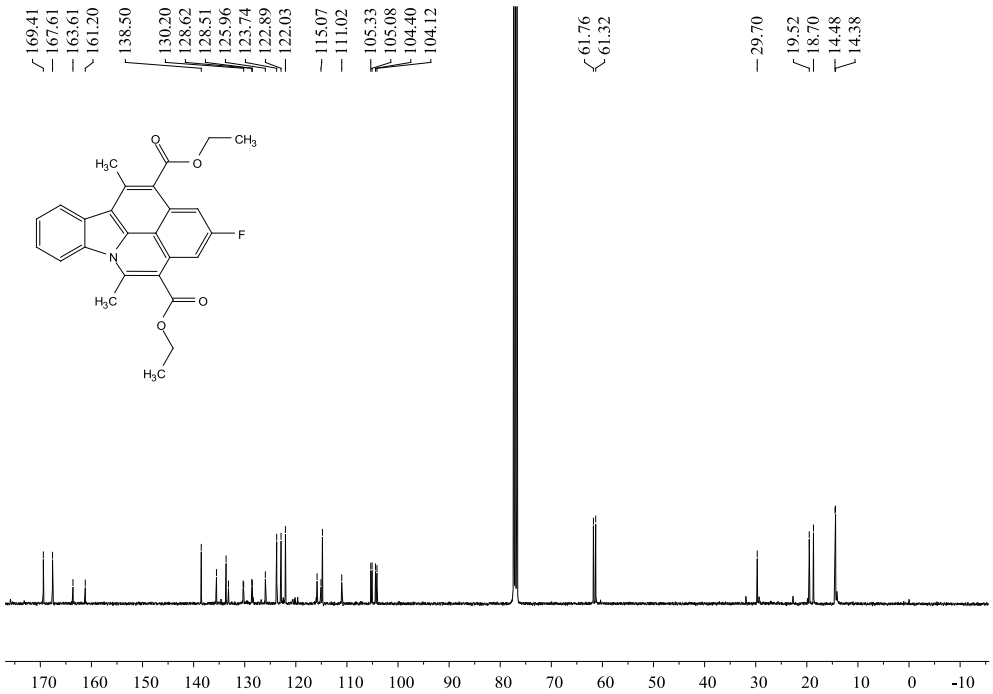
36) Diethyl 2,5,11-trimethylisoquinolino[2,1,8-lma]carbazole-4,12-dicarboxylate (**4d**) (Using $CDCl_3$ as solvent)



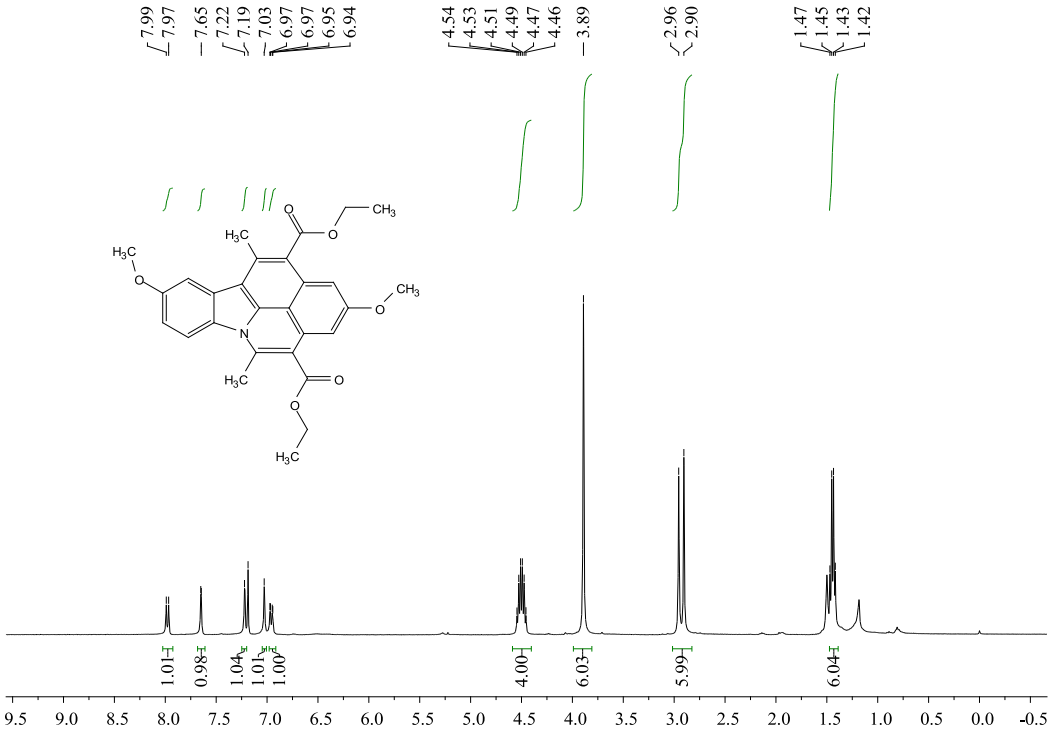


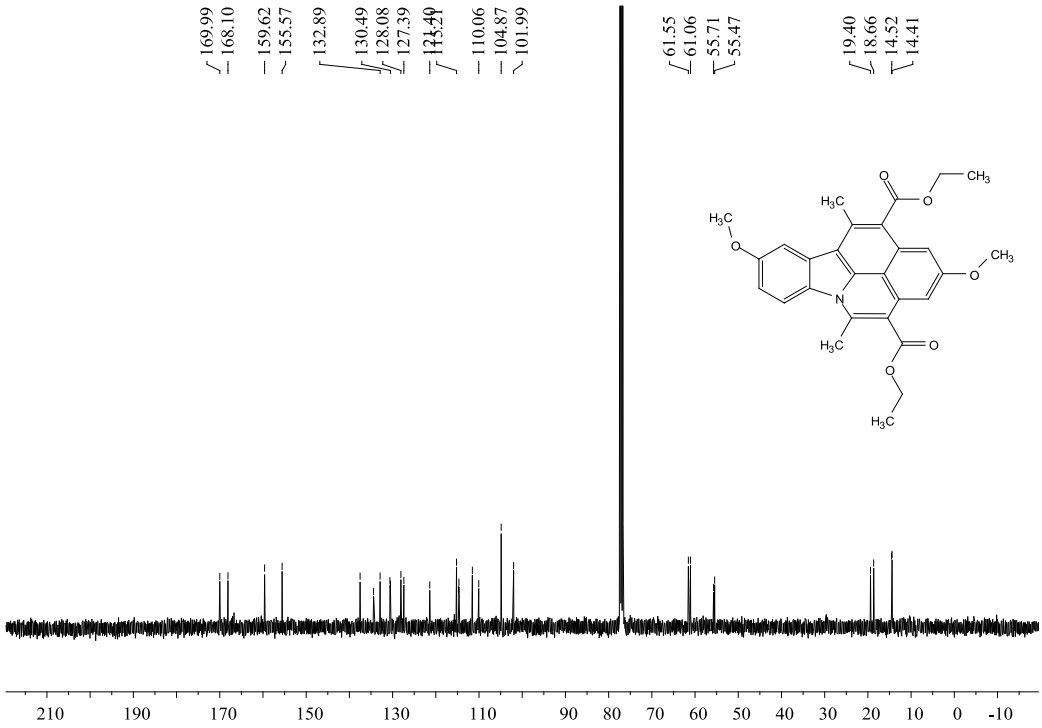
37) Diethyl 2-fluoro-5,11-dimethylisoquinolino[2,1,8-lma]carbazole-4,12-dicarboxylate (**4e**) (Using $CDCl_3$ as solvent)



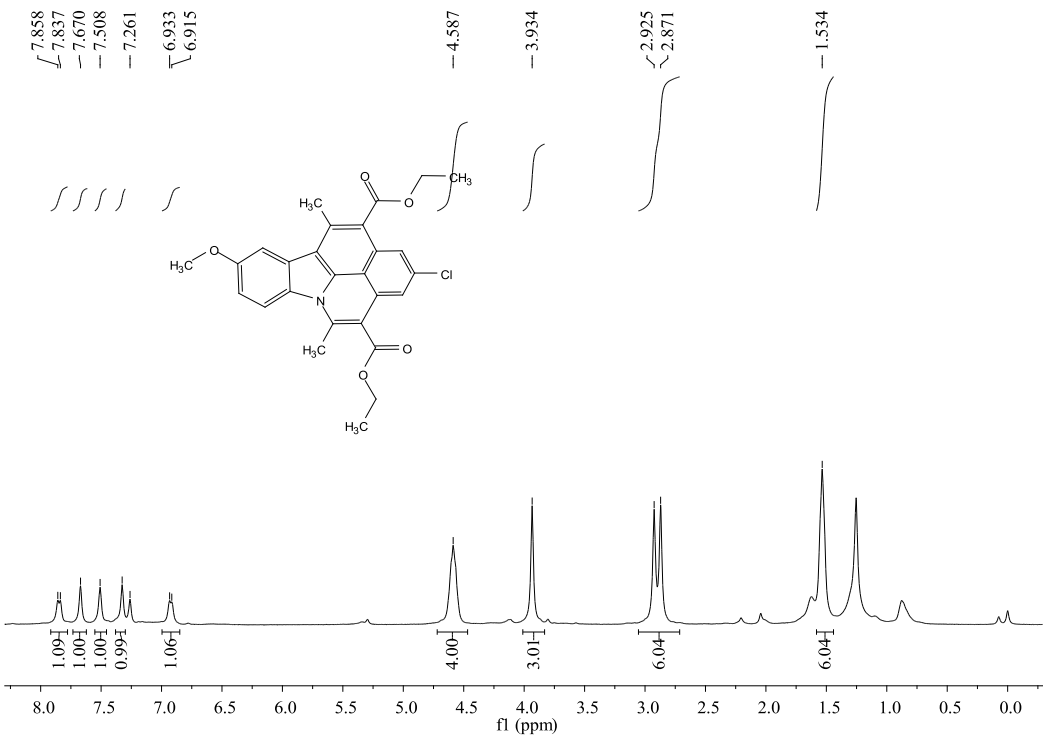


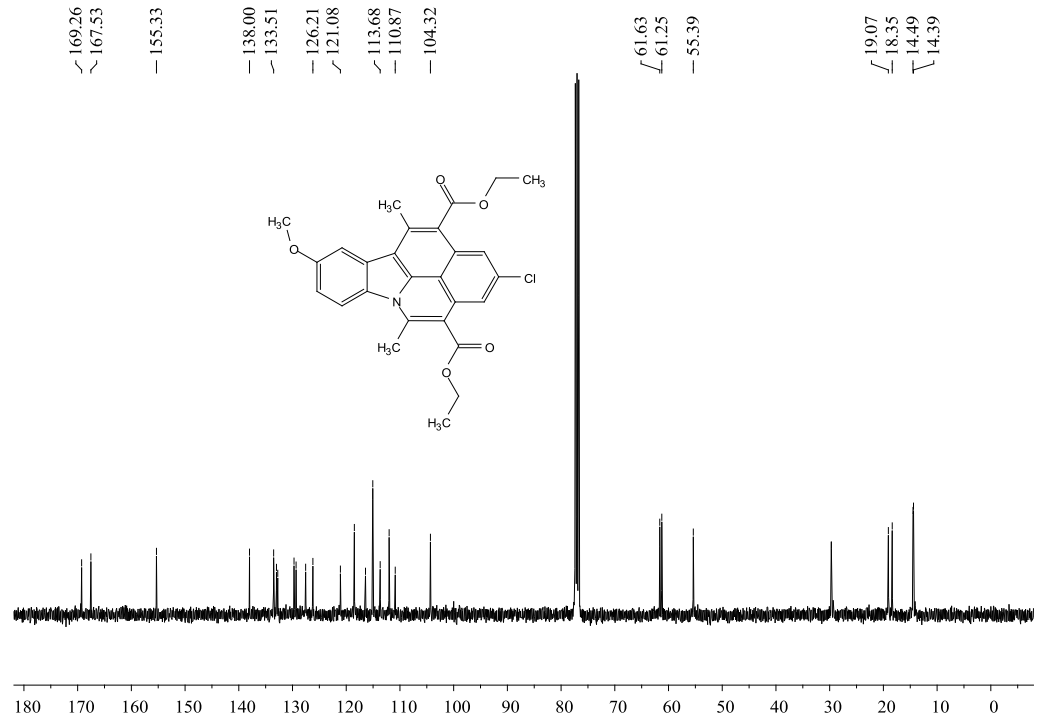
38) Diethyl 2,9-dimethoxy-5,11-dimethylisoquinolino[2,1,8-lma]carbazole-4,12-dicarboxylate (**4f**) (Using $CDCl_3$ as solvent)





39) Diethyl 2-chloro- 9- methoxy-5,11-dimethylisoquinolino[2,1,8-lma] carbazole-4,12-dicarboxylate (**4g**) (Using $CDCl_3$ as solvent)





40) Ethyl 6,11-dimethyl-11H-benzo[a]carbazole-5-carboxylate (**5a**) (Using $CDCl_3$ as solvent)