Supplementary Information

Direct C–H alkylation and indole formation of anilines with diazo compounds under rhodium catalysis

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General methods

Commercially available reagents were used without additional purification, unless otherwise stated. Sealed tubes (13 × 100 mm^2) were purchased from Fischer Scientific and dried in oven for overnight and cooled under a stream of nitrogen prior to use. Thin layer chromatography was carried out using plates coated with Kieselgel $60F_{254}$ (Merck). For flash column chromatography, E. Merck Kieselgel 60 (230-400 mesh) was used. Nuclear magnetic resonance spectra (^1H and ^{13}C NMR) were recorded on a Bruker Unity 500 MHz and 700 MHz spectrometer for $CDCl_3$ solutions and chemical shifts are reported as parts per million (ppm) relative to, respectively, residual $CHCl_3$ δ_H (7.24 ppm) and $CDCl_3$ δ_C (77.23 ppm) as internal standards. Resonance patterns are reported with the notations s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). In addition, the notation br is used to indicate a broad signal. Coupling constants (*J*) are reported in hertz (Hz). IR spectra were recorded on a Varian 2000 Infrared spectrophotometer and are reported as cm^{-1}. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 spectrometer.

General procedure for the synthesis of pyrimidyl arylamines:[1-3] To an oven-dried flask charged with aniline (977.8 mg, 10.5 mmol, 150 mol %), 2-chloropyrimidine (801.7 mg, 7.0 mmol, 100 mol %) and acetic acid (7 mL) in 1,4-dioxane (19 mL) was added. The reaction mixture was stirred at 110 ^{o}C for 24 h and monitored by TLC. Upon completion, the mixture was extracted with CH_2Cl_2 (3 × 20 mL) and washed with brine. The organic layer was dried over Mg_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc) to give *N*-phenylpyrimidin-2-amine **1a** (990.6 mg) in 82% yield.

General procedure for the synthesis of pyridinyl arylamines:[1-3] To an oven-dried flask charged with aniline (1.4 g, 15 mmol, 100 mol %), 2-bromopyridine (2.4 g, 15 mmol, 100 mol %) wad added. The reaction mixture was stirred at 160 ^{o}C for 7 h and monitored by TLC. Upon completion, saturated $NaHCO_3$ was added and the mixture was extracted with EtOAc (3 × 15 mL). The combined organic phase was washed with brine and dried over Mg_2SO_4. The solid was filtered off and the filtrate was evaporated in vacuum. The crude product was purified by flash column chromatography (*n*-hexanes/EtOAc) to give *N*-phenylpyridin-2-amine **4a** (2.44 g) in 95% yield.

General procedure for the synthesis of diazo substrates: Diazo substrates were prepared according to the previous literature.[4]

References:

[1] X. Huang, S. Xu, Q. Tan, M. Gao, M. Lia and B. Xu, *Chem. Commun*., 2014, **50**, 1465.

[2] L. Ackermann and A. V. Lygin, *Org. Lett*., 2012, **14**, 764.

[3] G. Qian, B. Liu, Q. Tan, S. Zhang and B. Xu, *Eur. J. Org. Chem*., 2014, 4837.

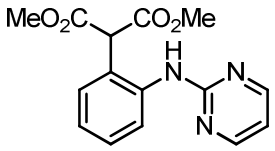
[4] N. D. Koduri, H. Scott, B. Hileman, J. D. Cox, M. Coffin, L. Glicksberg and S. R. Hussaini, *Org. Lett*., 2012, **14**, 440.

Typical procedure for the alkylation of *N*-phenylpyrimidin-2-amines (3a–3u)

To an oven-dried sealed tube charged with *N*-phenylpyrimidin-2-amine (**1a**) (34.2 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), and AgOAc (5 mg, 0.03 mmol, 15 mol %) in MeOH (1 mL) was added dimethyl 2-diazomalonate (**2a**) (37.9 mg, 0.24 mmol, 120 mol %) under air. The reaction mixture was allowed to stir at 60 °C for 24 h, and cooled to room temperature. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc: 3:1) to afford **3a** (37.2 mg) in 62% yield.

Characterization data for alkylated products (3a–3u)

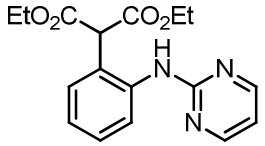
Dimethyl 2-(2-(pyrimidin-2-ylamino)phenyl)malonate (3a)



3a

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 4.5 Hz, 2H), 7.99 (br s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.39–7.35 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.67 (t, *J* = 4.5 Hz, 1H), 4.79 (s, 1H), 3.64 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 160.7, 158.1, 137.6, 130.9, 129.1, 127.7, 126.5, 125.4, 112.4, 55.4, 52.9, 29.6; IR (KBr) υ 3359, 2953, 2924, 1728, 1577, 1509, 1438, 1404, 1246, 1149, 1024, 799, 755 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{15}N_3O_4$ $[M]^+$ 301.1063, found 301.1058.

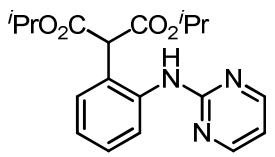
Diethyl 2-(2-(pyrimidin-2-ylamino)phenyl)malonate (3b)



3b

^{1}H NMR (700 MHz, $CDCl_3$) δ 8.34 (d, *J* = 4.9 Hz, 2H), 8.16 (br s, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.38–7.35 (m, 2H), 7.16 (d, *J* = 7.7 Hz, 1H), 6.65 (t, *J* = 4.9 Hz, 1H), 4.72 (s, 1H), 4.17–4.13 (m, 2H), 4.11–4.06 (m, 2H), 1.17 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.7, 160.6, 158.0, 137.7, 131.0, 128.9, 127.4, 125.9, 125.0, 112.3, 62.0, 56.0, 13.8; IR (KBr) υ 3350, 2981, 2927, 1724, 1577, 1513, 1439, 1402, 1300, 1245, 1148, 1029, 799, 754 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{19}N_3O_4$ $[M]^+$ 329.1376, found 329.1375.

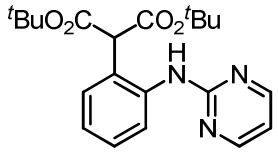
Diisopropyl 2-(2-(pyrimidin-2-ylamino)phenyl)malonate (3c)



3c

^{1}H NMR (700 MHz, $CDCl_3$) δ 8.34 (d, *J* = 4.9 Hz, 2H), 8.31 (br s, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.35–7.41 (m, 2H), 7.13 (d, *J* = 7.7 Hz, 1H), 6.64 (t, *J* = 4.5 Hz, 1H), 5.01–4.97 (m, 2H), 4.67 (s, 1H), 1.21 (d, *J* = 6.3 Hz, 6H), 1.13 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.3, 160.5, 158.0, 137.8, 131.1, 128.8, 127.1, 125.2, 124.6, 112.3, 69.8, 56.5, 21.4, 21.3; IR (KBr) υ 3351, 2980, 2925, 1722, 1578, 1516, 1442, 1405, 1239, 1159, 1097, 995, 905, 799, 754 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{23}N_3O_4$ $[M]^+$ 357.1689, found 357.1691.

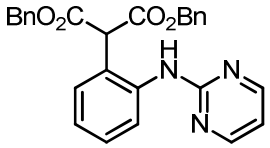
Di-*tert*-butyl 2-(2-(pyrimidin-2-ylamino)phenyl)malonate (3d)



3d

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (br s, 1H), 8.36 (d, *J* = 5.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.36–7.32 (m, 2H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.41 (t, *J* = 5.0 Hz, 1H), 4.58 (s, 1H), 1.39 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.0, 160.6, 158.0, 137.8, 131.2, 128.5, 127.2, 124.9, 124.4, 112.2, 82.6, 58.3, 27.7; IR (KBr) υ 3342, 2978, 2930, 1712, 1578, 1519, 1441, 1367, 1247, 1131, 799, 754 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{27}N_3O_4$ $[M]^+$ 385.2002, found 385.2002.

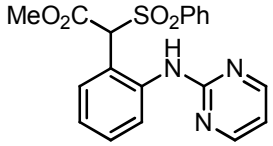
Dibenzyl 2-(2-(pyrimidin-2-ylamino)phenyl)malonate (3e)



3e

^{1}H NMR (700 MHz, $CDCl_3$) δ 8.28 (d, *J* = 4.9 Hz, 2H), 8.03 (br s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.41–7.38 (m, 2H), 7.30–7.29 (m, 6H), 7.26–7.25 (m, 4H), 7.19 (d, *J* = 7.7 Hz, 1H), 6.63 (t, *J* = 4.9 Hz, 1H), 5.15 (d, *J* = 11.9 Hz, 2H), 5.04 (d, *J* = 12.6 Hz, 2H), 4.90 (s, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.4, 160.6, 158.0, 137.6, 135.0, 130.9, 129.1, 128.4, 128.3, 128.2, 127.6, 126.1, 125.3, 112.4, 67.6, 55.4; IR (KBr) υ 3358, 2957, 2924, 1725, 1577, 1440, 1218, 1136, 1002, 799, 748, 697 cm^{-1}; HRMS (EI) calcd for $C_{27}H_{23}N_3O_4$ $[M]^+$ 453.1689, found 453.1683.

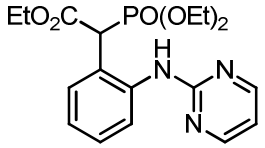
Methyl 2-(phenylsulfonyl)-2-(2-(pyrimidin-2-ylamino)phenyl)acetate (3f)



3f

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 4.5 Hz, 2H), 7.94 (br s, 1H), 7.72–7.71 (m, 3H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 9.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 4.5 Hz, 1H), 5.69 (s, 1H), 3.65 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.3, 160.6, 158.1, 138.6, 135.8, 134.3, 130.3, 130.2, 130.1, 128.5, 126.1, 125.2, 121.9, 112.9, 69.9, 53.0; IR (KBr) υ 3354, 2954, 2923, 1743, 1577, 1513, 1440, 1405, 1322, 1309, 1144, 1080, 799, 758, 686 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{17}N_3O_4S$ $[M]^+$ 383.0940, found 383.0949.

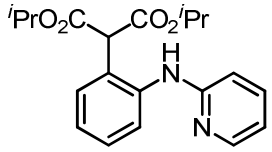
Ethyl 2-(diethoxyphosphoryl)-2-(2-(pyrimidin-2-ylamino)phenyl)acetate (3g)



3g

^{1}H NMR (700 MHz, $CDCl_3$) δ 8.63 (br s, 1H), 8.38 (br s, 2H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 7.7 Hz, 1H), 6.68 (t, *J* = 4.9 Hz, 1H), 4.57 (d, *J* = 2.8 Hz, 1H), 4.16–3.99 (m, 6H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.21 (t, *J* = 7.0 Hz, 3H), 7.15 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 167.5, 160.3, 158.0, 137.5 (d, $J_{C\text{-}P}$ = 5.6 Hz), 130.1 (d, $J_{C\text{-}P}$ = 5.0 Hz), 128.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 125.5, 125.0 (d, $J_{C\text{-}P}$ = 2.1 Hz), 124.5 (d, $J_{C\text{-}P}$ = 8.5 Hz), 112.2, 64.0 (d, $J_{C\text{-}P}$ = 7.0 Hz), 63.3 (d, $J_{C\text{-}P}$ = 7.0 Hz), 61.8, 48.1 (d, $J_{C\text{-}P}$ = 137.3 Hz), 16.3 (d, $J_{C\text{-}P}$ = 5.6 Hz), 16.2 (d, $J_{C\text{-}P}$ = 5.9 Hz), 13.8; IR (KBr) υ 3262, 2981, 2926, 1730, 1577, 1517, 1439, 1405, 1237, 1016, 962, 797, 751 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{24}N_3O_5P$ $[M]^+$ 393.1454, found 393.1452.

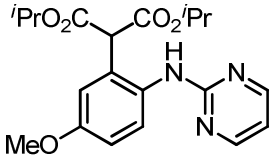
Diisopropyl 2-(2-(pyridin-2-ylamino)phenyl)malonate (3h)



3h

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 5.0 Hz, 1H), 7.60 (br s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.36–7.30 (m, 2H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.65 (t, *J* = 5.0 Hz, 1H), 6.60 (d, *J* = 8.5 Hz, 1H), 4.98–4.93 (m, 2H), 4.70 (s, 1H), 1.19 (d, *J* = 6.0 Hz, 6H), 1.14 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 156.5, 147.9, 139.3, 137.5, 131.5, 129.1, 128.4, 124.9, 124.6, 108.4, 56.2, 21.4; IR (KBr) υ 3362, 2981, 2931, 1715, 1592, 1441, 1299, 1220, 1161, 1097, 769 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{24}N_2O_4$ $[M]^+$ 356.1736, found 356.1737.

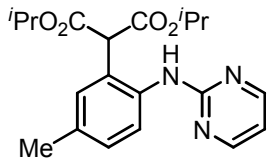
Diisopropyl 2-(5-methoxy-2-(pyrimidin-2-ylamino)phenyl)malonate (3i)



3i

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 4.5 Hz, 2H), 7.75 (br s, 1H), 7.51 (d, *J* = 9.0 Hz, 1H), 6.97 (d, *J* = 2.5 Hz, 1H), 6.91 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.61 (t, *J* = 5.0 Hz, 1H), 5.01–4.96 (m, 2H), 4.67 (s, 1H), 3.80 (s, 3H), 1.22 (d, *J* = 6.0 Hz, 6H), 1.14 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.0, 161.1, 158.0, 156.9, 130.3, 129.7, 127.6, 116.0, 114.3, 111.9, 69.7, 55.8, 55.4, 21.5, 21.4; IR (KBr) υ 3364, 2980, 2930, 1724, 1582, 1505, 1445, 1231, 1160, 1096, 1039, 983, 903, 800 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{25}N_3O_5$ $[M]^+$ 387.1794, found 387.1797.

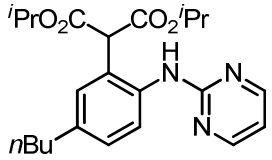
Diisopropyl 2-(5-methyl-2-(pyrimidin-2-ylamino)phenyl)malonate (3j)



3j

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 4.8 Hz, 2H), 8.07 (br s, 1H), 7.57 (d, *J* = 6.8 Hz, 1H), 7.16 (d, *J* = 6.4 Hz, 2H), 6.62 (t, *J* = 4.8 Hz, 1H), 5.02–4.96 (m, 2H), 4.64 (s, 1H), 2.33 (s, 3H), 1.21 (d, *J* = 6.4 Hz, 6H), 1.13 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.3, 160.8, 158.0, 134.9, 134.7, 131.6, 129.5, 127.5, 125.7, 112.0, 69.7, 56.2, 21.5,21.4, 20.8; IR (KBr) υ 3347, 2980, 2925, 1723, 1581, 1517, 1444, 1410, 1242, 1163, 1097, 987, 905, 800 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{25}N_3O_4$ $[M]^+$ 371.1845, found 371.1843.

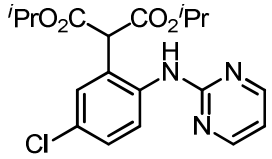
Diisopropyl 2-(5-butyl-2-(pyrimidin-2-ylamino)phenyl)malonate (3k)



3k

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (br s, 2H), 8.05 (br s, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 6.5 Hz, 2H), 6.61 (t, *J* = 8.5 Hz, 1H), 5.01–4.96 (m, 2H), 4.65 (s, 1H), 2.58 (t, *J* = 7.5 Hz, 2H), 1.61–1.56 (m, 2H), 1.38–1.34 (m, 2H), 1.22 (d, *J* = 6.5 Hz, 6H), 1.13 (d, *J* = 6.0 Hz, 6H), 0.91(t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 160.9, 158.0, 139.5, 135.2, 130.9, 128.8, 127.2, 125.4, 112.0, 69.6, 56.2, 35.0, 33.4, 22.3, 21.5, 21.4, 13.9; IR (KBr) υ 3349, 2980, 2930, 1725, 1581, 1518, 1446, 1164, 1099, 987, 907, 799 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{31}N_3O_4$ $[M]^+$ 413.2315, found 413.2315.

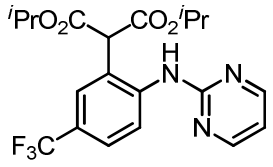
Diisopropyl 2-(5-chloro-2-(pyrimidin-2-ylamino)phenyl)malonate (3l)



3l

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 4.5 Hz, 2H), 8.26 (br s, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.34 (s, 1H), 7.30 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.66 (t, *J* = 5.0 Hz, 1H), 5.02–4.97 (m, 2H), 4.61 (s, 1H), 1.21 (d, *J* = 6.5 Hz, 6H), 1.13 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 160.4, 158.0, 136.6, 131.0, 129.4, 128.8, 128.4, 126.4, 112.7, 70.1, 56.2, 21.4, 21.3; IR (KBr) υ 3341, 2981, 2933, 1720, 1577, 1508, 1444, 1407, 1245, 1165, 1095, 976, 903, 798 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{22}ClN_3O_4$ $[M]^+$ 391.1299, found 391.1299.

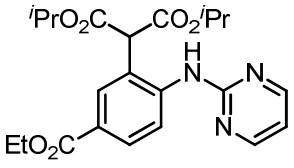
Diisopropyl 2-(2-(pyrimidin-2-ylamino)-5-(trifluoromethyl)phenyl)malonate (3m)



3m

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.40 (d, J = 4.5 Hz, 2H), 8.08 (d, J = 8.5 Hz, 1H), 7.60–7.57 (m, 2H), 6.73 (t, J = 5.0 Hz, 1H), 5.04–5.00 (m, 2H), 4.68 (s, 1H), 1.22 (d, J = 6.0 Hz, 6H), 1.14 (d, J = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 160.0, 158.1, 141.5, 128.5 (q, $J_{C\text{-}F}$ = 3.6 Hz), 126.0, 125.9 (q, $J_{C\text{-}F}$ = 3.6 Hz), 125.4 (q, $J_{C\text{-}F}$ = 32.6 Hz), 125.1, 124.2, 122.9, 113.3, 56.9, 21.4, 21.3; IR (KBr) υ 3353, 2984, 2936, 1722, 1578, 1525, 1447, 1423, 1330, 1303, 1163, 1101 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{22}F_3N_3O_4$ $[M]^+$ 425.1562, found 425.1565.

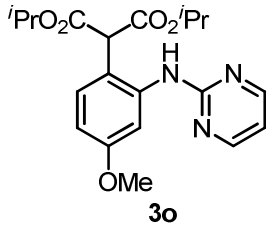
Diisopropyl 2-(5-(ethoxycarbonyl)-2-(pyrimidin-2-ylamino)phenyl)malonate (3n)



3n

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.40 (d, J = 5.0 Hz, 2H), 8.10 (d, J = 8.5 Hz, 1H), 7.96 (s, 1H), 6.70 (t, J = 5.0 Hz, 1H), 5.05–5.00 (m, 2H), 4.69 (s, 1H), 4.35 (q, J = 7.0 Hz, 2H), 1.37 (t, J = 7.5 Hz, 3H), 1.22 (d, J = 6.0 Hz, 6H), 1.12 (d, J = 6.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 166.0, 160.0, 158.0, 142.7, 133.2, 130.3, 125.2, 125.0, 123.0, 113.2, 70.2, 60.8, 57.4, 21.4, 21.3, 14.3; IR (KBr) υ 3335, 2980, 2923, 1711, 1576, 1519, 1444, 1415, 1278, 1171, 1095, 1017, 988, 913, 797, 766 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{27}N_3O_6$ $[M]^+$ 429.1900, found 429.1902.

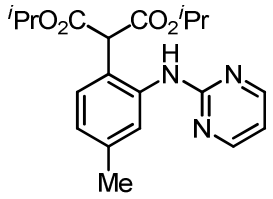
Diisopropyl 2-(4-methoxy-2-(pyrimidin-2-ylamino)phenyl)malonate (3o)



3o

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36–8.35 (m, 3H), 7.44 (d, *J* = 2.5 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 6.68–6.64 (m, 2H), 5.02–4.97 (m, 2H), 4.60 (s, 1H), 3.80 (s, 3H), 1.21 (d, *J* = 6.0 Hz, 6H), 1.14 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6, 160.4, 159.8, 158.0, 138.8, 131.9, 118.9, 112.4, 110.5, 110.0, 69.7, 55.9, 55.2, 21.5, 21.4; IR (KBr) υ 3345, 2980, 2925, 1720, 1577, 1520, 1442, 1254, 1165, 1098, 800 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{25}N_3O_5$ $[M]^+$ 387.1794, found 387.1793.

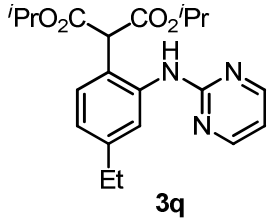
Diisopropyl 2-(4-methyl-2-(pyrimidin-2-ylamino)phenyl)malonate (3p)



3p

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 4.8 Hz, 2H), 8.26 (br s, 1H), 7.57 (s, 1H), 7.28 (d, *J* = 2.8 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.66 (t, *J* = 4.8 Hz, 1H), 5.05–4.99 (m, 2H), 4.67 (s, 1H), 2.37 (s, 3H), 1.23 (d, *J* = 6.4 Hz, 6H), 1.15 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.4, 160.5, 157.9, 138.8, 137.3, 130.9, 125.9, 125.8, 124.4, 112.1, 69.6, 56.0, 21.5, 21.4, 21.3; IR (KBr) υ 3354, 2980, 2927, 1723, 1576, 1524, 1444, 1253, 1165, 1099, 801 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{25}N_3O_4$ $[M]^+$ 371.1845, found 371.1843.

Diisopropyl 2-(4-ethyl-2-(pyrimidin-2-ylamino)phenyl)malonate (3q)

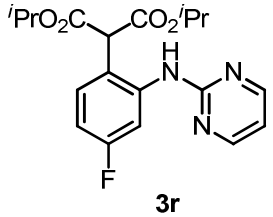


3q

^{1}H NMR (700 MHz, $CDCl_3$) δ 8.35 (d, *J* = 4.9 Hz, 2H), 8.23 (br s, 1H), 7.54 (s, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.65 (t, *J* = 4.9 Hz, 1H), 5.02–4.98 (m, 2H), 4.65 (s, 1H), 2.68 (q, *J* = 7.7 Hz, 2H), 1.23–1.21 (m, 9H), 1.14 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.4, 160.4, 158.0, 145.0, 137.2, 130.9, 125.0, 124.8, 124.7, 112.1, 69.7, 55.8, 28.5, 21.5, 21.4, 15.0; IR (KBr) υ 3350, 2978, 2932, 1721, 1574, 1523, 1445,

1428, 1402, 1160, 1097, 800 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{27}N_3O_4$ $[M]^+$ 385.2002, found 385.1999.

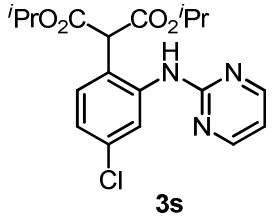
Diisopropyl 2-(4-fluoro-2-(pyrimidin-2-ylamino)phenyl)malonate (3r)



3r

^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.37 (d, *J* = 4.8 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.34–7.28 (m, 1H), 6.87 (t, *J* = 8.8 Hz, 1H), 6.68 (t, *J* = 4.8 Hz, 1H), 5.08 (s, 1H), 5.02–4.96 (m, 2H), 1.22 (d, *J* = 6.4 Hz, 6H), 1.11 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.2, 160.9 (d, $J_{C\text{-}F}$ = 243.9 Hz), 160.0, 157.9, 138.8, 129.4 (d, $J_{C\text{-}F}$ = 10.1 Hz), 120.2, 114.6, 112.7, 110.6 (d, $J_{C\text{-}F}$ = 22.9 Hz), 70.2, 48.7, 21.4, 21.3.; IR (KBr) υ 3337, 2982, 2926, 1721, 1575, 1517. 1438, 1401, 1235, 1171, 1098, 798 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{22}FN_3O_4$ $[M]^+$ 375.1594, found 375.1595.

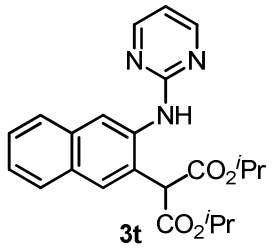
Diisopropyl 2-(4-chloro-2-(pyrimidin-2-ylamino)phenyl)malonate (3s)



3s

^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.37 (d, *J* = 4.8 Hz, 2H), 7.92 (d, *J* = 2.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.08 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.70 (t, *J* = 4.8 Hz, 1H), 5.04–4.98 (m, 2H), 4.63 (s, 1H), 1.21 (d, *J* = 6.4 Hz, 6H), 1.13 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.0, 160.0, 158.0, 139.0, 134.3, 132.1, 124.7, 124.6, 124.3, 112.9, 70.0, 56.1, 21.4, 21.3; IR (KBr) υ 3272, 2980, 2924, 1576, 1519, 1446, 1417, 1240, 1098, 994, 935, 796, 772 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{22}ClN_3O_4$ $[M]^+$ 391.1299, found 391.1300.

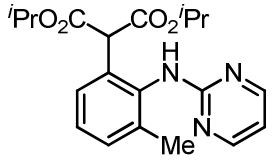
Diisopropyl 2-(3-(pyrimidin-2-ylamino)naphthalen-2-yl)malonate (3t)



3t

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (br s, 1H), 8.22 (br s, 2H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.89–7.86 (m, 2H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.50–7.44 (m, 2H), 6.58 (t, *J* = 5.0 Hz, 1H), 5.16 (s, 1H), 5.04–4.99 (m, 2H), 1.24 (d, *J* = 6.5 Hz, 6H), 1.15 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 162.1, 158.3, 134.1, 133.1, 131.1, 129.4, 128.2, 127.4, 127.0, 126.5, 126.3, 123.6, 111.9, 69.3, 54.4, 21.6, 21.5; IR (KBr) υ 3199, 2980, 2933, 1726, 1585, 1519, 1446, 1374, 1263, 1162, 1100, 995, 904, 801 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{25}N_3O_4$ $[M]^+$ 407.1845, found 407.1840.

Diisopropyl 2-(3-methyl-2-(pyrimidin-2-ylamino)phenyl)malonate (3u)



3u

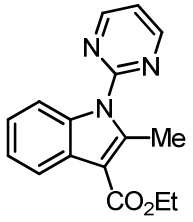
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 4.8 Hz, 2H), 7.54 (br s, 1H), 7.32 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.27–7.20 (m, 2H), 6.63 (t, *J* = 4.8 Hz, 1H), 4.97–4.90 (m, 2H), 4.77 (s, 1H), 2.23 (s, 3H), 1.21 (d, *J* = 6.4 Hz, 6H), 1.15 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 168.0, 160.7, 158.1, 136.9, 135.4, 131.5, 130.9, 128.1, 127.0, 111.6, 69.4, 55.2, 21.5, 18.9; IR (KBr) υ 3216, 2979, 2932, 1725, 1580, 1445, 1228, 1157, 1097, 994, 913, 800 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{25}N_3O_4$ $[M]^+$ 371.1845, found 371.1844.

Typical procedure for the synthesis of indoles (5a–5p)

To an oven-dried sealed tube charged with *N*-phenylpyridin-2-amine (**4a**) (34.0 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), and AgOAc (5 mg, 0.03 mmol, 15 mol %) in MeOH (1 mL) was added ethyl 2-diazo-3-oxobutanoate (**2h**) (37.5 mg, 0.24 mmol, 120 mol %) under air. The reaction mixture was allowed to stir at 60 °C for 24 h, and cooled to room temperature. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc: 5:1) to afford **5b** (52.8 mg) in 94% yield.

Characterization data for indole products (5a–5p)

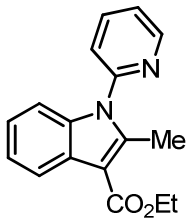
Ethyl 2-methyl-1-(pyrimidin-2-yl)-1*H*-indole-3-carboxylate (5a)



5a

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 4.8 Hz, 2H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 4.8 Hz, 1H), 7.29–7.22 (m, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 2.95 (s, 3H), 1.48 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.9, 158.5, 157.3, 145.5, 135.9, 127.1, 123.2, 122.9, 121.3, 118.8, 112.4, 108.3, 59.8, 14.5, 14.3; IR (KBr) υ 2978, 2929, 1659, 1564, 1551, 1456, 1418, 1399, 1193, 1094, 1024, 748 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{15}N_3O_2$ $[M]^+$ 281.1164, found 281.1167.

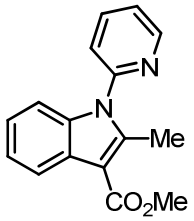
Ethyl 2-methyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (5b)



5b

^{1}H NMR (700 MHz, $CDCl_3$) δ 8.81 (br s, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.03 (t, *J* = 7.7 Hz, 1H), 7.52–7.48 (m, 2H), 7.36–7.34 (m, 1H), 7.30–7.25 (m, 2H), 4.53 (q, *J* = 7.1 Hz, 2H), 2.80 (s, 3H), 1.56 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 166.0, 150.0, 149.9, 145.0, 138.6, 136.5, 126.7, 123.3, 122.7, 122.3, 122.1, 121.4, 110.2, 106.2, 59.6, 14.5, 13.1; IR (KBr) υ 2924, 1691, 1588, 1543, 1468, 1436, 1397, 1268, 1178, 1115, 1078, 784, 747 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{16}N_2O_2$ $[M]^+$ 280.1212, found 280.1215.

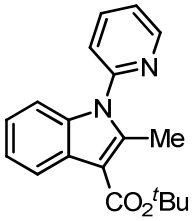
Methyl 2-methyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (5c)



5c

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (d, *J* = 5.0 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.98 (td, *J* = 8.5, 2.0 Hz, 1H), 7.48–7.43 (m, 2H), 7.32–7.26 (m, 1H), 7.24–7.21 (m, 2H), 4.01 (s, 3H), 2.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 150.1, 150.0, 145.1, 138.6, 136.6, 126.6, 123.3, 122.7, 122.3, 122.1, 121.4, 110.3, 106.1, 50.8, 13.1; IR (KBr) υ 3055, 2946, 1698, 1588, 1544, 1469, 1435, 1394, 1270, 1192, 1116, 1082, 784, 749 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{14}N_2O_2$ $[M]^+$ 266.1055, found 266.1057.

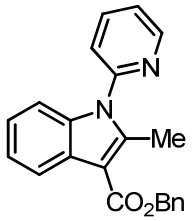
***tert*-Butyl 2-methyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (5d)**



5d

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (br s, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.00 (td, *J* = 8.5, 2.0 Hz, 1H), 7.50–7.45 (m, 2H), 7.32–7.26 (m, 1H), 7.24–7.21 (m, 2H), 2.75 (s, 3H), 1.74 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 150.3, 150.0, 144.5, 138.5, 136.5, 126.8, 123.2, 122.6, 122.2, 122.1, 121.4, 110.2, 107.5, 80.0, 28.7, 13.2; IR (KBr) υ 2974, 2928, 1685, 1588, 1541, 1468, 1435, 1391, 1364, 1276, 1201, 1159, 1113, 1098, 1079, 1022, 993, 785, 740 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{20}N_2O_2$ $[M]^+$ 308.1525, found 308.1524.

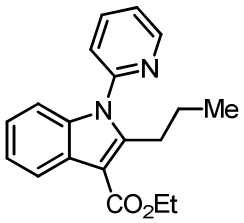
Benzyl 2-methyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (5e)



5e

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.5 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.97 (td, *J* = 8.5, 2.0 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.47–7.43 (m, 4H), 7.38 (t, *J* = 7.0 Hz, 1H), 7.30–7.20 (m, 3H), 5.50 (s, 2H), 2.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 150.1, 150.0, 145.4, 138.5, 136.8, 136.6, 128.5, 127.9, 127.8, 126.7, 123.3, 122.7, 122.4, 122.1, 121.5, 110.3, 105.9, 65.4, 13.2; IR (KBr) υ 3056, 2980, 2931, 1693, 1587, 1541, 1469, 1437, 1400, 1267, 1177, 1115, 1075, 1025, 995, 783, 748, 698 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{18}N_2O_2$ $[M]^+$ 342.1368, found 342.1370.

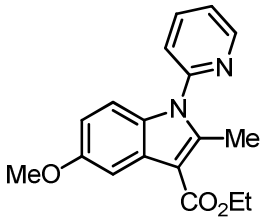
Ethyl 2-propyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (5f)



5f

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (d, *J* = 3.5 Hz, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 8.07 (td, *J* = 8.5, 2.0 Hz, 1H), 7.58–7.54 (m, 2H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 4.58 (q, *J* = 7.0 Hz, 2H), 3.28 (t, *J* = 6.5 Hz, 2H), 1.74–1.69 (m, 2H), 1.61 (t, *J* = 7.0 Hz, 3H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 150.4, 150.0, 149.6, 138.5, 136.8, 126.8, 123.4, 122.7, 122.4, 122.3, 121.6, 110.2, 105.7, 59.5, 27.9, 22.9, 14.5, 14.0; IR (KBr) υ 3362, 2961, 2929, 1692, 1587, 1532, 1467, 1436, 1321, 1273, 1180, 1069, 993, 746, 696 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{20}N_2O_2$ $[M]^+$ 308.1525, found 308.1523.

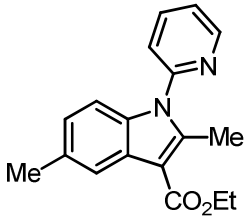
Ethyl 5-methoxy-2-methyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (5h)



5h

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.92 (dt, *J* = 8.5, 1.5 Hz, 1H), 7.71 (d, *J* = 2.5 Hz, 1H), 7.41–7.37 (m, 2H), 7.10 (d, *J* = 9.0 Hz, 1H), 6.80 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.42 (q, *J* = 7.0 Hz, 2H), 3.89 (s, 3H), 2.69 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 156.0, 150.3, 149.9, 145.0, 138.5, 131.6, 127.7, 123.2, 121.9, 112.3, 111.1, 106.1, 103.6, 59.5, 55.7, 14.5, 13.3; IR (KBr) υ 2980, 2927, 1688, 1581, 1539, 1469, 1434, 1399, 1270, 1186, 1160, 1078, 1032, 851, 780, 747 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{18}N_2O_3$ $[M]^+$ 310.1317, found 310.1312.

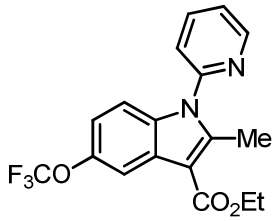
Ethyl 2,5-dimethyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (5i)



5i

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 3.5 Hz, 1H), 7.98 (s, 1H), 7.92 (dt, *J* = 8.5, 2.0 Hz, 1H), 7.41–7.37 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 4.43 (q, *J* = 7.0 Hz, 2H), 2.69 (s, 3H), 2.48 (s, 3H), 1.47 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 150.3, 149.9, 144.8, 138.5, 135.0, 131.7, 127.0, 124.1, 123.1, 122.0, 121.2, 109.9, 105.9, 59.5, 21.6, 14.6, 13.2; IR (KBr) υ 2976, 2923, 1687, 1588, 1541, 1469, 1434, 1397, 1268, 1197, 1150, 1132, 1075, 1035, 993, 883, 782 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{18}N_2O_2$ $[M]^+$ 294.1368, found 294.1363.

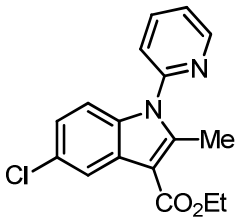
Ethyl 2-methyl-1-(pyridin-2-yl)-5-(trifluoromethoxy)-1*H*-indole-3-carboxlate (5j)



5j

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.5 Hz, 1H), 8.04 (br s, 1H), 7.96 (td, *J* = 8.6, 2.0 Hz, 1H), 7.48–7.44 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 9.0 Hz, 1H), 7.03 (dd, *J* = 8.8 Hz, 1H), 4.43 (q, *J* = 7.0 Hz, 2H), 2.70 (s, 3H), 1.47 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 150.1, 149.8, 146.6, 144.9, 138.8, 134.8, 127.3, 123.6, 122.0, 120.7 (q, $J_{C\text{-}F}$ = 254.4 Hz), 116.4, 114.0, 111.1, 106.5, 59.8, 14.4, 13.2; IR (KBr) υ 3474, 2982, 2931, 1695, 1467, 1245, 1148, 1078, 781 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{15}F_3N_2O_3$ $[M]^+$ 364.1035, found 364.1031.

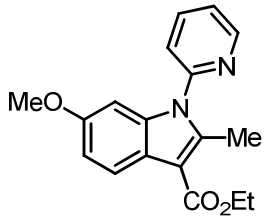
Ethyl 5-chloro-2-methyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (5k)



5k

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 3.5 Hz, 1H), 8.15 (s, 1H), 7.95 (dt, *J* = 8.5, 1.5 Hz, 1H), 7.45–7.43 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.11 (s, 1H), 4.43 (q, *J* = 7.0 Hz, 2H), 3.89 (s, 3H), 2.69 (s, 3H), 1.47 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 150.1, 149.8, 146.1, 138.7, 128.1, 127.8, 123.5, 122.9, 122.0, 121.1, 111.4, 106.0, 59.8, 14.5, 13.2; IR (KBr) υ 3062, 2978, 2926, 1692, 1587, 1541, 1435, 1396, 1183, 1085, 877, 780, 746 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{15}ClN_2O_2$ $[M]^+$ 314.0822, found 314.0821.

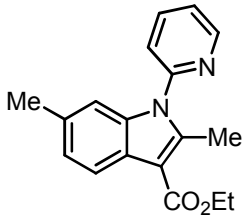
Ethyl 6-methoxy-2-methyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (5l)



5l

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 5.0 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 1H), 7.94 (td, *J* = 8.5, 2.0 Hz, 1H), 7.44–7.40 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 6.90 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.71 (d, *J* = 2.0 Hz, 1H), 4.42 (q, *J* = 7.0 Hz, 2H), 3.76 (s, 3H), 2.66 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 156.7, 150.2, 150.0, 143.9, 138.6, 137.3, 123.3, 122.1, 122.0, 120.8, 111.1, 106.1, 94.7, 59.5, 55.6, 14.5, 13.1; IR (KBr) υ 3053, 2978, 2927, 1691, 1586, 1548, 1468, 1435, 1266, 1186, 1159, 1078, 1027, 819, 780, 747 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{18}N_2O_3$ $[M]^+$ 310.1317, found 310.1317.

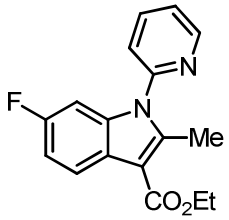
Ethyl 2,6-dimethyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (5m)



5m

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 3.5 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.94 (td, *J* = 8.5, 2.0 Hz, 1H), 7.43–7.38 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.99 (s, 1H), 4.42 (q, *J* = 7.0 Hz, 2H), 2.68 (s, 3H), 2.40 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 150.3, 149.9, 144.3, 138.5, 137.0, 132.6, 124.5, 123.9, 123.2, 122.1, 121.1, 110.2, 106.1, 59.5, 21.6, 14.5, 13.0; IR (KBr) υ 3053, 2979, 2923, 1691, 1542, 1468, 1436, 1387, 1267, 1192, 1129, 1078, 1031, 810, 781, 747 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{18}N_2O_2$ $[M]^+$ 294.1368, found 294.1367.

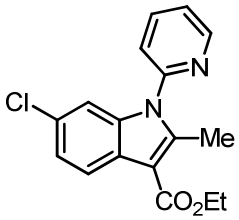
Ethyl 6-fluoro-2-methyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (5n)



5n

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 3.5 Hz, 1H), 7.95 (td, *J* = 9.0, 2.0 Hz, 1H), 7.46–7.44 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.10–7.06 (m, 1H), 6.95–6.89 (m, 2H), 4.40 (q, *J* = 7.0 Hz, 2H), 2.61 (s, 3H), 1.43 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 155.7 (d, $J_{C\text{-}F}$ = 250.0 Hz), 150.1 (d, $J_{C\text{-}F}$ = 8.6 Hz), 144.2, 139.3 (d, $J_{C\text{-}F}$ = 10.0 Hz), 138.7, 123.6, 123.3 (d, $J_{C\text{-}F}$ = 8.0 Hz), 122.3, 114.7 (d, $J_{C\text{-}F}$ = 19.0 Hz), 108.5 (d, $J_{C\text{-}F}$ = 21.8 Hz), 106.4 (q, $J_{C\text{-}F}$ = 3.8 Hz), 105.8 (d, $J_{C\text{-}F}$ = 3.0 Hz), 60.1, 14.3, 13.0; IR (KBr) υ 3056, 2980, 2929, 1692, 1587, 1542, 1468, 1434, 1398, 1219, 1154, 1079, 766, 726 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{15}FN_2O_2$ $[M]^+$ 298.1118, found 298.1121.

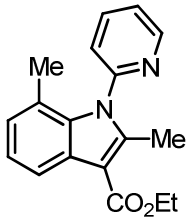
Ethyl 6-chloro-2-methyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (5o)



5o

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.5 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.96 (td, *J* = 8.5, 2.0 Hz, 1H), 7.47–7.43 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.22–7.20 (m, 2H), 4.42 (q, *J* = 7.5 Hz, 2H), 2.68 (s, 3H), 1.46 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 150.1, 149.6, 145.5, 138.8, 136.9, 128.6, 125.3, 123.6, 122.8, 122.4, 122.0, 110.4, 106.3, 59.7, 14.5, 13.1; IR (KBr) υ 3055, 2978, 2930, 1693, 1587, 1545, 1470, 1437, 1396, 1262, 1196, 1125, 1063, 813, 786, 747 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{15}ClN_2O_2$ $[M]^+$ 314.0822, found 314.0821.

Ethyl 2,7-dimethyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (5p)



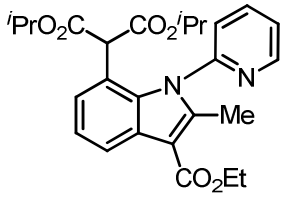
5p

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (d, *J* = 3.5 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.88 (td, *J* = 8.5, 2.0 Hz, 1H), 7.48–7.46 (m, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 7.0 Hz, 1H), 4.42 (q, *J* = 7.0 Hz, 2H), 2.50 (s, 3H), 1.78 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 152.1, 149.4, 145.5, 138.1, 135.6, 127.2, 125.3, 124.3, 124.2, 122.0, 120.8, 119.4, 105.5, 59.5, 18.8, 14.5, 12.6; IR (KBr) υ 3048, 2978, 2927, 1692, 1587, 1551, 1469, 1438, 1399, 1245, 1201, 1098, 792, 744 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{18}N_2O_2$ $[M]^+$ 294.1368, found 294.1363.

General procedure and characterization for C7-alkylation of indole 5b

To an oven-dried sealed tube charged with ethyl 2-methyl-1-(pyridin-2-yl)-*1H*-indole-3-carboxylate (**5b**) (56.1 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), and $AgSbF_6$ (6.8 mg, 0.02 mmol, 10 mol %) in EtOH (1 mL) was diisopropyl 2-diazomalonate (**2c**) (64.2 mg, 0.24 mmol, 150 mol %). The reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc: 4:1) to afford **3a** (83.7 mg) in 90% yield.

Diisopropyl 2-(3-(ethoxycarbonyl)-2-methyl-1-(pyridin-2-yl)-1*H*-indol-7-yl)malonate (7a)



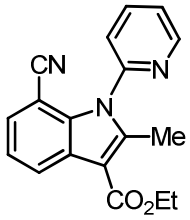
7a

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 5.0 Hz, 1H), 8.20 (d, *J* = 7.5 Hz, 1H), 7.91 (t, *J* = 8.0 Hz, 1H), 7.50–7.48 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.26–7.21 (m, 2H), 4.92–4.87 (m, 2H), 4.42 (q, *J* = 7.0 Hz, 2H), 3.96 (s, 1H), 2.42 (s, 3H), 1.43 (t, *J* = 7.5 Hz, 3H), 1.14 (d, *J* = 6.5 Hz, 6H), 1.12 (t, *J* = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 165.8, 151.7, 150.4, 146.1, 138.9, 135.0, 128.0, 124.5, 124.3, 124.2, 122.1, 121.5, 116.4, 106.0, 69.2, 59.6, 52.7, 21.5, 21.4, 14.5, 12.6; IR (KBr) υ 3051, 2980, 2933, 1726, 1695, 1467, 1438, 1241, 1167, 1097, 993, 801, 747 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{30}N_2O_6$ $[M]^+$ 466.2104, found 466.2104.

General procedure and characterization for C7-cyanation of indole 5b

To an oven-dried sealed tube charged with ethyl 2-methyl-1-(pyridin-2-yl)-*1H*-indole-3-carboxylate (**5b**) (56.1 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol %), $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %), and NaOAc (4.9 mg, 0.06 mmol, 30 mol %) in DCE (1 mL) was added *N*-cyano-*N*-phenyl-*p*-methylbenzenesulfonamide (NCTS) (**6a**) (108.9 mg, 0.4 mmol, 200 mol %). The reaction mixture was allowed to stir at 110 ^oC for 24 h, and cooled to room temperature. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 4:1) to afford **7b** (28.1 mg) in 46% yield.

Ethyl 7-cyano-2-methyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (7b)



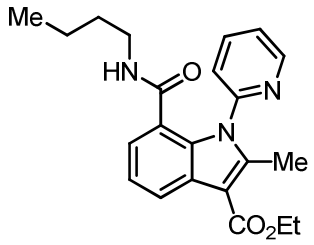
7b

^1H NMR (500 MHz, $CDCl_3$) δ 8.76 (d, *J* = 5.5 Hz, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.01 (td, *J* = 9.0, 2.0 Hz, 1H), 7.60–7.57 (m, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 4.43 (q, *J* = 7.0 Hz, 2H), 2.59 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.1, 150.2, 148.9, 146.9, 138.8, 135.7, 128.9, 128.0, 126.8, 125.4, 124.3, 121.9, 116.0, 106.2, 94.8, 60.0, 14.5, 12.7; IR (KBr) υ 3054, 2923, 2853, 1698, 1468, 1443, 1258, 1087, 799, 740 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{15}N_3O_2$ $[M]^+$ 305.1164, found 305.1168.

General procedure and characterization for C7-amidation of indole 5b

To an oven-dried sealed tube charged with ethyl 2-methyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (**5b**) (56.1 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (6.2 mg, 0.01 mmol, 5 mol %) and $AgSbF_6$ (13.7 mg, 0.04 mmol, 20 mol %) was added *n*-butyl isocyanate (**6b**) (67.5 μL, 0.6 mmol, 300 mol %) and DCE (1 mL) under N_2 atmosphere. The reaction mixture was allowed to stir at 100 °C for 24 h and cooled to room temperature. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (n-hexanes/EtOAc = 2:1) to afford **7c** (46.2 mg) in 61% yield.

Ethyl 7-(butylcarbamoyl)-2-methyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (7c)



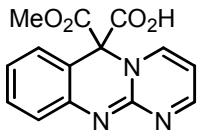
7c

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.5 Hz, 1H), 8.32–8.29 (m, 1H), 7.94 (td, *J* = 9.0, 2.0 Hz, 1H), 7.43–7.40 (m, 2H), 7.27–7.25 (m, 2H), 5.75 (t, *J* = 5.0 Hz, 1H), 4.43 (q, *J* = 7.0 Hz, 2H), 2.88 (q, *J* = 6.0 Hz, 2H), 2.61 (s, 3H), 1.48 (t, *J* = 7.0 Hz, 3H), 1.37–1.28 (m, 4H), 0.91 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 165.7, 151.3, 149.0, 146.4, 138.7, 132.5, 128.3, 123.7, 123.6, 123.2, 122.4, 121.8, 121.7, 106.3, 59.8, 39.5, 31.2, 20.0, 14.5, 13.7, 13.0; IR (KBr) υ 3325, 2956, 2926, 1698, 1630, 1553, 1468, 1250, 1184, 1091, 744 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{25}N_3O_3$ $[M]^+$ 379.1896, found 379.1889.

General procedure and characterization for the transformation of 3a

To an oven-dried sealed tube charged with dimethyl 2-(2-(pyrimidin-2-ylamino)phenyl)malonate (**3a**) (60.2 mg, 0.2 mmol, 100 mol %) in toluene (5 mL) was added DBU (121.7 mg, 0.8 mmol, 400 mol %). The reaction mixture was allowed to stir at 110 ^{o}C for 12 h. Upon completion, the solvent was removed under vacuum. The mixture was extracted with EtOAc (3 × 10 mL) and washed with brine. The organic layer was dried over Mg_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 1:1.5) to afford **8a** (23.9 mg) in 42% yield.

6-(Methoxycarbonyl)-6*H*-pyrimido[2,1-b]quinazoline-6-carboxylic acid (8a)



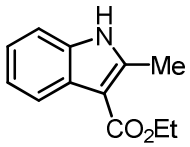
8a

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (d, *J* = 4.5 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.43–7.38 (m, 2H), 7.30 (t, *J* = 4.9 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 4.42 (br s, 1H), 3.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.8, 170.0, 158.6, 155.6, 142.0, 130.6, 126.0, 124.7, 124.0, 119.1, 113.8, 77.5, 54.1; IR (KBr) υ 3055, 2929, 1693, 1587, 1541, 1468, 1436, 1399, 1267, 1176, 1115, 1074, 995, 782 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{11}N_3O_4$ $[M]^+$ 285.0750, found 285.0750.

General procedure and characterization for deprotection of 5b

To a stirred solution of ethyl 2-methyl-1-(pyridin-2-yl)-1*H*-indole-3-carboxylate (**5b**) (56.1 mg, 0.2 mmol, 100 mol %) in DCM (5 mL) was added dropwise MeOTf (27 μL, 0.24 mmol, 120 mol %) at 0 ^{o}C. The reaction mixture was allowed to stir for 24 h at room temperature. The solvent was removed under vacuum, and the residue was dissolved in EtOH (2.5 mL). An aqueous solution of 2 N NaOH (1.2 mL) was added to the reaction mixture, and the resulting mixture was stirred at 60 ^{o}C for 12 h and cooled to room temperature. The solvent was removed under reduced pressure and the mixture was diluted with EtOAc and washed with brine. The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 4:1) to afford **9a** (25.7 mg) in 63% yield.

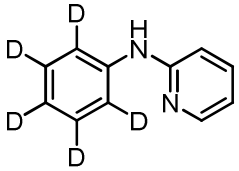
Ethyl 2-methyl-1*H*-indole-3-carboxylate (9a)



9a

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (br s, 1H), 8.10 (d, *J* = 7.0 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.22–7.18 (m, 2H), 4.40 (q, *J* = 7.0 Hz, 2H), 2.74 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.0, 143.8, 134.5, 127.2, 122.3, 121.6, 121.3, 110.4, 104.7, 59.4, 14.6, 14.2; IR (KBr) υ 3303, 2922, 1714, 1659, 1550, 1456, 1367, 1271, 1196, 1120, 1091, 1010, 782, 732 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{13}NO_2$ $[M]^+$ 203.0946, 203.0945.

Experimental procedure and characterization for the synthesis of deuterio-4a



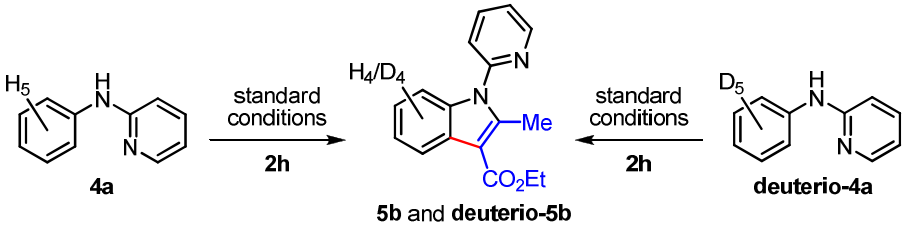
To an oven-dried flask charged with 2-bromopyridine (316 mg, 2 mmol, 100 mol %), aniline-d5 (385 mg, 2.4 mmol, 120 mol %), potassium *tert*-butoxide (449 mg, 4 mmol, 200 mol%), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol, 5 mol%) and (±)-BINAP (62.2 mg, 0.1 mmol, 5 mol%) were taken and the reaction vessel was flushed with N_2. Dry toluene (6 mL) was added to it through the septum. The reaction mixture was stirred at 120 ^oC for 6 h and monitored by TLC. Upon completion, water was added and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic phase was washed with brine and dried over Mg_2SO_4. The organic layer was evaporated in vacuum. The crude product was purified by flash column chromatography (*n*-hexanes/EtOAc = 6:1) to give **deuterio-4a** (297 mg) in 85% yield.

2′,3′,4′,5′,6′-Pentadeuterium-*N*-phenylpyridin-2-amine (**deuterio-4a**)[5]: ^1H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 4.5 Hz, 1H), 7.48 (t, *J* = 8.5 Hz, 1H), 6.98 (br s, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.74-6.71 (m, 1H).

Reference:

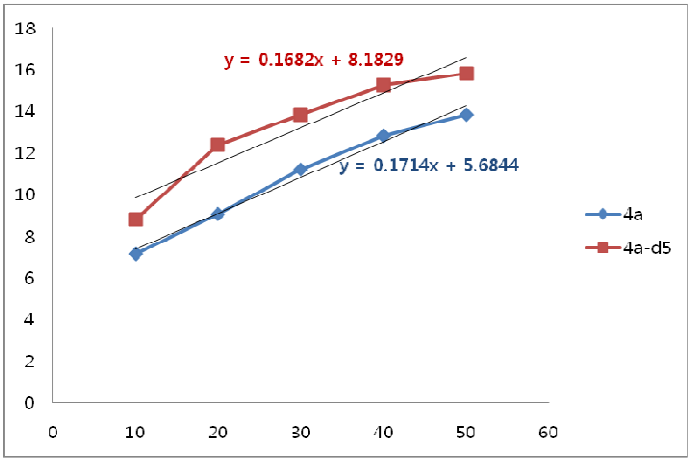
[5] M. Koley, N. Dastbaravardeh, M. Schnurch, and M. D. Mihovilovic, *ChemCatChem*, 2012, **4**, 1345

Kinetic Isotope Effect (KIE) experiments



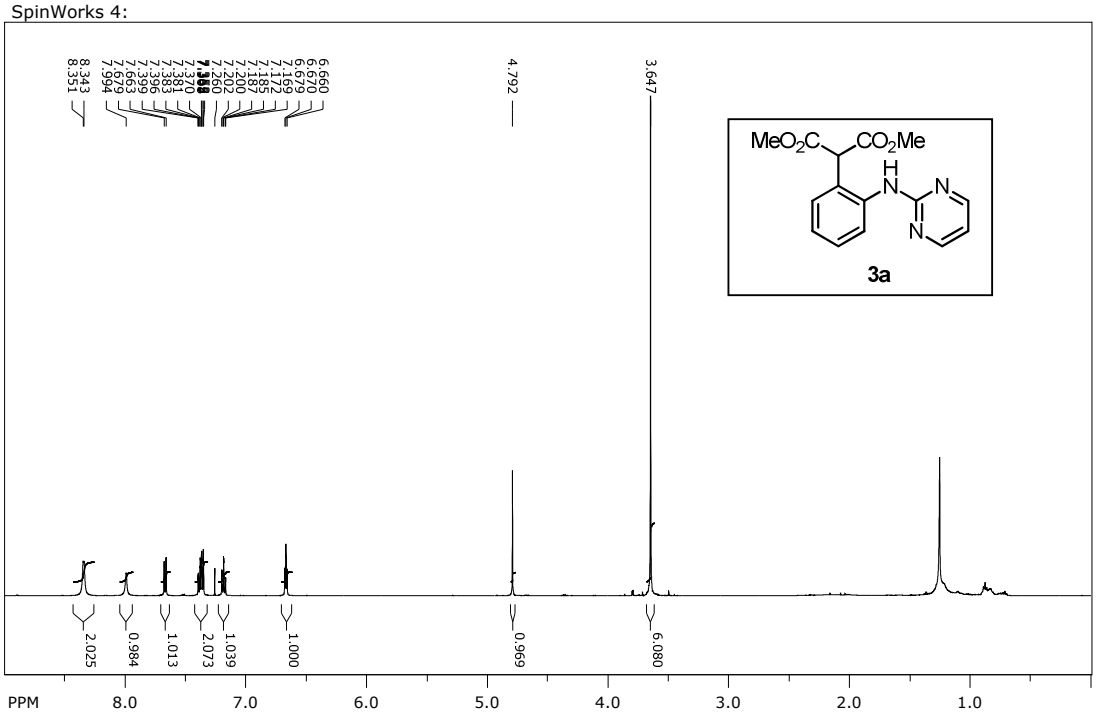
To an oven-dried sealed tube charged with *N*-phenylpyridin-2-amine (**4a**) (34.0 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %) and AgOAc (5 mg, 0.03 mmol, 15 mol %) in MeOH (1 mL) was added ethyl 2-diazo-3-oxobutanoate (**2h**) (37.5 mg, 0.24 mmol, 120 mol %) and cyclohexanemethanol (22.8 mg, 0.2 mmol, 100 mol%) as an internal standard. In another reaction tube, **deuterio-4a** (35.0 mg, 0.2 mmol, 100 mol %) was used as a substrate under otherwise identical conditions. The two reactions were allowed to stir at 60 °C. An aliquot of each reaction mixture was taken at the time of 10 min, 20 min, 30 min, 40 min, and 50 min. The corresponding yield of each product was determined by GC (cyclohexanemethanol as an internal standard). A kinetic isotope effect value (k_H/k_D) of 1.02 was observed.

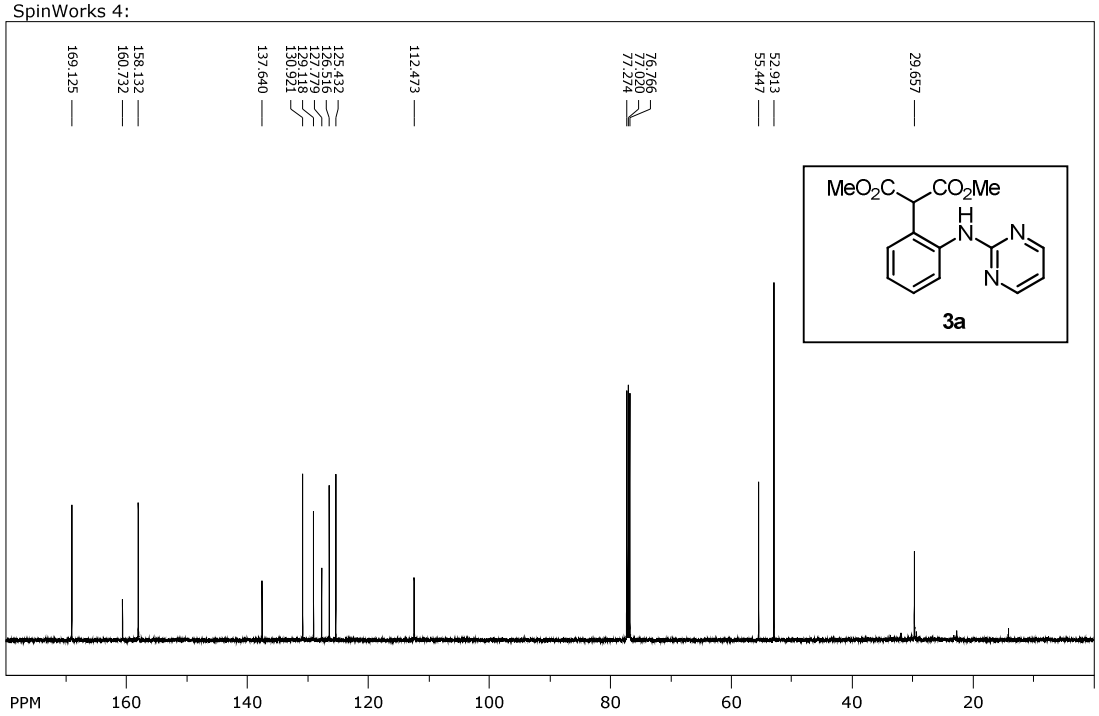
	Relative yield (%) based on cyclohexanemethanol				
	10 min	20 min	30 min	40 min	50 min
4a	7.1615048	9.0632375	11.23016	12.835847	13.847292
deuterio-4a	8.837547	12.390344	13.843618	15.252313	15.814402

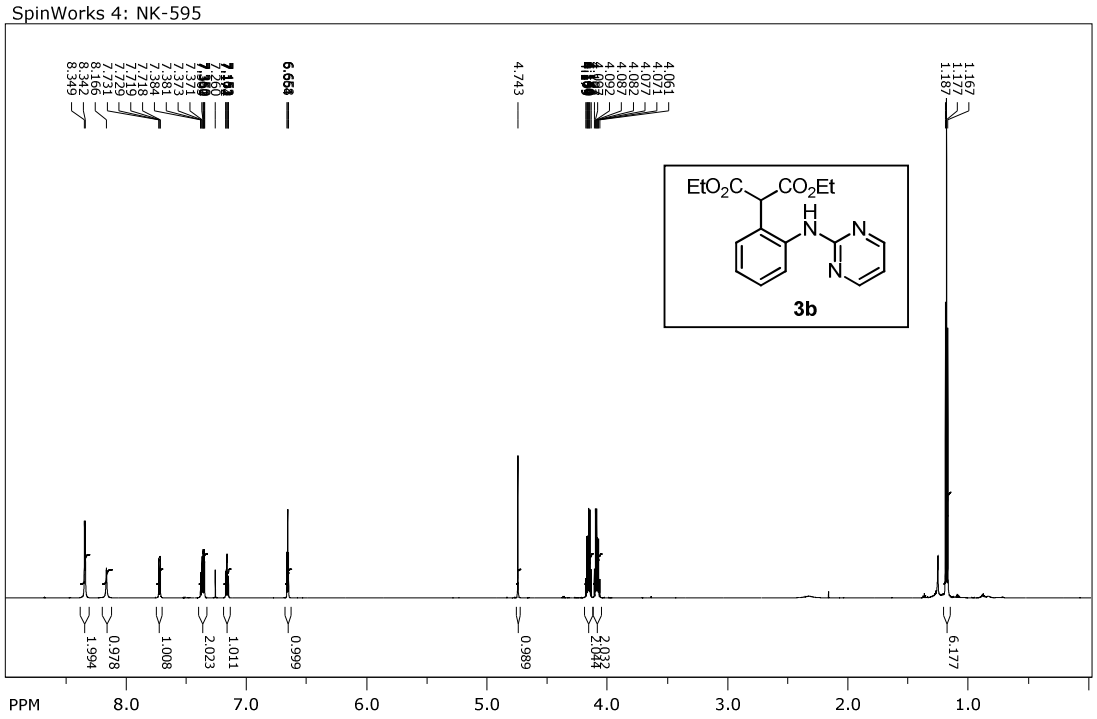


k_H	0.171
k_D	0.168
k_H/k_D	1.02

^{1}H NMR and ^{13}C NMR copies of all products



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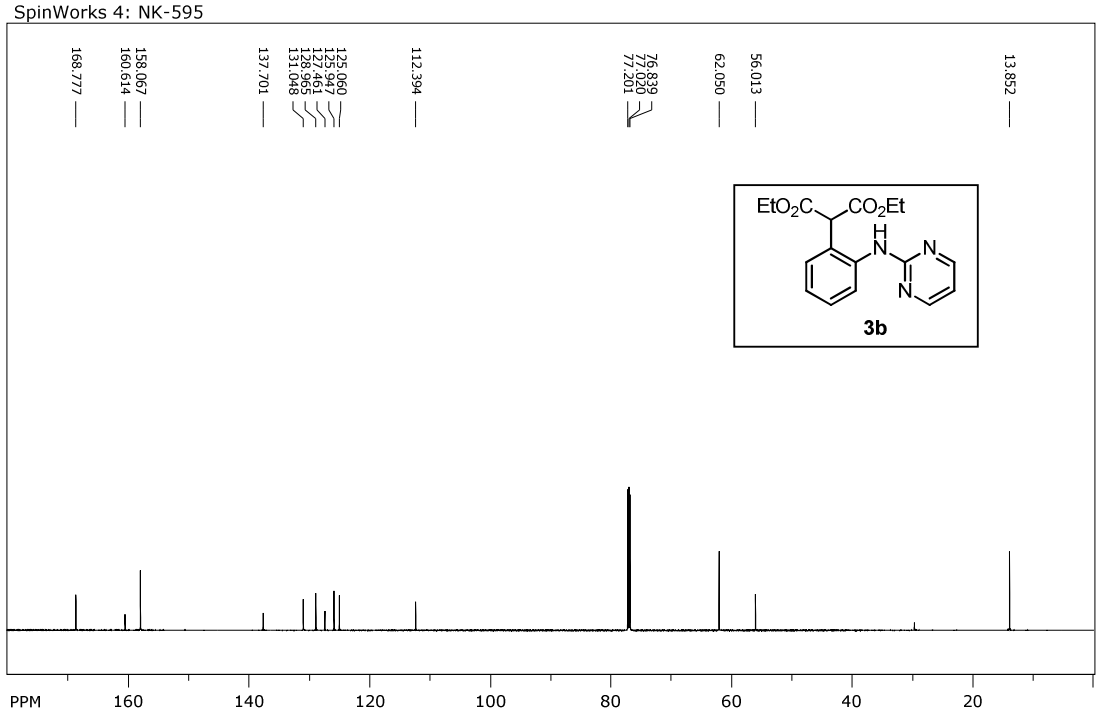
8.342
7.731
7.729
7.719
7.718
7.384
7.383
7.371
7.260
6.653
4.743
4.091
4.077
4.087
4.082
4.092
1.167
1.177
1.187
EtO2C
CO2Et
H
N
N
N
3b
1.994
0.978
1.008
2.023
1.011
0.999
0.989
2.032
2.044
6.177
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0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137.701
131.048
128.965
127.461
125.947
125.060
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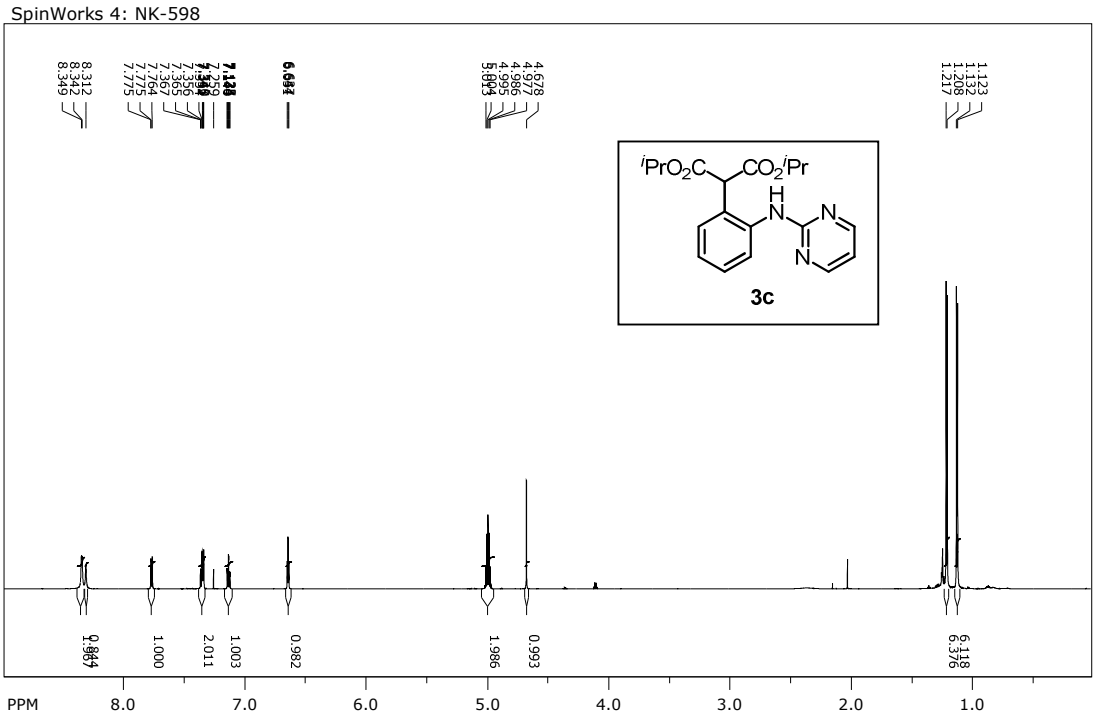
76.839
77.020
62.050
56.013
13.852
EtO2C
CO2Et
H
N
N
N
3b
PPM
160
140
120
100
80
60
40
20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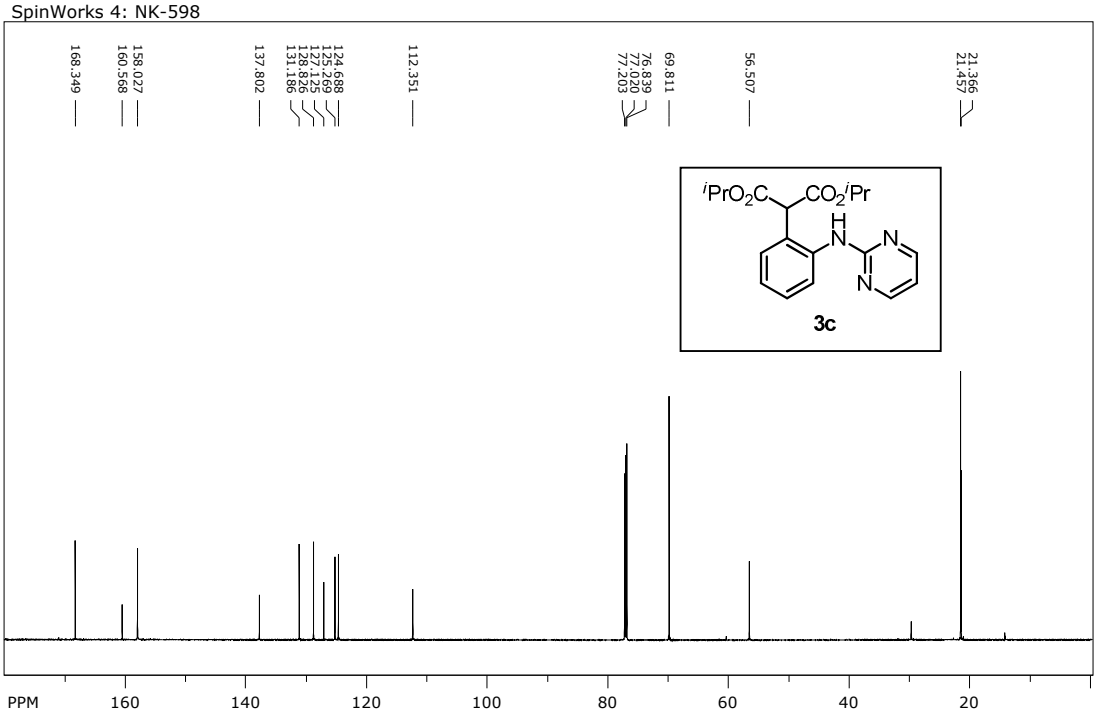
8.349
7.775
7.365
7.356
4.678
4.977
4.965
4.995
1.123
1.132
1.208
1.217
iPrO2C
CO2iPr
H
N
N
N
3c
0.964
1.000
2.011
1.003
0.982
1.986
0.993
6.118
6.376
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0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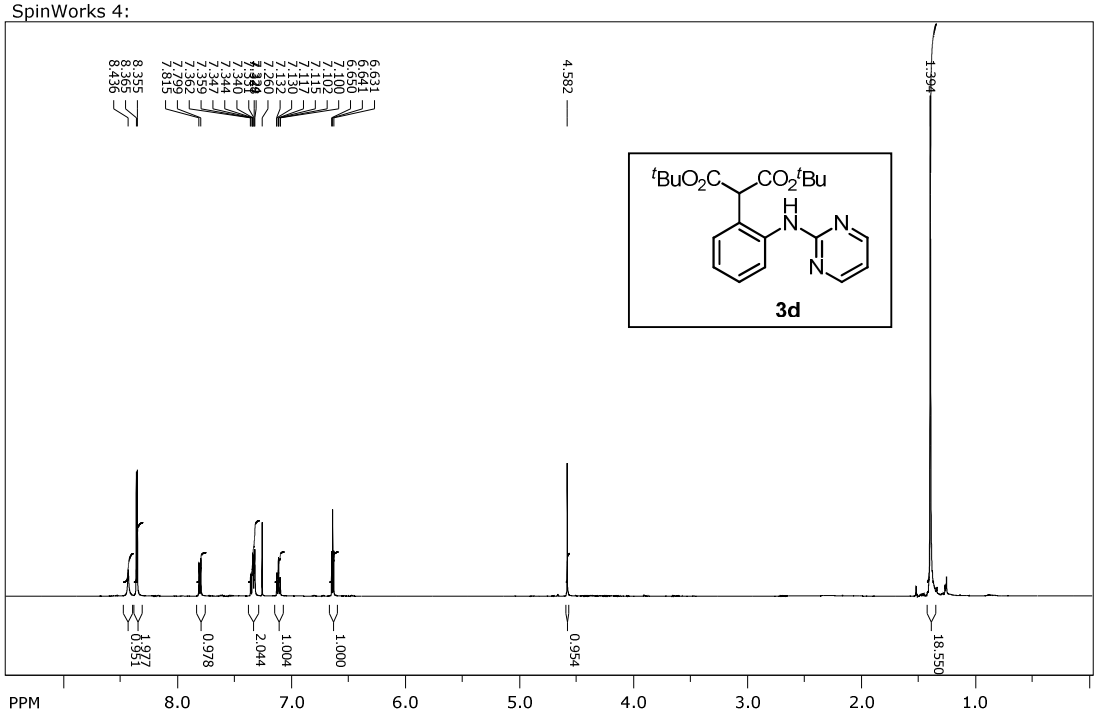
137.802
131.186
128.826
127.125
125.269
124.688
112.351
77.203
77.020
76.839
69.811
56.507
21.457
21.366
iPrO2C
CO2iPr
H
N
N
N
3c
PPM
160
140
120
100
80
60
40
20

SpinWorks 4:



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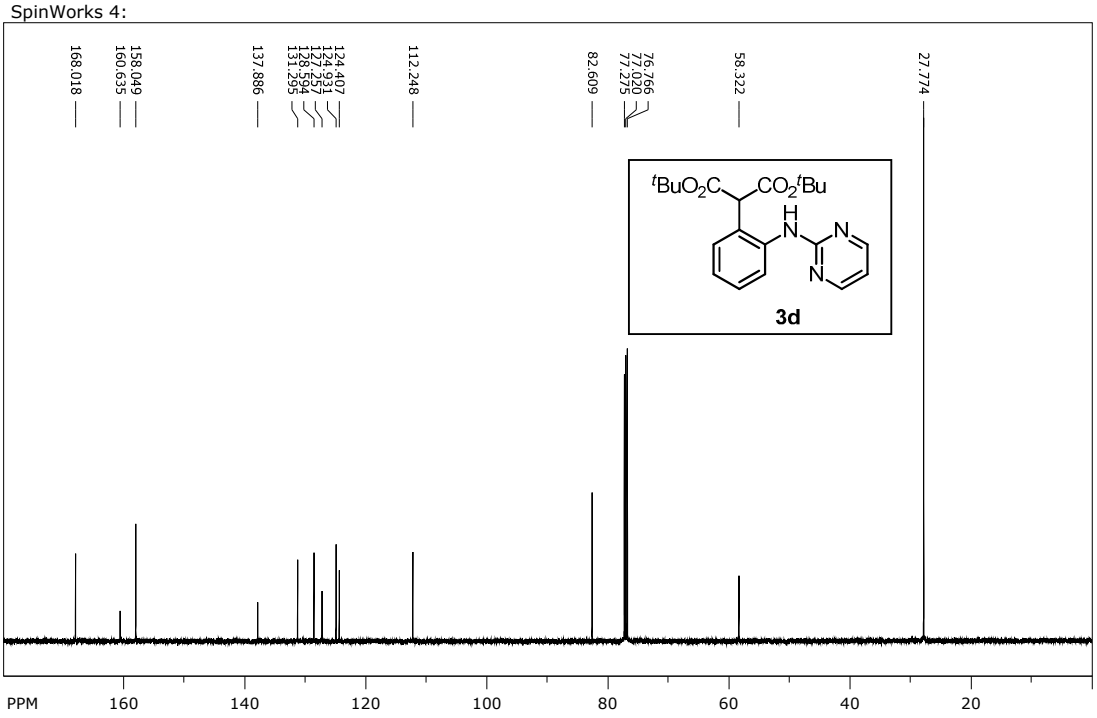

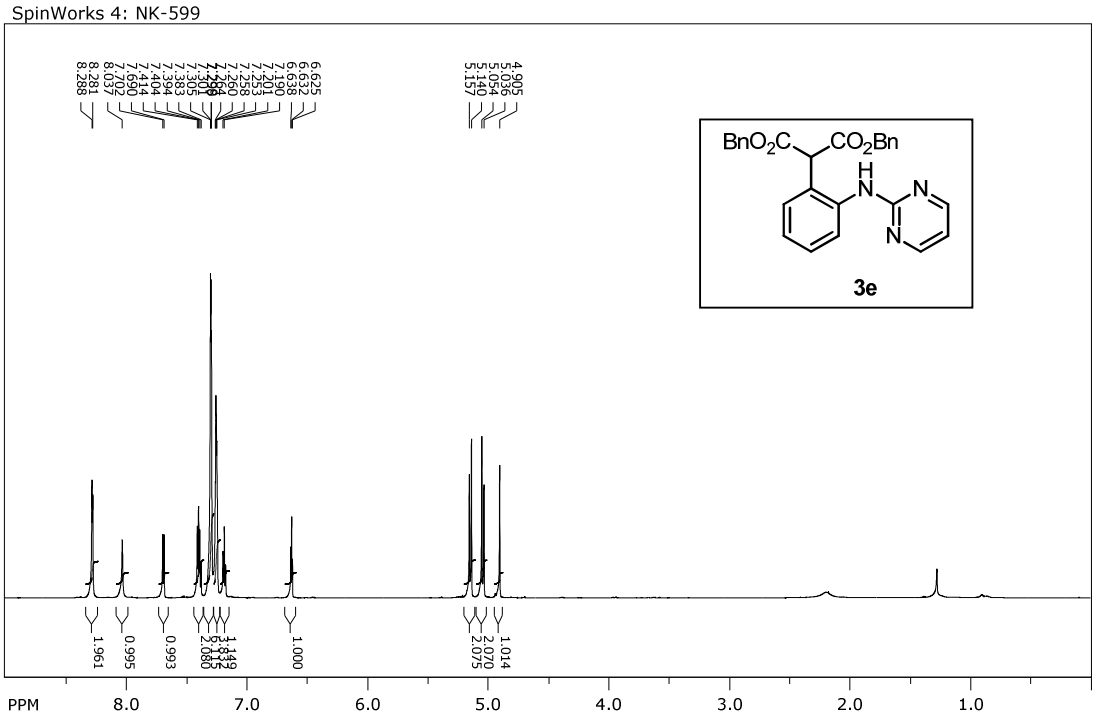
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7.690
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7.404
7.383
7.305
7.301
7.260
7.258
7.253
7.201
6.638
6.632
6.625
5.157
5.140
5.054
5.035
4.905
1.961
0.995
0.993
2.080
1.000
2.075
2.070
1.014
PPM
8.0
7.0
6.0
5.0
4.0
3.0
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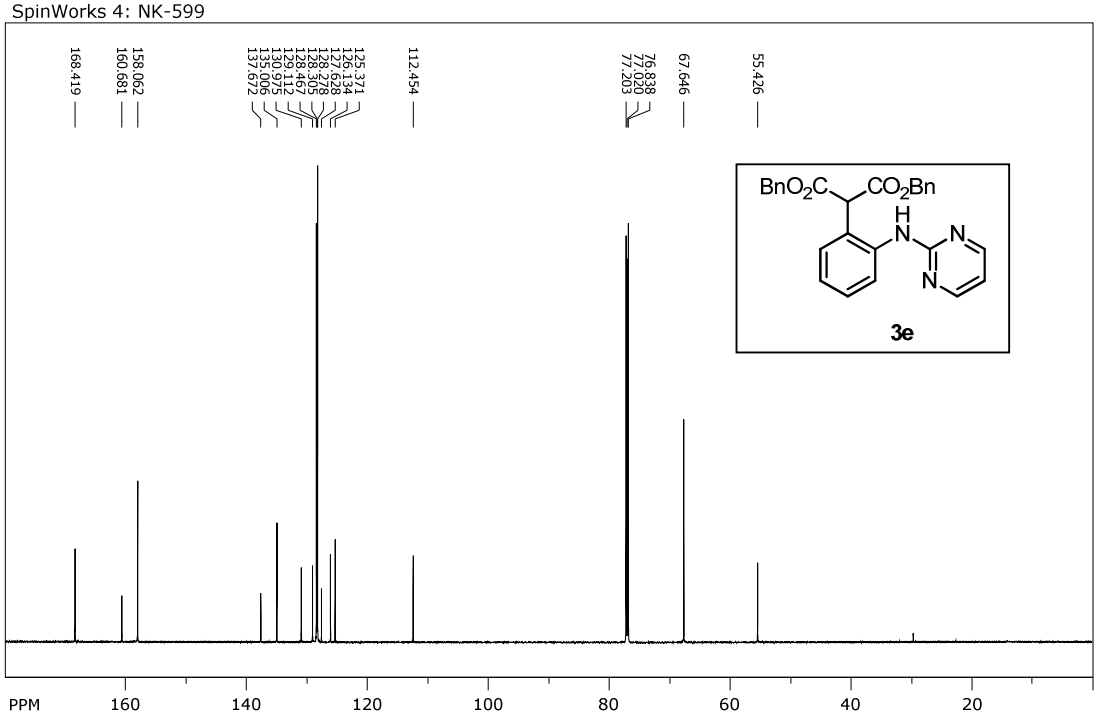
BnO2C
CO2Bn
H
N
N
N
3e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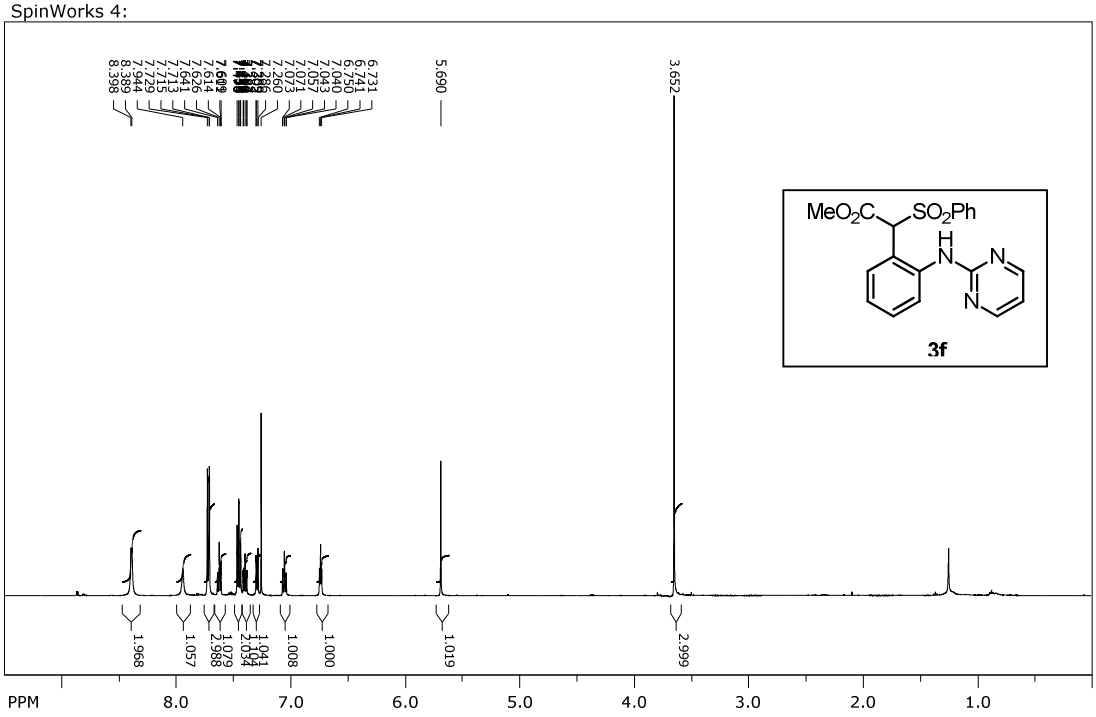
128.305
128.278
127.658
125.371
112.454
77.203
77.020
76.838
67.646
55.426
PPM
160
140
120
100
80
60
40
20
BnO2C
CO2Bn
H
N
N
N
3e

SpinWorks 4:



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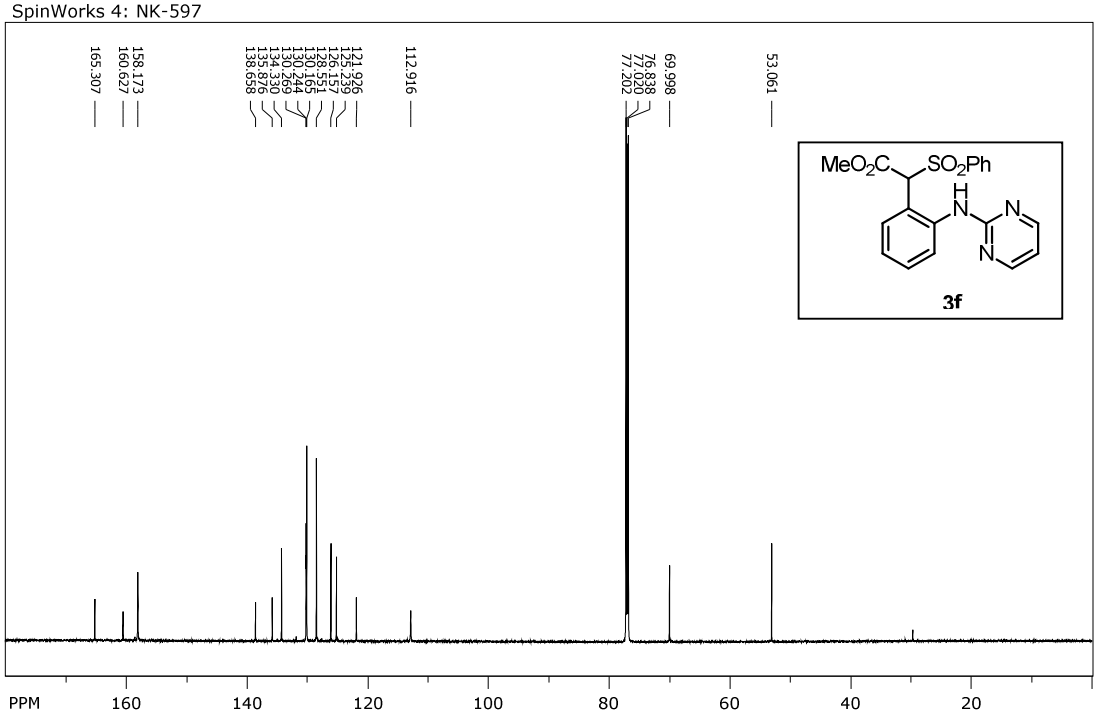

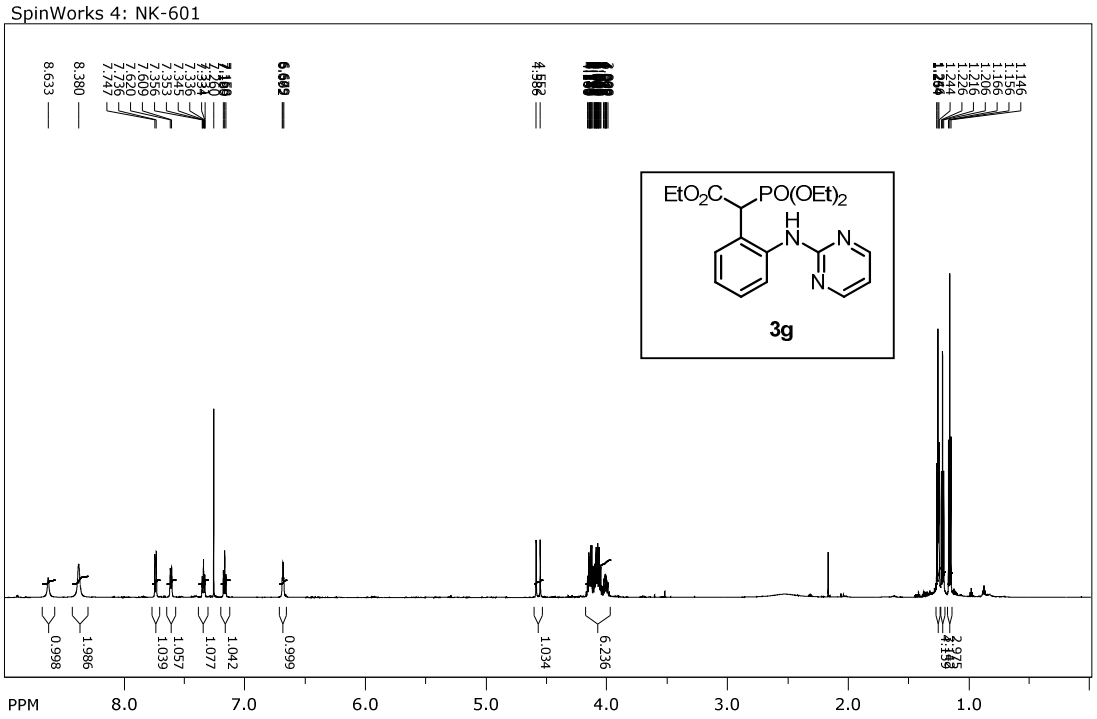
SpinWorks 4: NK-601
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PO(OEt)2
H
N
N
N
3g
PPM
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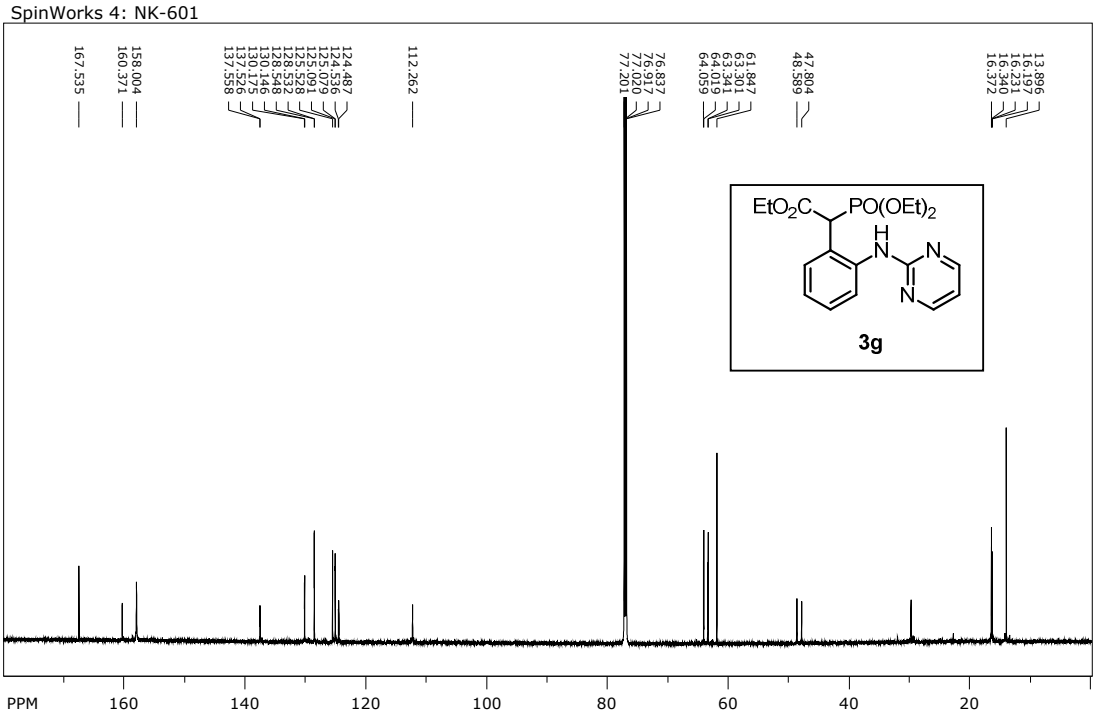
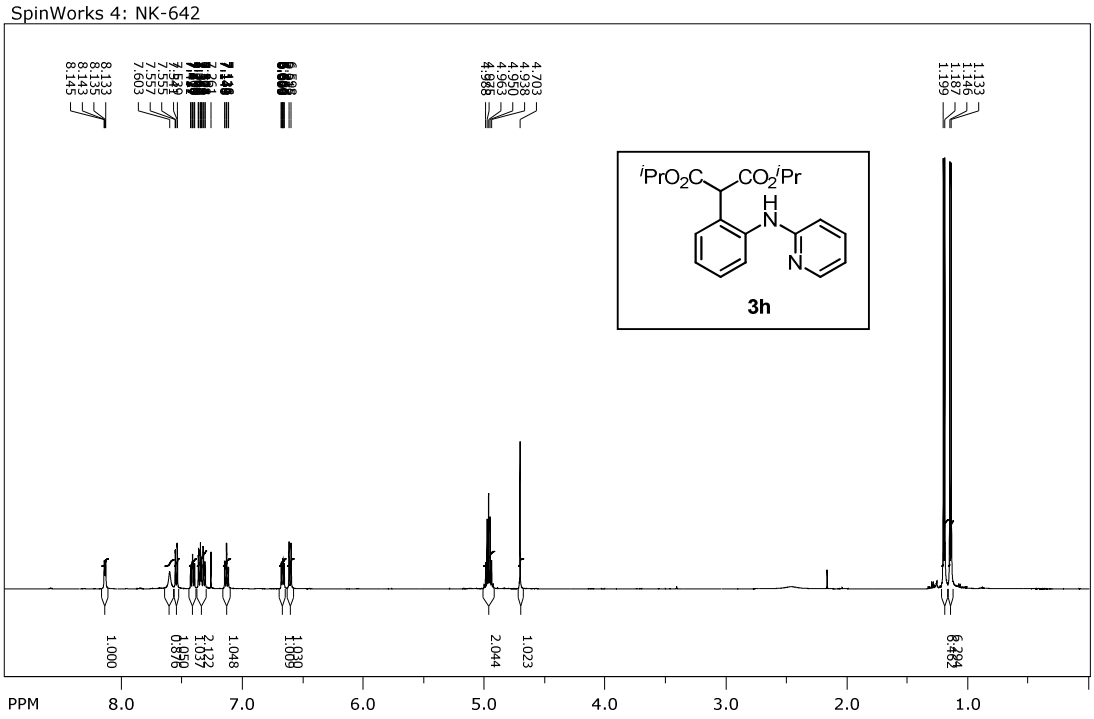
7.0
6.0
5.0
4.0
3.0
2.0
1.0


SpinWorks 4: NK-601
EtO2C
PO(OEt)2
H
N
N
N
3g
PPM
160
140
120
100
80
60
40
20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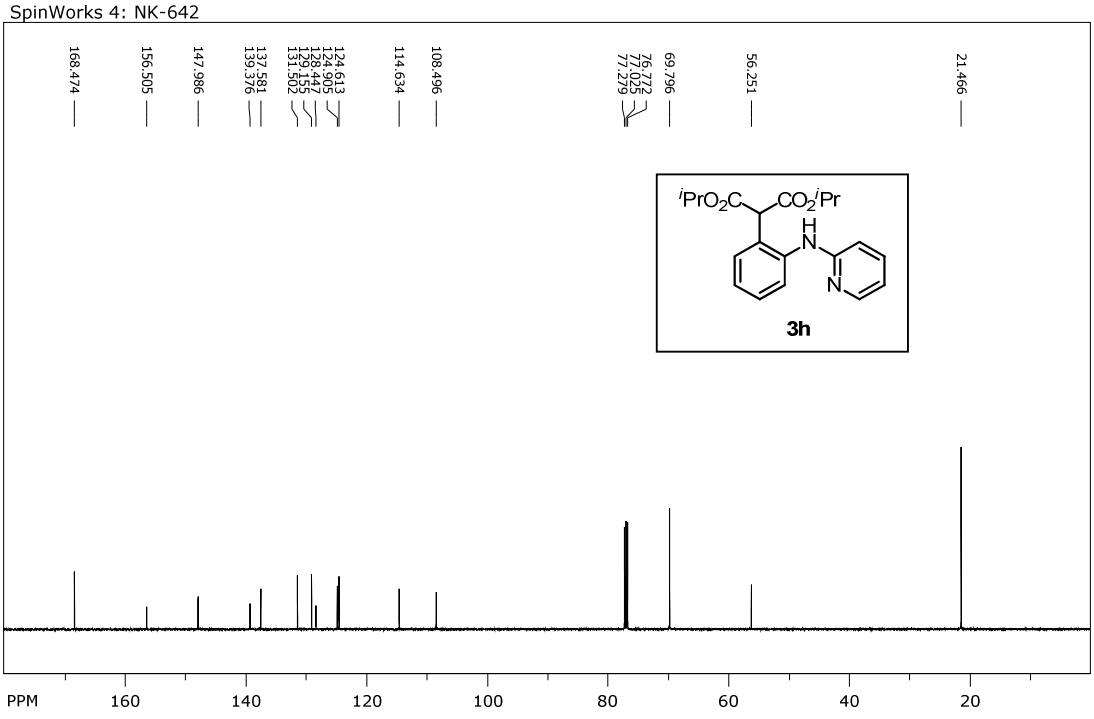
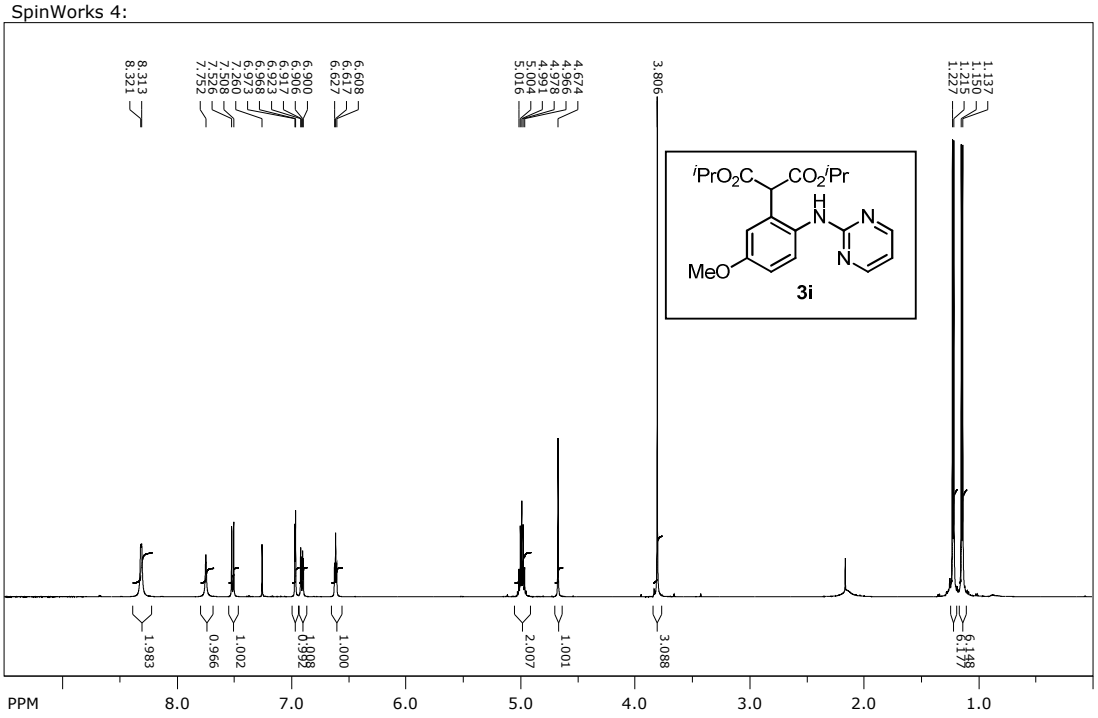
3h
PPM


SpinWorks 4: NK-642
3h
PPM

SpinWorks 4:



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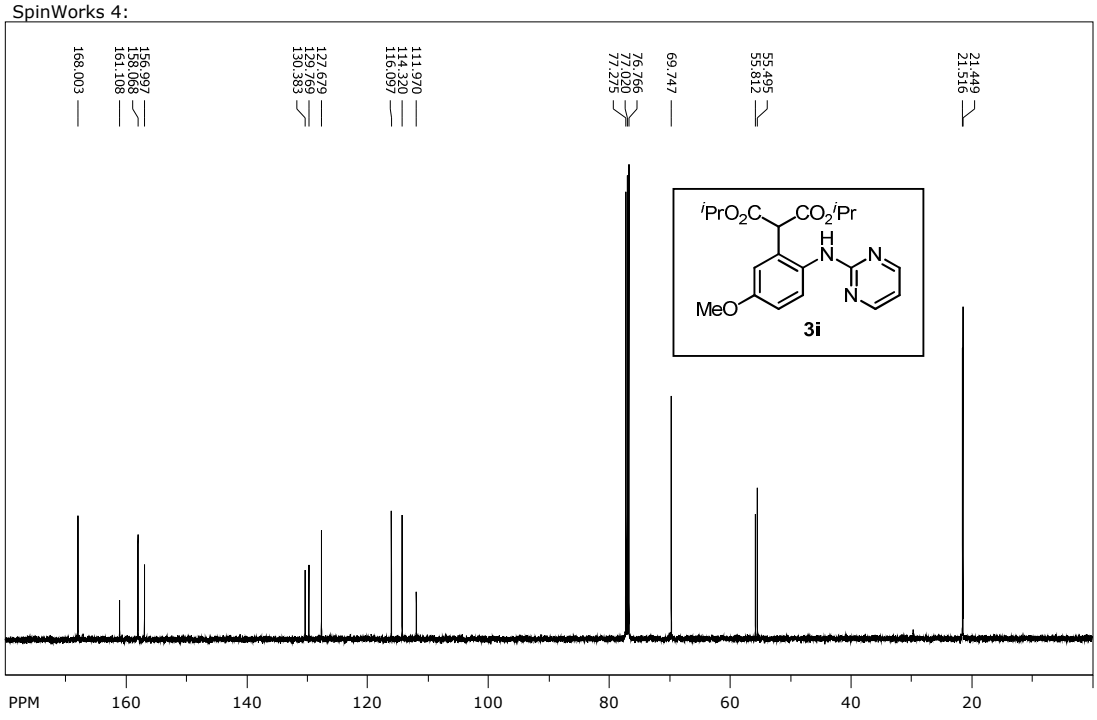
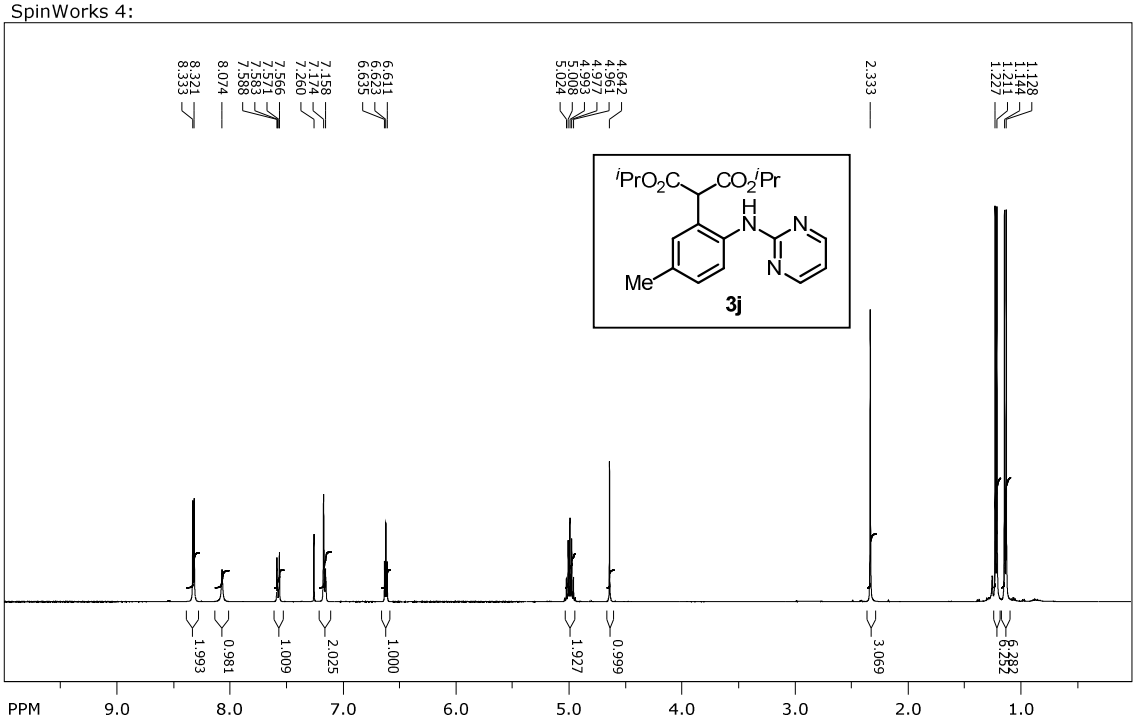


SpinWorks 4:



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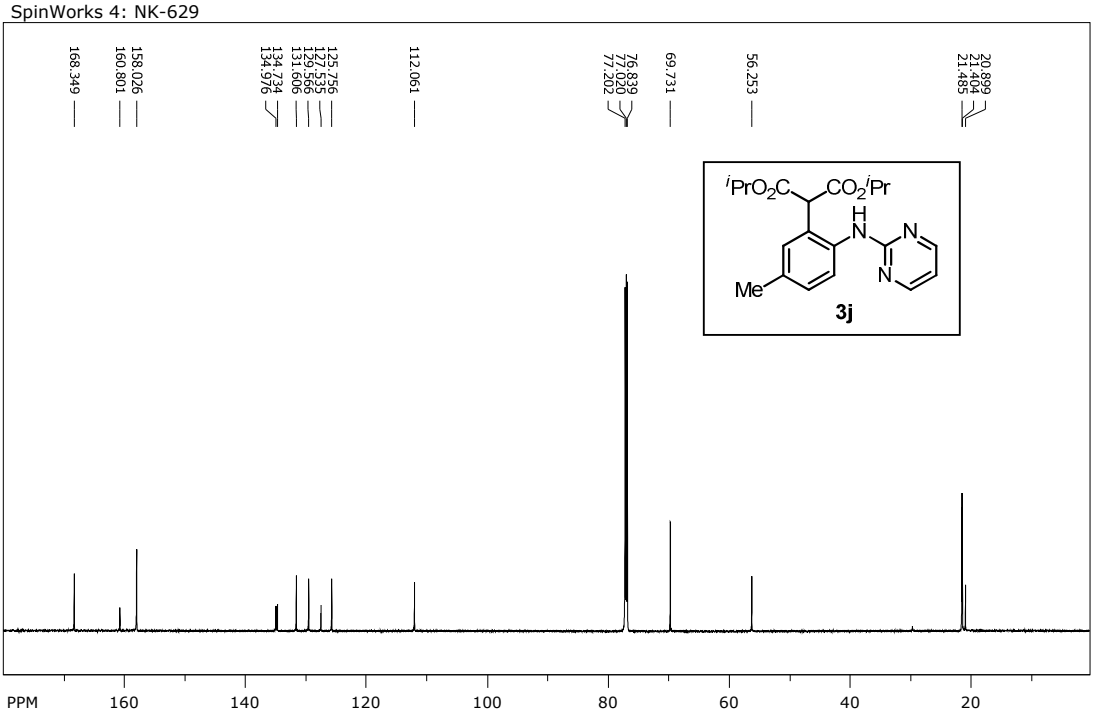
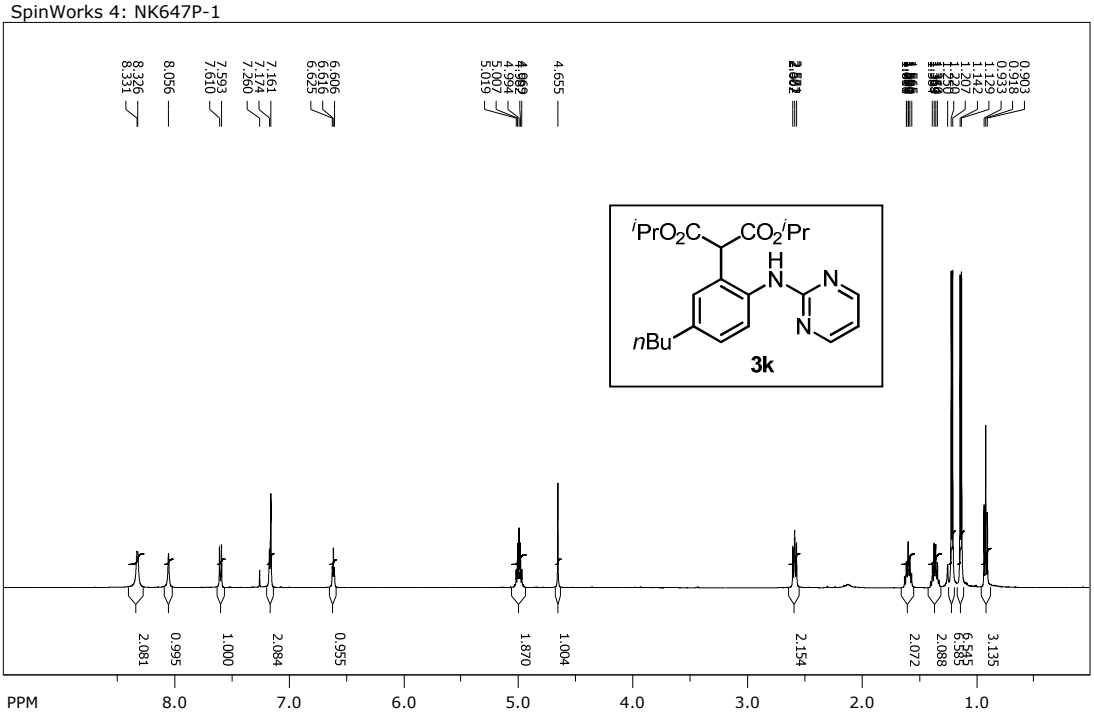
freq. of 0 ppm: 400.130011 MHz
processed size: 131072 complex points
LB: 0.300 GF: 0.0000

SpinWorks 4: NK-629



SpinWorks 4: NK647P-1



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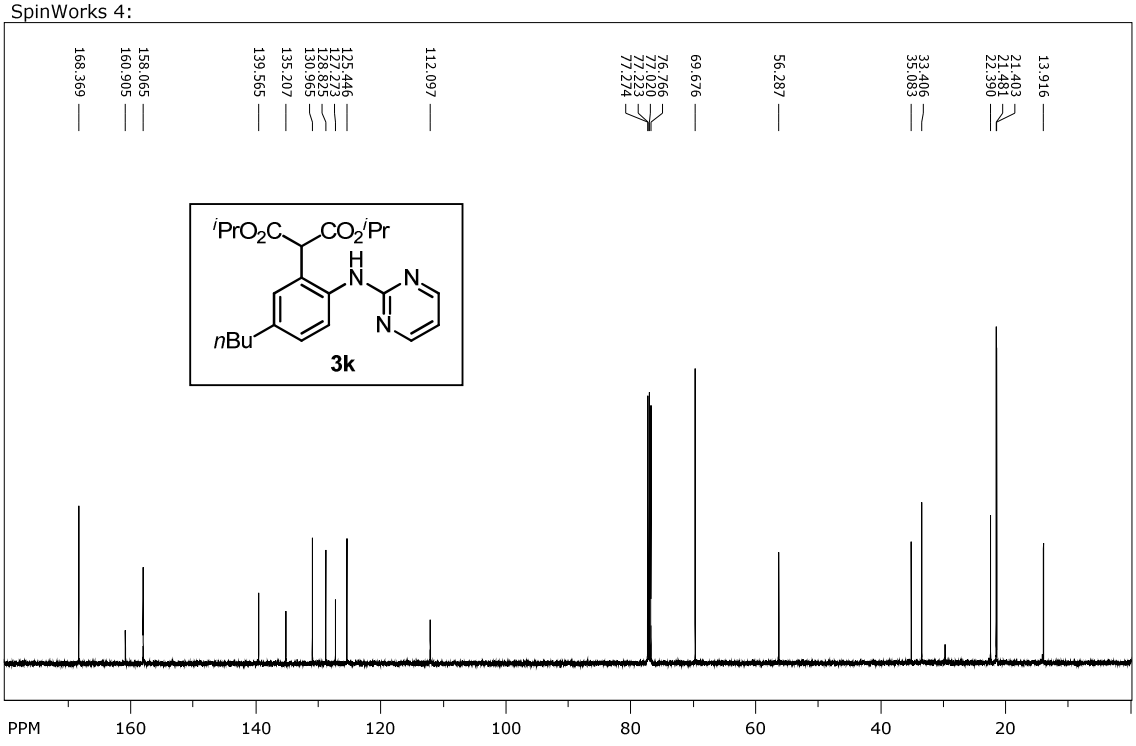
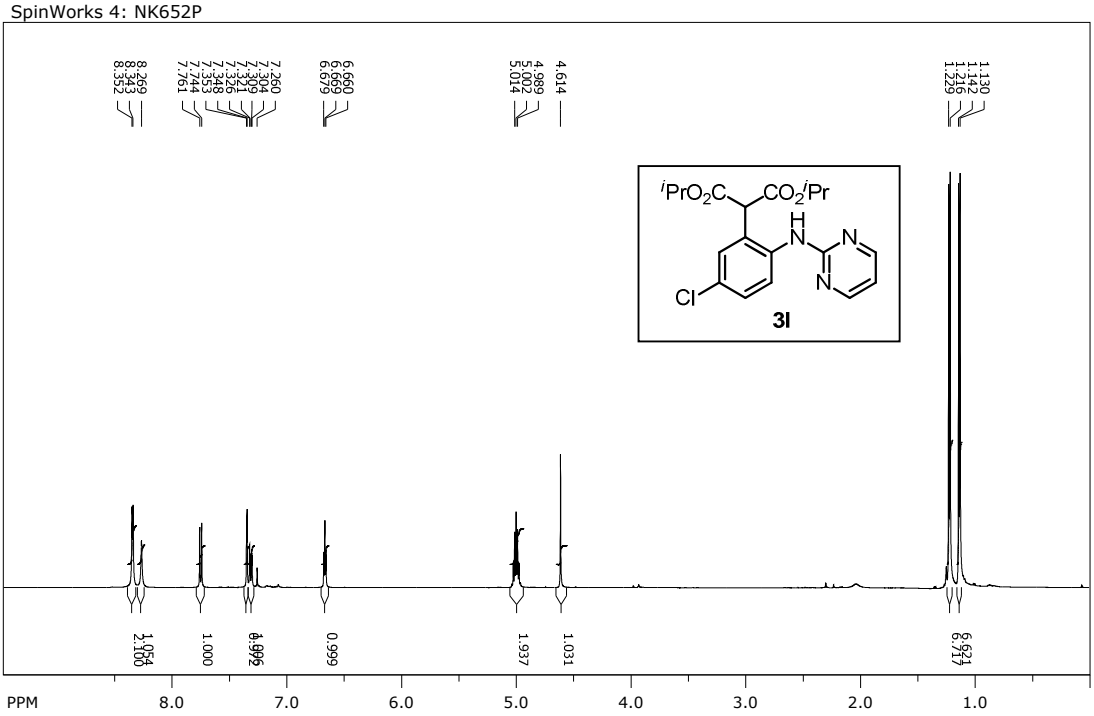
SpinWorks 4:



SpinWorks 4: NK652P



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number of scans: 32

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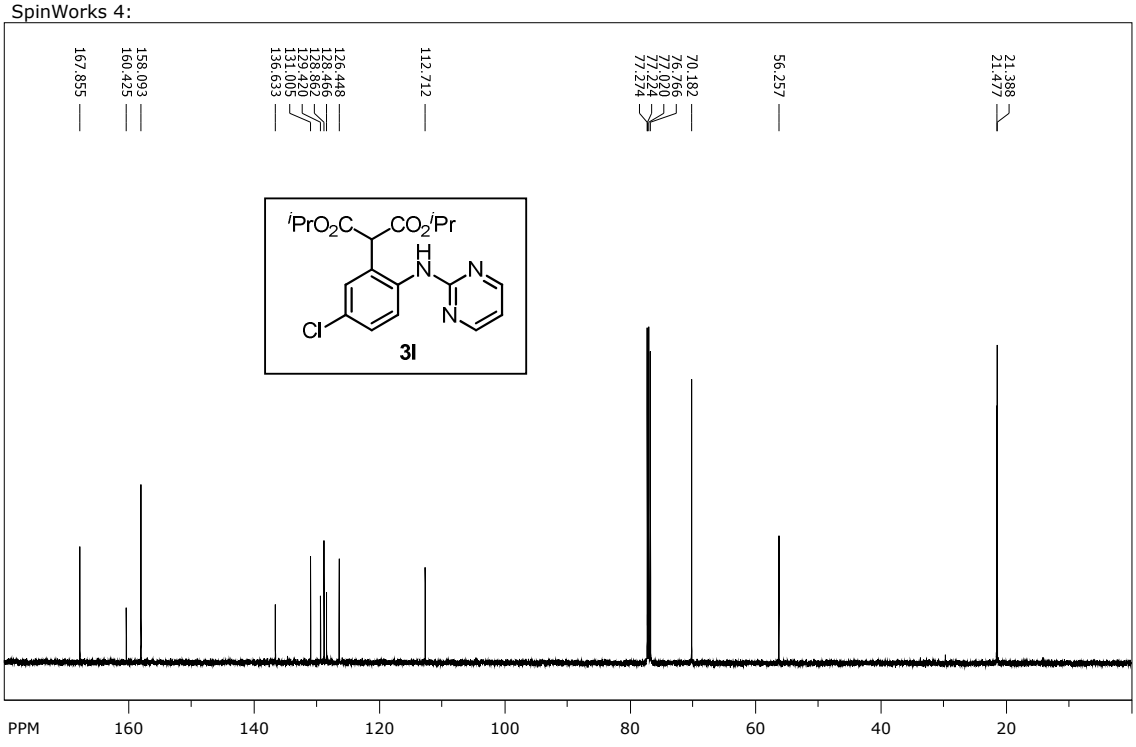
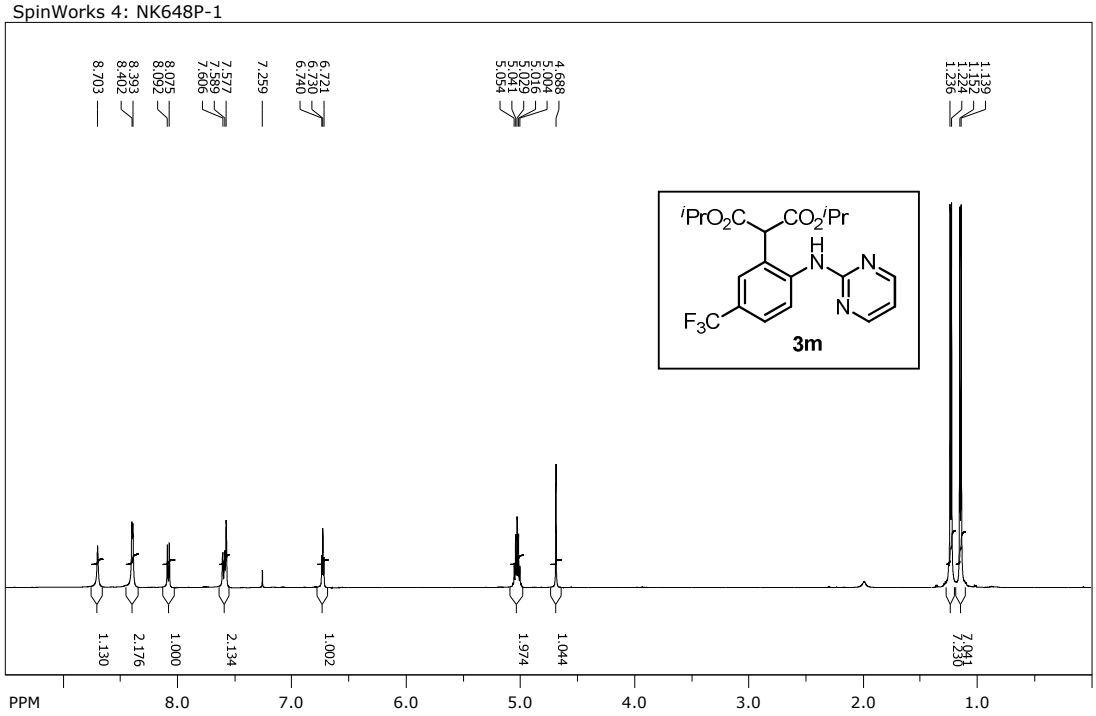
processed size: 65536 complex points
LB: 1.000 GF: 0.0000

SpinWorks 4:



SpinWorks 4: NK648P-1



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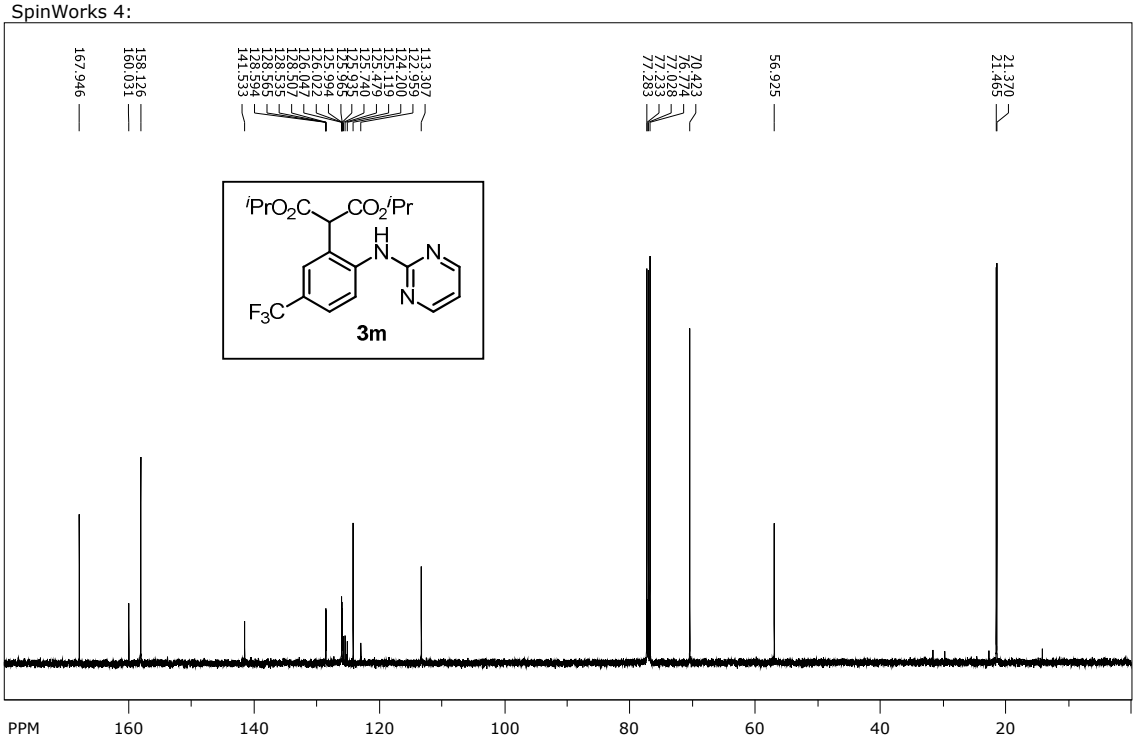
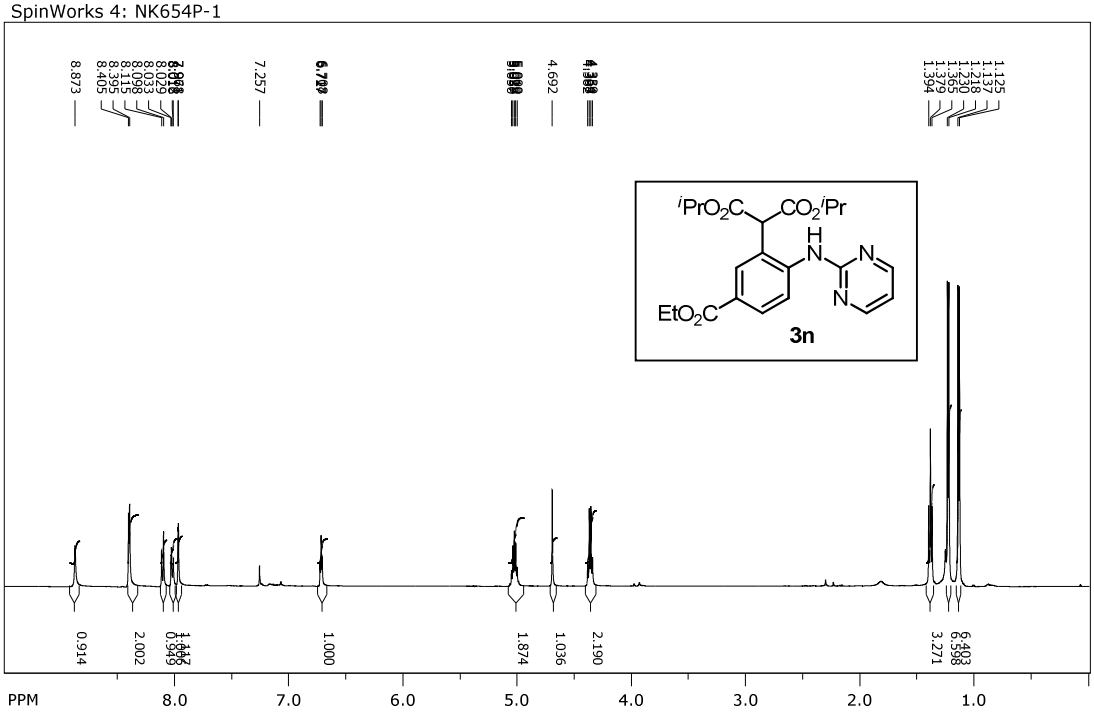
transmitter freq.: 499.960210 MHz
time domain size: 36372 points
width: 9611.92 Hz = 19.2254 ppm = 0.264267 Hz/pt
number of scans: 32

freq. of 0 ppm: 499.957021 MHz
processed size: 65536 complex points
LB: 1.000 GF: 0.0000

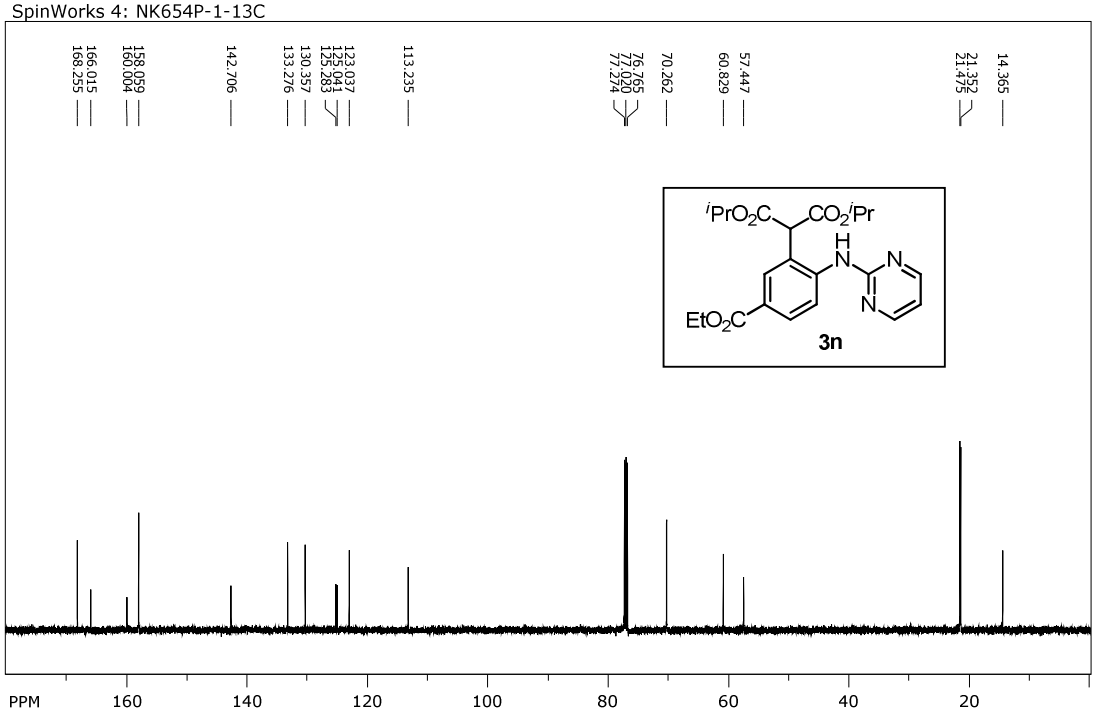
SpinWorks 4:

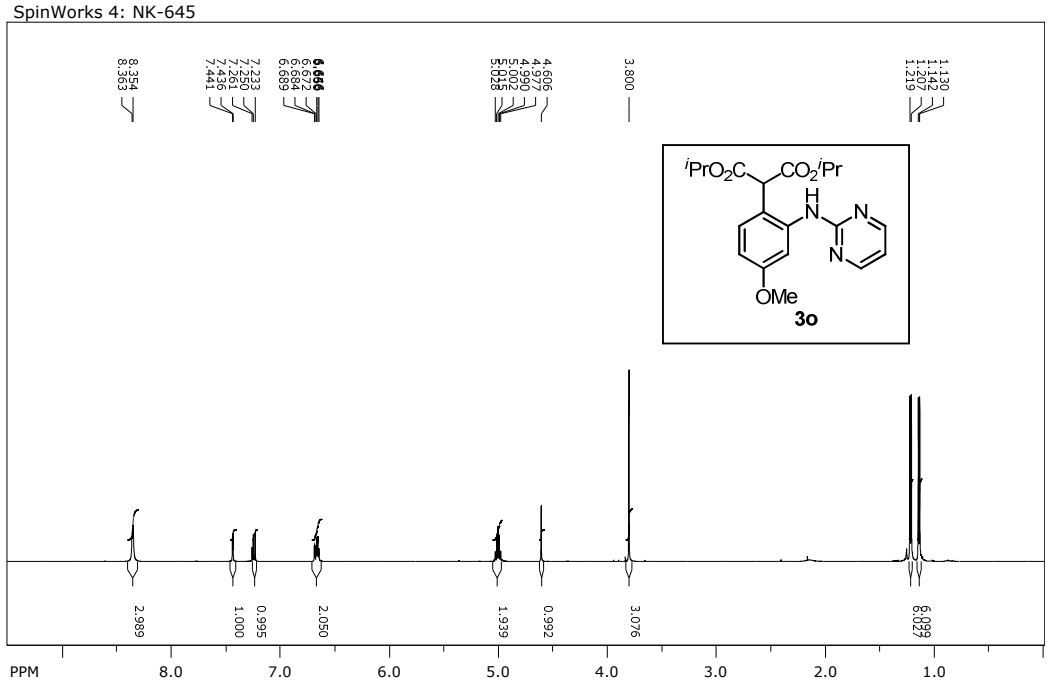


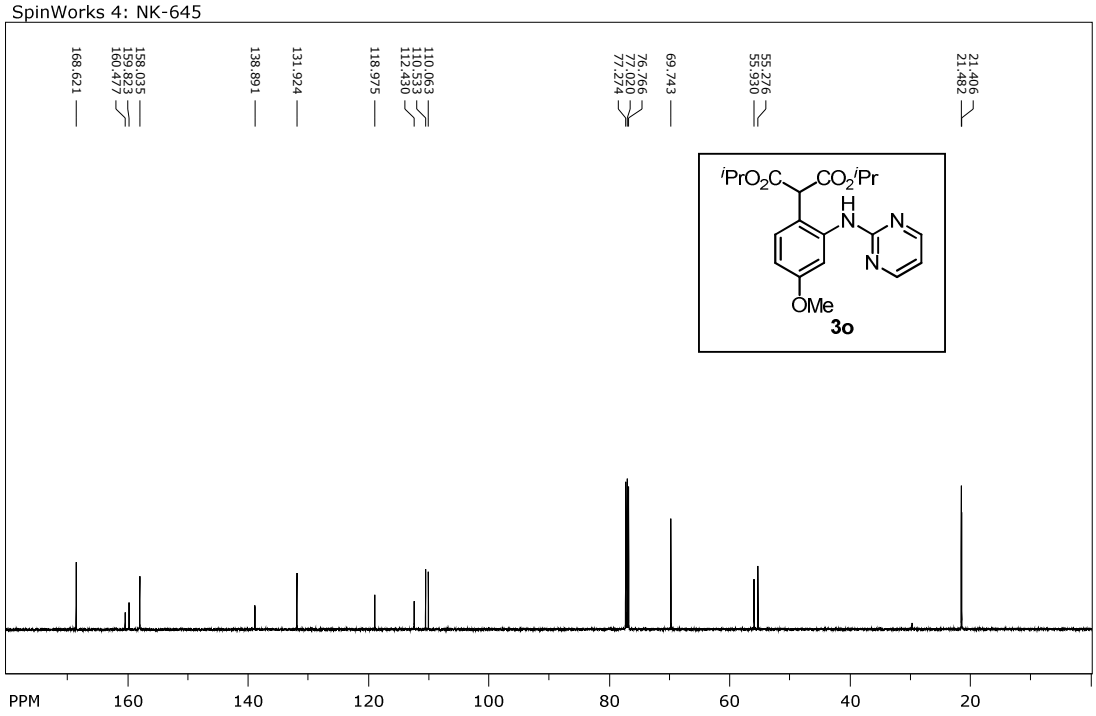
SpinWorks 4: NK654P-1



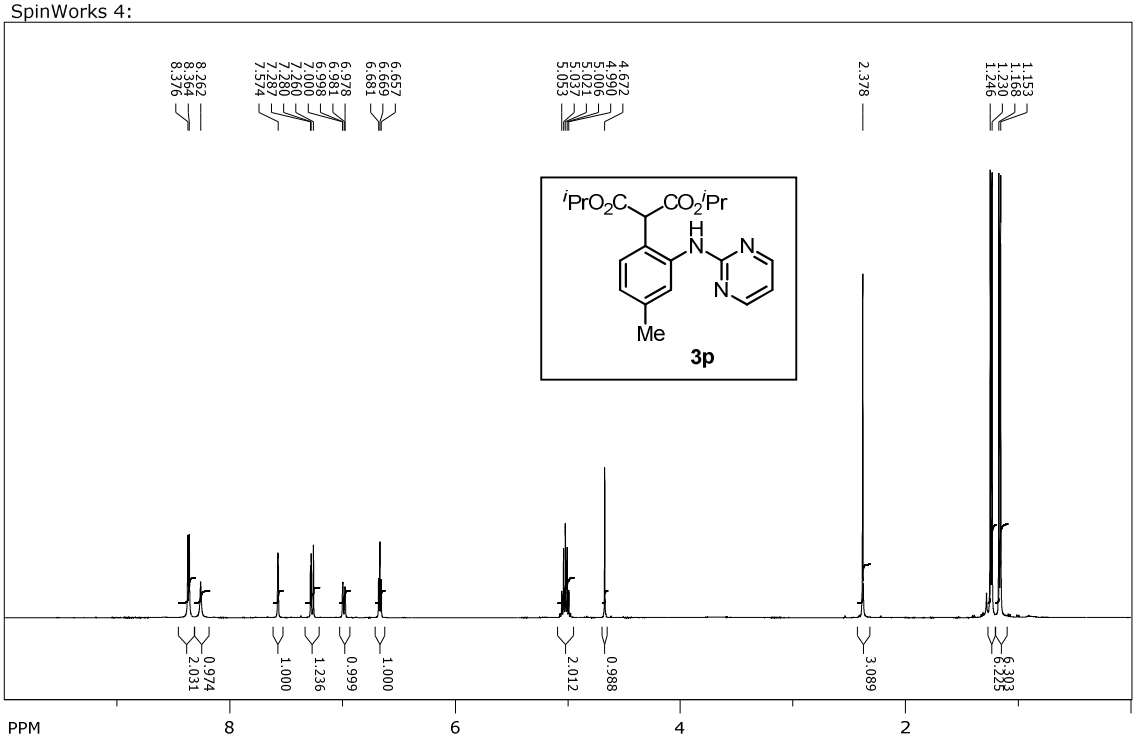
SpinWorks 4: NK654P-1-13C




SpinWorks 4: NK-645
8.354
8.363
7.441
7.439
7.250
7.233
6.689
6.684
6.672
6.667
5.028
5.012
4.990
4.977
4.606
3.800
1.219
1.207
1.130
2.989
1.000
0.995
2.050
1.939
0.992
3.076
6.099
6.027
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
iPrO2C
CO2iPr
H
N
N
N
OMe
3o


SpinWorks 4: NK-645
168.621
159.823
158.035
160.477
138.891
131.924
118.975
110.063
110.533
112.430
77.274
77.020
76.766
69.743
55.930
55.276
21.482
21.406
PPM
160
140
120
100
80
60
40
20
iPrO2C
CO2iPr
H
N
N
N
OMe
3o

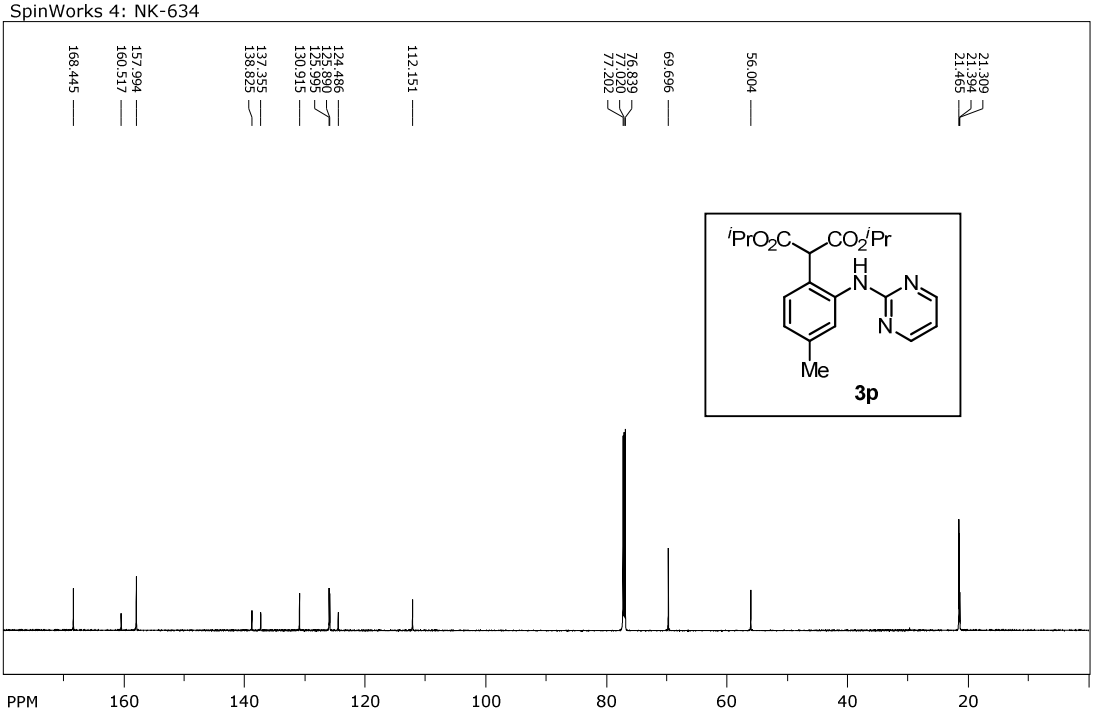
SpinWorks 4:

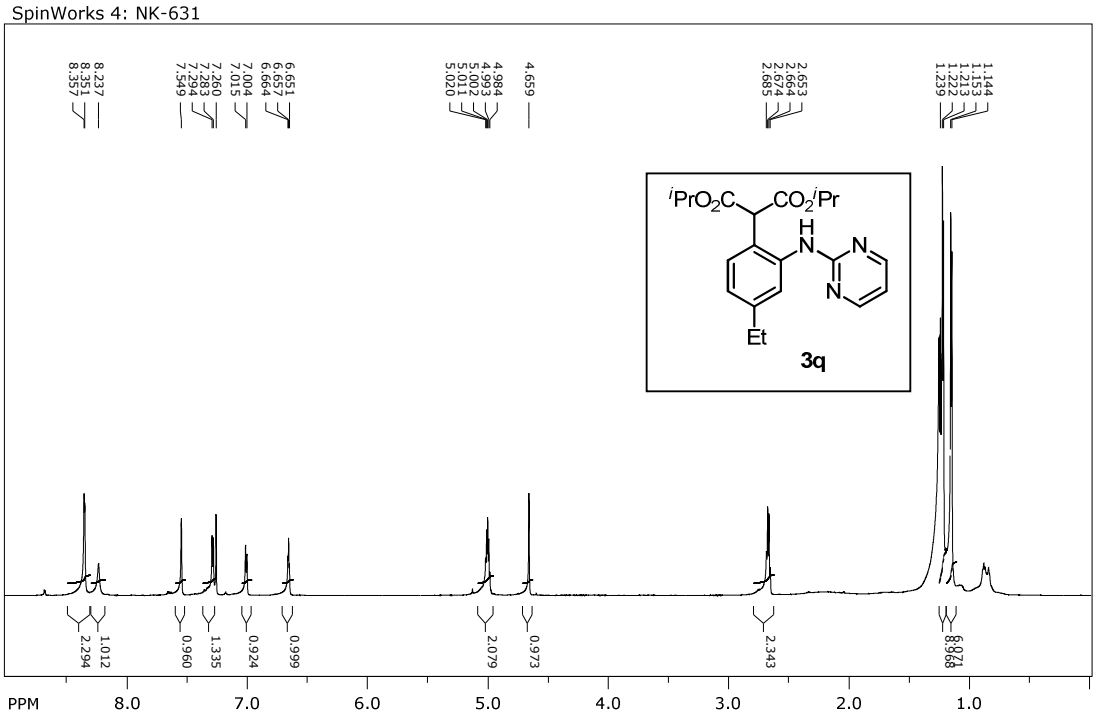


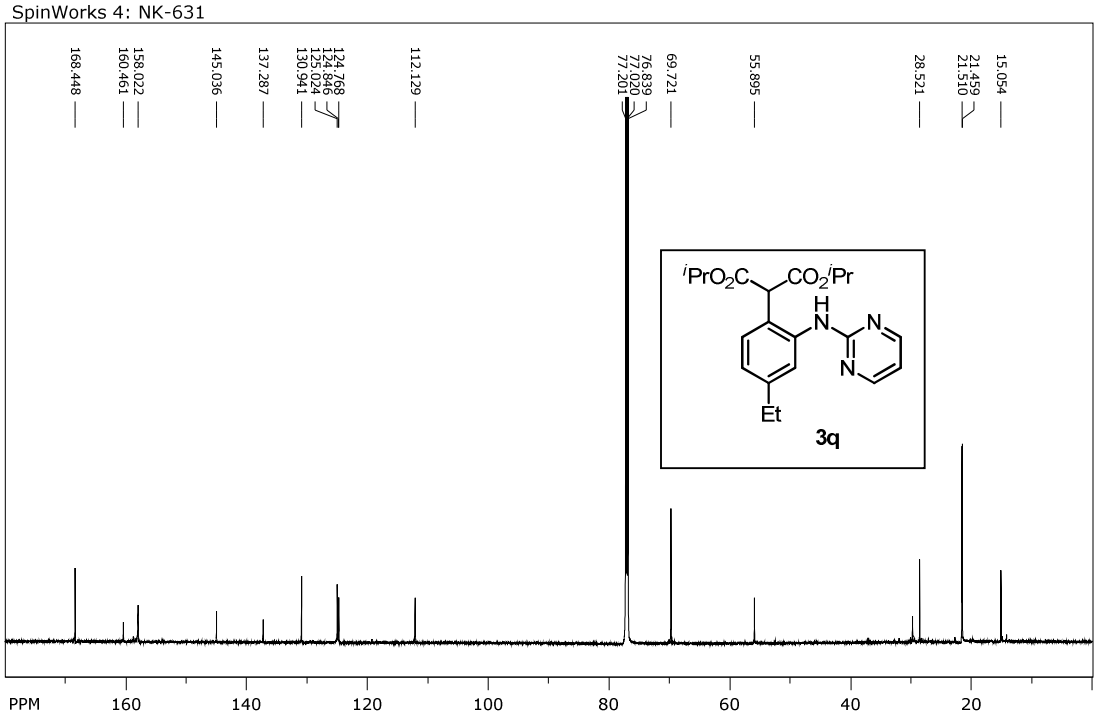
file: ...p\Rest carbon and NMR\NK-634\1\fid expt: <zg30>
transmitter freq.: 400.131601 MHz
time domain size: 65536 points
width: 8012.82 Hz = 20.0255 ppm = 0.122266 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130000 MHz
processed size: 131072 complex points
LB: 0.300 GF: 0.0000

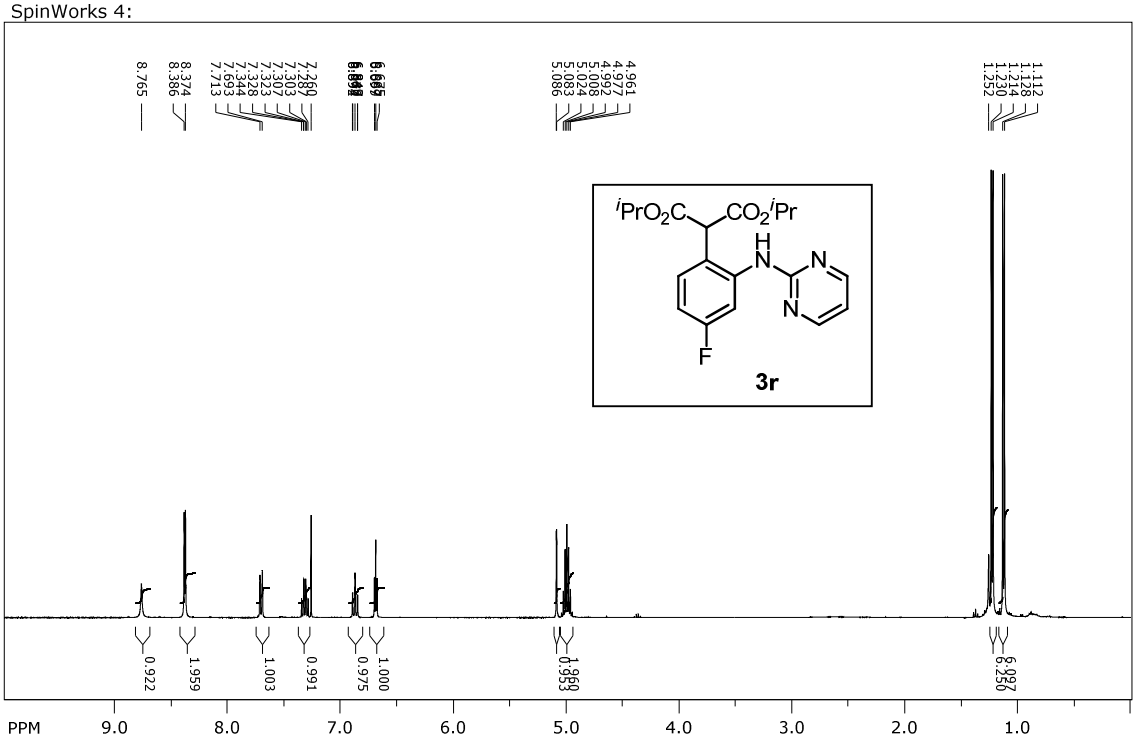
SpinWorks 4: NK-634




SpinWorks 4: NK-631
8.357
8.351
8.237
7.549
7.294
7.283
7.260
7.015
7.004
6.664
6.657
6.651
5.020
5.011
5.002
4.993
4.984
4.659
2.685
2.674
2.664
2.653
1.239
1.223
1.153
1.144
2.294
1.012
0.960
1.335
0.924
0.999
2.079
0.973
2.343
8.968
8.074
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
iPrO2C
CO2iPr
H
N
N
N
Et
3q


SpinWorks 4: NK-631
168.448
160.461
158.022
145.036
137.287
130.941
125.024
124.846
124.768
112.129
77.201
77.020
76.839
69.721
55.895
28.521
21.510
21.459
15.054
PPM
160
140
120
100
80
60
40
20
iPrO2C
CO2iPr
H
N
N
N
Et
3q

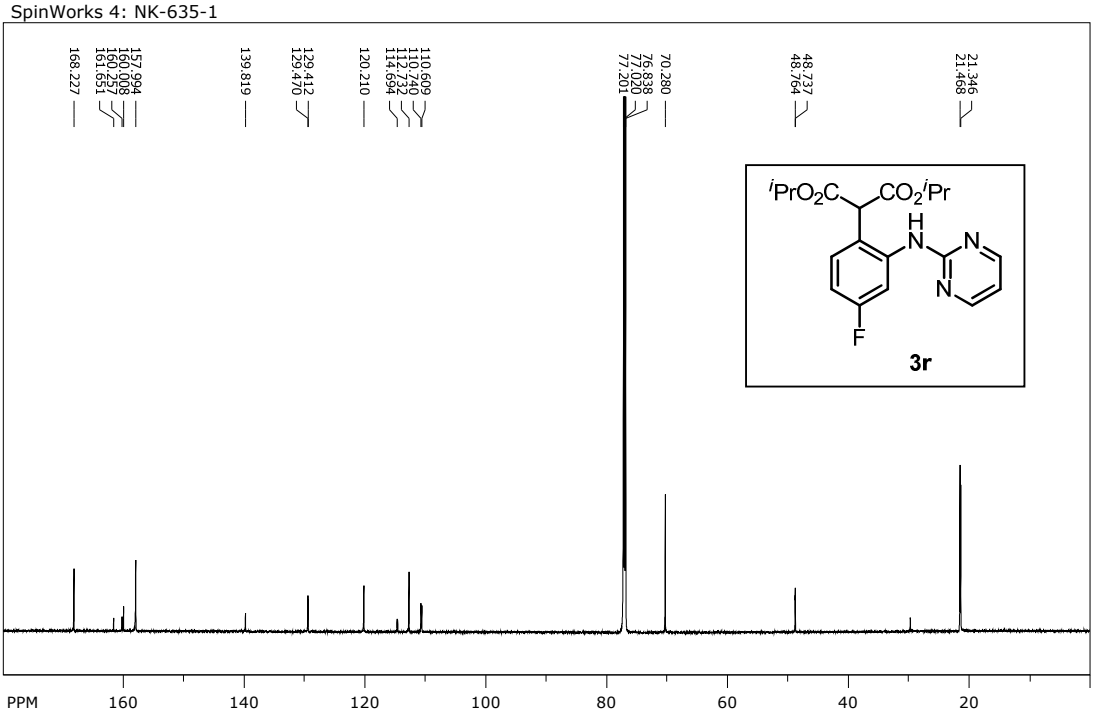
SpinWorks 4:



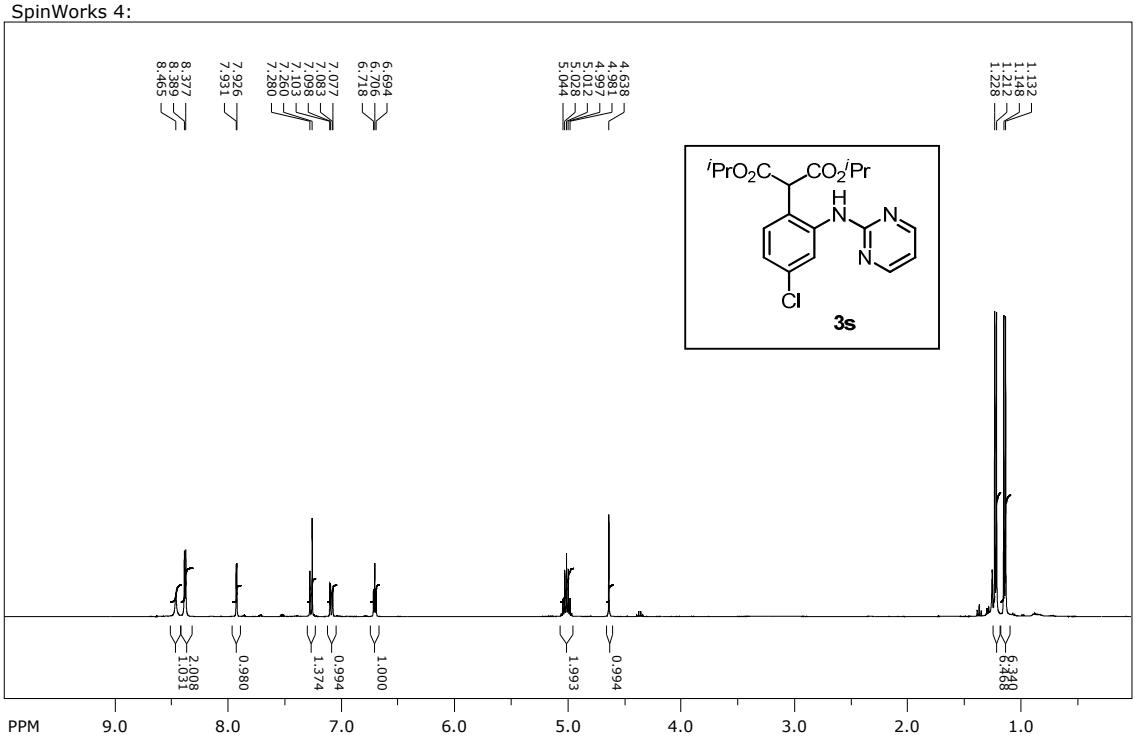
file: ...p\Rest carbon and NMR\NK-635\1\fid expt: <zg30>
transmitter freq.: 400.131601 MHz
time domain size: 65536 points
width: 8012.82 Hz = 20.0255 ppm = 0.122266 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130011 MHz
processed size: 131072 complex points
LB: 0.300 GF: 0.0000

SpinWorks 4: NK-635-1



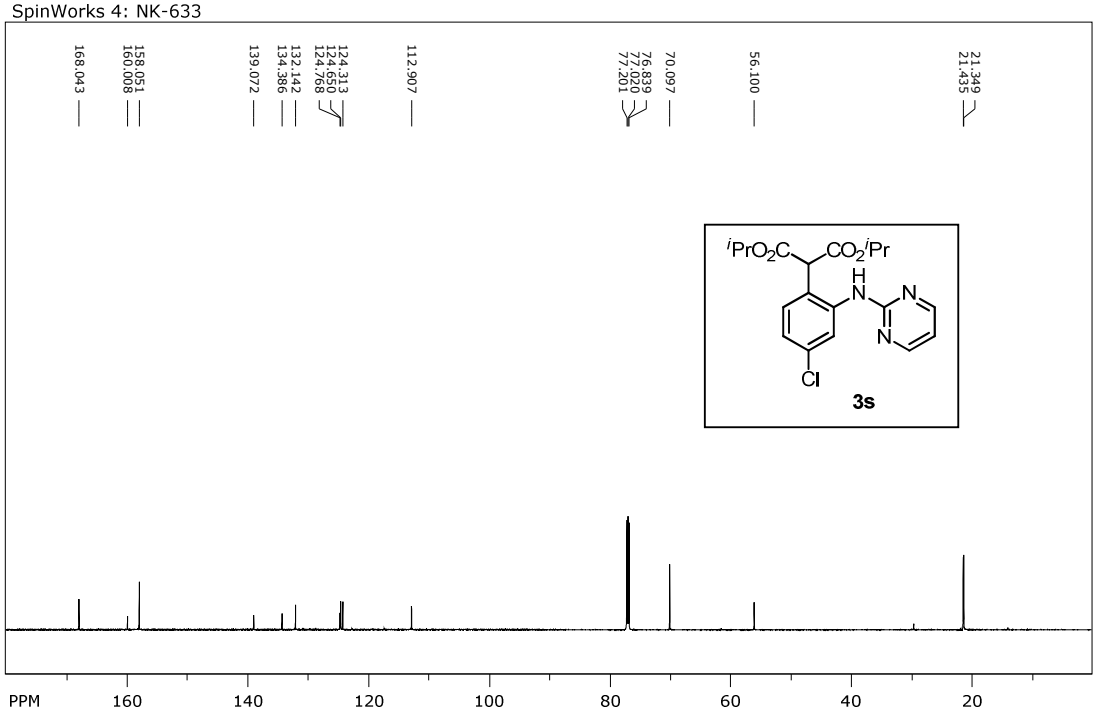
SpinWorks 4:



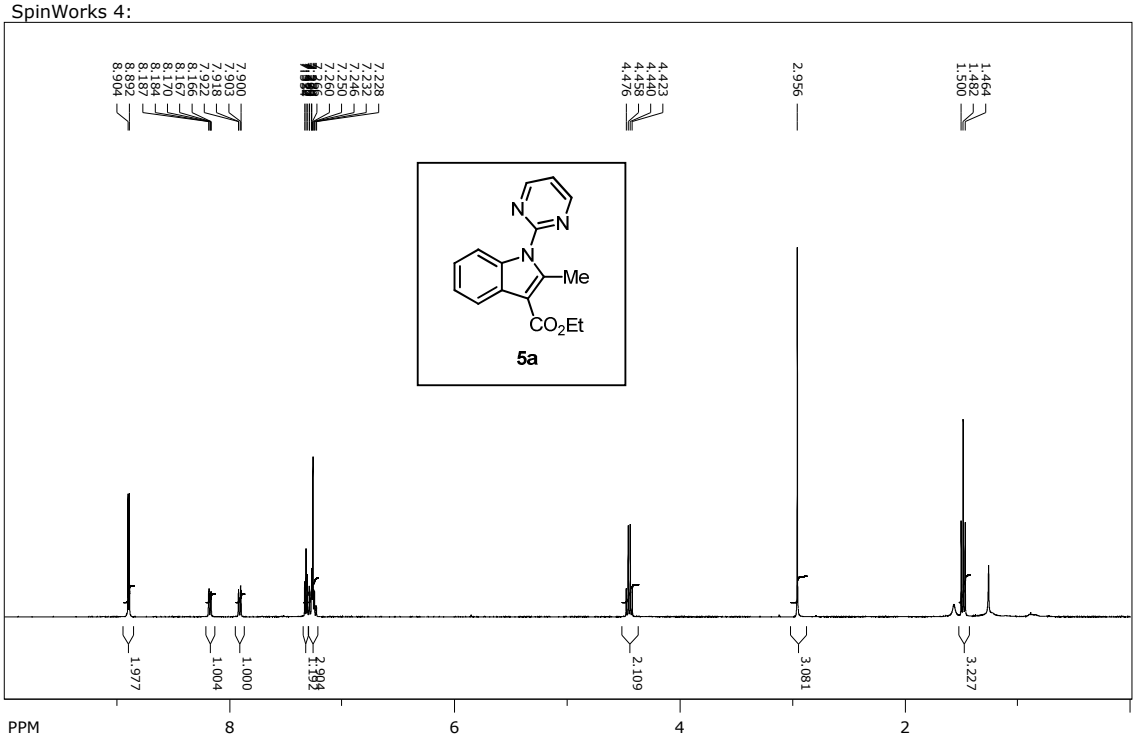
file: ...p\Rest carbon and NMR\NK-633\1\fid expt: <zg30>
transmitter freq.: 400.131601 MHz
time domain size: 65536 points
width: 8012.82 Hz = 20.0255 ppm = 0.122266 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130011 MHz
processed size: 131072 complex points
LB: 0.300 GF: 0.0000

SpinWorks 4: NK-633



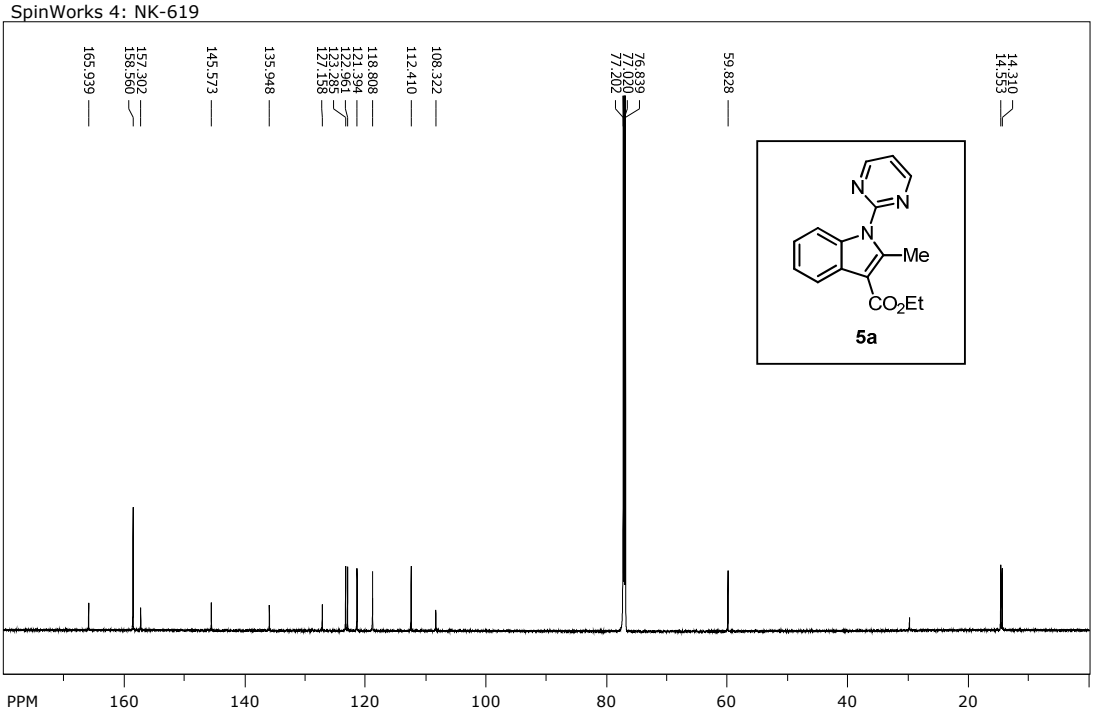
SpinWorks 4:



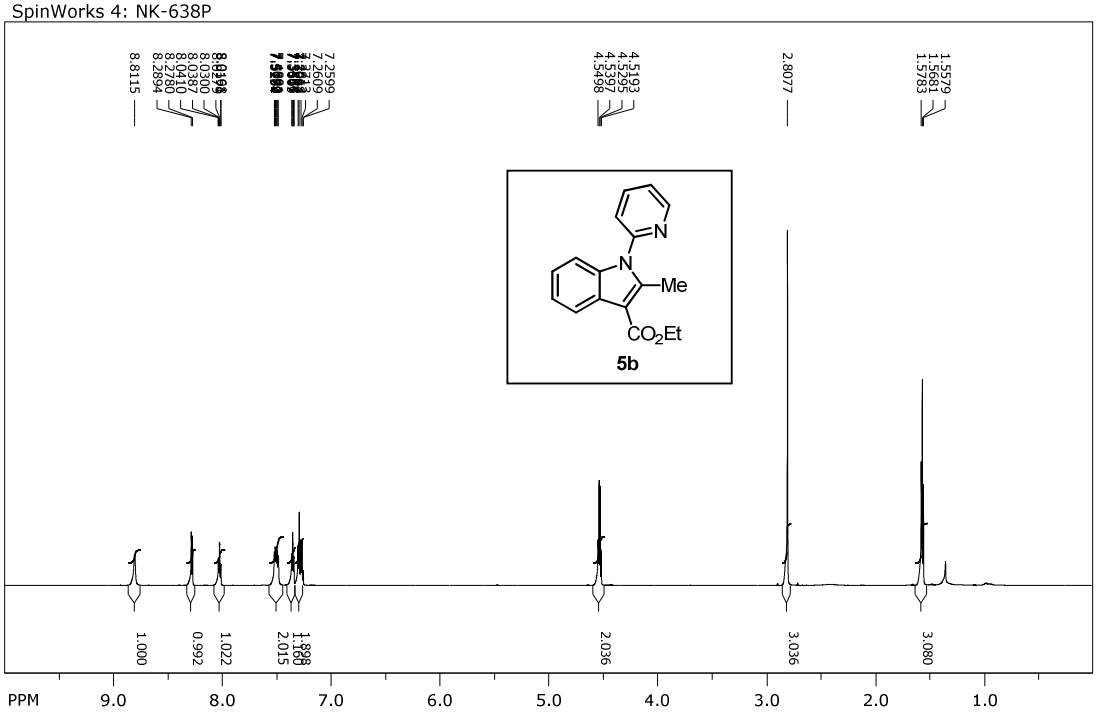
file: ...p\Rest carbon and NMR\NK-619\1\fid expt: <zg30>
transmitter freq.: 400.131601 MHz
time domain size: 65536 points
width: 8012.82 Hz = 20.0255 ppm = 0.122266 Hz/pt
number of scans: 16

freq. of 0 ppm: 400.130011 MHz
processed size: 131072 complex points
LB: 0.300 GF: 0.0000

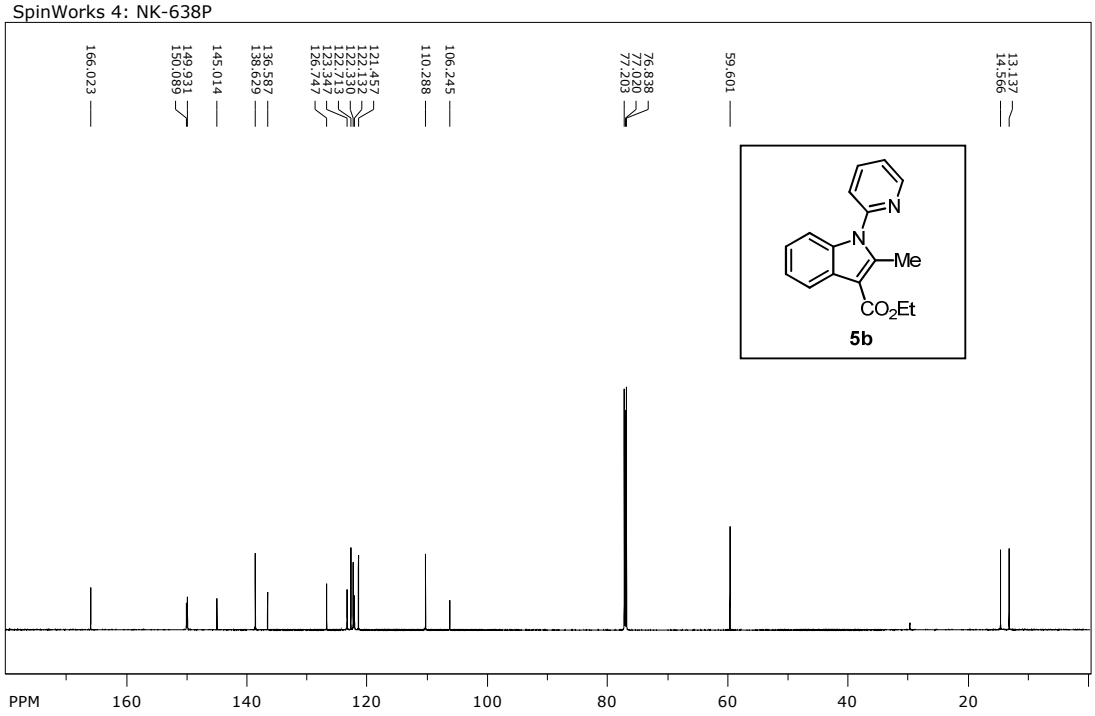
SpinWorks 4: NK-619



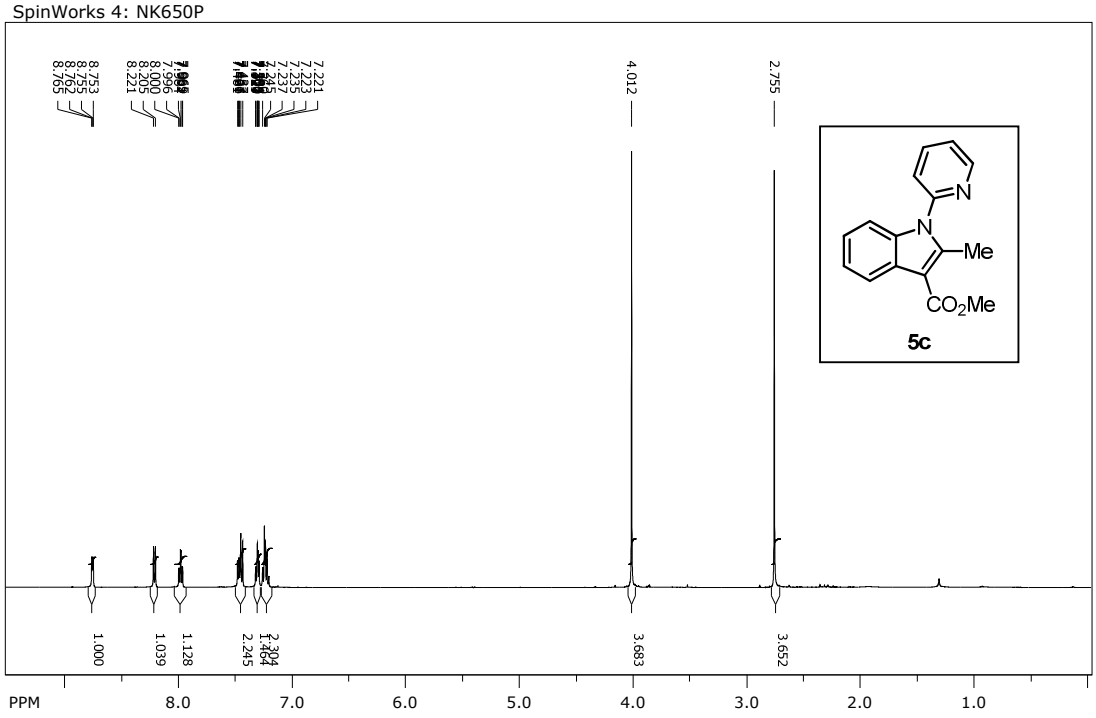
SpinWorks 4: NK-638P



SpinWorks 4: NK-638P



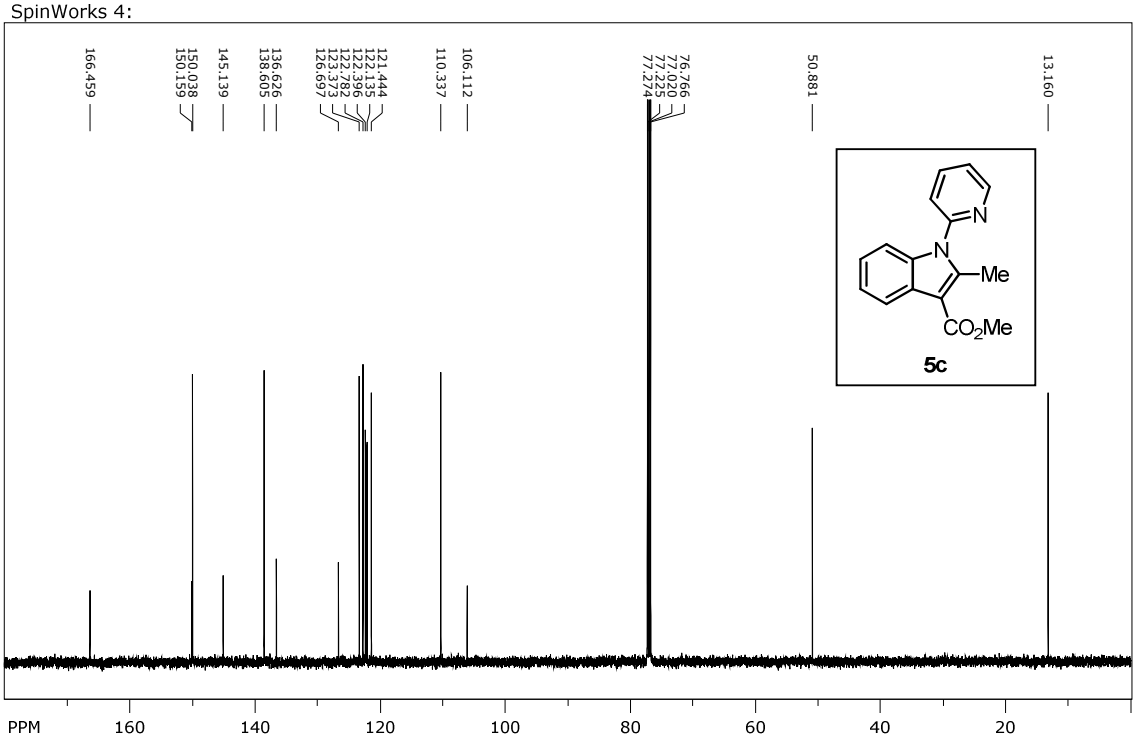
SpinWorks 4: NK650P



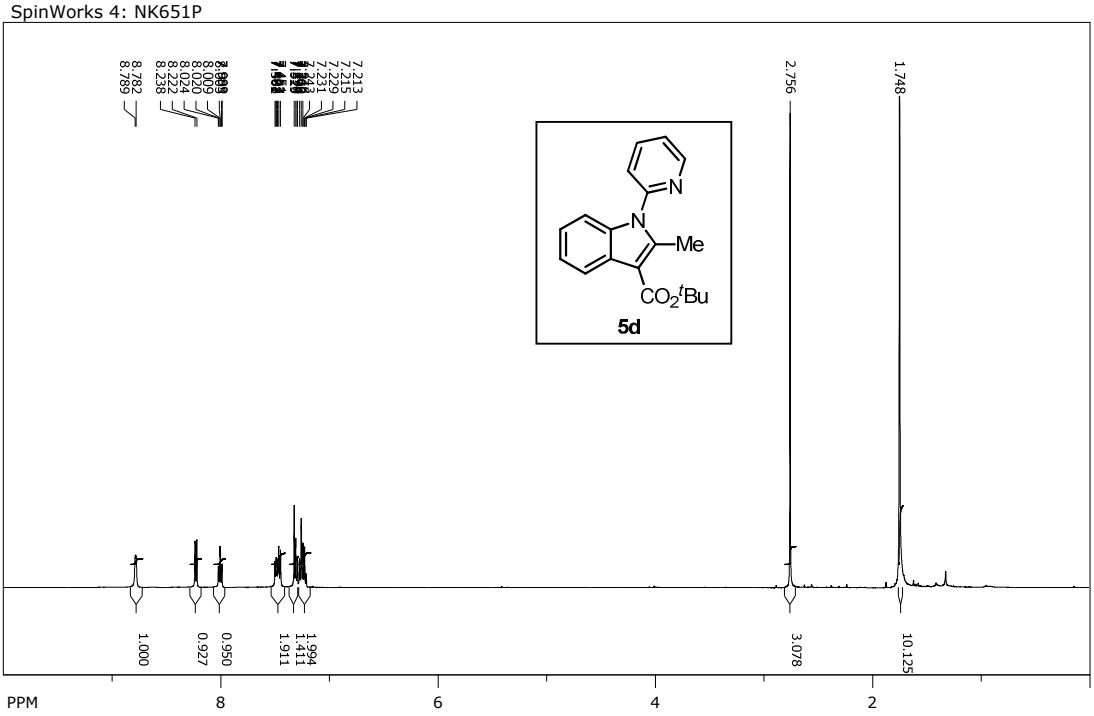
file: ...\Desktop\NMR_Neeraj\NK650P.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 499.960210 MHz
time domain size: 36372 points
width: 9611.92 Hz = 19.2254 ppm = 0.264267 Hz/pt
number of scans: 32

freq. of 0 ppm: 499.957000 MHz
processed size: 65536 complex points
LB: 1.000 GF: 0.0000

SpinWorks 4:



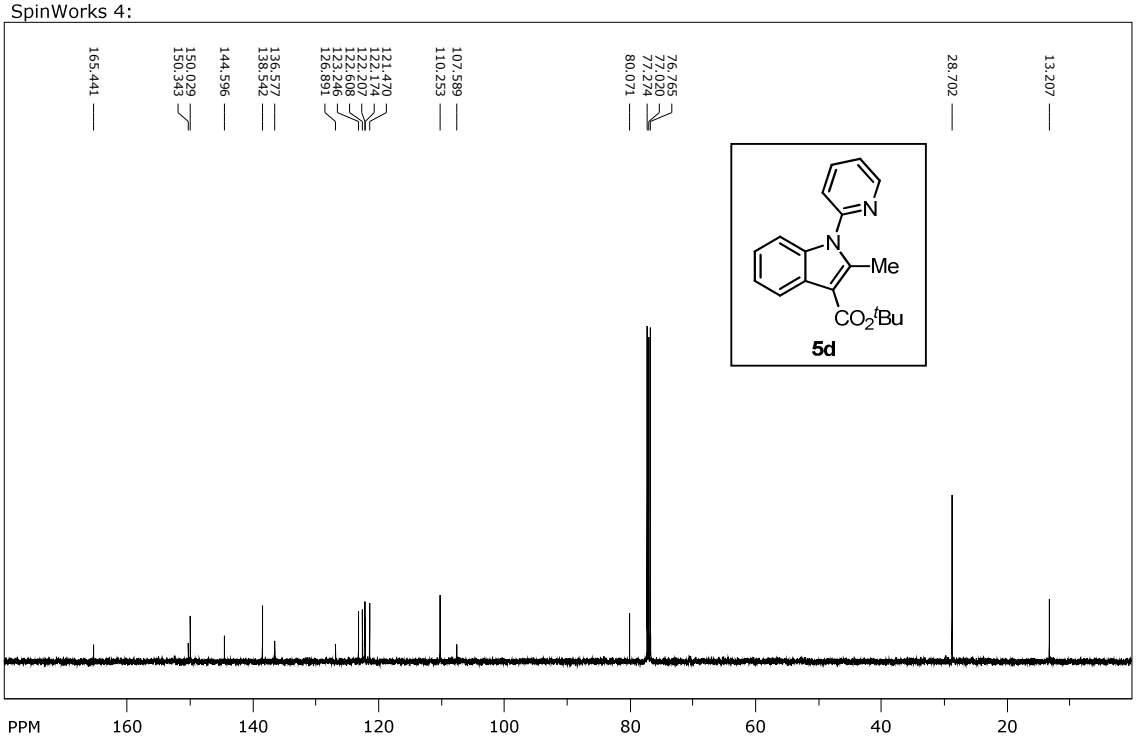
SpinWorks 4: NK651P



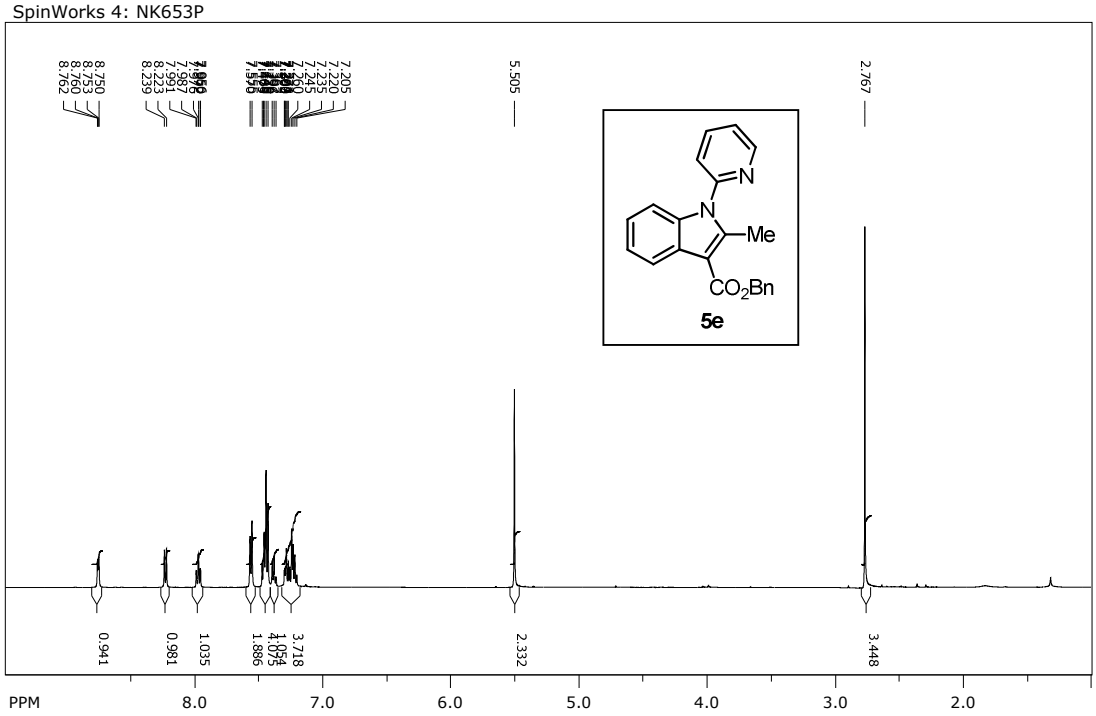
file: ...\Desktop\NMR_Neeraj\NK651P.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 499.960210 MHz
time domain size: 36372 points
width: 9611.92 Hz = 19.2254 ppm = 0.264267 Hz/pt
number of scans: 32

freq. of 0 ppm: 499.956988 MHz
processed size: 65536 complex points
LB: 1.000 GF: 0.0000

SpinWorks 4:



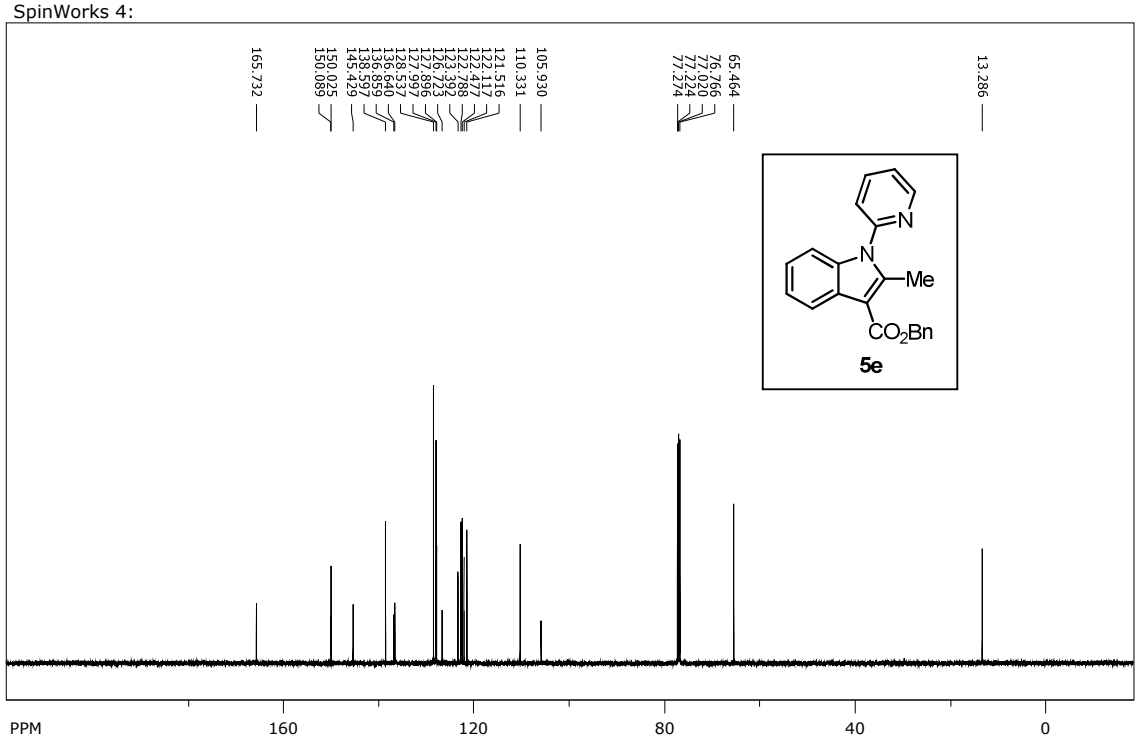
SpinWorks 4: NK653P



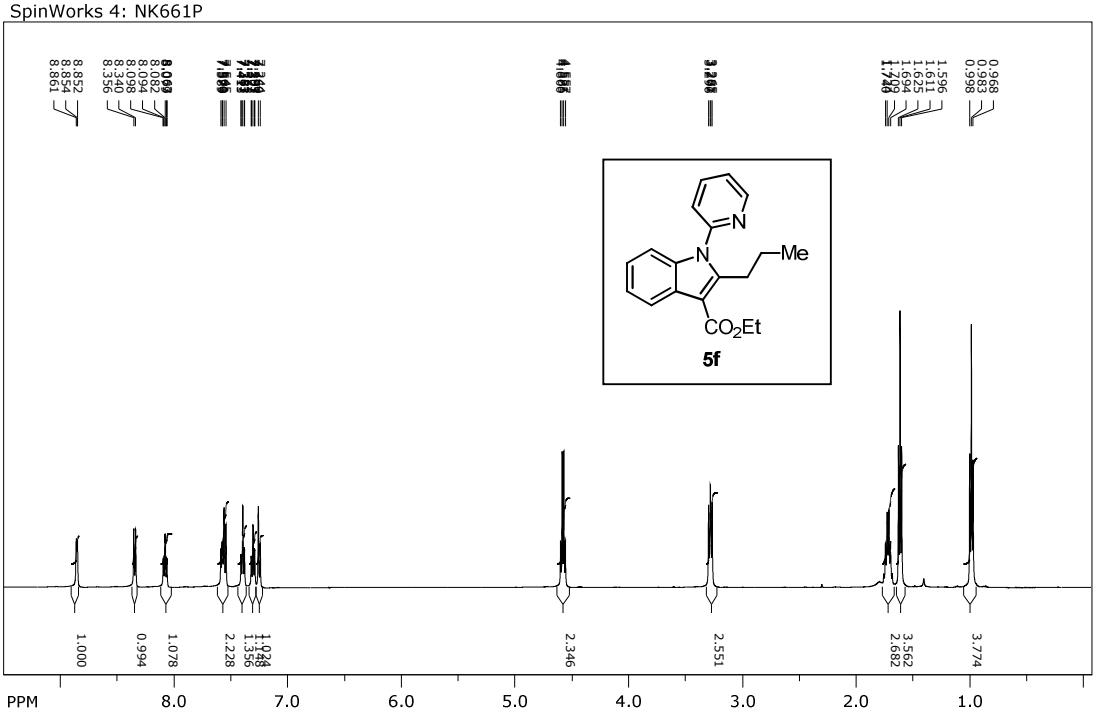
file: ...\Desktop\NMR_Neeraj\NK653P.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 499.960210 MHz
time domain size: 36372 points
width: 9611.92 Hz = 19.2254 ppm = 0.264267 Hz/pt
number of scans: 32

freq. of 0 ppm: 499.957003 MHz
processed size: 65536 complex points
LB: 1.000 GF: 0.0000

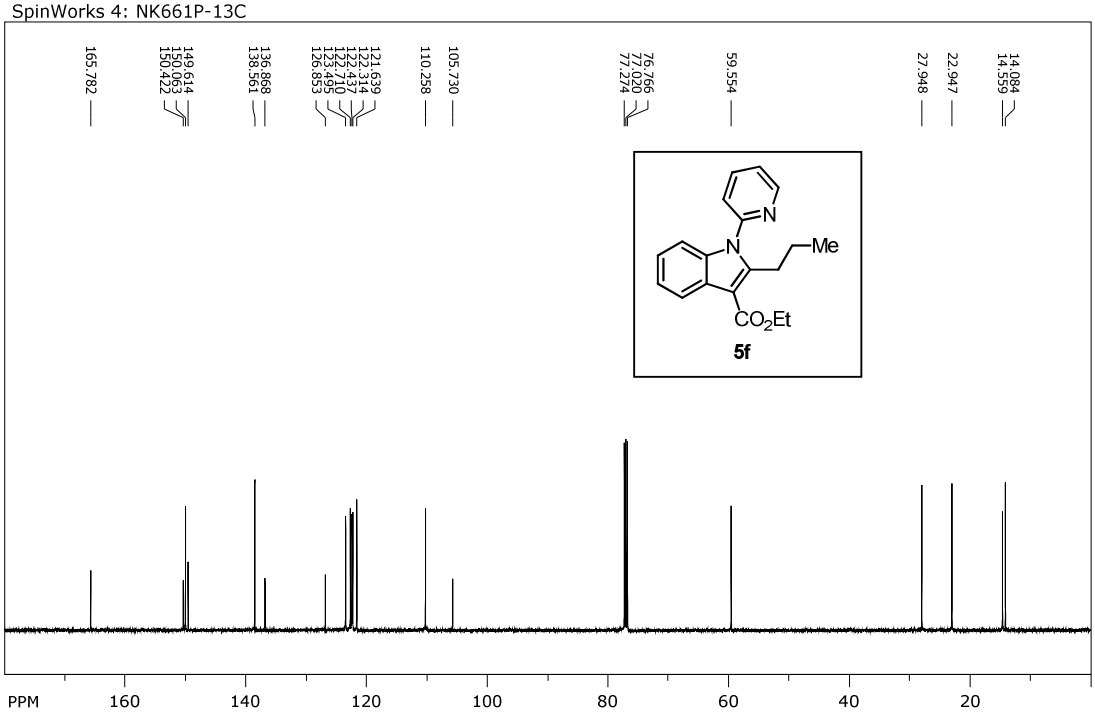
SpinWorks 4:



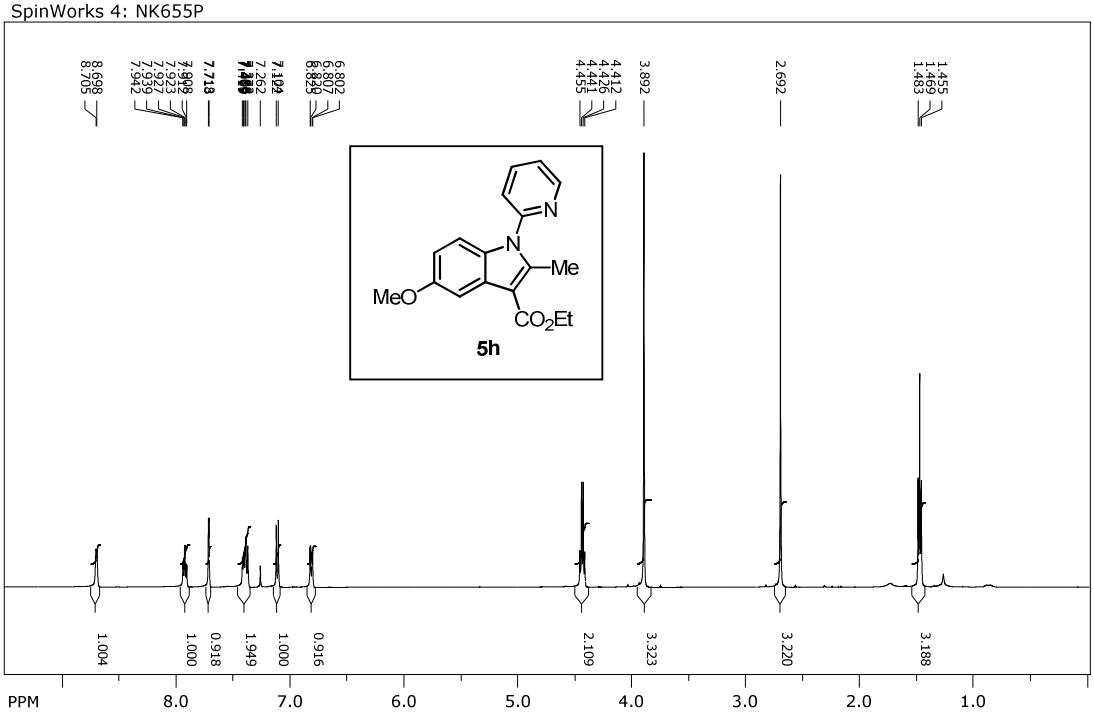
SpinWorks 4: NK661P



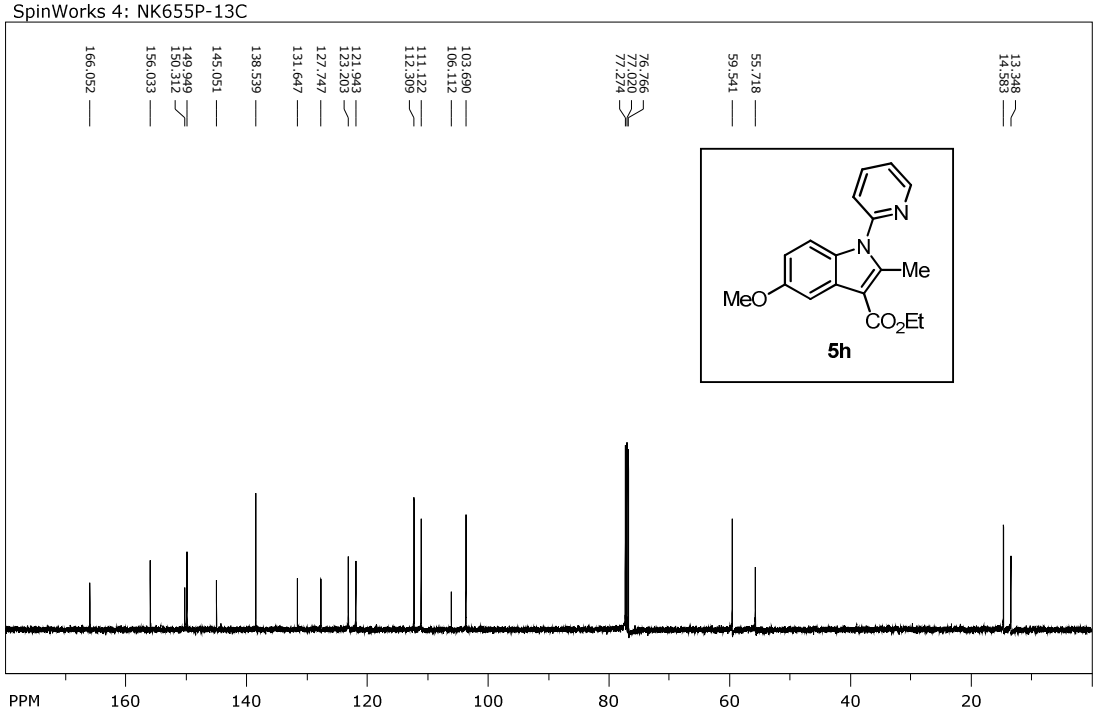
SpinWorks 4: NK661P-13C



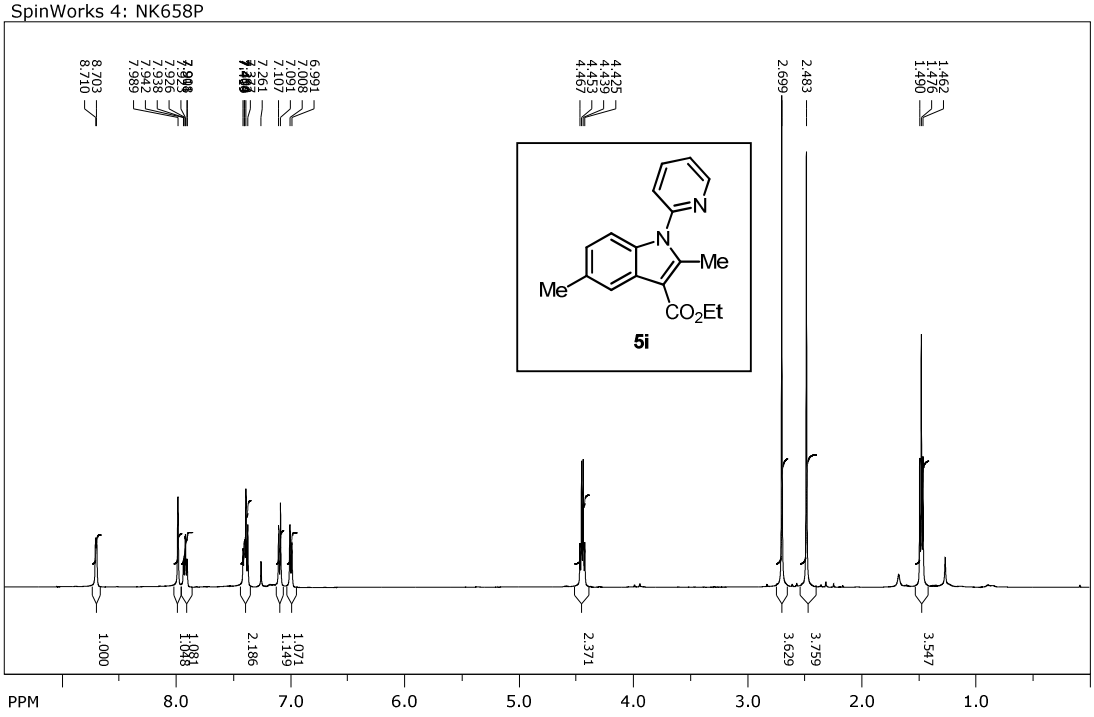
SpinWorks 4: NK655P



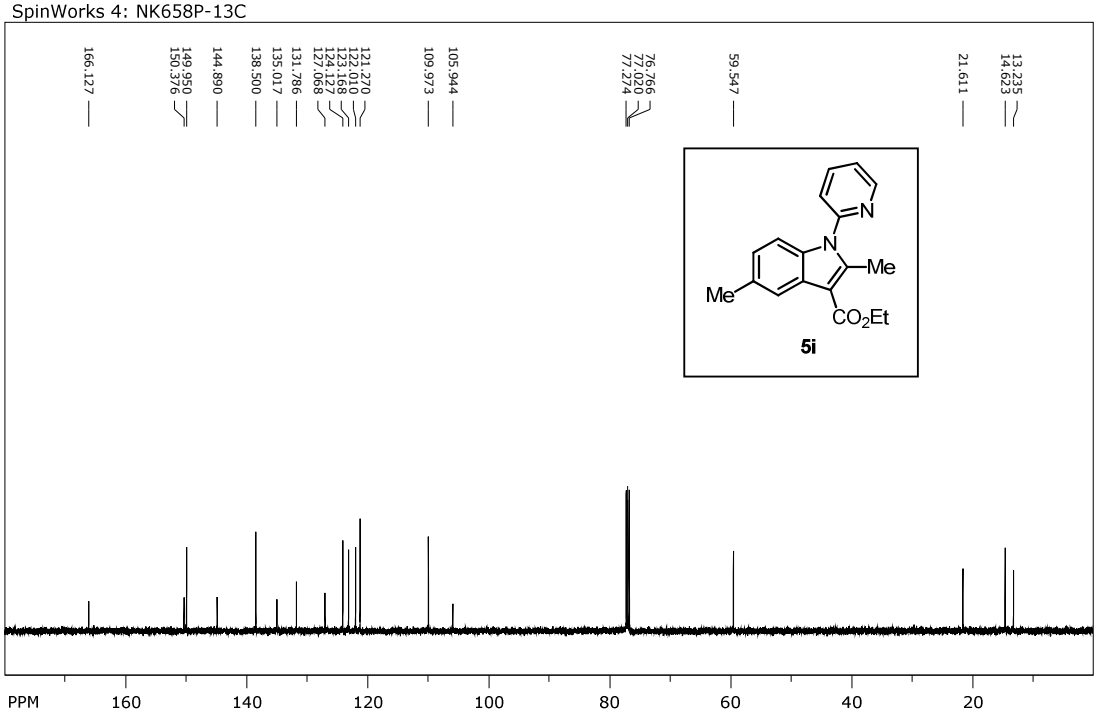
SpinWorks 4: NK655P-13C



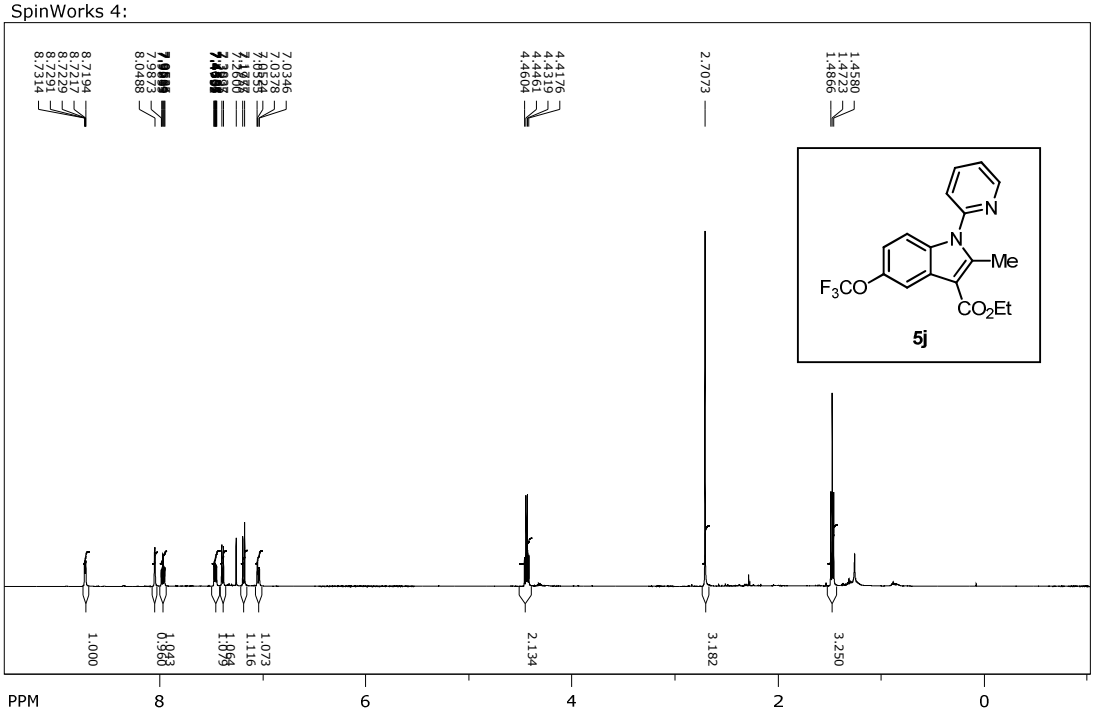
SpinWorks 4: NK658P



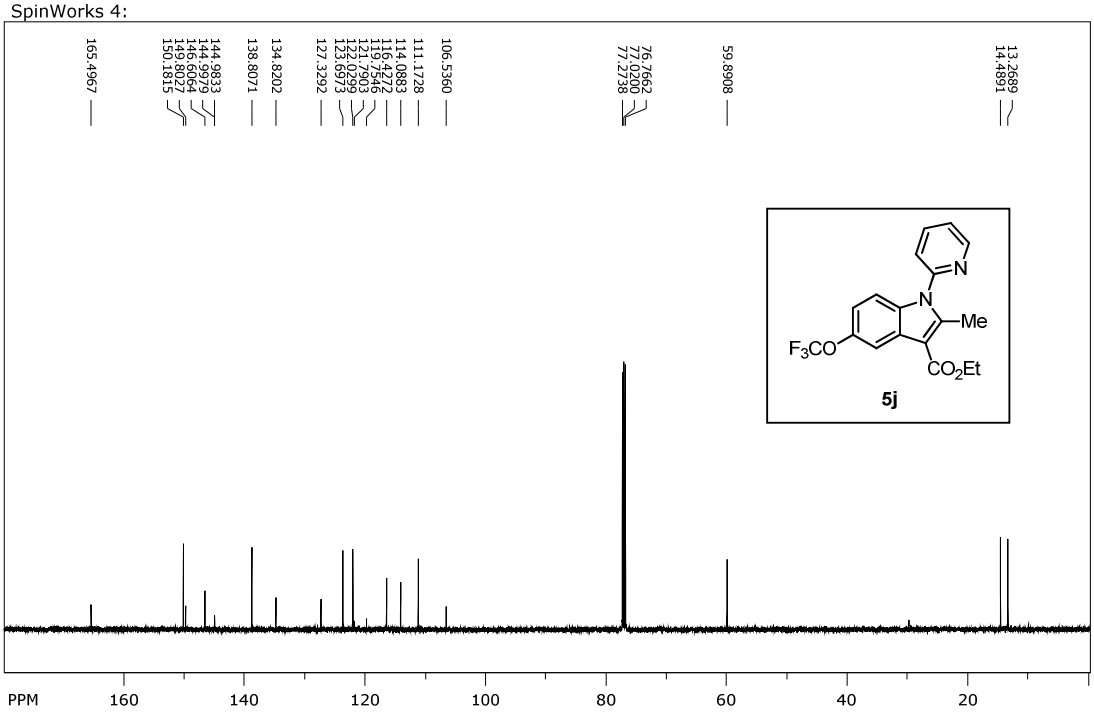
SpinWorks 4: NK658P-13C



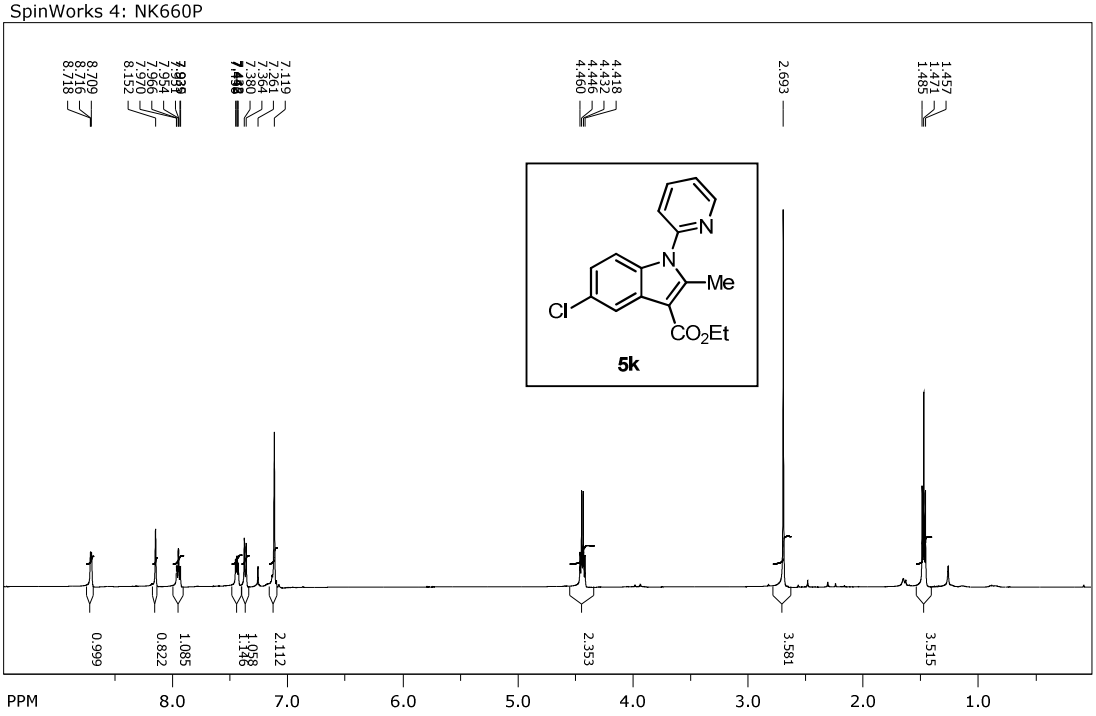
SpinWorks 4:



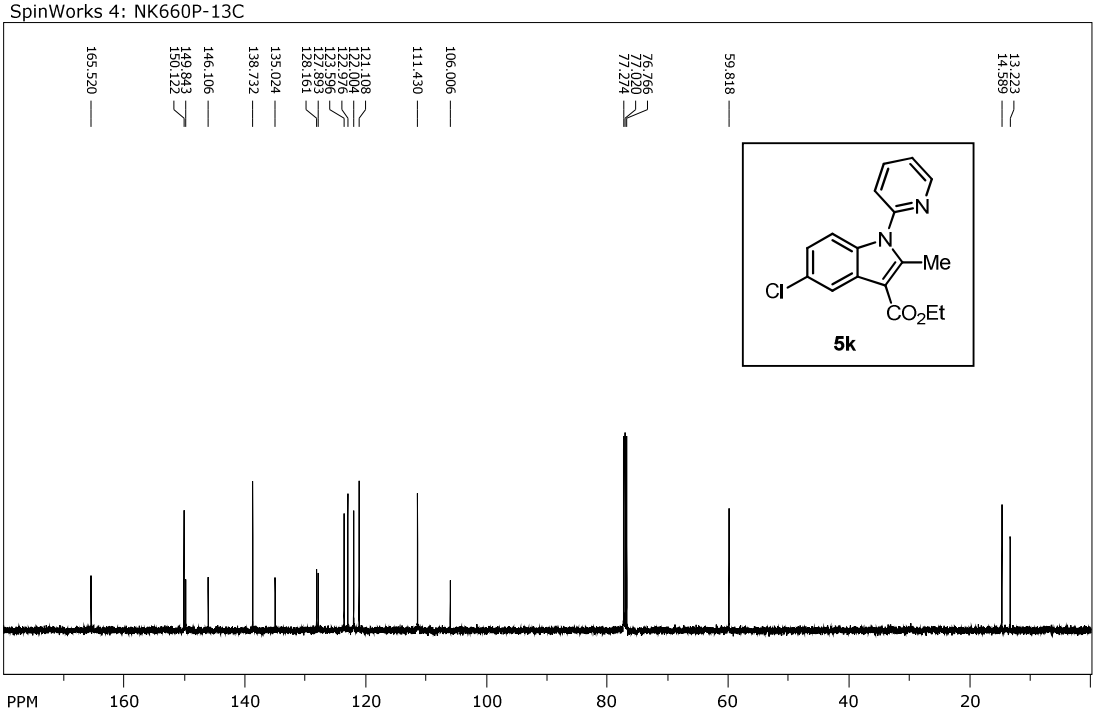
SpinWorks 4:



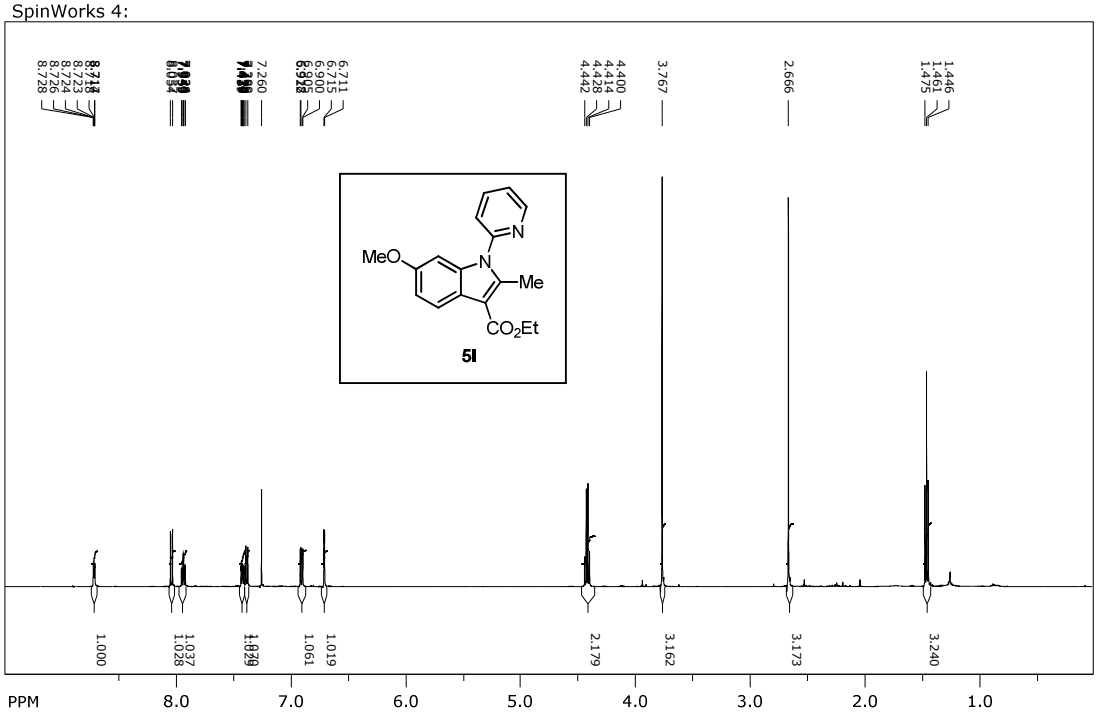
SpinWorks 4: NK660P



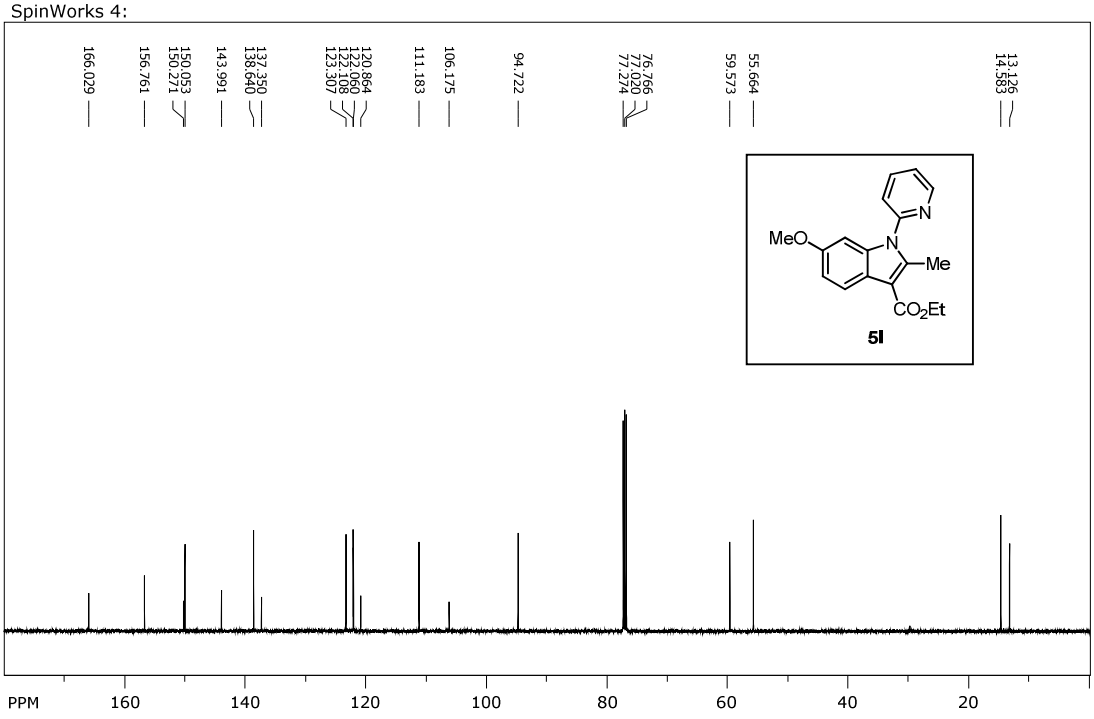
SpinWorks 4: NK660P-13C



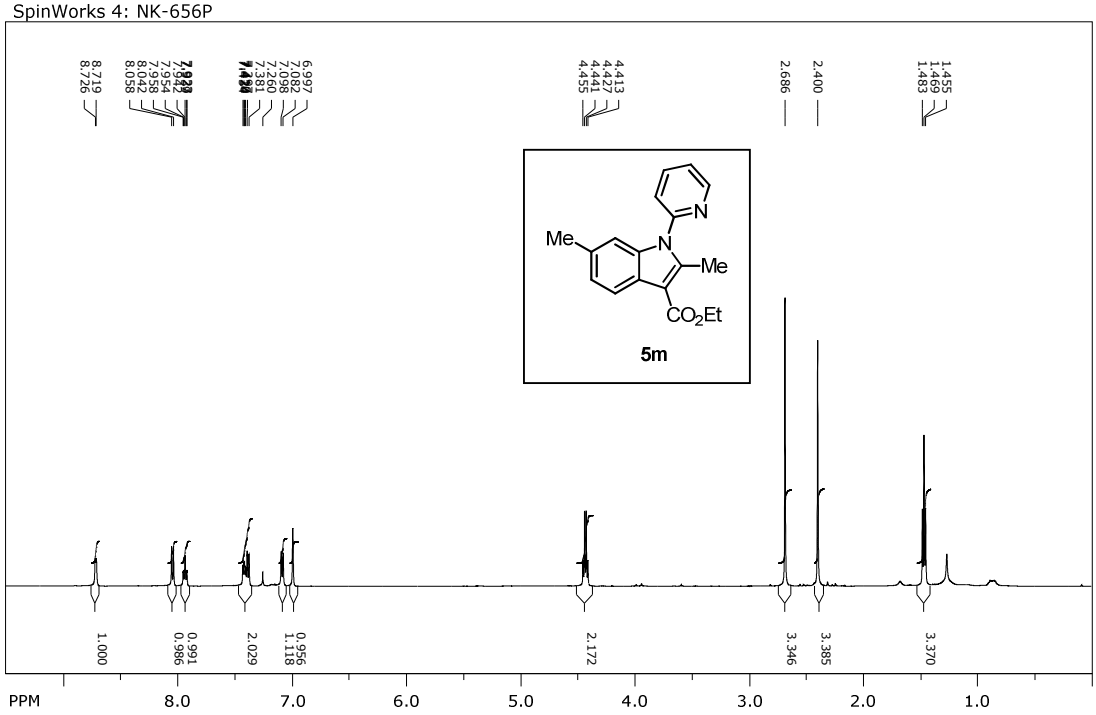
SpinWorks 4:



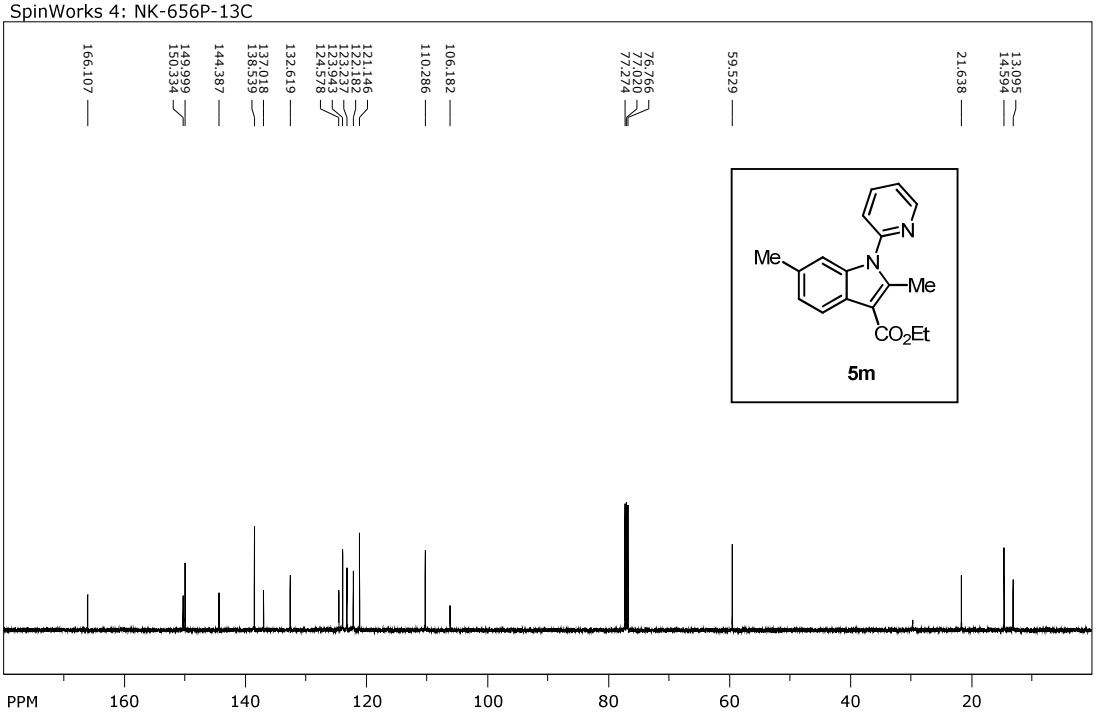
SpinWorks 4:

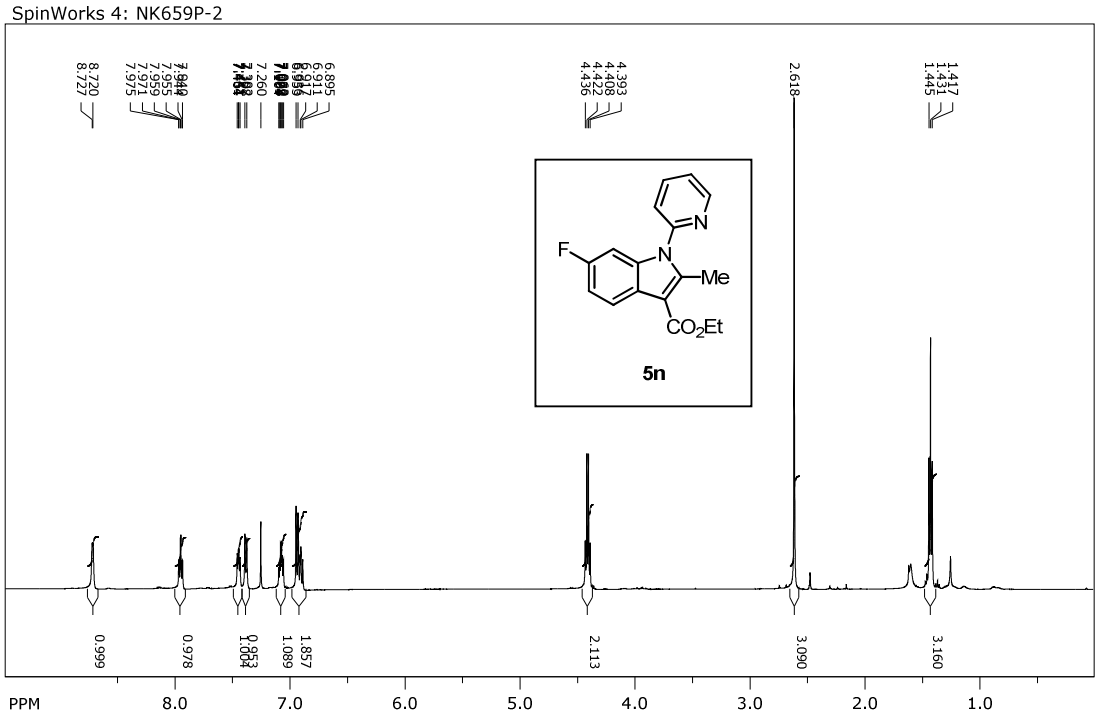


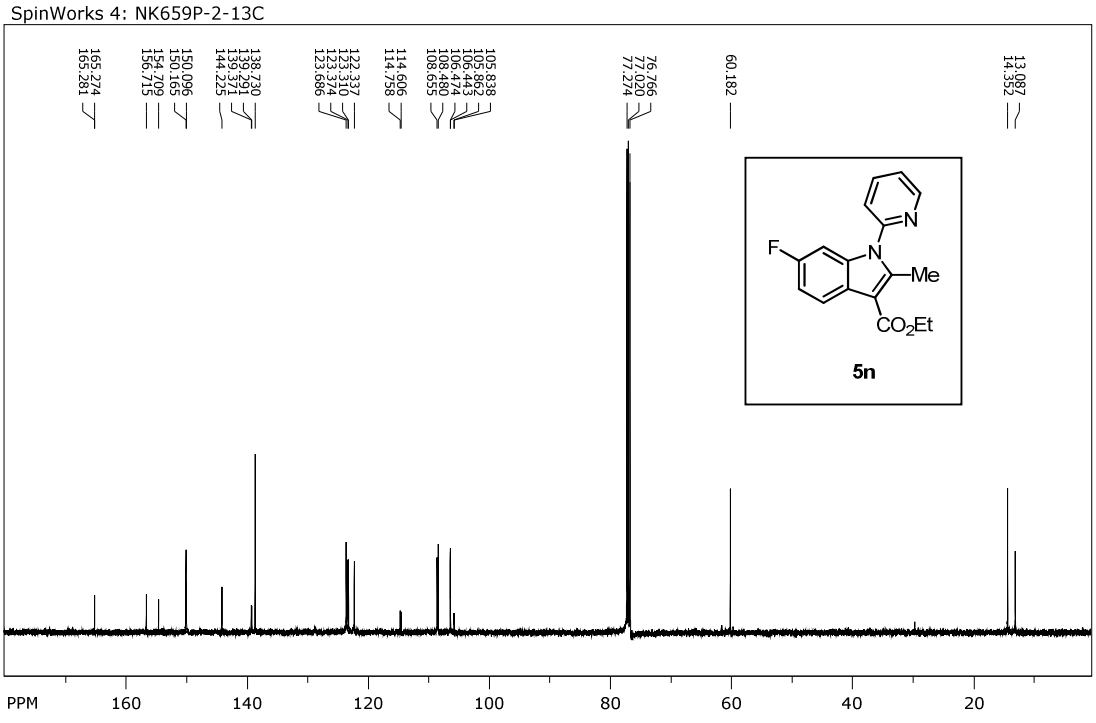
SpinWorks 4: NK-656P



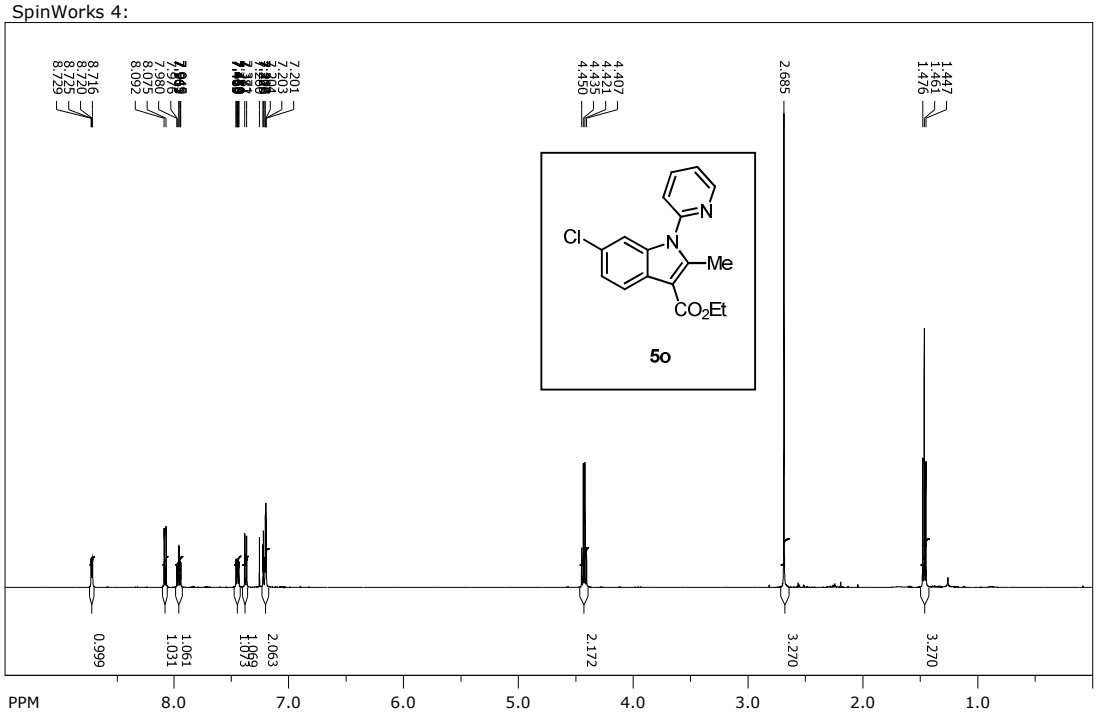
SpinWorks 4: NK-656P-13C



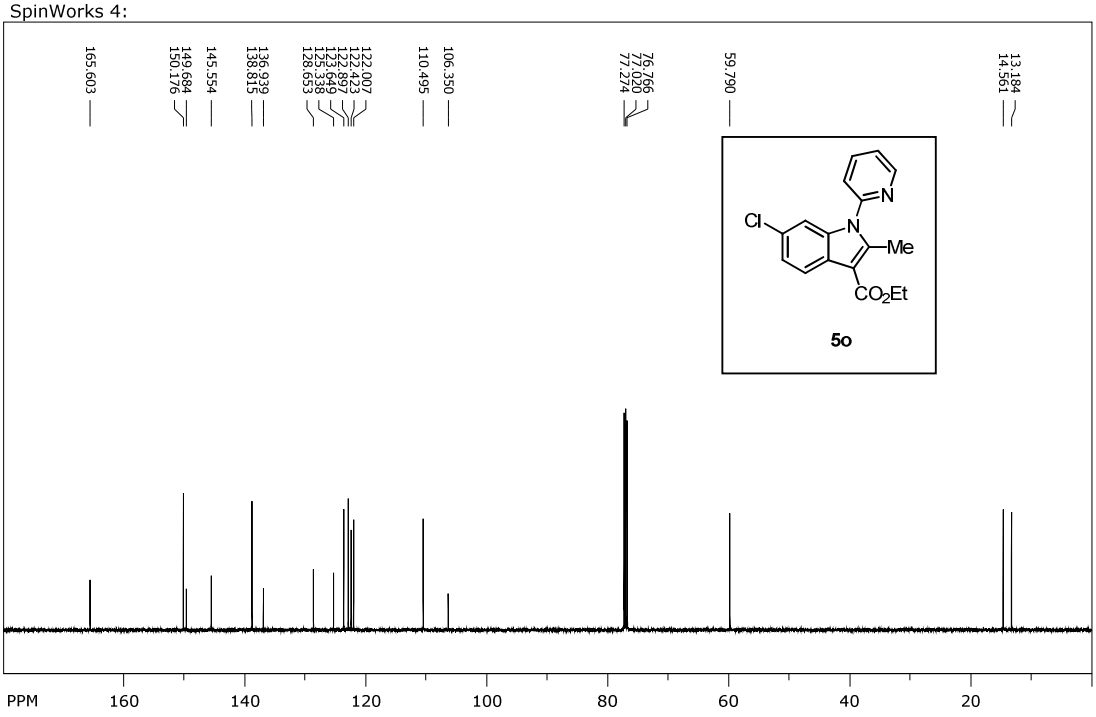

SpinWorks 4: NK659P-2
8.720
8.727
7.975
7.959
7.955
7.944
7.260
6.911
6.895
4.436
4.422
4.408
4.393
2.618
1.445
1.431
1.417
F
N
N
Me
CO2Et
5n
0.999
0.978
1.063
1.089
1.857
2.113
3.090
3.160
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


SpinWorks 4: NK659P-2-13C
165.274
163.261
156.715
154.709
150.165
150.096
144.225
139.371
139.291
138.730
123.686
123.374
123.310
122.337
114.758
114.606
108.655
108.480
106.474
106.443
105.862
105.838
77.274
77.020
76.766
60.182
14.392
13.987
F
N
N
Me
CO2Et
5n
PPM
160
140
120
100
80
60
40
20

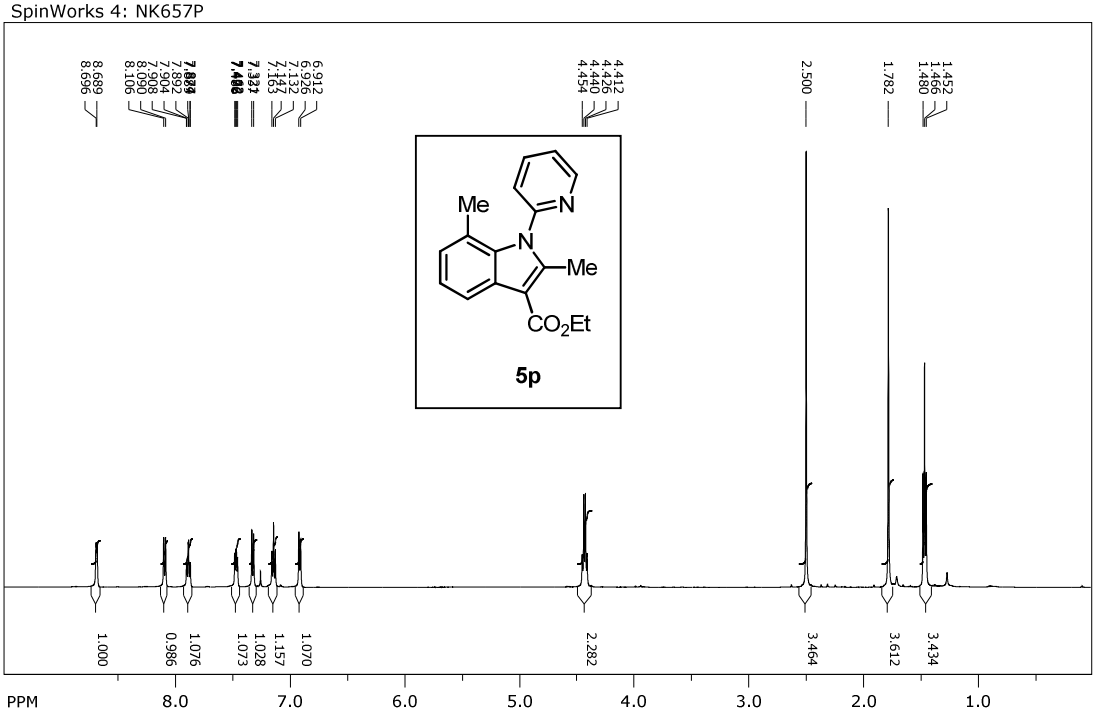
SpinWorks 4:



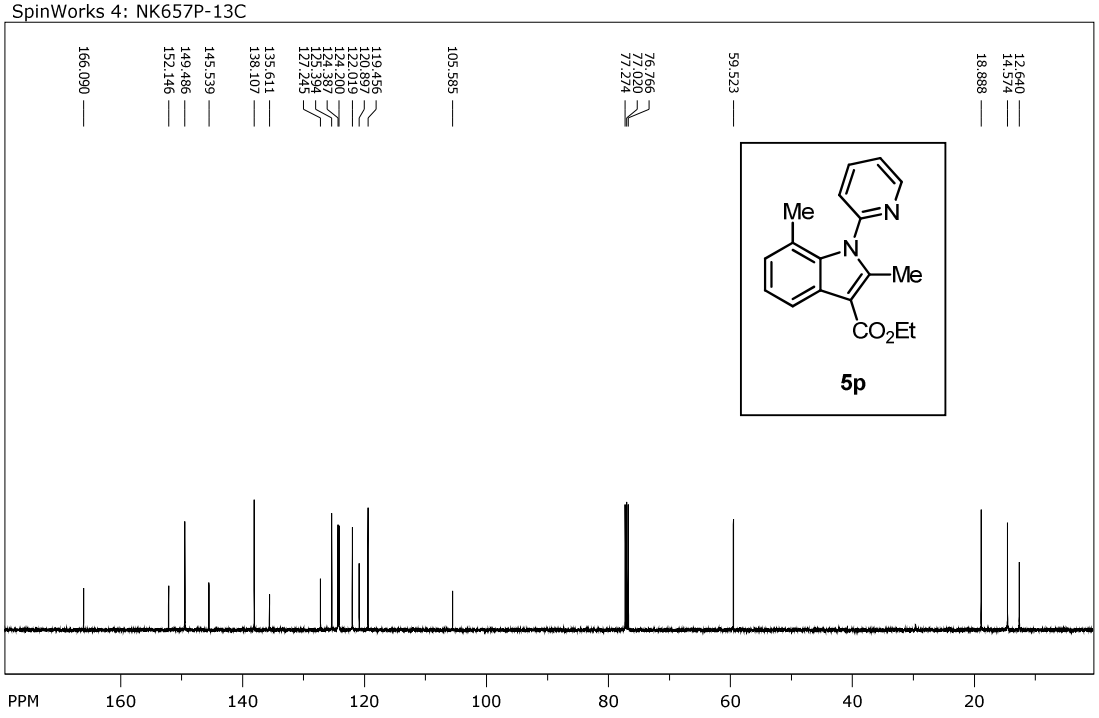
SpinWorks 4:

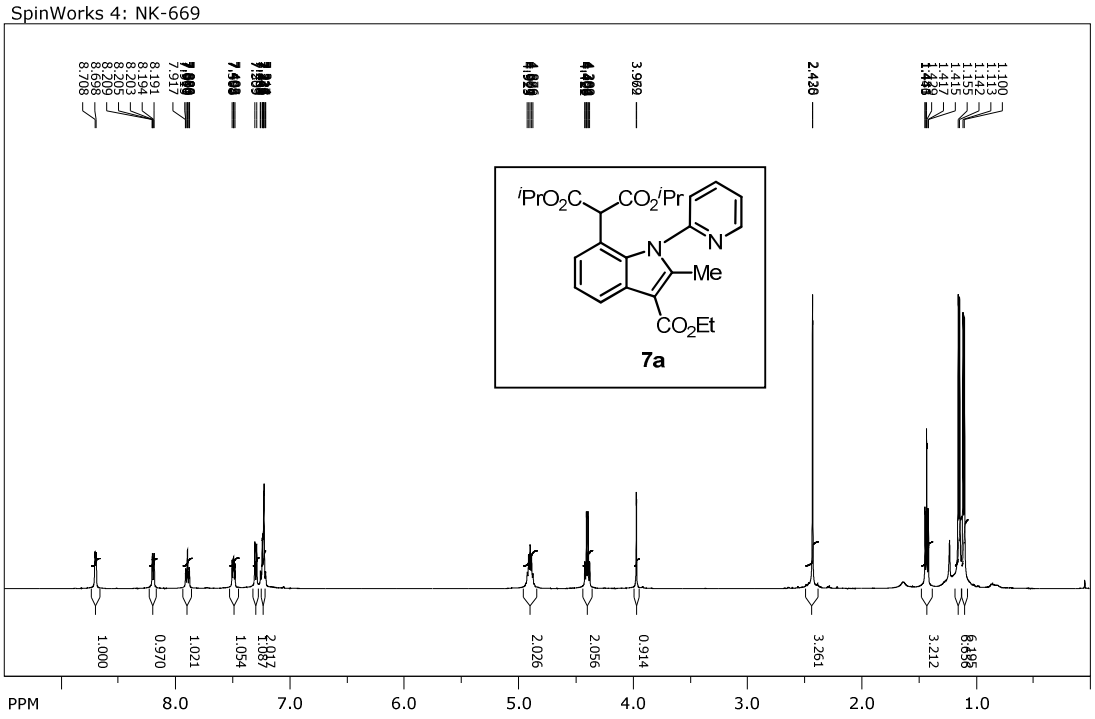


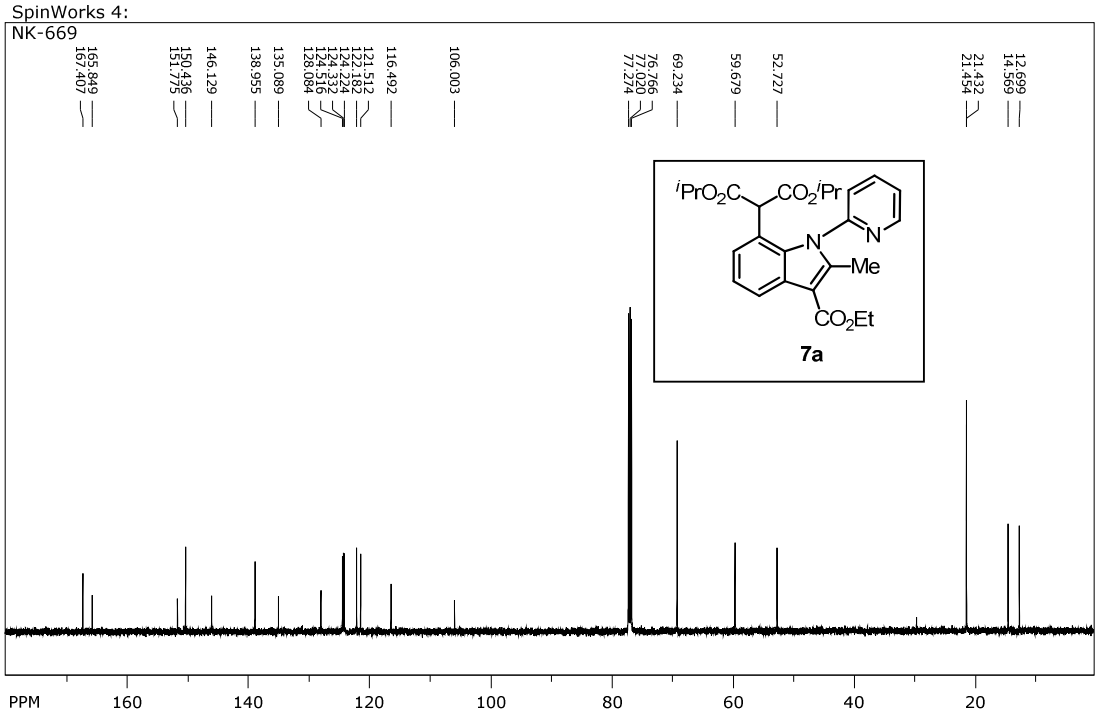
SpinWorks 4: NK657P



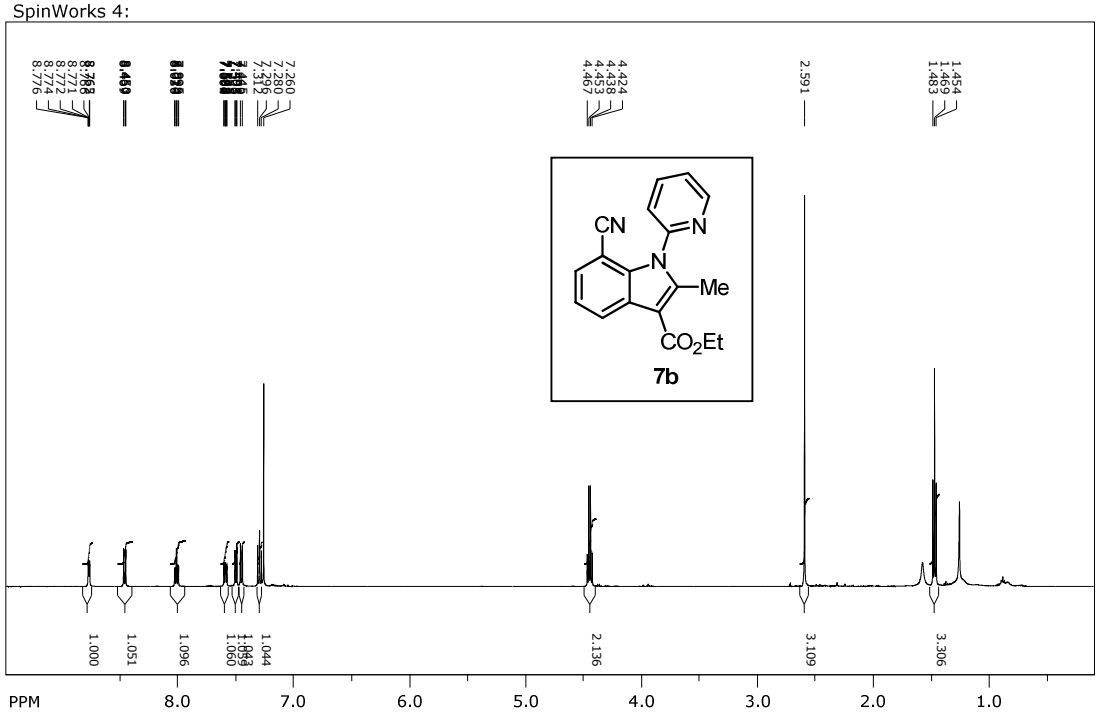
SpinWorks 4: NK657P-13C



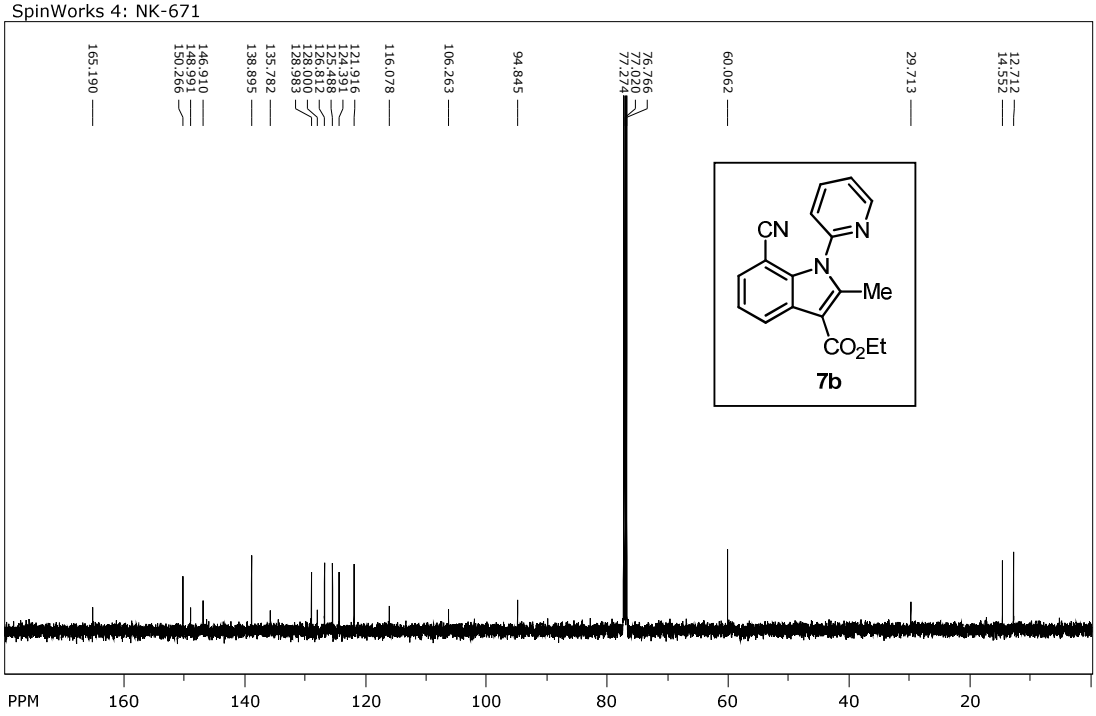

SpinWorks 4: NK-669
8.708
8.699
8.689
8.205
8.203
8.194
8.191
7.917
3.962
2.426
1.155
1.142
1.110
1.103
1.000
0.970
1.021
1.054
2.026
2.056
0.914
3.261
3.212
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Me
CO2Et
7a


SpinWorks 4:
NK-669
167.407
165.849
151.775
150.436
146.129
138.955
135.089
128.084
124.516
124.332
124.224
122.182
121.512
116.492
106.003
77.274
76.766
77.020
69.234
59.679
52.727
21.454
21.432
14.569
12.699
PPM
160
140
120
100
80
60
40
20
Me
CO2Et
7a

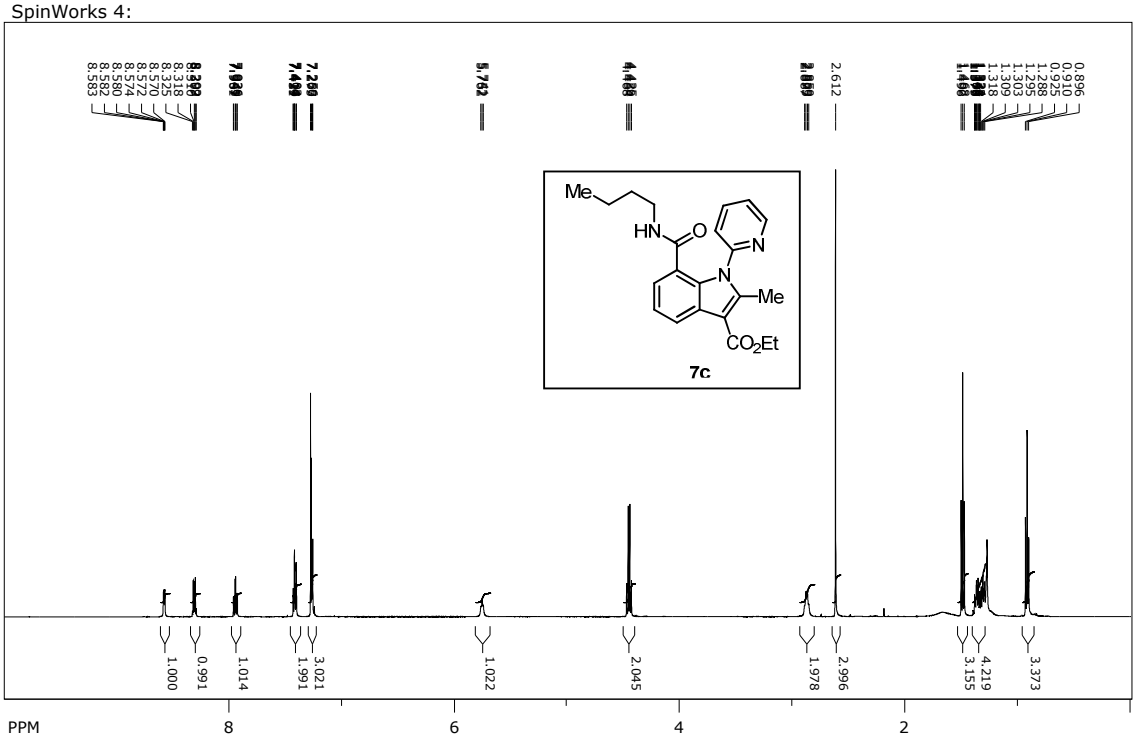
SpinWorks 4:



SpinWorks 4: NK-671



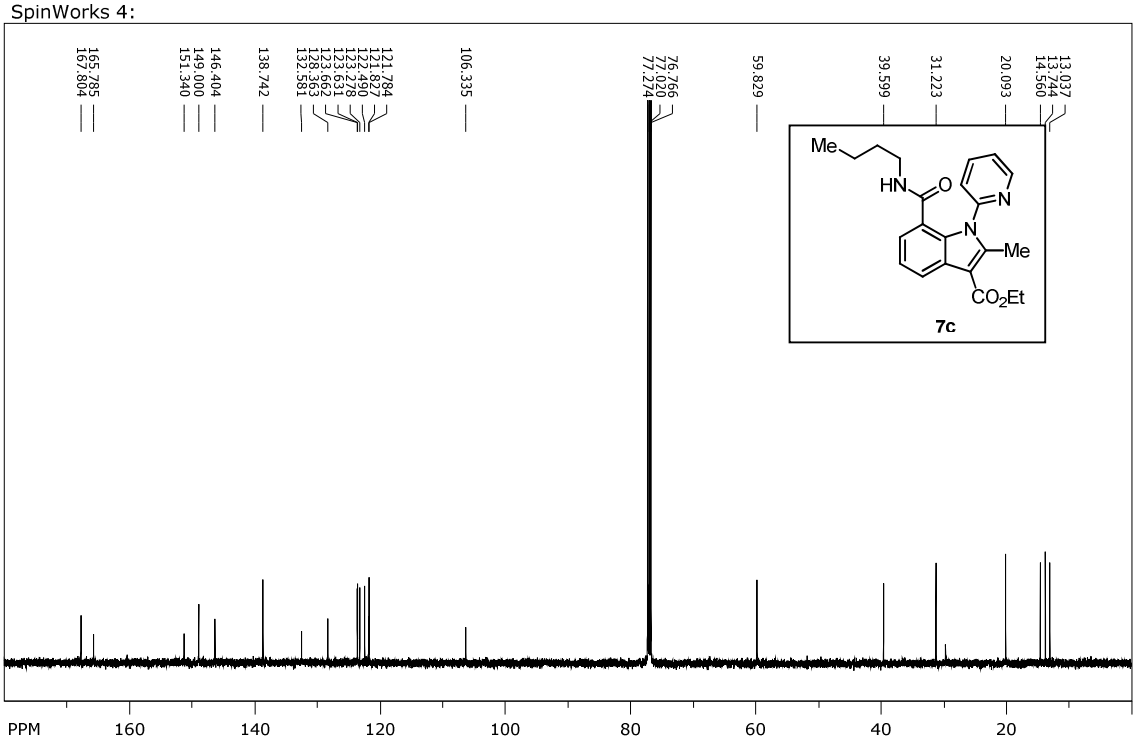
SpinWorks 4:

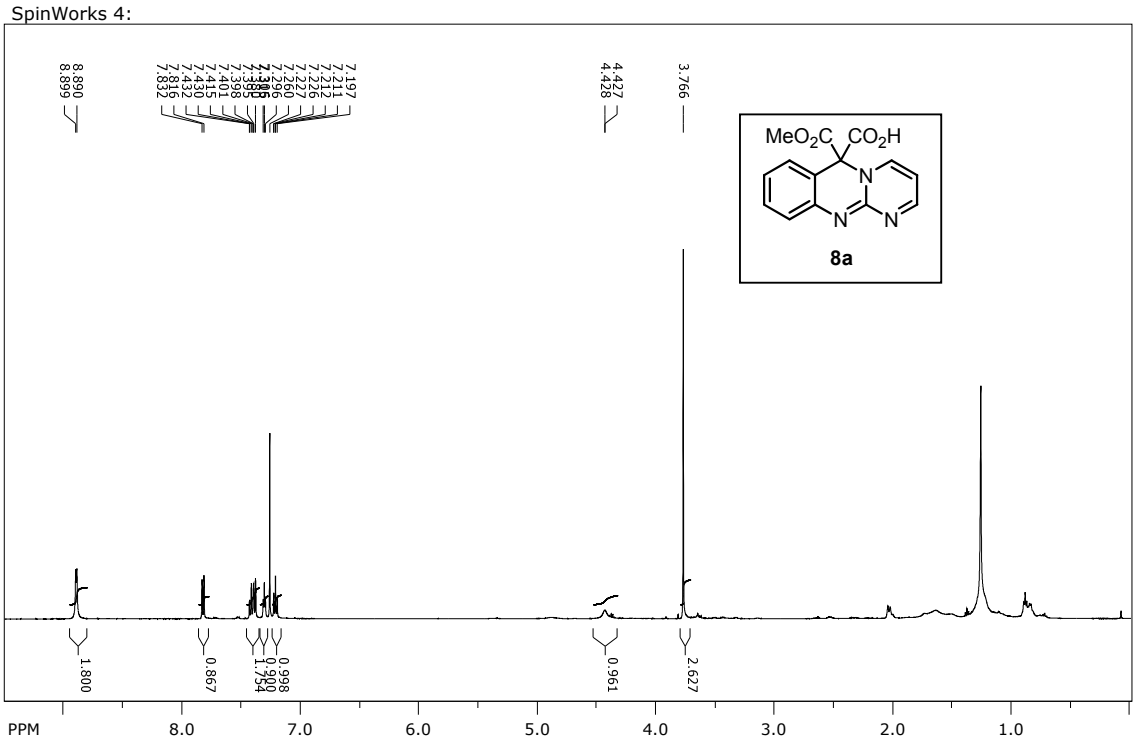


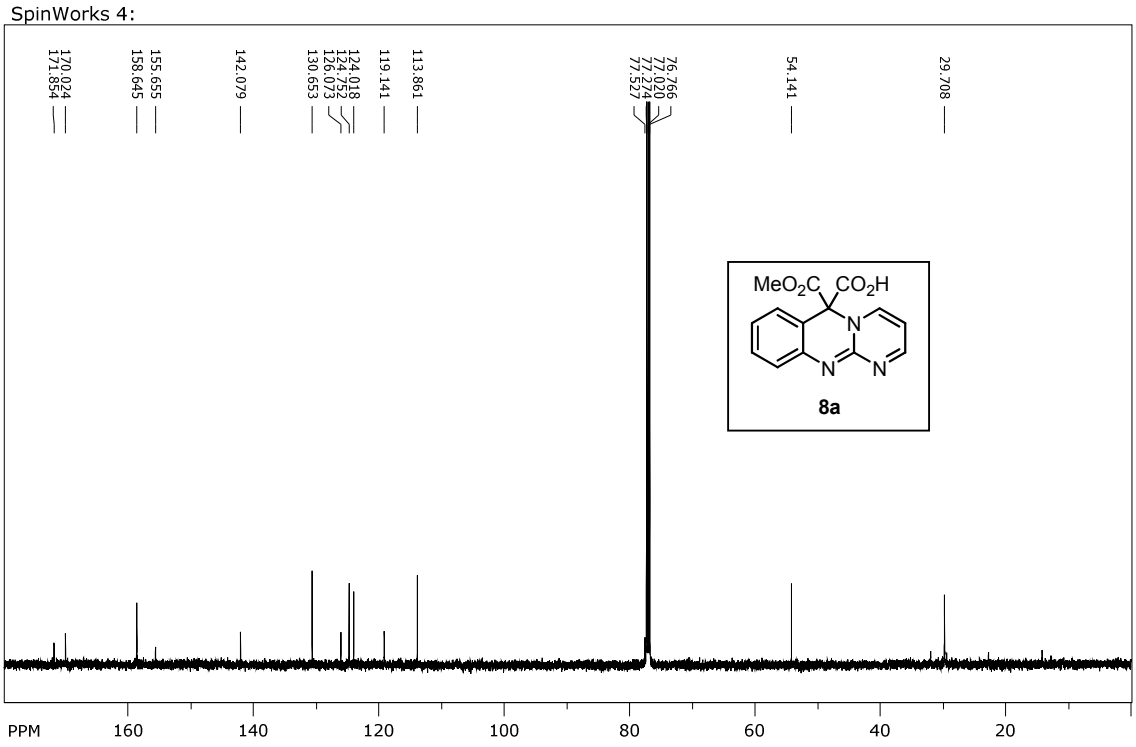
file: ...p\Rest carbon and NMR\NK.672\3\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10000.00 Hz = 19.9947 ppm = 0.152588 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130006 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

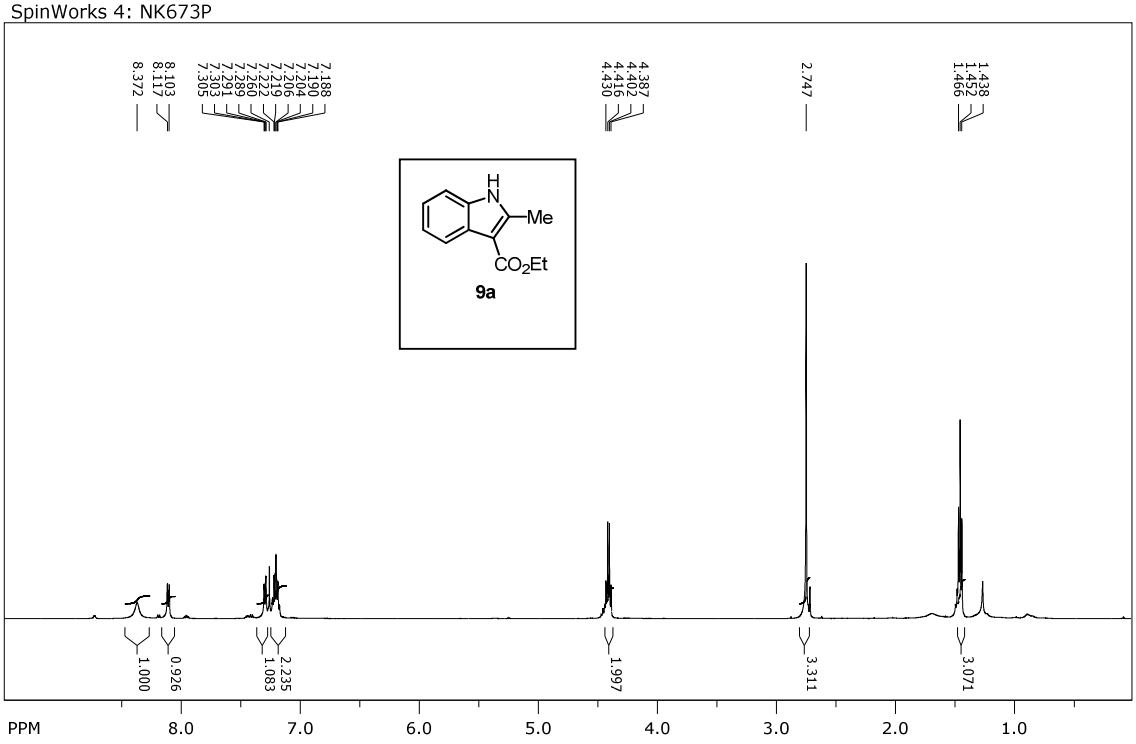
SpinWorks 4:




SpinWorks 4:
8.890
8.899
7.832
7.816
7.432
7.415
7.401
7.398
7.296
7.260
7.227
7.226
7.211
7.197
4.427
4.428
3.766
MeO2C
CO2H
N
N
N
8a
1.800
0.867
1.754
0.900
0.998
0.961
2.627
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


SpinWorks 4:
170.024
171.854
155.655
158.645
142.079
130.653
124.018
124.752
126.073
119.141
113.861
76.766
77.020
77.527
54.141
29.708
MeO2C
CO2H
N
N
N
8a
PPM
160
140
120
100
80
60
40
20

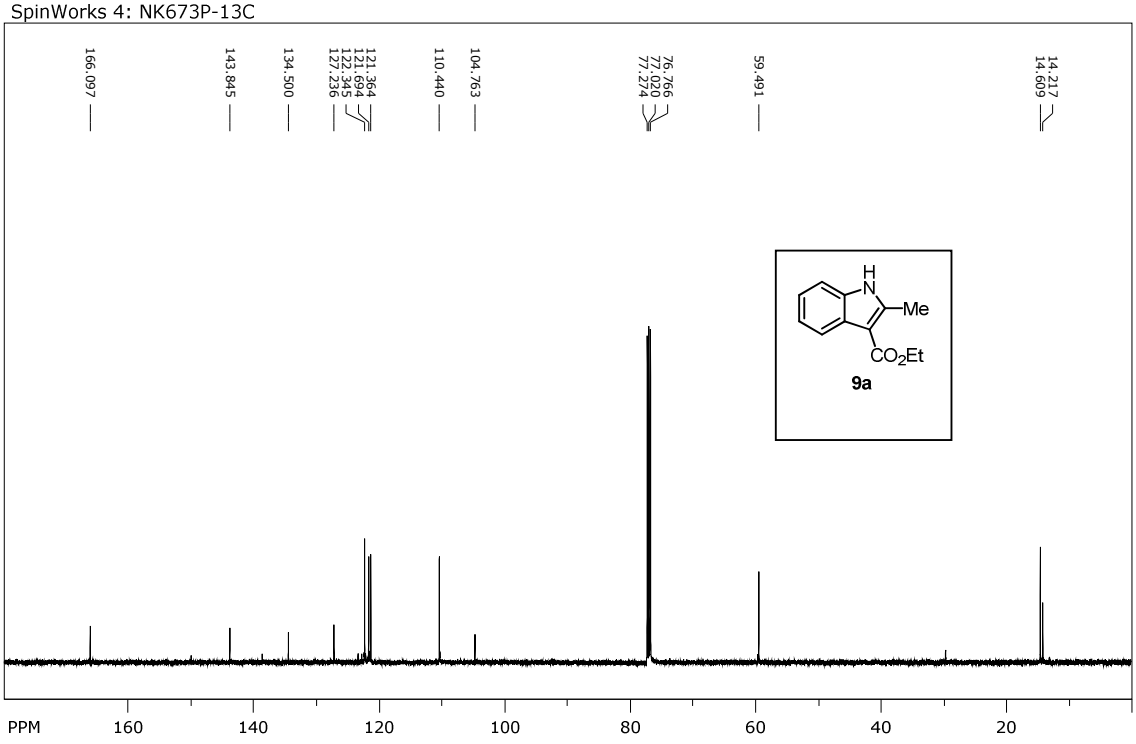
SpinWorks 4: NK673P

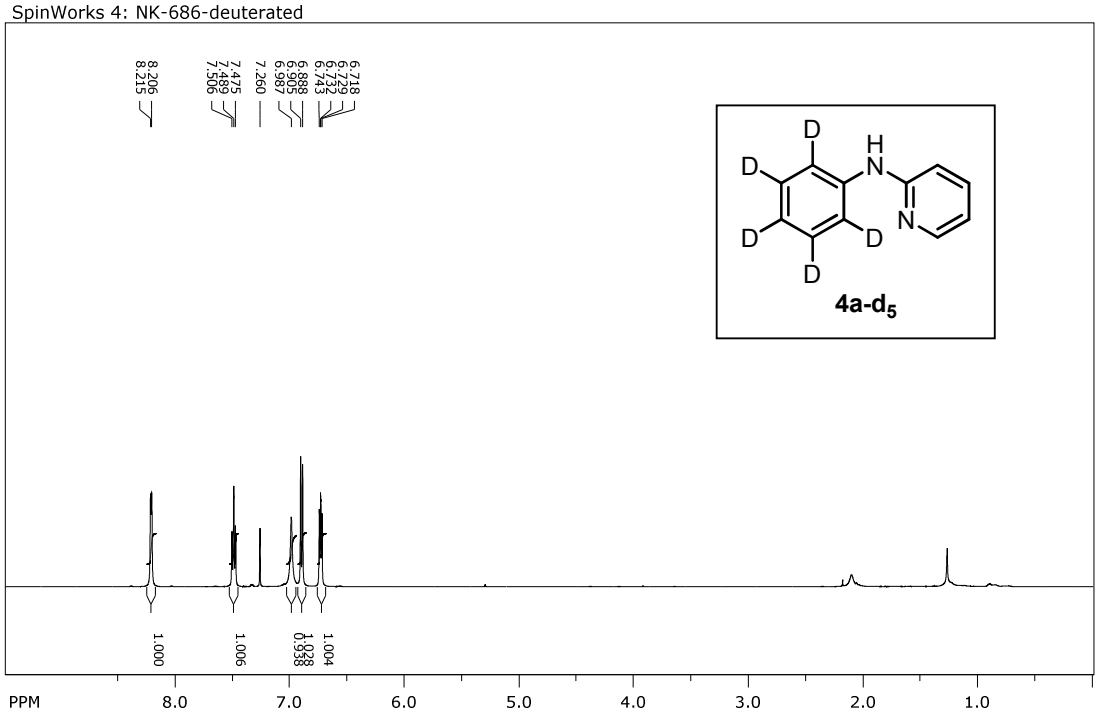


file: ...Rest carbon and NMR\NK673P.fid\fid block# 1 expt: "s2pul"
transmitter freq.: 499.960210 MHz
time domain size: 36372 points
width: 9611.92 Hz = 19.2254 ppm = 0.264267 Hz/pt
number of scans: 32

freq. of 0 ppm: 499.957020 MHz
processed size: 65536 complex points
LB: 1.000 GF: 0.0000

SpinWorks 4: NK673P-13C




SpinWorks 4: NK-686-deuterated
8.206
8.215
7.475
7.489
7.506
7.260
6.987
6.905
6.888
6.743
6.732
6.729
6.718
D
H
N
D
N
D
D
D
4a-d5
1.000
1.006
1.928
0.938
1.004
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0