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Supporting Information

Regio-selective synthesis of diversely substituted benzo[*a*]carbazoles through Rh(III)-catalyzed annulation of 2-arylindoles with α-diazo carbonyl compounds

Bin Li, Beibei Zhang, Xinying Zhang* and Xuesen Fan*

School of Chemistry and Chemical Engineering, School of Environment, Collaborative Innovation Centre of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Henan Normal University, Xinxiang, Henan 453007, P. R. China.

E-mail: xuesen.fan@htu.cn; xinyingzhang@htu.cn

Contents

I. General experimental information

All the commercial reagents were used without further purification. 2-Aryl-1*H*-indoles (**1**),[1] α-diazo carbonyl compounds (**2**),[2,3] 2-aryl-1*H*-indole-3-carbonitriles (**4**),[4] and $[RhCp^*Cl_2]_2$[5] were prepared according to literature procedures. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^1H NMR spectra were recorded at 400 MHz or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), q (quadruple), dd (doublet of doublet), m (multiplet), etc. The coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental procedures and spectroscopic data

1. General synthetic procedure and spectroscopic data of 3a-3y.

2-Aryl-1*H*-indole (**1**, 0.5 mmol), α-diazo carbonyl compound (**2**, 0.75 mmol), $[RhCp^*Cl_2]_2$ (0.025 mmol), $Cu(OAc)_2$ (0.05 mmol), and CH_3CN (3 mL) were charged into a sealed tube. The mixture was then stirred at 120 ℃. Upon completion, it was cooled to room temperature, quenched with saturated brine (10 mL) and extracted with EtOAc (10 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford **3**.

Ethyl 6-phenyl-11*H*-benzo[*a*]carbazole-5-carboxylate (3a): Eluent: petroleum ether-ethyl acetate (10:1); white solid (130 mg, 71%); mp: 168-169 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.96 (t, *J* = 7.2 Hz, 3H), 4.12 (q, *J* = 7.2 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.51-7.55 (m, 6H), 7.57-7.61 (m, 2H), 8.14-8.15 (m, 1H), 8.17-8.18 (m, 1H), 9.06 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.8, 61.4, 111.3, 116.4, 119.9, 120.2, 121.1, 121.8, 123.2, 124.0, 124.9, 125.7, 126.0, 126.6, 128.0, 128.4, 128.8, 129.5, 135.4, 136.0, 139.1, 139.3, 170.5. HRMS calcd for $C_{25}H_{19}NNaO_2$: 388.1308 $[M+Na]^+$, found: 388.1307.

Ethyl 6-phenyl-3-(trifluoromethyl)-11*H*-benzo[*a*]carbazole-5-carboxylate (3b): Eluent: petroleum ether-ethyl acetate (10:1); white solid (149 mg, 69%); mp: 200-201 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.97 (t, *J* = 7.2 Hz, 3H), 4.15 (q, *J* = 7.2 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 1H), 7.00-7.02 (m, 1H), 7.37-7.39 (m, 1H), 7.50-7.57 (m, 6H), 7.74 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 8.26 (d, *J* = 9.0 Hz, 1H), 8.47 (s, 1H), 9.25 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 61.4, 111.2, 118.3, 120.5, 121.3, 121.5 (q, $^3J_{C\text{-}F}$ = 2.55 Hz), 121.7, 122.2, 123.8, 123.9, 124.2 (q, $^3J_{C\text{-}F}$ = 4.5 Hz), 124.4 (q, $^1J_{C\text{-}F}$ = 269.55 Hz), 125.8, 127.8, 128.16 (q, $^2J_{C\text{-}F}$ = 33.3 Hz),

128.19, 128.5, 129.2, 135.0, 136.9, 138.7, 139.1, 169.2. HRMS calcd for $C_{26}H_{18}F_3NNaO_2$: 456.1182 $[M+Na]^+$, found: 456.1180.

Ethyl 3-fluoro-6-phenyl-11*H*-benzo[*a*]carbazole-5-carboxylate (3c): Eluent: petroleum ether-ethyl acetate (10:1); white solid (130 mg, 68%); mp: 151-152 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.94 (t, J = 7.2 Hz, 3H), 4.11 (q, J = 7.2 Hz, 2H), 6.85 (d, J = 7.8 Hz, 1H), 6.97 (dd, J_1 = 7.8 Hz, J_2 = 0.6 Hz, 1H), 7.28-7.34 (m, 2H), 7.49-7.52 (m, 6H), 7.81 (dd, J_1 = 10.8 Hz, J_2 = 1.8 Hz, 1H), 8.11 (dd, J_1 = 9.0 Hz, J_2 = 5.4 Hz, 1H), 9.16 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 61.2, 110.6 (d, $^2J_{C\text{-}F}$ = 22.05 Hz), 111.0, 115.6 (d, $^2J_{C\text{-}F}$ = 24.9 Hz), 116.3, 117.0, 120.3, 121.8, 122.8 (d, $^4J_{C\text{-}F}$ = 4.8 Hz), 123.0 (d, $^3J_{C\text{-}F}$ = 9.3 Hz), 124.0, 125.1, 128.0, 128.4, 129.2, 130.2 (d, $^3J_{C\text{-}F}$ = 9.15 Hz), 135.8, 136.9, 138.9, 139.0, 161.2 (d, $^1J_{C\text{-}F}$ = 244.35 Hz), 169.5. HRMS calcd for $C_{25}H_{19}FNO_2$: 384.1394 $[M+H]^+$, found: 384.1406.

Ethyl 3-chloro-6-phenyl-11*H*-benzo[*a*]carbazole-5-carboxylate (3d): Eluent: petroleum ether-ethyl acetate (10:1); white solid (142 mg, 71%); mp: 134-135 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.94 (t, J = 7.2 Hz, 3H), 4.12 (q, J = 7.2 Hz, 2H), 6.86 (d, J = 8.4 Hz, 1H), 6.97-6.99 (m, 1H), 7.32-7.35 (m, 1H), 7.45 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 7.49-7.52 (m, 6H), 8.03 (d, J = 9.0 Hz, 1H), 8.12 (d, J = 1.8 Hz, 1H), 9.16 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 61.3, 111.1, 116.9, 118.2, 120.3, 121.9, 122.2, 122.6, 123.9, 125.3, 125.4, 126.4, 128.1, 128.4, 129.2, 129.7, 132.5, 135.5, 136.7, 138.9, 139.0, 169.5. HRMS calcd for $C_{25}H_{19}ClNO_2$: 400.1099 $[M+H]^+$, found: 400.1108.

Ethyl 3-bromo-6-phenyl-11*H*-benzo[*a*]carbazole-5-carboxylate (3e): Eluent: petroleum ether-ethyl acetate (10:1); white solid (164 mg, 74%); mp: 144-145 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.94 (t, J = 7.2 Hz, 3H), 4.12 (q, J = 7.2 Hz, 2H), 6.84 (d, J = 7.8 Hz, 1H), 6.95-6.98 (m, 1H), 7.31 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.45-7.51 (m, 7H), 7.89 (d, J = 9.0 Hz, 1H), 8.26 (d, J = 1.8 Hz, 1H), 9.26 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 61.4, 111.2, 116.9, 118.5, 120.3, 120.7, 121.9, 122.3, 122.4, 123.9, 125.3, 128.1, 128.4, 128.5,

128.9, 129.2, 130.0, 135.5, 136.6, 138.9, 139.0, 169.6. HRMS calcd for $C_{25}H_{18}BrNNaO_2$: 466.0413 $[M+Na]^+$, found: 466.0393.

Ethyl 3-methyl-6-phenyl-11*H*-benzo[*a*]carbazole-5-carboxylate (3f): Eluent: petroleum ether-ethyl acetate (10:1); white solid (144 mg, 76%); mp: 206-207 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.94 (t, J = 7.2 Hz, 3H), 2.51 (s, 3H), 4.11 (q, J = 7.2 Hz, 2H), 6.88 (d, J = 7.8 Hz, 1H), 6.97 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.31-7.33 (m, 1H), 7.40 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.50-7.55 (m, 6H), 7.88 (s, 1H), 8.04 (d, J = 8.4 Hz, 1H), 9.03 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 22.0, 61.0, 110.9, 116.0, 118.1, 120.0, 120.5, 121.8, 123.1, 124.3, 124.8, 125.4, 127.9, 128.3, 129.2, 129.4, 135.2, 135.8, 136.5, 138.8, 139.3, 170.0. HRMS calcd for $C_{26}H_{21}NNaO_2$: 402.1465 $[M+Na]^+$, found: 402.1455.

Ethyl 3-methoxy-6-phenyl-11*H*-benzo[*a*]carbazole-5-carboxylate (3g): Eluent: petroleum ether-ethyl acetate (10:1); white solid (144 mg, 73%); mp: 206-207 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.94 (t, J = 7.2 Hz, 3H), 3.82 (s, 3H), 4.11 (q, J = 7.2 Hz, 2H), 6.83 (d, J = 8.4 Hz, 1H), 6.94 (td, J_1 = 7.2 Hz, J_2 = 0.8 Hz, 1H), 7.08 (dd, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 1H), 7.24-7.28 (m, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.48-7.53 (m, 6H), 7.95 (d, J = 9.2 Hz, 1H), 9.16 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 55.3, 61.1, 105.6, 111.0, 115.1, 115.2, 117.4, 119.9, 121.6, 122.2, 122.4, 124.2, 124.6, 127.9, 128.3, 129.3, 130.5, 136.30, 136.35, 138.9, 139.5, 158.3, 170.4. HRMS calcd for $C_{26}H_{22}NO_3$: 396.1594 $[M+H]^+$, found: 396.1579.

Ethyl 1-chloro-6-phenyl-11*H*-benzo[*a*]carbazole-5-carboxylate (3h): Eluent: petroleum ether-ethyl acetate (10:1); white solid (140 mg, 70%); mp: 164-165 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.95 (t, J = 7.2 Hz, 3H), 4.10 (q, J = 7.2 Hz, 2H), 6.84 (d, J = 8.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 7.35-7.39 (m, 1H), 7.43-7.47 (m, 1H), 7.53 (s, 5H), 7.59 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 8.03 (dd, J_1 = 8.8 Hz, J_2 = 0.8 Hz, 1H), 10.50 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 61.2, 111.3, 118.1, 118.2, 120.1, 121.9, 122.6, 124.2, 125.41, 125.43, 126.0, 127.4, 128.2, 128.5, 128.9, 129.4, 131.0, 134.1, 135.9, 138.3, 138.6, 169.5. HRMS calcd for $C_{25}H_{19}ClNO_2$: 400.1099 $[M+H]^+$, found: 400.1090.

Ethyl 1-methyl-6-phenyl-11*H*-benzo[*a*]carbazole-5-carboxylate (3i): Eluent: petroleum ether-ethyl acetate (10:1); white solid (138 mg, 73%); mp: 185-186 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.96 (t, J = 7.2 Hz, 3H), 3.09 (s, 3H), 4.11 (q, J = 7.2 Hz, 2H), 6.84 (d, J = 8.0 Hz, 1H), 6.97 (td, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.30-7.34 (m, 2H), 7.37-7.41 (m, 1H), 7.49-7.54 (m, 6H), 7.92 (d, J = 7.6 Hz, 1H), 9.34 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.8, 24.0, 61.1, 111.0, 117.3, 120.0, 120.5, 121.8, 123.0, 124.4, 124.79, 124.83, 126.0, 128.0, 128.2, 128.4, 129.6, 129.9, 132.0, 134.6, 136.1, 138.6, 139.0, 170.2. HRMS calcd for $C_{26}H_{21}NNaO_2$: 402.1465 $[M+Na]^+$, found: 402.1462.

Ethyl 2-chloro-6-phenyl-11*H*-benzo[*a*]carbazole-5-carboxylate (3j): Eluent: petroleum ether-ethyl acetate (10:1); white solid (140 mg, 70%); mp: 215-216 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.95 (t, J = 7.2 Hz, 3H), 4.14 (q, J = 7.2 Hz, 2H), 6.84 (d, J = 8.0 Hz, 1H), 6.93 (td, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.20-7.26 (m, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.36 (dd, J_1 = 9.2 Hz, J_2 = 2.0 Hz, 1H), 7.48 (s, 5H), 8.03 (d, J = 9.2 Hz, 1H), 8.10 (d, J = 2.0 Hz, 1H), 9.47 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 61.5, 111.2, 117.3, 120.1, 120.3, 120.9, 121.9, 122.9, 123.8, 125.3, 127.0, 127.1, 127.8, 128.1, 128.4, 129.3, 131.5, 134.9, 135.8, 138.9, 139.1, 170.2. HRMS calcd for $C_{25}H_{18}ClNNaO_2$: 422.0918 $[M+Na]^+$, found: 422.0904.

Ethyl 2-bromo-6-phenyl-11*H*-benzo[*a*]carbazole-5-carboxylate (3k): Eluent: petroleum ether-ethyl acetate (10:1); white solid (162 mg, 73%); mp: 240-241 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.95 (t, J = 7.2 Hz, 3H), 4.14 (q, J = 7.2 Hz, 2H), 6.83 (d, J = 7.6 Hz, 1H), 6.93 (td, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.25 (td, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.48 (s, 5H), 7.52 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.98 (d, J = 9.2 Hz, 1H), 8.29 (d, J = 2.0 Hz, 1H), 9.37 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 61.5, 111.2, 117.4, 119.7, 120.2, 121.3, 122.0, 123.1, 123.5, 123.8, 125.3, 127.3, 128.0, 128.1, 128.4, 129.3, 129.6, 134.7, 135.9, 138.9, 139.1, 170.0. HRMS calcd for $C_{25}H_{18}BrNNaO_2$: 466.0413 $[M+Na]^+$, found: 466.0421.

Ethyl 2-methyl-6-phenyl-11*H*-benzo[*a*]carbazole-5-carboxylate (3l): Eluent: petroleum ether-ethyl acetate (10:1); white solid (137 mg, 72%); mp: 239-240 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 0.95 (t, J = 7.2 Hz, 3H),

2.57 (s, 3H), 4.11 (q, *J* = 7.2 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.49-7.53 (m, 6H), 7.94 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 9.05 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 21.8, 61.1, 111.0, 116.6, 119.9, 120.1, 120.3, 121.8, 123.3, 124.2, 124.8, 126.1, 127.1, 127.8, 128.3, 128.7, 129.5, 134.4, 135.4, 135.7, 138.9, 139.3, 170.1. HRMS calcd for $C_{26}H_{22}NO_2$: 380.1645 $[M+H]^+$, found: 380.1657.

Ethyl 8-fluoro-6-phenyl-11*H*-benzo[*a*]carbazole-5-carboxylate (3m): Eluent: petroleum ether-ethyl acetate (10:1); white solid (128 mg, 67%); mp: 207-208 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.96 (t, *J* = 7.2 Hz, 3H), 4.13 (q, *J* = 7.2 Hz, 2H), 6.48 (dd, J_1 = 10.0 Hz, J_2 = 2.4 Hz, 1H), 7.01 (td, J_1 = 9.2 Hz, J_2 = 2.8 Hz, 1H), 7.32 (dd, J_1 = 8.8 Hz, J_2 = 4.4 Hz, 1H), 7.40-7.52 (m, 7H), 8.03-8.08 (m, 2H), 9.31 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 61.3, 107.3 (d, $^2J_{C\text{-}F}$ = 26.65 Hz), 111.6 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 112.9 (d, $^2J_{C\text{-}F}$ = 27 Hz), 116.2 (d, $^4J_{C\text{-}F}$ = 4.35 Hz), 120.1, 120.8, 123.4, 124.5 (d, $^3J_{C\text{-}F}$ = 9.75 Hz), 125.8, 126.2, 126.8, 128.2, 128.5, 129.0, 129.2, 135.2, 135.3, 137.0, 138.6, 157.4 (d, $^1J_{C\text{-}F}$ = 233.1 Hz), 170.1. HRMS calcd for $C_{25}H_{19}FNO_2$: 384.1394 $[M+H]^+$, found: 384.1402.

Ethyl 8-chloro-6-phenyl-11*H*-benzo[*a*]carbazole-5-carboxylate (3n): Eluent: petroleum ether-ethyl acetate (10:1); white solid (138 mg, 69%); mp: 163-164 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.96 (t, *J* = 7.2 Hz, 3H), 4.13 (q, *J* = 7.2 Hz, 2H), 6.78 (d, *J* = 2.0 Hz, 1H), 7.23 (dd, J_1 = 8.8 Hz, J_1 = 1.2 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 1H), 7.48-7.53 (m, 7H), 8.05-8.09 (m, 2H), 9.26 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 61.3, 112.0, 115.8, 120.0, 120.7, 121.4, 123.8, 125.1, 125.2, 125.5, 125.9, 126.2, 126.9, 128.3, 128.5, 129.0, 129.2, 135.1, 136.4, 137.2, 138.5, 169.9. HRMS calcd for $C_{25}H_{19}ClNO_2$: 400.1099 $[M+H]^+$, found: 400.1111.

Ethyl 8-methyl-6-phenyl-11*H*-benzo[*a*]carbazole-5-carboxylate (3o): Eluent: petroleum ether-ethyl acetate (10:1); white solid (133 mg, 70%); mp: 117-118 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.95 (t, *J* = 7.2 Hz, 3H), 2.24 (s, 3H), 4.12 (q, *J* = 7.2 Hz, 2H), 6.63 (s, 1H), 7.11-7.13 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.44-7.54 (m,

7H), 8.07 (d, *J* = 7.6 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 9.13 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.8, 21.6, 61.4, 110.7, 116.3, 120.1, 120.8, 121.7, 123.1, 124.3, 125.7, 126.2, 126.4, 126.5, 127.9, 128.3, 128.8, 129.2, 129.4, 135.4, 136.0, 137.2, 139.3, 170.1. HRMS calcd for $C_{26}H_{22}NO_2$: 380.1645 $[M+H]^+$, found: 380.1658.

Ethyl 8-phenyl-13*H*-naphtho[1,2-*a*]carbazole-7-carboxylate (3p): Eluent: petroleum ether-ethyl acetate (10:1); white solid (137 mg, 66%); mp: 261-262 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.91 (t, *J* = 7.2 Hz, 3H), 4.09 (q, *J* = 7.2 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 7.40-7.52 (m, 1H), 7.60-7.61 (m, 2H), 7.60-7.61 (m, 3H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.92-7.97 (m, 2H), 8.02 (d, *J* = 8.8 Hz, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 9.32 (d, *J* = 8.4 Hz, 1H), 12.28 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 61.2, 111.2, 116.2, 120.1, 120.4, 122.2, 123.6, 124.3, 124.4, 125.1, 125.6, 126.2, 127.4, 127.5, 128.0, 128.1, 128.4, 129.3, 129.4, 129.5, 132.3, 134.8, 136.7, 138.8, 140.2, 170.1. HRMS calcd for $C_{29}H_{21}NNaO_2$: 438.1465 $[M+Na]^+$, found: 438.1476.

Ethyl 5-phenyl-10*H*-thieno[3,2-*a*]carbazole-4-carboxylate (3q): Eluent: petroleum ether-ethyl acetate (10:1); white solid (141 mg, 76%); mp: 182-183 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.91 (t, *J* = 7.2 Hz, 3H), 4.09 (q, *J* = 7.2 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.94 (td, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.29 (td, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.45-7.51 (m, 6H), 7.87 (d, *J* = 5.2 Hz, 1H), 8.74 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.7, 60.9, 111.0, 117.9, 119.7, 120.2, 122.2, 124.2, 125.4, 125.5, 125.6, 127.6, 128.3, 129.3, 135.0, 135.6, 137.5, 139.5, 139.9, 169.3. HRMS calcd for $C_{23}H_{17}NNaO_2S$: 394.0872 $[M+Na]^+$, found: 394.0873.

Ethyl 6-(4-(trifluoromethyl)phenyl)-11*H*-benzo[*a*]carbazole-5-carboxylate (3r): Eluent: petroleum ether-ethyl acetate (10:1); white solid (149 mg, 69%); mp: 208-209 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.95 (t, *J* = 7.2 Hz, 3H), 4.12 (q, *J* = 7.2 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.99-7.03 (m, 1H), 7.33-7.37 (m, 1H), 7.52 (d,

J = 8.4 Hz, 1H), 7.56 (dd, J_1 = 6.4 Hz, J_2 = 3.2 Hz, 2H), 7.66 (d, J = 7.6 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 8.14 (dd, J_1 = 6.4 Hz, J_2 = 3.2 Hz, 2H), 9.20 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.5, 61.3, 111.2, 115.8, 120.2, 120.3, 120.8, 121.5, 123.5, 123.7, 124.2 (q, $^1J_{C\text{-}F}$ = 270.45 Hz), 125.2, 125.3 (q, $^3J_{C\text{-}F}$ = 2.85 Hz), 126.23, 126.25, 126.4, 126.8, 128.8, 130.0, 130.2 (q, $^2J_{C\text{-}F}$ = 31.5 Hz), 133.6, 135.8, 138.9, 169.5. HRMS calcd for $C_{26}H_{19}F_3NO_2$: 434.1362 $[M+H]^+$, found: 434.1353.

Ethyl 6-(4-fluorophenyl)-11*H*-benzo[*a*]carbazole-5-carboxylate (3s): Eluent: petroleum ether-ethyl acetate (10:1); white solid (130 mg, 68%); mp: 182-183 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.02 (t, J = 7.2 Hz, 3H), 4.17 (q, J = 7.2 Hz, 2H), 6.86 (d, J = 8.0 Hz, 1H), 6.98 (td, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.18-7.22 (m, 2H), 7.30 (td, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.43-7.52 (m, 5H), 8.06-8.10 (m, 2H), 9.30 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.9, 61.3, 111.2, 115.4 (d, $^2J_{C\text{-}F}$ = 25.15 Hz), 116.5, 120.10, 120.14, 120.8, 121.6, 123.7, 123.9, 125.1, 125.9, 126.2, 126.6, 128.8, 131.2 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 134.0, 135.1 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 135.7, 138.9, 162.7 (d, $^1J_{C\text{-}F}$ = 245.85 Hz), 170.0. HRMS calcd for $C_{25}H_{18}FNNaO_2$: 406.1214 $[M+Na]^+$, found: 406.1221.

Ethyl 6-(4-chlorophenyl)-11*H*-benzo[*a*]carbazole-5-carboxylate (3t): Eluent: petroleum ether-ethyl acetate (10:1); white solid (132 mg, 66%); mp: 203-204 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.03 (t, J = 7.2 Hz, 3H), 4.16 (q, J = 7.2 Hz, 2H), 6.90 (d, J = 8.4 Hz, 1H), 6.99-7.02 (m, 1H), 7.30-7.34 (m, 1H), 7.44-7.54 (m, 7H), 8.10 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H), 9.27 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.9, 61.3, 111.2, 116.2, 120.16, 120.18, 120.8, 121.6, 123.6, 123.9, 125.1, 126.0, 126.2, 126.7, 128.6, 128.8, 130.9, 133.8, 134.0, 135.8, 137.7, 138.9, 169.8. HRMS calcd for $C_{25}H_{19}ClNO_2$: 400.1099 $[M+H]^+$, found: 400.1079.

Ethyl 6-(4-bromophenyl)-11*H*-benzo[*a*]carbazole-5-carboxylate (3u): Eluent: petroleum ether-ethyl acetate (10:1); white solid (160 mg, 72%); mp: 223-224 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.03 (t, J = 7.2 Hz, 3H), 4.16 (q, J = 7.2 Hz, 2H), 6.92 (d, J = 8.0 Hz, 1H), 7.01 (td, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 7.33 (td, J_1 = 8.0 Hz,

J_2 = 1.2 Hz, 1H), 7.40 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H), 7.48-7.54 (m, 3H), 7.65 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 2H), 8.09-8.12 (m, 2H), 9.25 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.8, 61.3, 111.2, 116.1, 120.16, 120.21, 120.8, 121.7, 122.2, 123.5, 123.8, 125.1, 126.0, 126.3, 126.7, 128.8, 131.2, 131.6, 133.8, 135.8, 138.2, 138.9, 169.8. HRMS calcd for $C_{25}H_{18}BrNNaO_2$: 466.0413 $[M+Na]^+$, found: 466.0415.

Ethyl 6-(*p*-tolyl)-11*H*-benzo[*a*]carbazole-5-carboxylate (3v): Eluent: petroleum ether-ethyl acetate (10:1); white solid (138 mg, 73%); mp: 223-224 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.00 (t, *J* = 7.2 Hz, 3H), 2.49 (s, 3H), 4.15 (q, *J* = 7.2 Hz, 2H), 6.96-6.99 (m, 2H), 7.30-7.34 (m, 3H), 7.41-7.43 (d, *J* = 7.6 Hz, 2H), 7.48-7.55 (m, 3H), 8.08-8.13 (m, 2H), 9.18 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.8, 21.5, 61.1, 111.0, 116.7, 119.97, 120.02, 120.7, 122.0, 123.7, 124.2, 124.9, 125.7, 126.2, 126.5, 128.9, 129.0, 129.2, 135.4, 135.7, 136.0, 137.5, 138.9, 170.1. HRMS calcd for $C_{26}H_{21}NNaO_2$: 402.1465 $[M+Na]^+$, found: 402.1446.

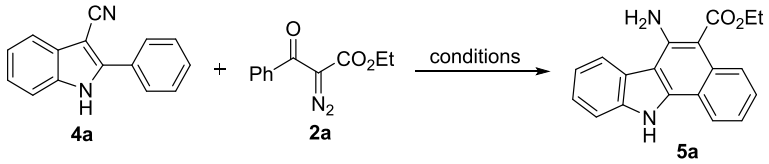
Ethyl 6-(4-methoxyphenyl)-11*H*-benzo[*a*]carbazole-5-carboxylate (3w): Eluent: petroleum ether-ethyl acetate (10:1); white solid (148 mg, 75%); mp: 216-217 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.04 (t, *J* = 7.2 Hz, 3H), 3.91 (s, 3H), 4.17 (q, *J* = 7.2 Hz, 2H), 6.99-7.00 (m, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 7.30-7.34 (m, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.48-7.55 (m, 3H), 8.07-8.13 (m, 2H), 9.19 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.9, 55.4, 61.1, 111.0, 113.8, 116.9, 120.0, 120.7, 121.9, 123.9, 124.2, 124.9, 125.7, 126.2, 126.5, 128.9, 130.6, 131.4, 134.9, 135.6, 138.9, 159.4, 170.2. HRMS calcd for $C_{26}H_{22}NO_3$: 396.1594 $[M+H]^+$, found: 396.1596

Ethyl 6-(thiophen-2-yl)-11H-benzo[a]carbazole-5-carboxylate (3x): Eluent: petroleum ether-ethyl acetate (10:1); white solid (130 mg, 70%); mp: 198-199 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.12 (t, *J* = 7.2 Hz, 3H), 4.25 (q, *J* = 7.2 Hz, 2H), 7.01-7.06 (m, 2H), 7.20-7.23(m, 2H),7.31-7.35 (m, 1H), 7.39-7.53 (m, 3H), 7.53-5.54 (m, 1H), 7.99-8.01 (m, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 9.22 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 14.0, 61.5, 111.1, 117.4, 120.2, 120.4, 120.7, 121.8, 123.8, 125.1, 125.7, 126.2, 126.45, 125.49, 127.1, 127.2, 128.0, 128.5, 135.5, 138.9, 139.0, 169.9. HRMS calcd for $C_{23}H_{18}NO_2S$: 372.1053 $[M+H]^+$, found: 372.1060.

1-(6-Methyl-11*H*-benzo[*a*]carbazol-5-yl)ethanone (3y): Eluent: petroleum ether-ethyl acetate (10:1); white solid (29 mg, 21%); mp: 165-166 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.71 (s, 3H), 2.88 (s, 3H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.42-7.53 (m, 3H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.71-7.73 (m, 1H), 8.07-8.09 (m, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 9.01 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 18.2, 34.0, 111.2, 117.2, 119.5, 120.3, 120.8, 122.2, 124.6, 124.8, 125.0, 125.1, 126.1, 127.5, 128.0, 131.7, 135.0, 138.8, 209.4. HRMS calcd for $C_{19}H_{16}NO$: 274.1226 $[M+H]^+$, found: 274.1230.

2. Optimization studies on the formation of 5a

Table 1. Optimization studies on the formation of **5a**[a]



Entry	Catalyst	Additive (equiv)	Solvent	Yield (%)[b]
1	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2$ (0.1)	CH_3CN	32
2	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (0.2)	CH_3CN	13
3	$[RhCp^*Cl_2]_2$	$Cu(OAc)_2$ (0.1) + $AgSbF_6$ (0.2)	CH_3CN	47
4	**$[RhCp^*Cl_2]_2$**	**AgOAc (0.2) + $AgSbF_6$ (0.2)**	**CH_3CN**	**68**
5	$[RhCp^*Cl_2]_2$	CsOAc (0.2) + $AgSbF_6$ (0.2)	CH_3CN	34
6	$[RhCp^*Cl_2]_2$	AgOAc (0.1) + $AgSbF_6$ (0.1)	CH_3CN	45
7	$[RhCp^*Cl_2]_2$	AgOAc (0.2) + $AgSbF_6$ (0.2)	DCE	12
8	$[RhCp^*Cl_2]_2$	AgOAc (0.2) + $AgSbF_6$ (0.2)	THF	28
9	-	AgOAc (0.2) + $AgSbF_6$ (0.2)	CH_3CN	-
10	$[RhCp^*Cl_2]_2$	-	CH_3CN	19
11	$[RhCp^*Cl_2]_2$	AgOAc (0.2)	CH_3CN	44

[a] Conditions: 0.5 mmol of **4a**, 0.75 mmol of **2a**, 0.025 mmol of catalyst, sealed tube, 120 ℃, 18 h. [b] Isolated yield.

3. General synthetic procedure and spectroscopic data of 5a-5h.

2-Aryl-1*H*-indole-3-carbonitrile (**4**, 0.5 mmol), α-diazo carbonyl compound (**2**, 0.75 mmol), $[RhCp^*Cl_2]_2$ (0.025 mmol), AgOAc (0.1 mmol), $AgSbF_6$ (0.1 mmol), and CH_3CN (3 mL) were charged into a sealed tube. The reaction mixture was then stirred at 120 ℃. Upon completion, it was cooled to room temperature, quenched with saturated brine (10 mL), and extracted with EtOAc (10 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford **5**.

Ethyl 6-amino-11*H*-benzo[*a*]carbazole-5-carboxylate (5a): Eluent: petroleum ether-ethyl actate (10:1); white solid (103 mg, 68%); mp: 177-178 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.50 (t, *J* = 7.2 Hz, 3H), 4.53 (q, *J* = 7.2 Hz, 2H), 6.68 (br s, 2H), 7.27-7.32 (m, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 8.68 (d, *J* = 9.0 Hz, 1H), 9.07 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 14.6, 60.5, 97.8, 108.0, 111.5, 116.4, 120.1, 120.6, 120.9, 122.1, 123.4, 124.4, 126.4, 127.1, 132.6, 138.2, 138.6, 148.8, 170.2. HRMS calcd for $C_{19}H_{16}N_2NaO_2$: 327.1104 $[M+Na]^+$, found: 327.1105.

Ethyl 6-amino-3-(trifluoromethyl)-11*H*-benzo[*a*]carbazole-5-carboxylate (5b): Eluent: petroleum ether-ethyl acetate (10:1); white solid (128 mg, 69%); mp: 197-198 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.53 (t, *J* = 7.2 Hz, 3H), 4.52 (q, *J* = 7.2 Hz, 2H), 6.94 (br s, 2H), 7.36-7.39 (m, 1H), 7.47-7.49 (m, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 8.96 (br s, 1H), 9.10 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 14.3, 60.7, 97.6, 109.3, 111.7, 117.7, 117.8 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 120.4, 121.1, 121.4, 123.1, 124.2 (q, $^3J_{C\text{-}F}$ = 4.35 Hz), 124.8 (q, $^1J_{C\text{-}F}$ = 270.3 Hz), 125.1, 128.5 (q, $^2J_{C\text{-}F}$ = 31.65 Hz), 131.9, 137.7, 138.2, 150.0, 169.7. HRMS calcd for $C_{20}H_{15}F_3N_2NaO_2$: 395.0978 $[M+Na]^+$, found: 395.0985.

Ethyl 6-amino-3-fluoro-11*H*-benzo[*a*]carbazole-5-carboxylate (5c): Eluent: petroleum ether-ethyl acetate (10:1); white solid (103 mg, 64%); mp: 180-181 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.52 (t, *J* = 7.2 Hz, 3H), 4.53 (q, *J* = 7.2 Hz, 2H), 6.93 (br s, 2H), 7.06-7.09 (m, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.87 (dd, J_1 = 8.4 Hz, J_2 = 6.0 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 8.47 (dd, J_1 = 13.8 Hz, J_2 = 2.4 Hz, 1H), 8.91 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 14.6, 60.6, 97.0 (d, $^{3}J_{C\text{-}F}$ = 4.35 Hz), 107.5, 111.1 (d, $^{2}J_{C\text{-}F}$ = 24 Hz), 111.5, 111.6 (d, $^{2}J_{C\text{-}F}$ = 25.2 Hz), 113.2, 120.0, 121.2, 122.4 (d, $^{3}J_{C\text{-}F}$ = 9.9 Hz), 123.4, 124.5, 134.5, 138.0, 138.6, 150.2, 162.1 (d, $^{1}J_{C\text{-}F}$ = 241.8 Hz), 169.9. HRMS calcd for $C_{19}H_{16}FN_2O_2$: 323.1190 $[M+H]^+$, found: 323.1210.

Ethyl 6-amino-3-chloro-11*H*-benzo[*a*]carbazole-5-carboxylate (5d): Eluent: petroleum ether-ethyl acetate (10:1); white solid (106 mg, 63%); mp: 218-219 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 1.43 (t, *J* = 7.2 Hz, 3H), 4.46 (q, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.397-7.402 (m, 3H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 8.66 (d, *J* = 1.8 Hz, 1H), 12.56 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 14.8, 60.6, 95.2, 107.5, 112.1, 115.3, 120.8, 121.4, 122.1, 122.9, 124.4, 124.9, 125.0, 132.3, 133.8, 138.97, 139.00, 150.0, 169.3. HRMS calcd for $C_{19}H_{16}ClN_2O_2$: 339.0895 $[M+H]^+$, found: 339.0901.

Ethyl 6-amino-3-bromo-11*H*-benzo[*a*]carbazole-5-carboxylate (5e): Eluent: petroleum ether-ethyl acetate (10:1); white solid (126 mg, 66%); mp: 209-210 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 1.43 (t, *J* = 7.2 Hz, 3H), 4.45 (q, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.39 (s, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.51 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 8.82 (d, *J* = 1.2 Hz, 1H), 12.56 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 14.8, 60.6, 95.1, 107.6, 112.1, 115.5, 120.8, 121.2, 121.4, 122.9, 124.5, 124.7, 124.9, 128.1, 134.1, 138.98, 139.00, 149.8, 169.3. HRMS calcd for $C_{19}H_{16}BrN_2O_2$: 383.0390 $[M+H]^+$, found: 383.0392.

Ethyl 6-amino-8-(trifluoromethyl)-11*H*-benzo[*a*]carbazole-5-carboxylate (5f): Eluent: petroleum ether-ethyl acetate (10:1); white solid (139 mg, 75%); mp: 218-219 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 1.42 (t, J = 7.2 Hz, 3H), 4.46 (q, J = 7.2 Hz, 2H), 7.26 (s, 2H), 7.40 (t, J = 7.8 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.75 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 8.41 (d, J = 7.8 Hz, 1H), 8.53 (d, J = 9.0 Hz, 1H), 8.83 (s, 1H), 12.88 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 14.8, 60.5, 97.7, 107.7, 112.5, 116.6, 119.1 (q, $^{3}J_{C\text{-}F}$ = 3.3 Hz), 121.2, 121.3 (q, $^{2}J_{C\text{-}F}$ = 31.8 Hz), 122.4, 122.6, 122.7, 126.00 (q, $^{1}J_{C\text{-}F}$ = 269.1 Hz), 126.01, 127.8, 132.9, 140.5, 140.8, 148.1, 169.7. HRMS calcd for $C_{20}H_{16}F_3N_2O_2$: 373.1158 $[M+H]^+$, found: 373.1160.

Ethyl 6-amino-8-fluoro-11*H*-benzo[*a*]carbazole-5-carboxylate (5g): Eluent: petroleum ether- ethyl acetate (10:1); white solid (105 mg, 65%); mp: 202-203 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.51 (t, J = 7.2 Hz, 3H), 4.54 (q, J = 7.2 Hz, 2H), 6.62 (br s, 2H), 7.17-7.20 (m, 1H), 7.35 (t, J = 7.2 Hz, 1H), 7.49-7.53 (m, 2H), 7.69 (d, J = 9.6 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 8.69 (d, J = 9.0 Hz, 1H), 8.91 (br s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 14.8, 60.4, 96.4, 107.0 (d, $^{2}J_{C\text{-}F}$ = 25.05 Hz), 107.4 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 112.3 (d, $^{2}J_{C\text{-}F}$ = 26.25 Hz), 112.7 (d, $^{3}J_{C\text{-}F}$ = 9.75 Hz), 116.8, 122.2, 122.4, 123.3 (d, $^{3}J_{C\text{-}F}$ = 10.95 Hz), 126.0, 127.6, 132.8, 135.5, 140.6, 148.5, 157.8 (d, $^{1}J_{C\text{-}F}$ = 231.9 Hz), 169.8. HRMS calcd for $C_{19}H_{15}FN_2NaO_2$: 345.1010 $[M+Na]^+$, found: 345.1030.

Ethyl 5-amino-10*H*-thieno[2,3-*a*]carbazole-4-carboxylate (5h): Eluent: petroleum ether-ethyl acetate (10:1); white solid (113 mg, 73%); mp: 191-192 ℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 1.51 (t, J = 7.2 Hz, 3H), 4.49 (q, J = 7.2 Hz, 2H), 6.89 (br s, 2H), 7.32 (t, J = 7.8 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.45 (d, J = 5.4 Hz, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H), 8.17 (d, J = 5.4 Hz, 1H), 8.51 (br s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 14.6, 60.3, 98.2, 107.9, 111.2, 114.3, 120.1, 121.0, 123.7, 124.4, 124.8, 127.8, 137.1, 138.4, 139.4, 149.1, 169.5. HRMS calcd for $C_{17}H_{15}N_2O_2S$: 311.0849 $[M+H]^+$, found: 311.0864.

4. Synthesis of 2-bromo-11*H*-benzo[*a*]carbazole-5-carboxylic acid (8)

4.1 Synthetic procedure and spectroscopic data of 5i

2-(3-Bromophenyl)-1*H*-indole-3-carbonitrile (**4i**, 0.5 mmol), ethyl 2-diazo-3-*oxo*-3-phenylpropanoate (**2a**, 0.75 mmol), $[RhCp^*Cl_2]_2$ (0.025 mmol), AgOAc (0.1 mmol), $AgSbF_6$ (0.1 mmol), and CH_3CN (3 mL) were charged into a sealed tube. The reaction mixture was then stirred at 120 ℃. Upon completion, it was cooled to room temperature, quenched with saturated brine (10 mL), and extracted with EtOAc (10 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford **5i**.

Ethyl 6-amino-2-bromo-11*H*-benzo[*a*]carbazole-5-carboxylate (5i): Eluent: petroleum ether-ethyl acetate (10:1); white solid (130 mg, 68%); mp: 167-168 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.40 (t, J = 7.2 Hz, 3H), 4.43 (q, J = 7.2 Hz, 2H), 7.28-7.33 (m, 3H), 7.45 (t, J = 7.6 Hz, 1H), 7.56 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 8.41 (d, J = 8.0 Hz, 1H), 8.49 (d, J = 9.2 Hz, 1H), 8.61 (d, J = 2.4 Hz, 1H), 12.54 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 14.3, 60.0, 95.6, 107.6, 111.6, 114.1, 117.8, 120.3, 121.0, 122.4, 124.0, 124.5, 127.8, 129.2, 130.9, 137.6, 138.5, 148.6, 169.0. HRMS calcd for $C_{19}H_{16}BrN_2O_2$: 383.0390 $[M+H]^+$, found: 383.0395.

4.2 Synthetic procedure and spectroscopic data of 7

To a flask containing ethyl 6-amino-2-bromo-11*H*-benzo[*a*]carbazole-5-carboxylate (**5i**, 77 mg, 0.2 mmol), DMSO (0.2 mL) and diluted HCl (2M, 2 mL) was added an aqueous solution of $NaNO_2$ (30% w/w in water, 0.07 mL) dropwisely at 0 ℃ with stirring. The resuling mixture was stirred at 0 ℃ for 0.5 h. Then, H_3PO_2 (50% w/w in water, 0.06 mL) was added in a drop-wise manner. It was then stirred at room temperature for 3 h. Upon completion as monitored by TLC, it was quenched with aqueous solution of $NaHCO_3$, and extracted with ethyl acetate (5 mL × 3). The combined organic phases were washed with brine, dried over anhydrous

Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography on silica gel using petroleum ether-ethyl acetate (10:1) as the eluent to give **7**.

Ethyl 2-bromo-11*H*-benzo[*a*]carbazole-5-carboxylate (7): Eluent: petroleum ether-ethyl acetate (10:1); yellow solid (39 mg, 53%); mp: 258-259 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ: 1.43 (t, J = 7.2 Hz, 3H), 4.42 (q, J = 7.2 Hz, 2H), 7.30 (t, J = 7.8 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.40 (d, J = 9.6 Hz, 1H), 8.25 (d, J = 7.8 Hz, 1H), 8.44 (s, 1H), 8.98 (s, 1H), 9.01 (d, J = 9.6 Hz, 1H), 12.61 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 14.8, 61.0, 112.3, 117.2, 117.6, 119.5, 120.6, 120.8, 123.0, 123.6, 125.1, 126.17, 126.22, 128.8, 129.2, 129.8, 137.7, 139.8, 167.3. HRMS calcd for $C_{19}H_{15}BrNO_2$: 368.0281 $[M+H]^+$, found: 368.0285.

4.3 Synthetic procedure and spectroscopic data of 8

To a flask containing ethyl 2-bromo-11*H*-benzo[*a*]carbazole-5-carboxylate (**7**, 73 mg, 0.2 mmol) were added methanol (10 mL) and an aqueous solution of NaOH (2M, 0.5 mL). It was stirred under reflux for 3 h, and then cooled to room temperature. To the resulting mixture was added an aqueous solution of HCl (1M) dropwisely until the pH value was about 5. The mixture was then extracted with EtOAc (10 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (2:1) as eluent to give **8**.

2-Bromo-11*H*-benzo[*a*]carbazole-5-carboxylic acid (8)[6]: Eluent: petroleum ether-ethyl acetate (2:1); white solid (63 mg, 93%); mp: 260-261 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.3 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.79 (dd, J_1 = 9.6 Hz, J_2 = 2.0 Hz, 1H), 8.30 (d, J = 8.4 Hz, 1H), 8.88 (d, J = 1.6 Hz, 1H), 9.09 (s, 1H), 9.20 (d, J = 9.2 Hz, 1H), 12.63 (s, 1H), 12.88 (br s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 14.3, 60.0, 95.6, 107.6, 111.6, 114.1, 117.8, 120.3, 121.0, 122.4, 124.0, 124.5, 127.8, 129.2, 130.9, 137.6, 138.5, 148.6, 169.0. HRMS calcd for $C_{17}H_9BrNO_2$: 337.9822 $[M-H]^-$, found: 337.9826.

III. Mechanism studies

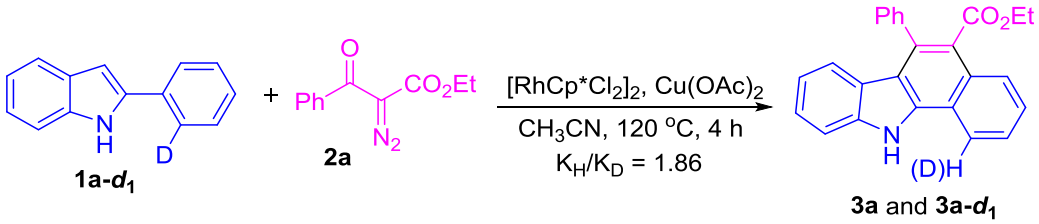
1. A control experiment

1-Methyl-2-phenyl-1*H*-indole (**6**, 0.5 mmol), ethyl 2-diazo-3-oxo-3-phenylpropanoate (**2a**, 0.75 mmol), $[RhCp^*Cl_2]_2$ (0.025 mmol), $Cu(OAc)_2$ (0.1 mmol), and CH_3CN (3 mL) were charged into a sealed tube. The mixture was then stirred at 120 ℃ for 18 h. From the resulting mixture, 93% of **6** was recovered.

Scheme 1. A control experiment

2. The intramolecular KIE experiment

2-(Phenyl-2-*d*)-1*H*-indole (**1a-*d*$_1$**, 0.5 mmol), ethyl 2-diazo-3-oxo-3-phenylpropanoate (**2a**, 0.75 mmol), $[RhCp^*Cl_2]_2$ (0.025 mmol), $Cu(OAc)_2$ (0.05 mmol), and CH_3CN (3 mL) were charged into a sealed tube. The mixture was then stirred at 120 ℃ for 4 h. Afterwards, it was cooled to room temperature, quenched with saturated brine (10 mL), and extracted with EtOAc (10 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford a mixture of **3a** and **3a-*d*$_1$**. Upon analyzing the corresponding ^{1}H NMR spectrum as shown in Fig 1, the ratio of **3a** and **3a-*d*$_1$** in the resulting mixture was determined as 0.65:0.35. Accordingly, the intramolecular KIE (k_H/k_D) was calculated as 1.86.



Scheme 2. The intramolecular KIE experiment

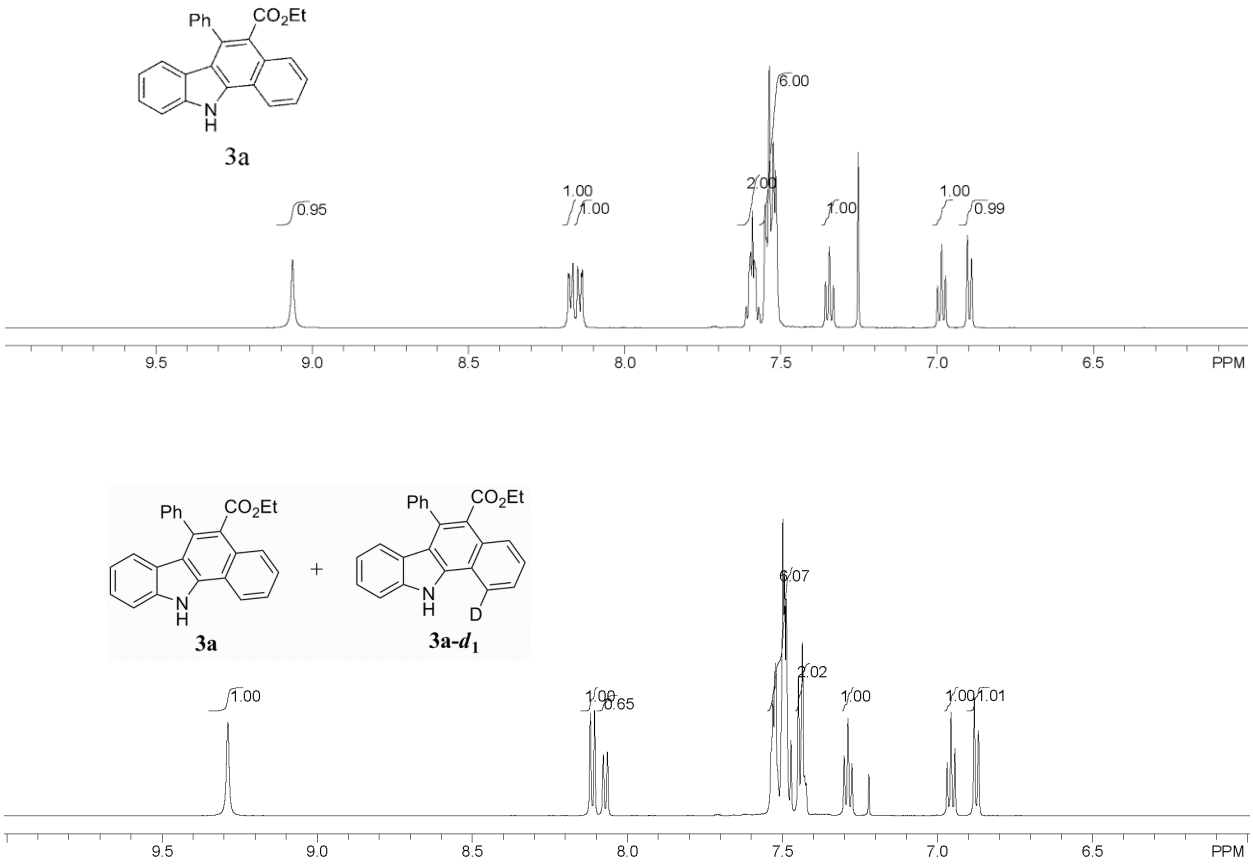
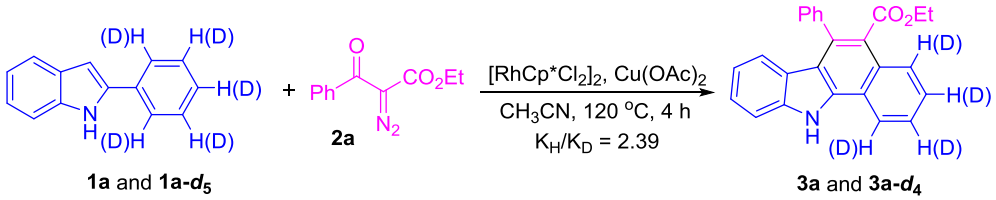


Fig 1. The ^{1}H NMR spectrum of the products obtained from the intramolecular KIE experiment

3. The intermolecular KIE experiments

2-Phenyl-1*H*-indole (**1a**, 0.25 mmol), 2-phenyl-d_5-1*H*-indole (**1a-*d*$_5$**, 0.25 mmol), ethyl 2-diazo-3-oxo-3-phenylpropanoate (**2a**, 0.5 mmol), $[RhCp^*Cl_2]_2$ (0.025 mmol), $Cu(OAc)_2$ (0.05 mmol), and CH_3CN (3 mL) were charged into a sealed tube. The mixture was then stirred at 120 ℃ for 4 h. Afterwards, it was cooled to room temperature, quenched with saturated brine (10 mL), and extracted with EtOAc (10 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford a mixture of **3a** and **3a-*d*$_4$**. Upon analyzing the corresponding ^{1}H NMR spectrum as shown in Fig 2, the ratio of **3a** and **3a-*d*$_4$** was determined as 1.41:0.59. Accordingly, the intermolecular KIE (K_H/K_D) was calculated as 2.39.



Scheme 3. The intermolecular KIE experiment

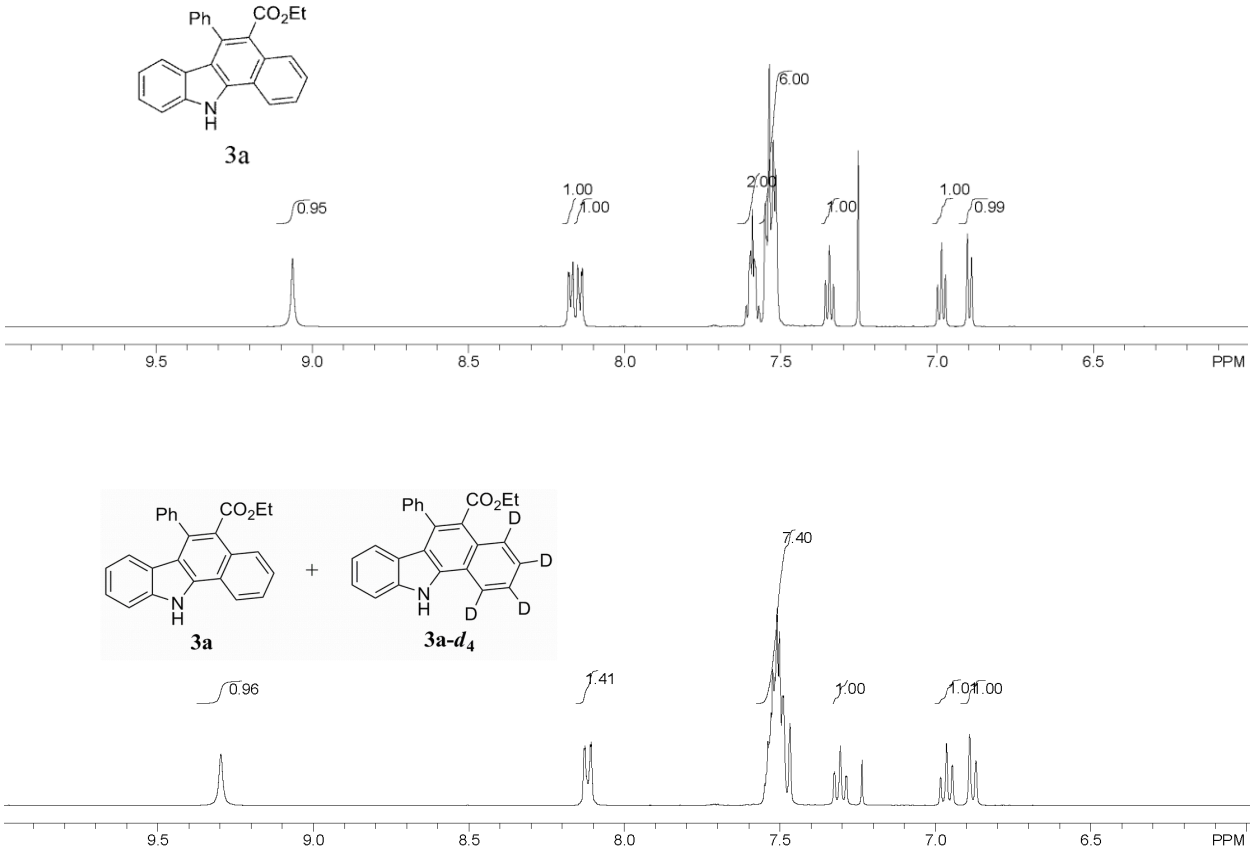


Fig 2. The ^{1}H NMR spectrum of the products obtained from the intermolecular KIE experiment

4. Identification of benzoic acid from the reaction mixture of 4a with 2a by GC-MS

3-Cyano-2-phenylindole (**4a**, 0.5 mmol), ethyl 2-diazo-3-*oxo*-3-phenylpropanoate (**2a**, 0.75 mmol), $[RhCp^*Cl_2]_2$ (0.025 mmol), AgOAc (0.1 mmol), $AgSbF_6$ (0.1 mmol), and CH_3CN (3 mL) were charged into a sealed tube. The mixture was then stirred at 120 ℃ for 8 h. Afterwards, it was cooled to room temperature, and filtered. A GC-MS study of the resulting mixture thus obtained showed that benzoic acid was formed.

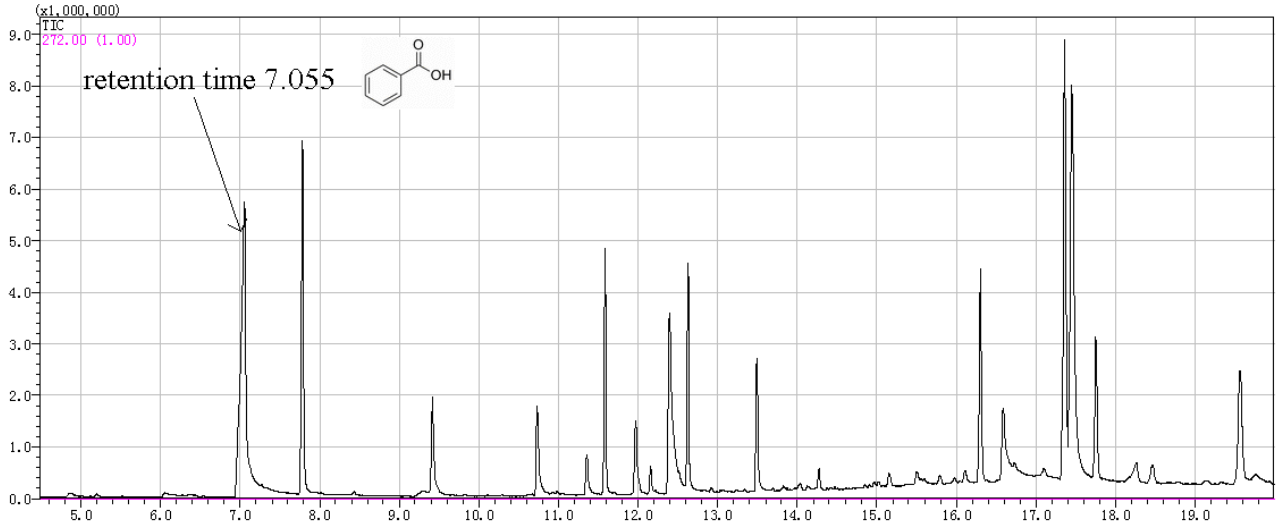


Fig 3. GC spectrum of the resulting mixture from the reaction of **4a** with **2a**

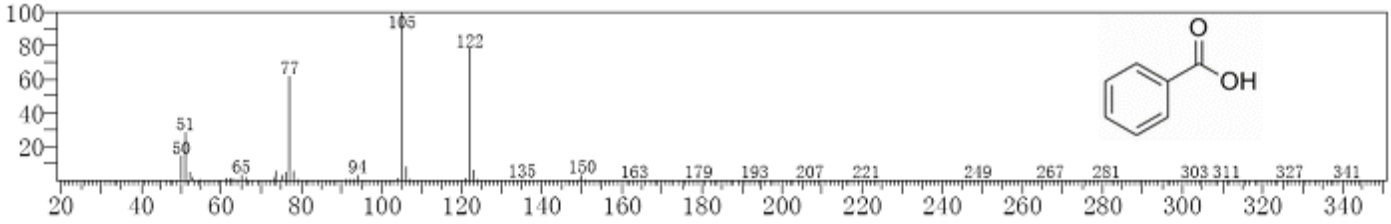
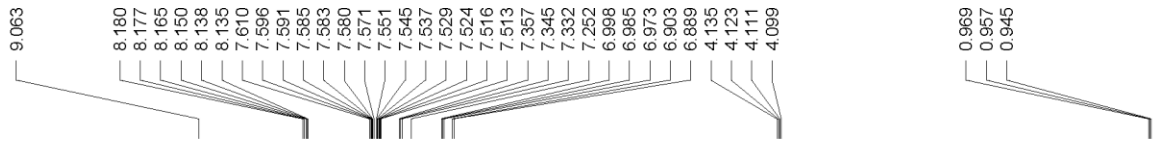
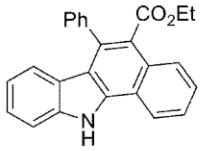


Fig 4. MS spectrum of the compound with a retention time of 7.055

IV. Copies of ^{1}H and ^{13}C NMR spectra of 3a-3y





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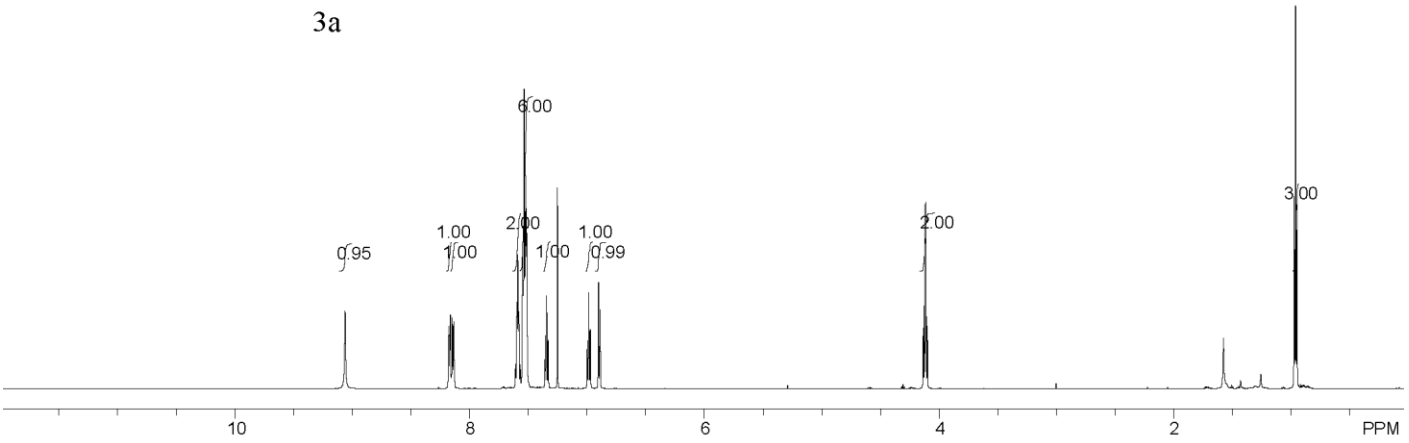

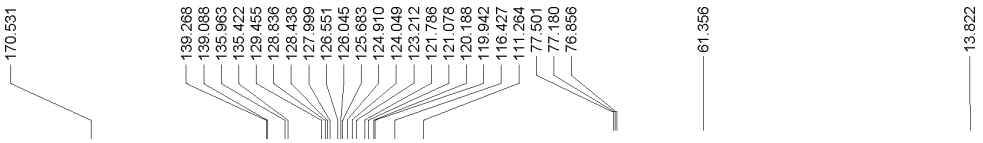

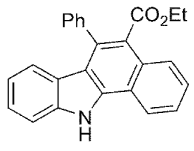

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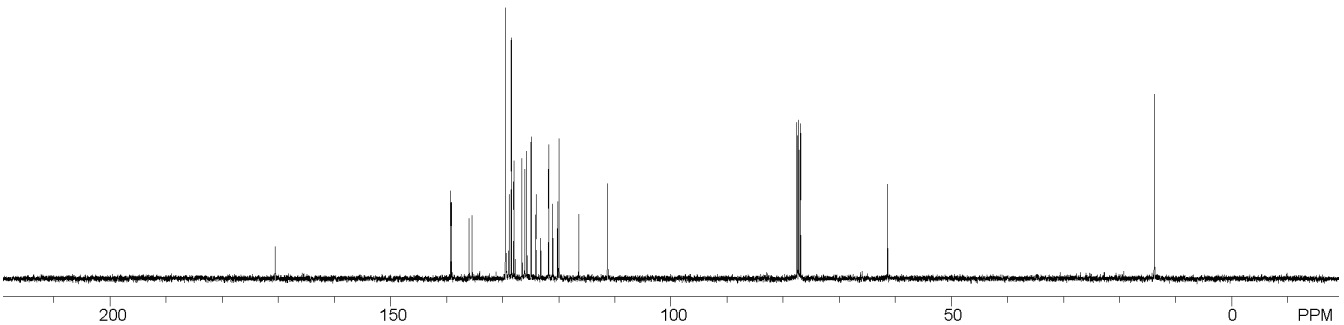

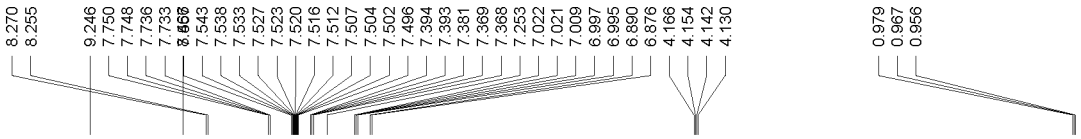
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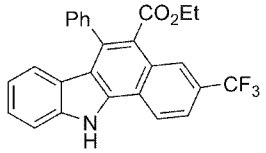
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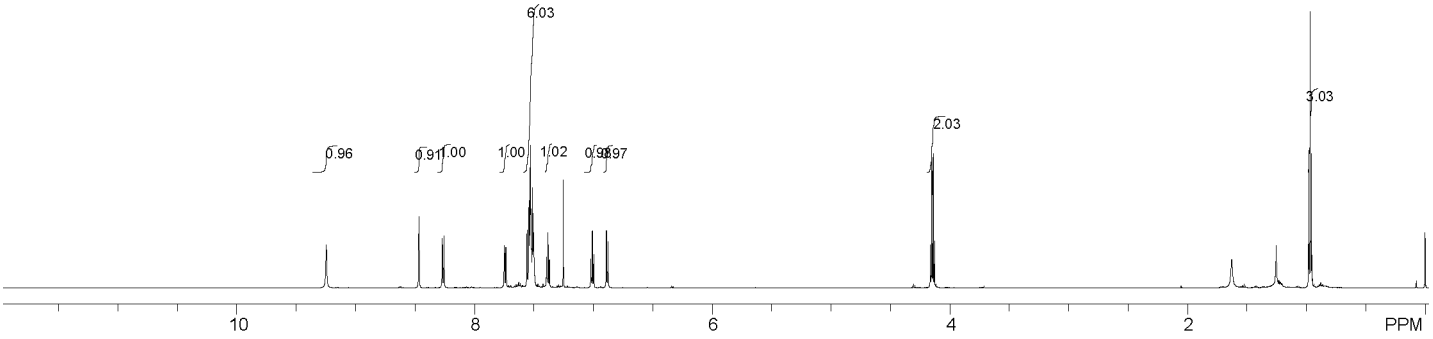
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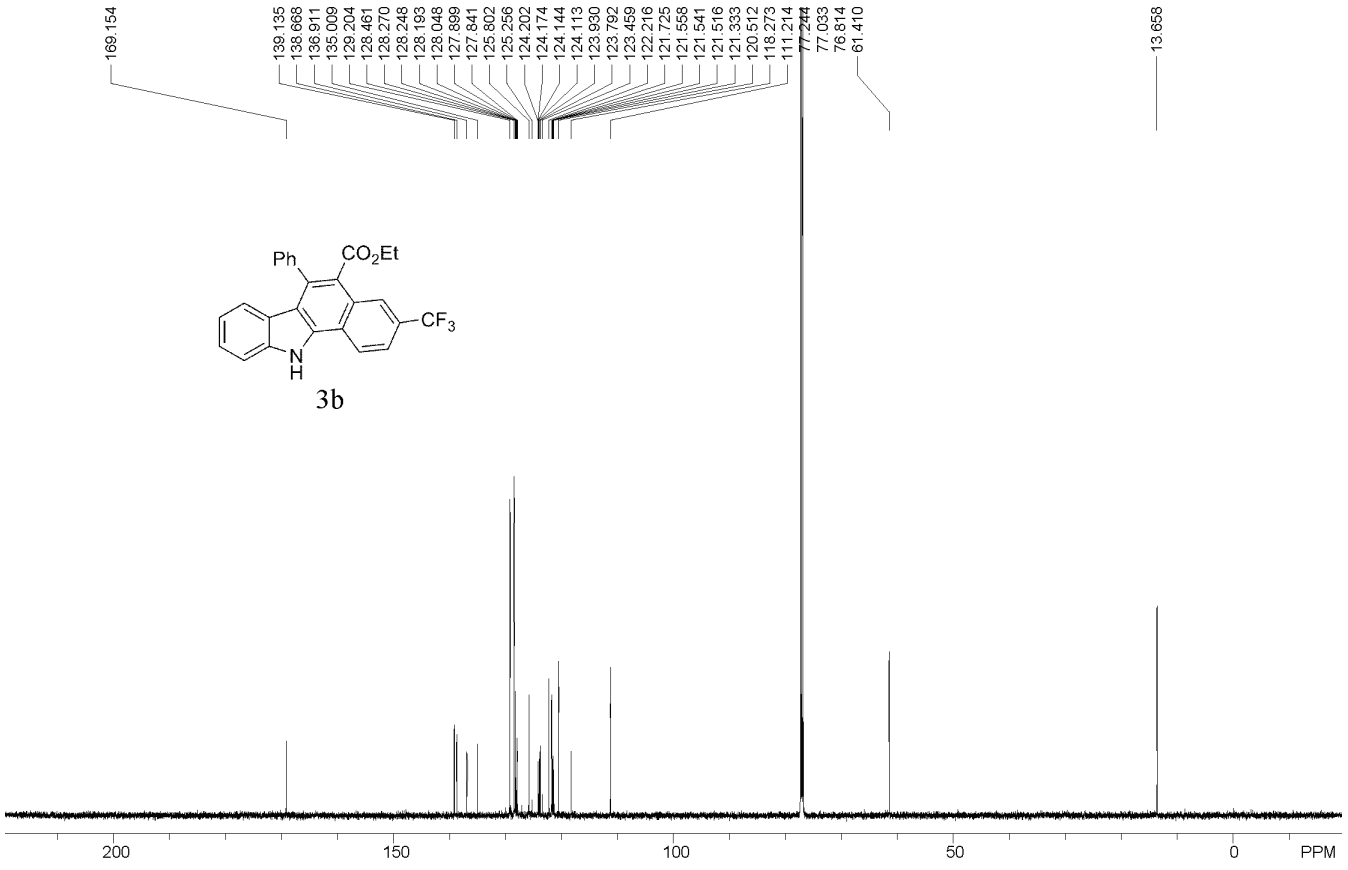
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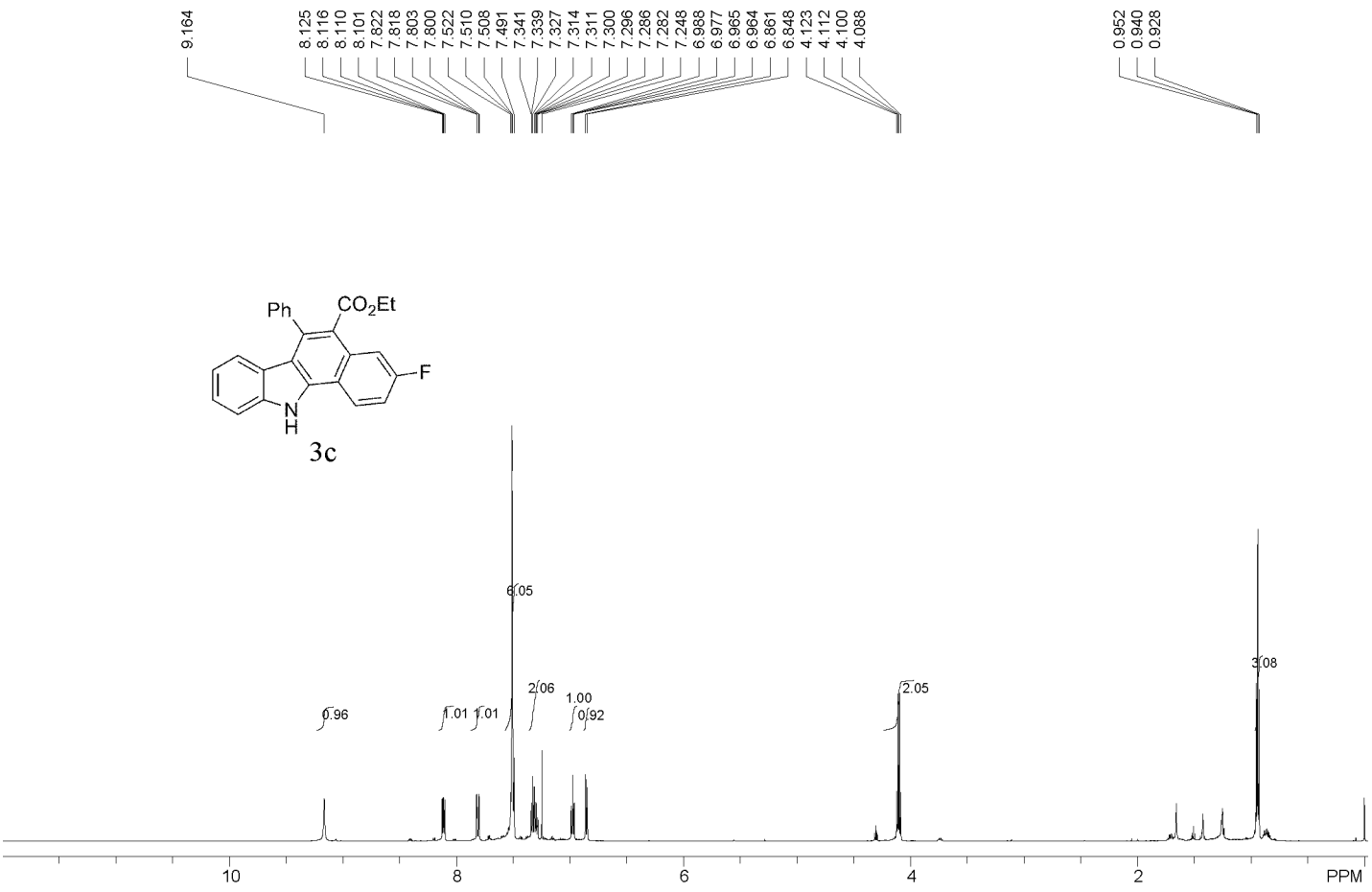
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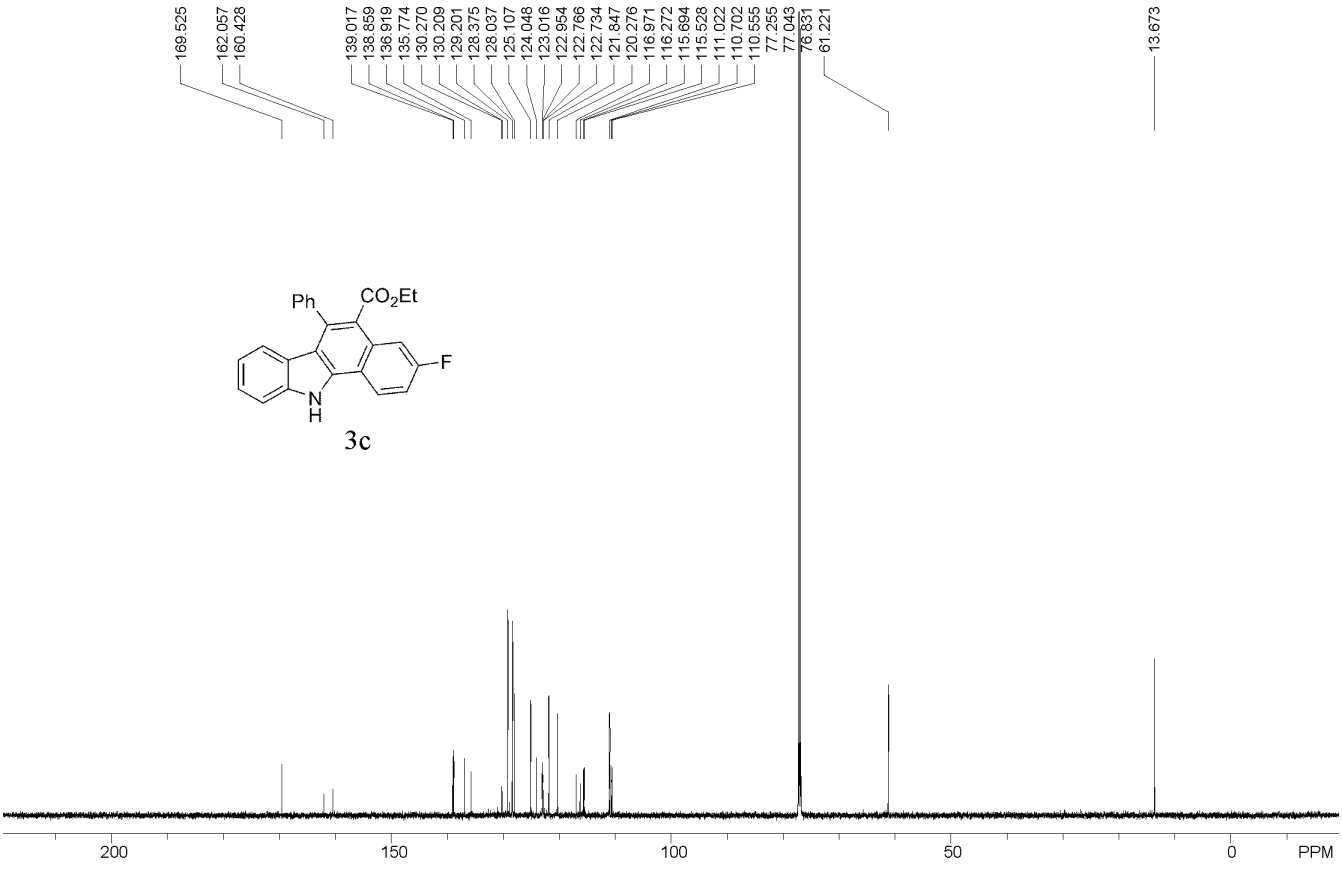
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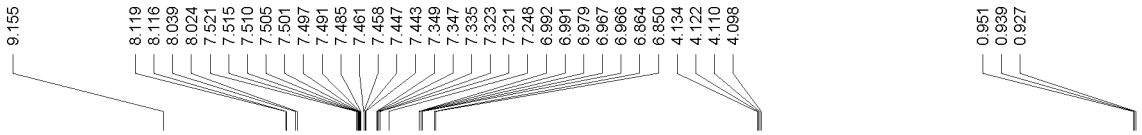
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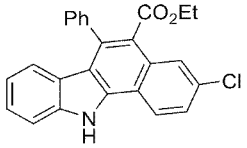
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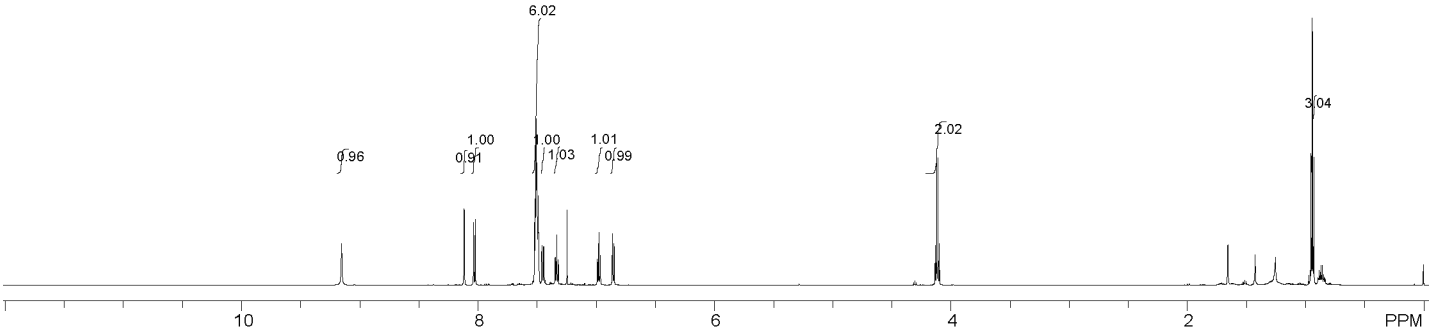
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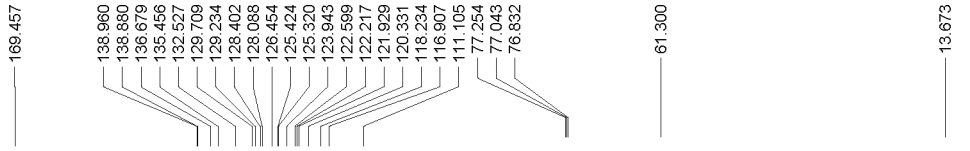
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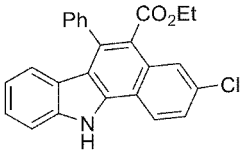
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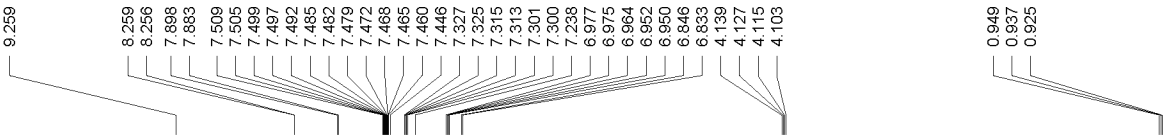
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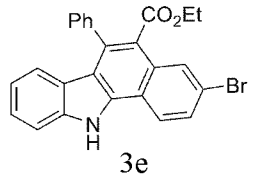
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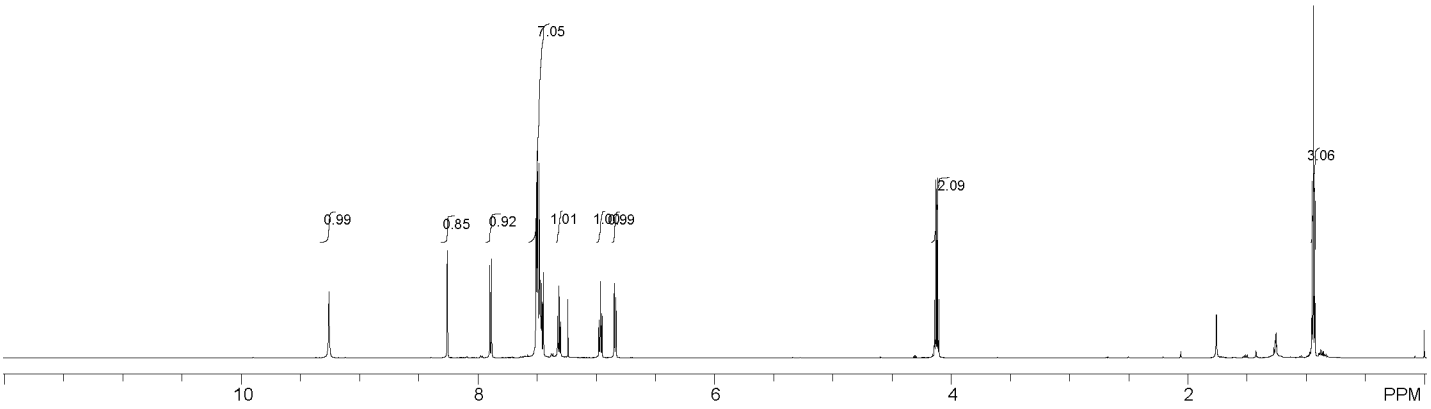
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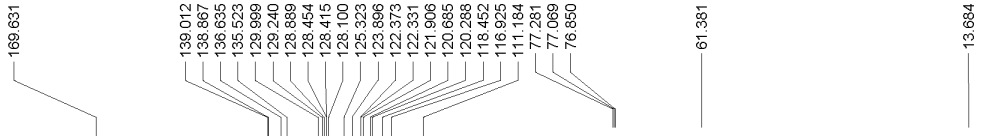
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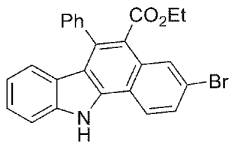
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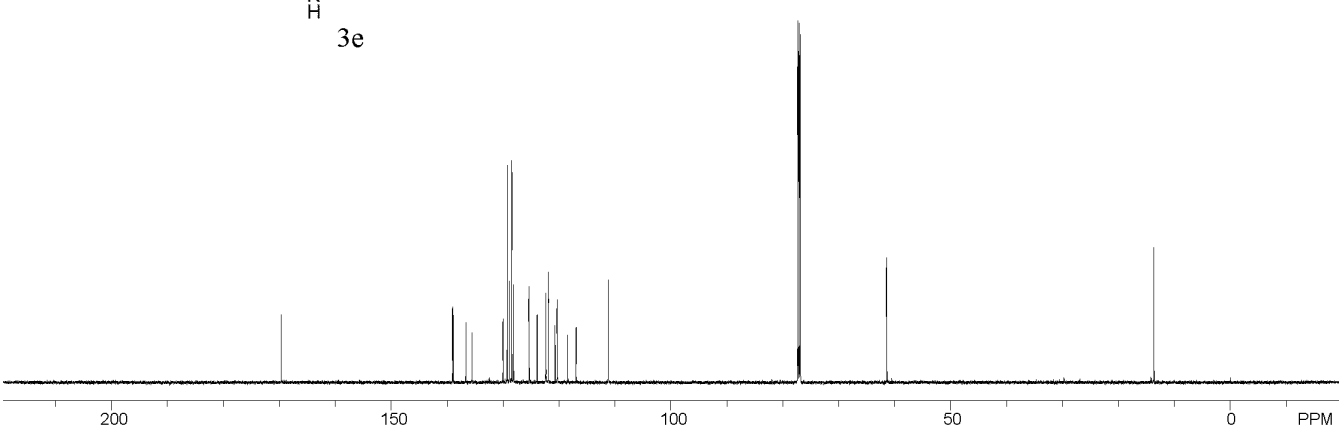
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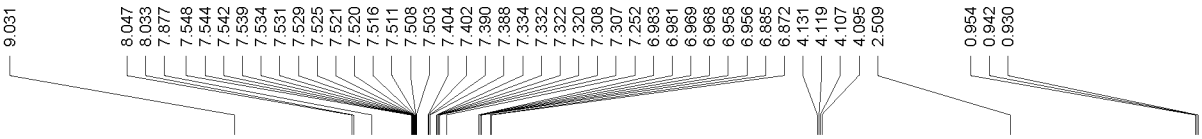
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7.252
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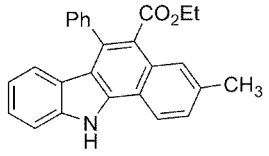
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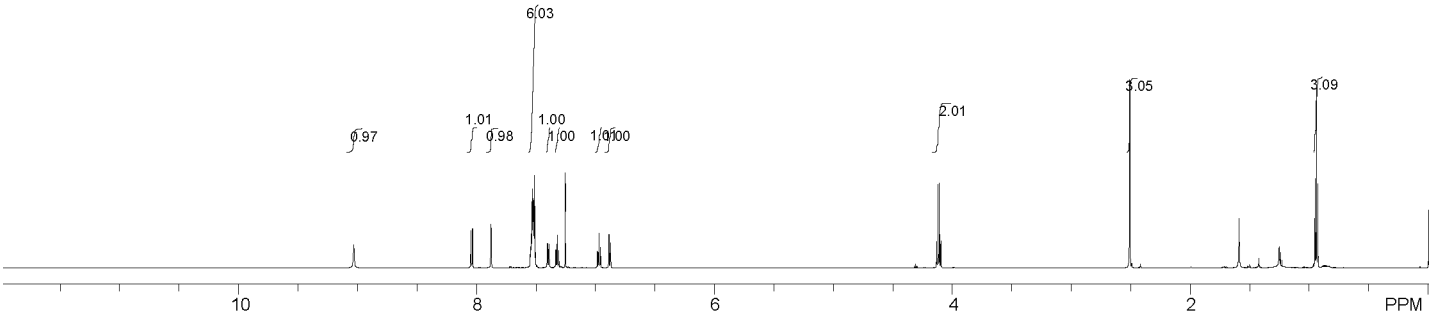
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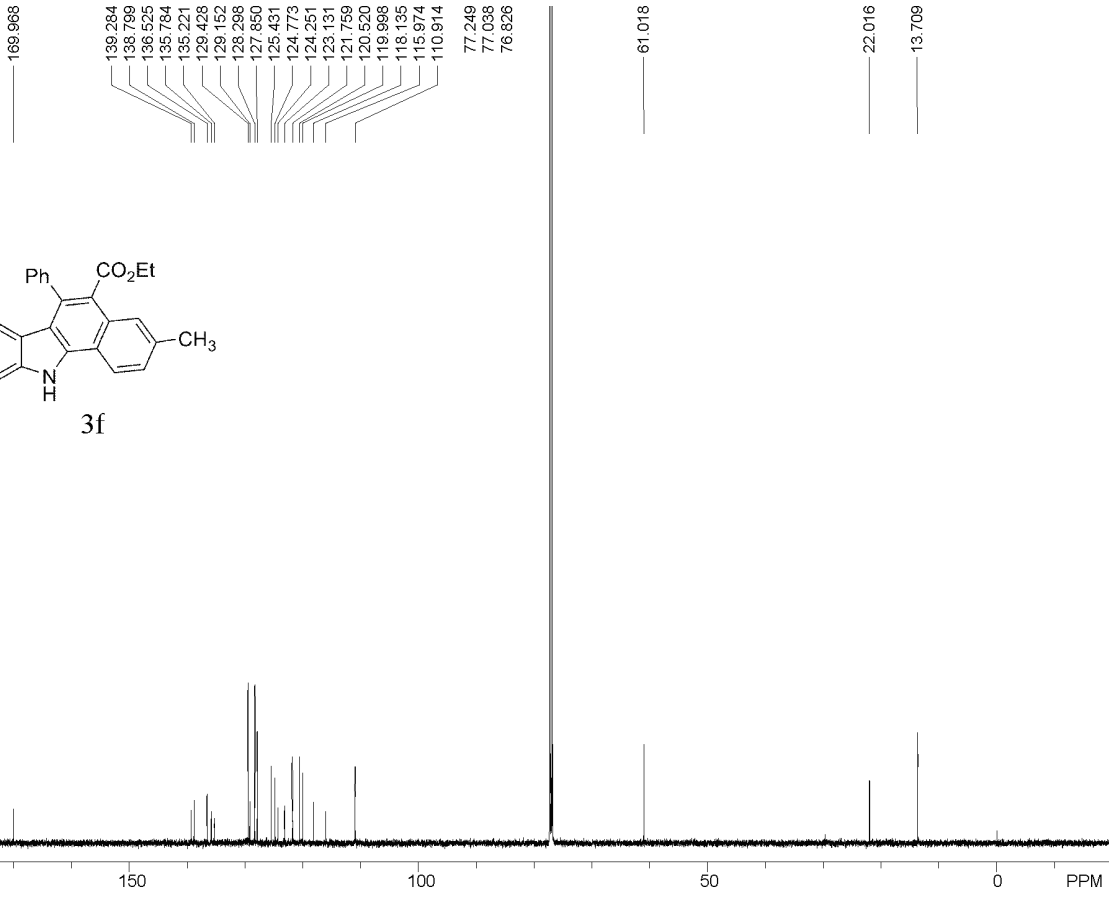
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H

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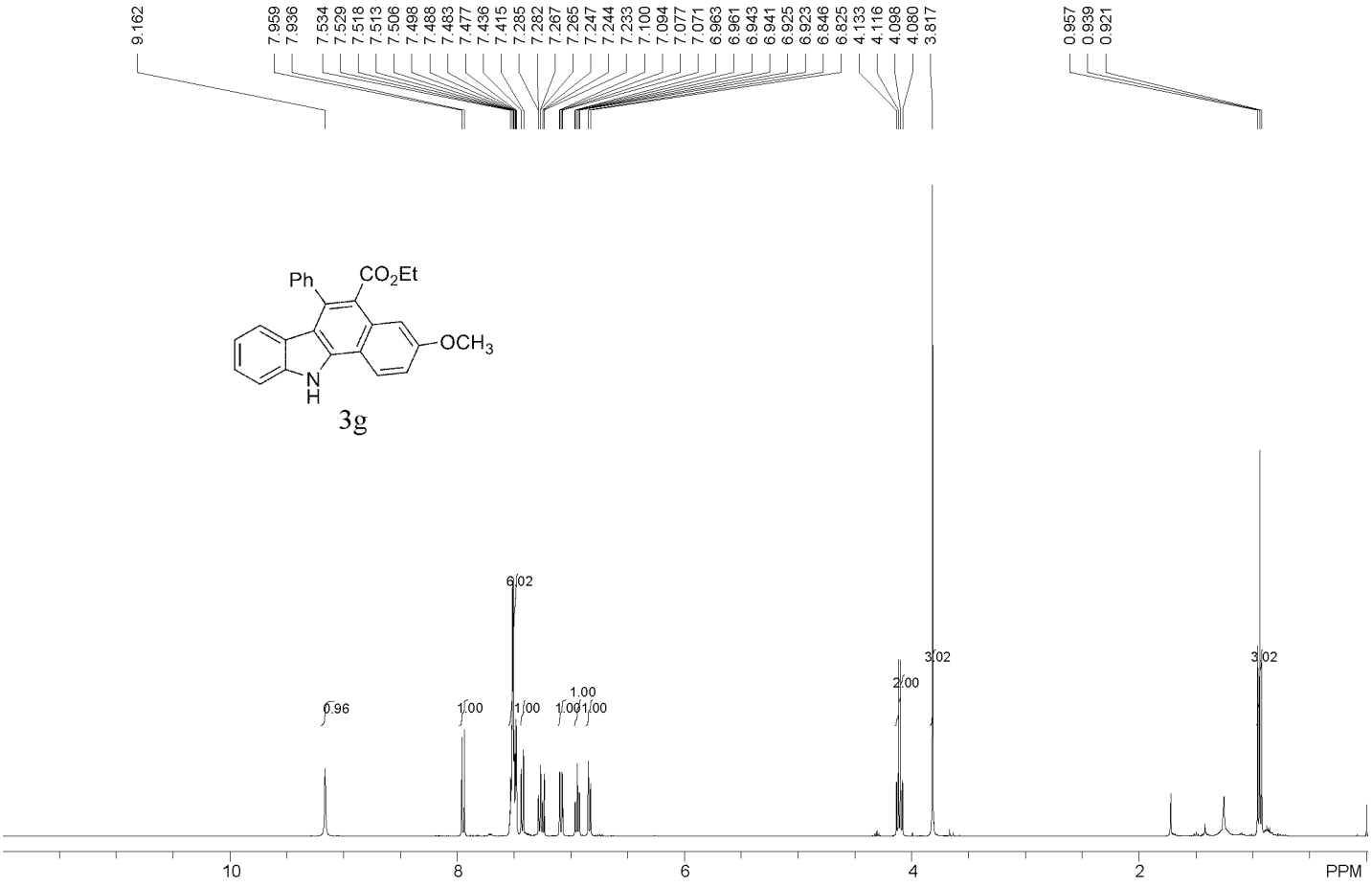
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7.071
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4.116
4.098
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0.921
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OCH3
N
H
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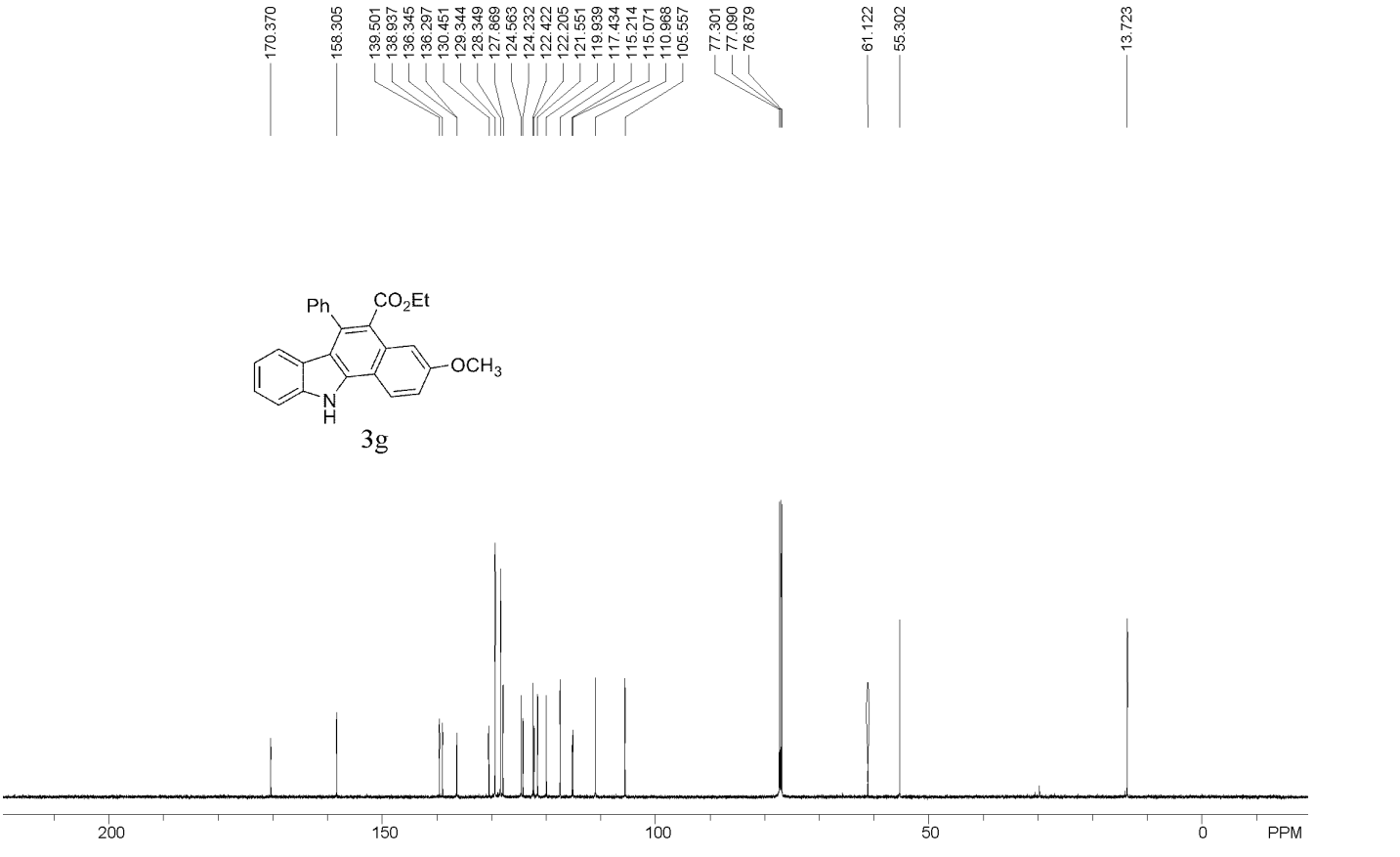
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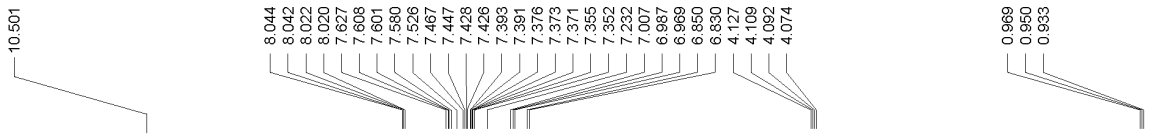
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7.376
7.373
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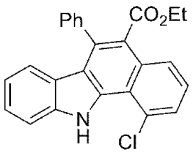
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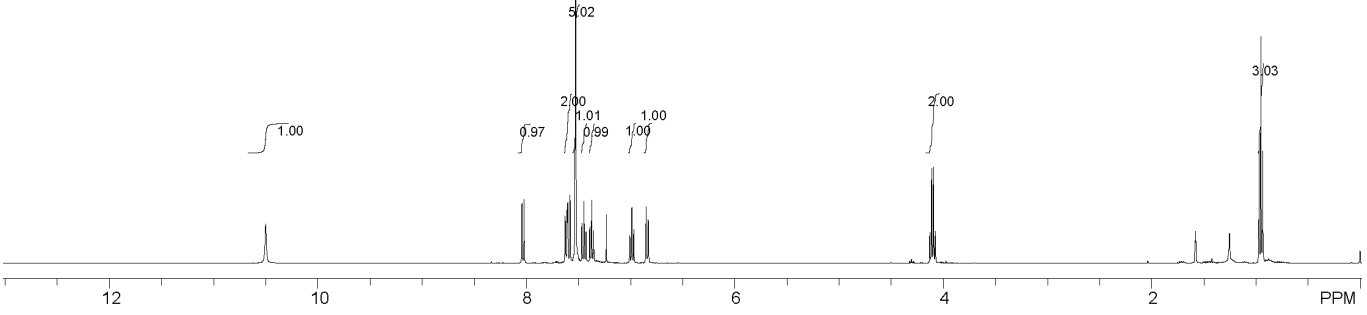
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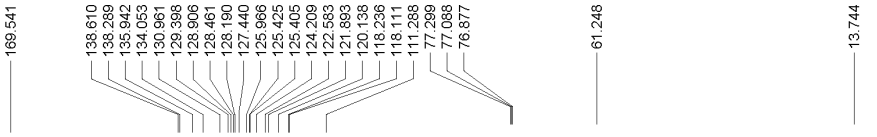
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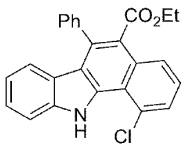
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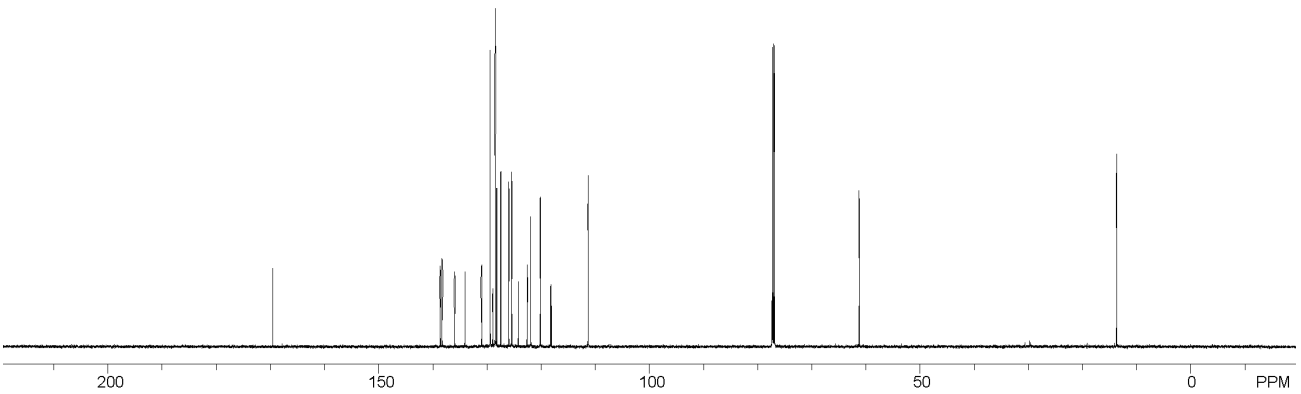
3h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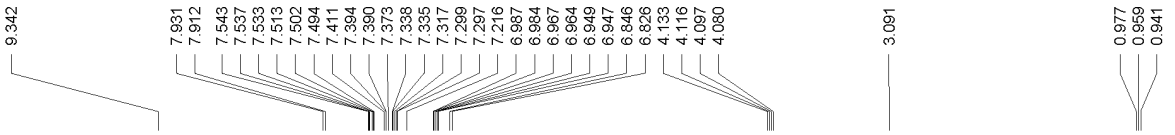
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7.297
7.216
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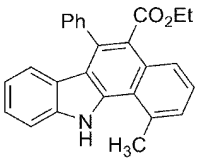
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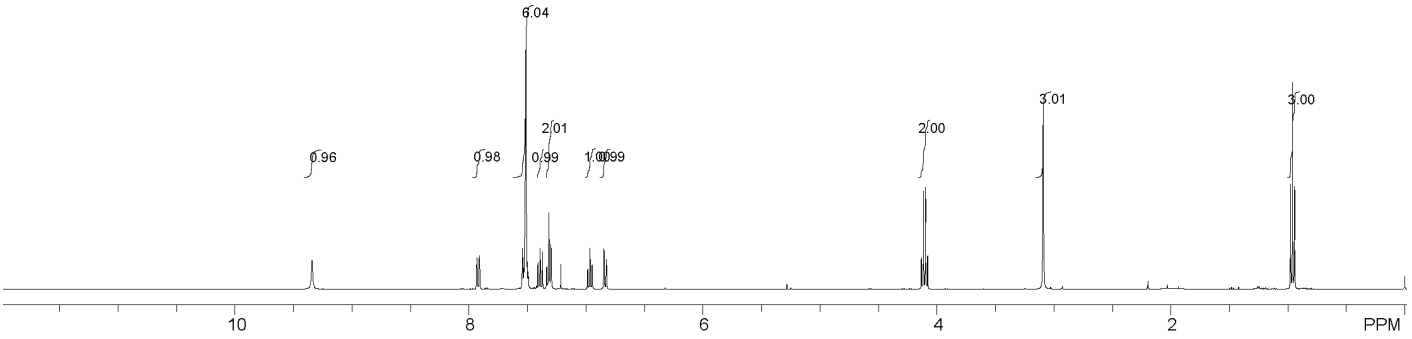
3i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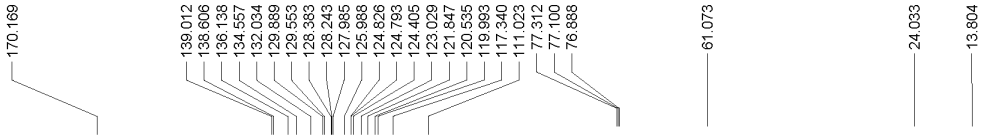
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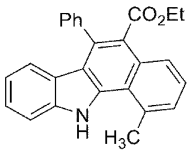
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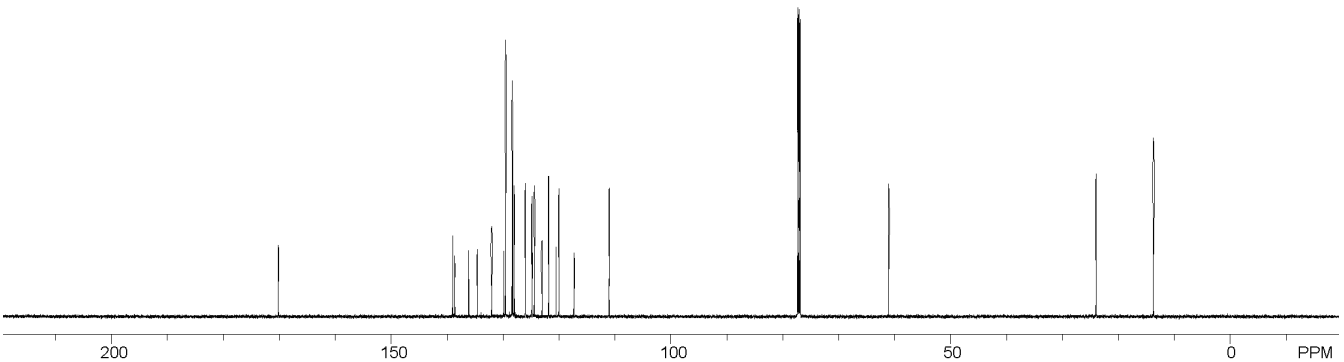
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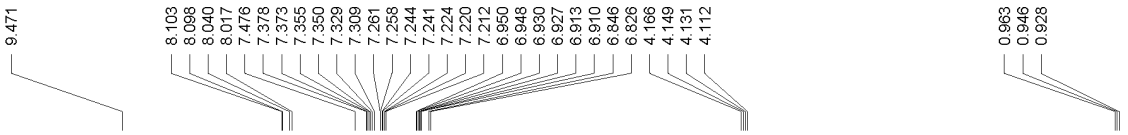
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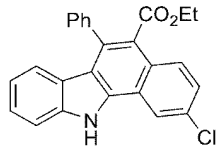
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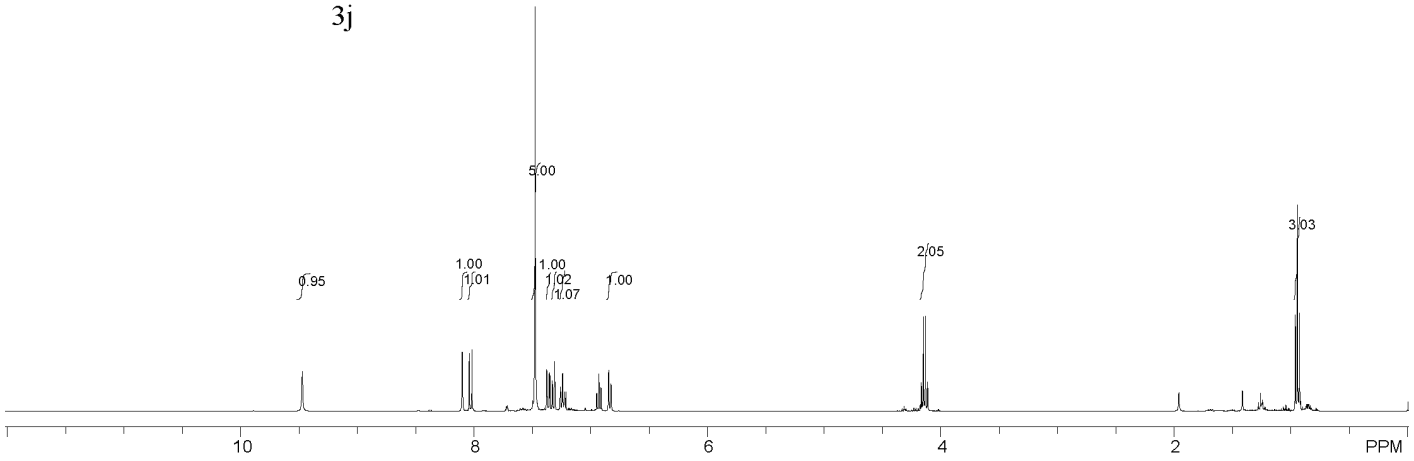
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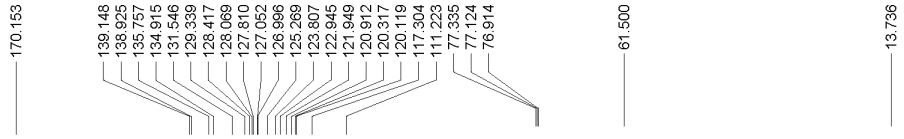
PPM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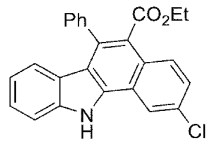
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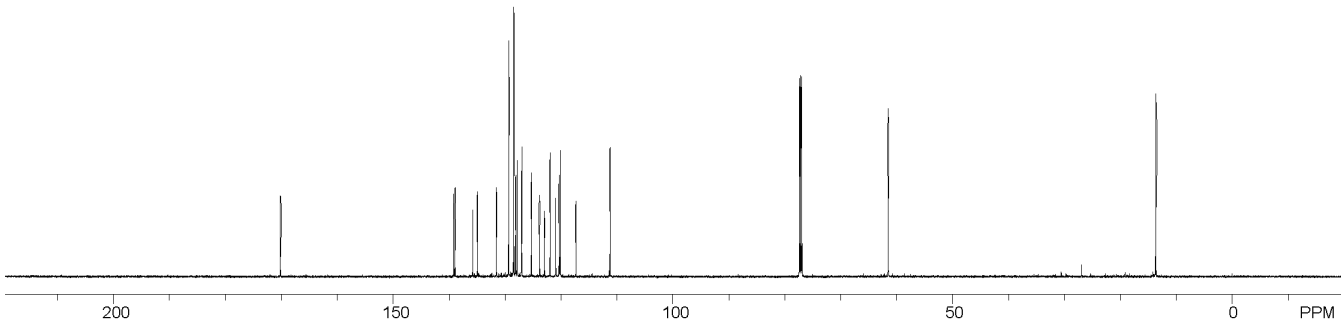
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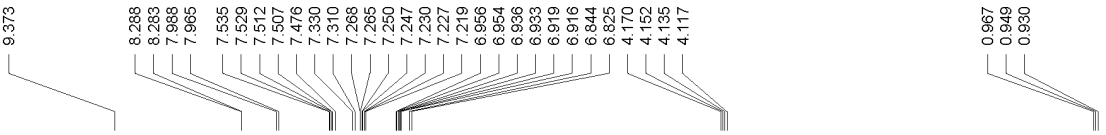
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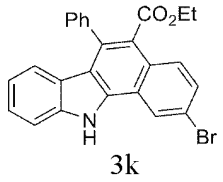
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3k

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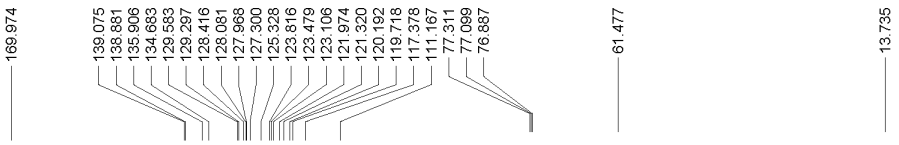
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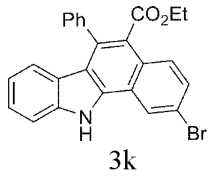
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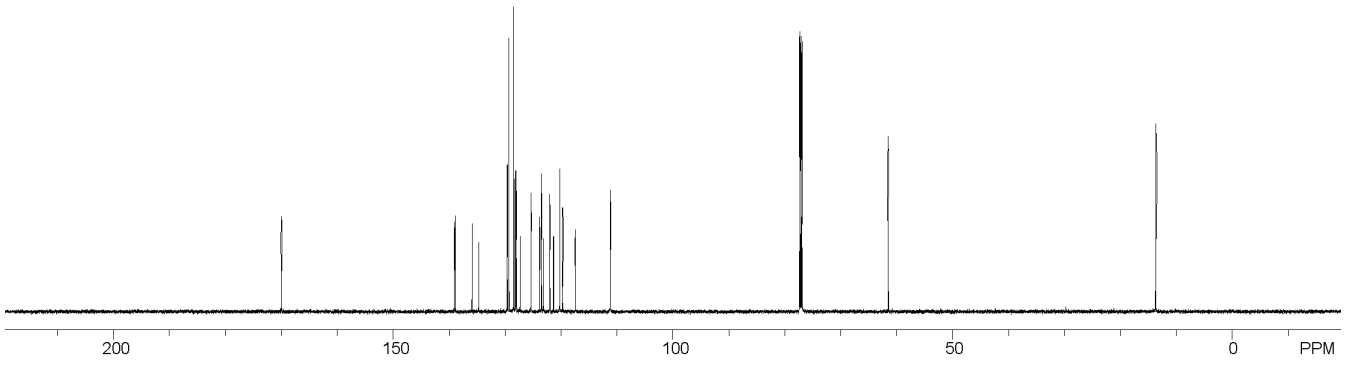
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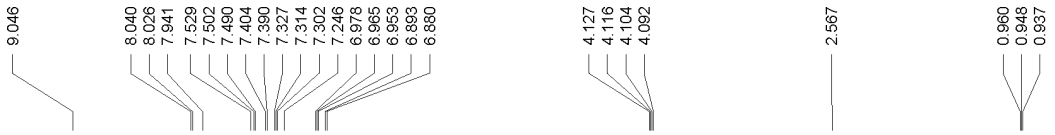
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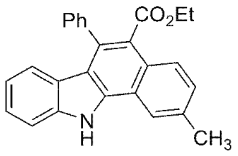
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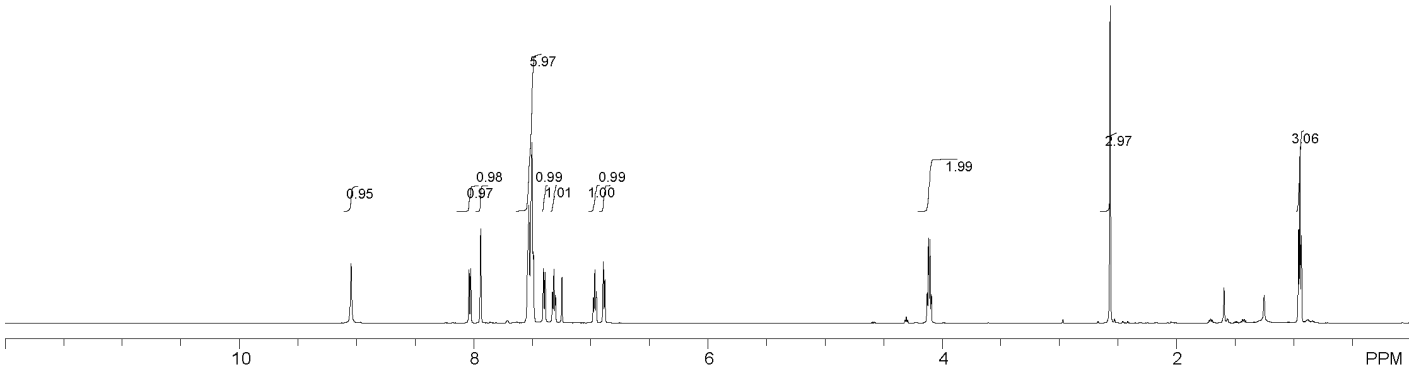
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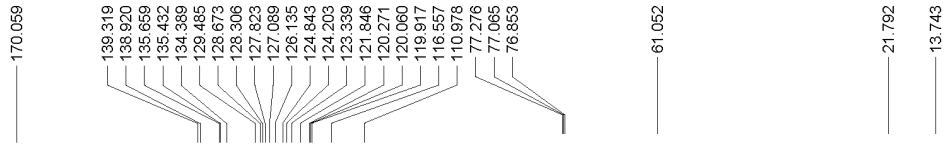
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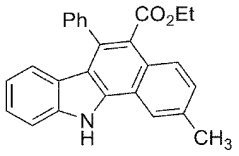
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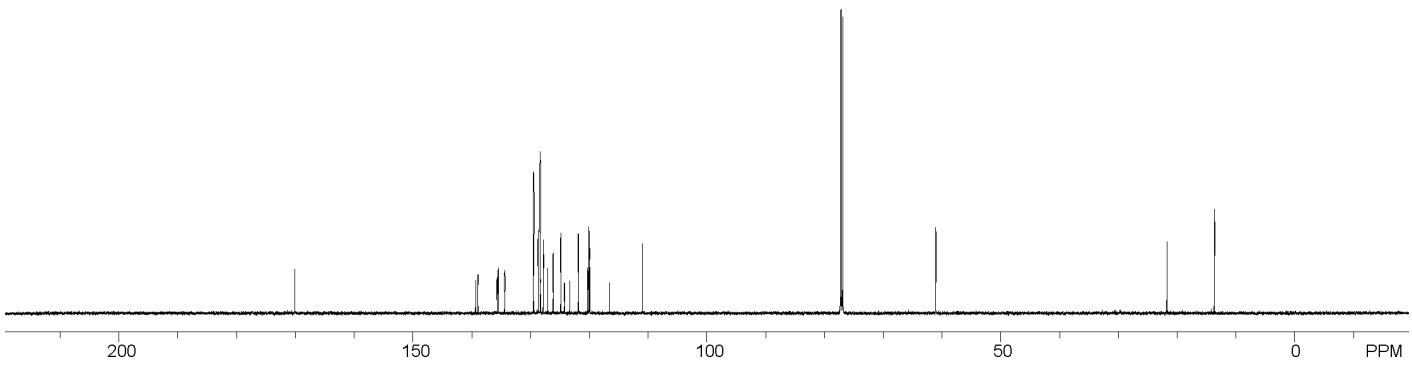
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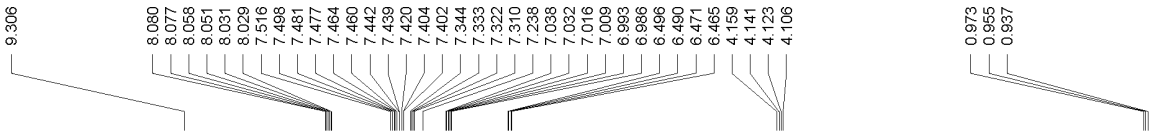
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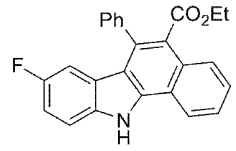
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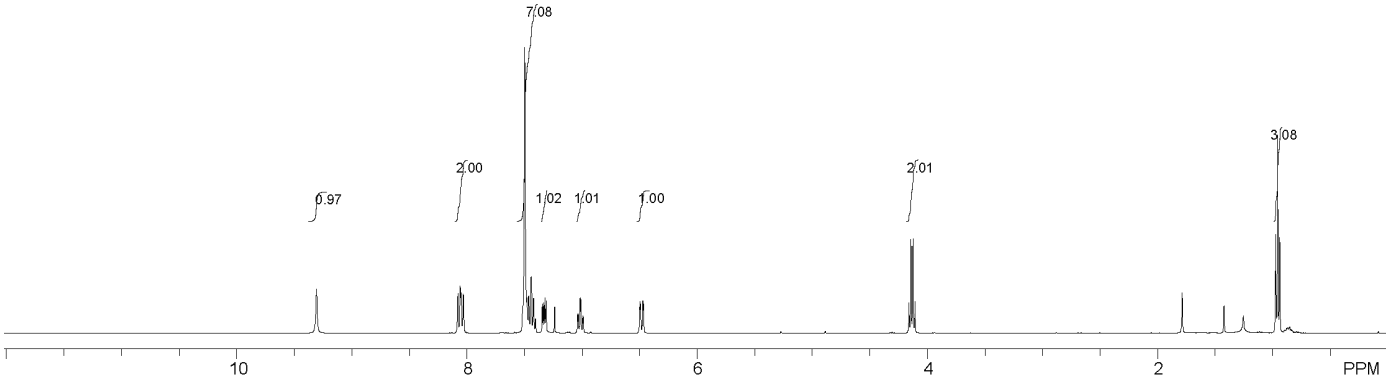
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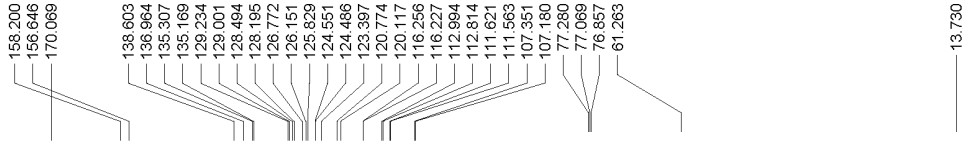
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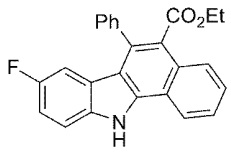
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F
N
H

3m

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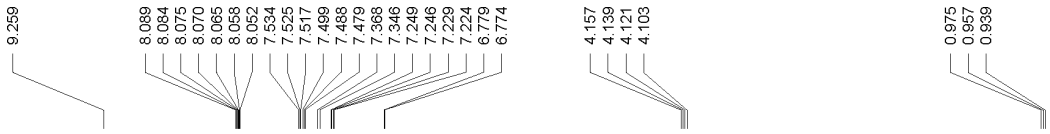
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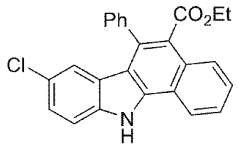
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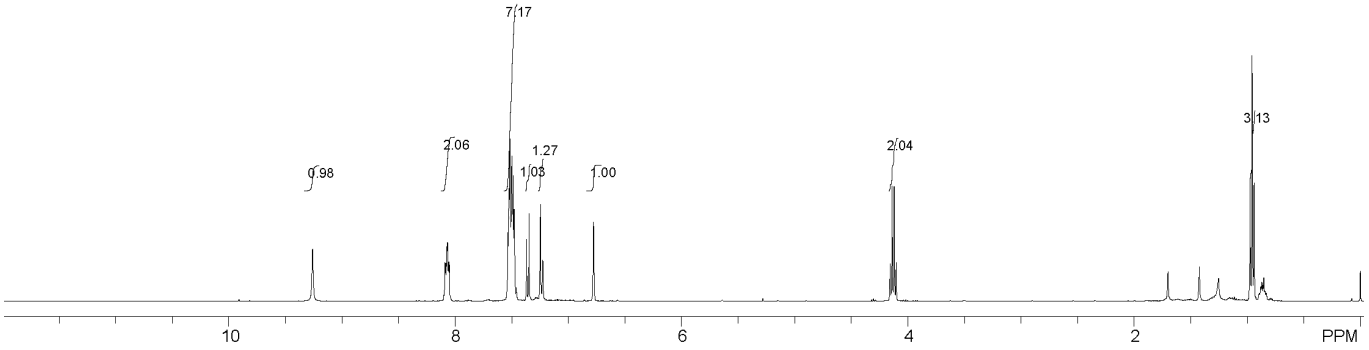
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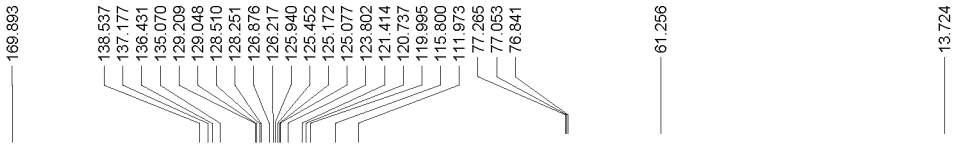
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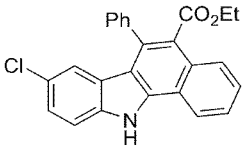
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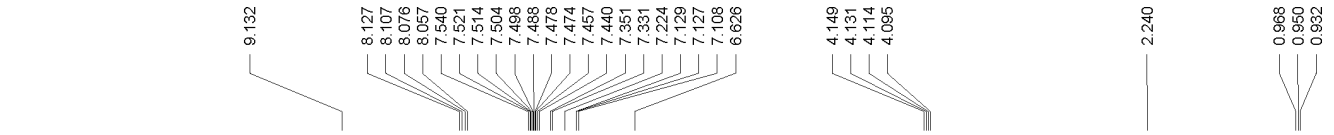
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7.331
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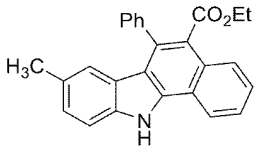
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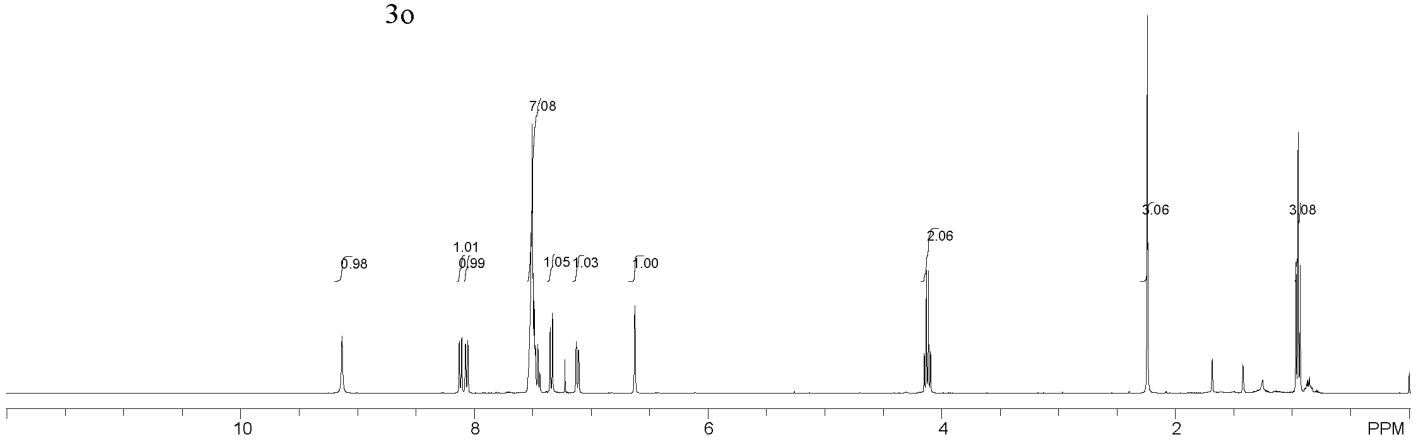
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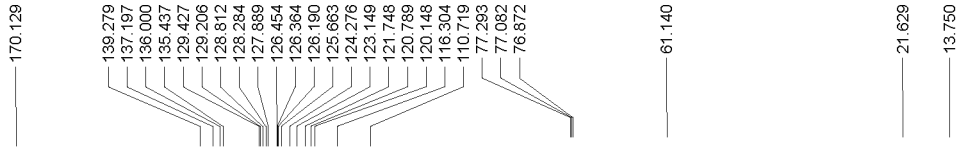
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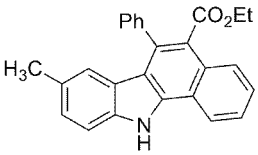
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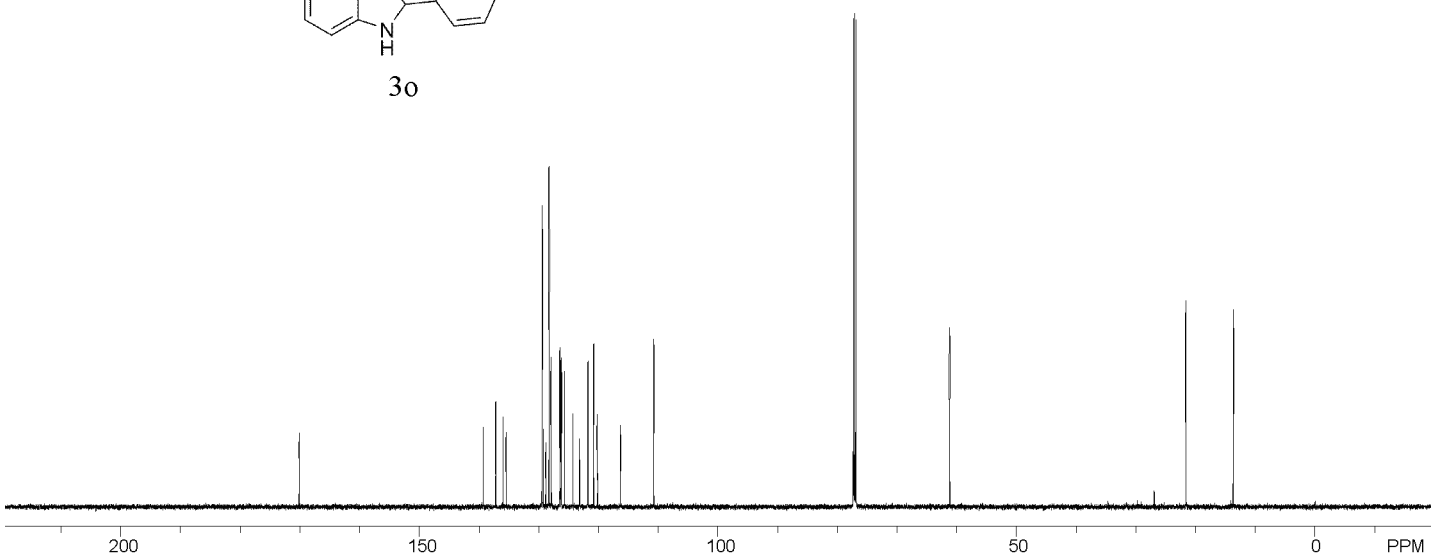
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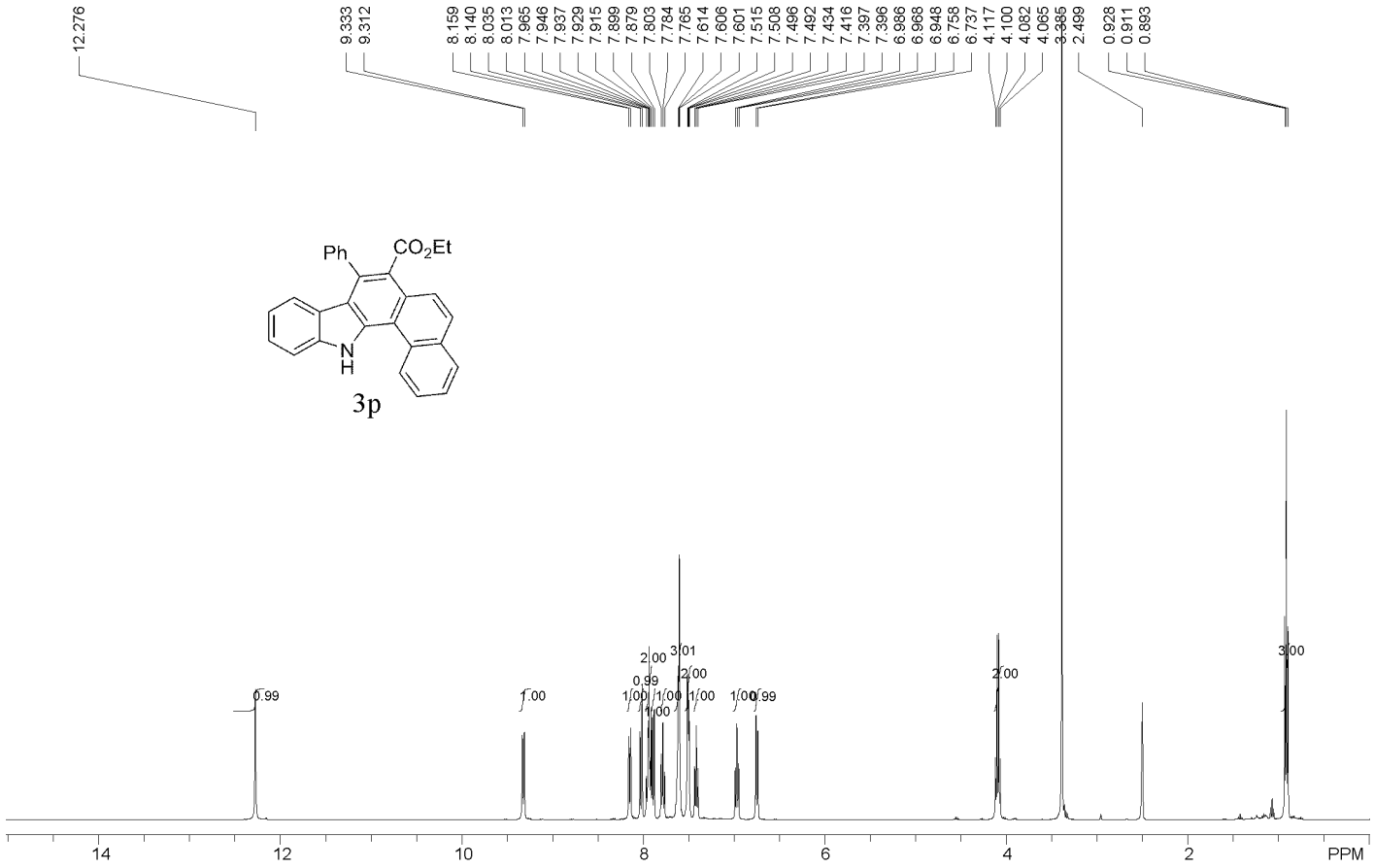
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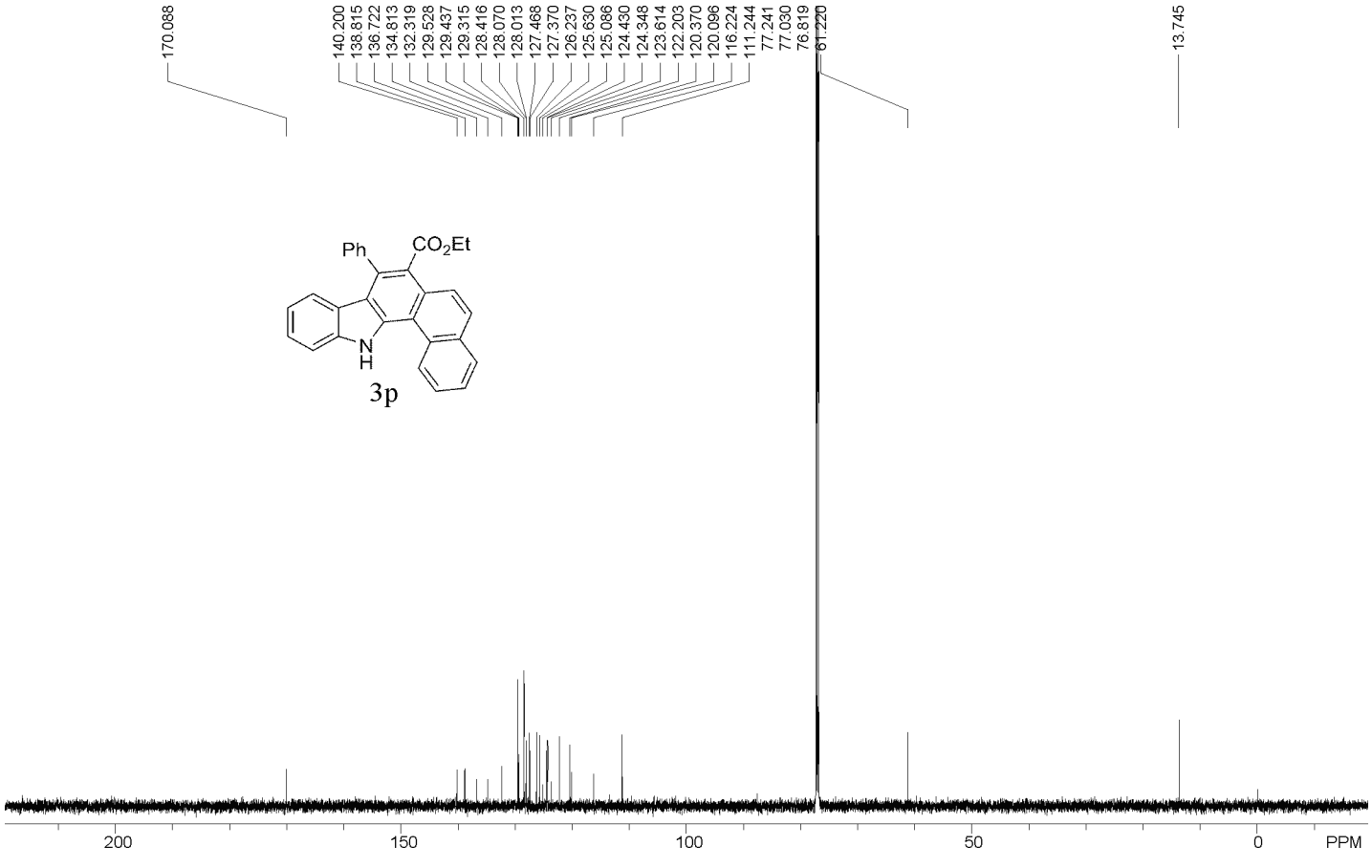
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125.086
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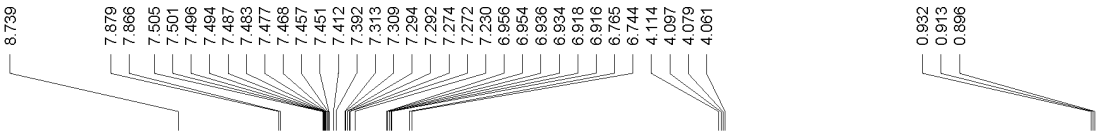
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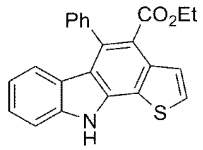
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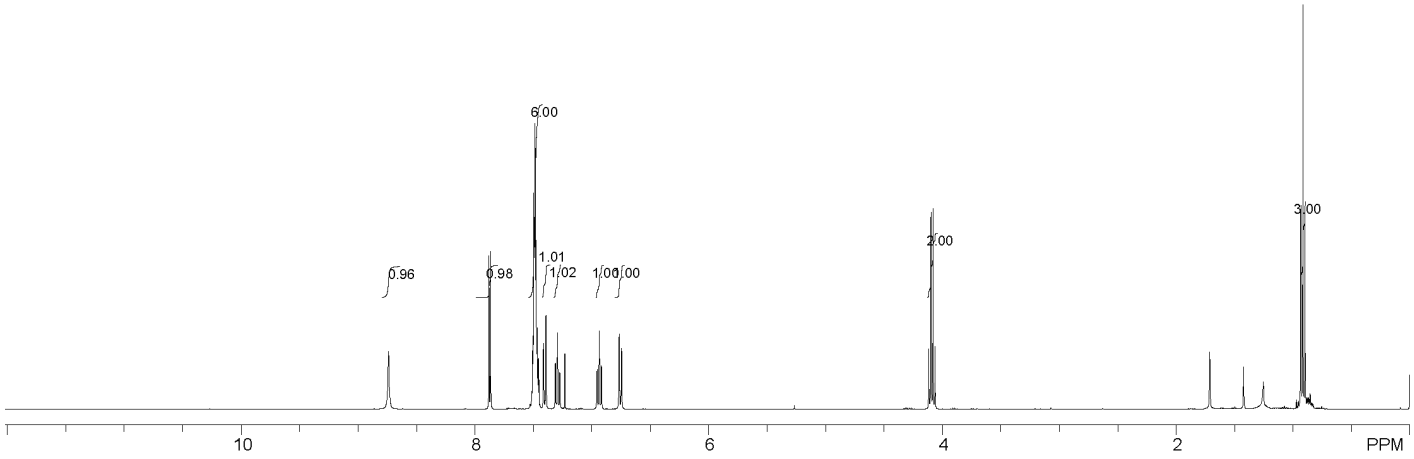
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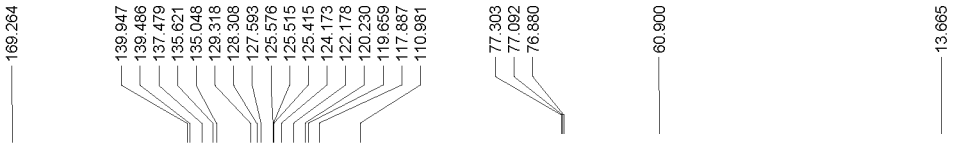
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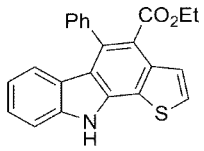
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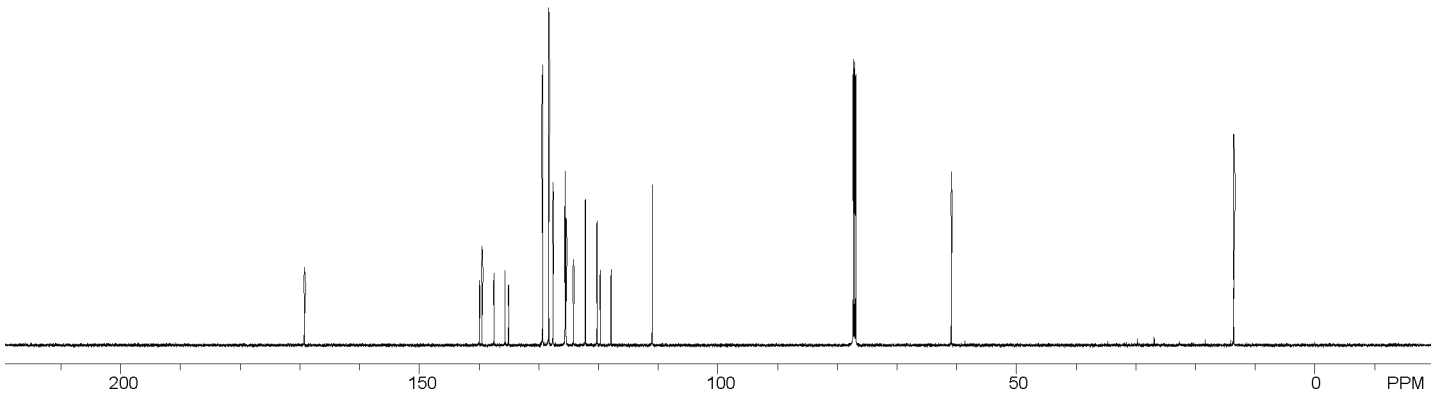
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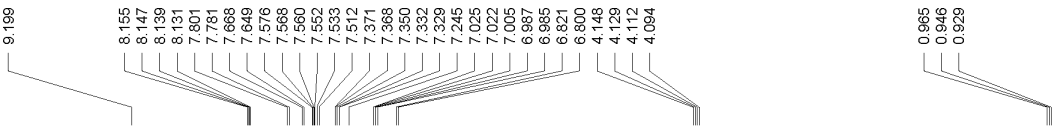
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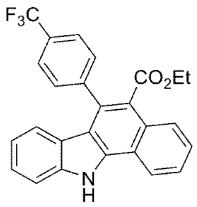
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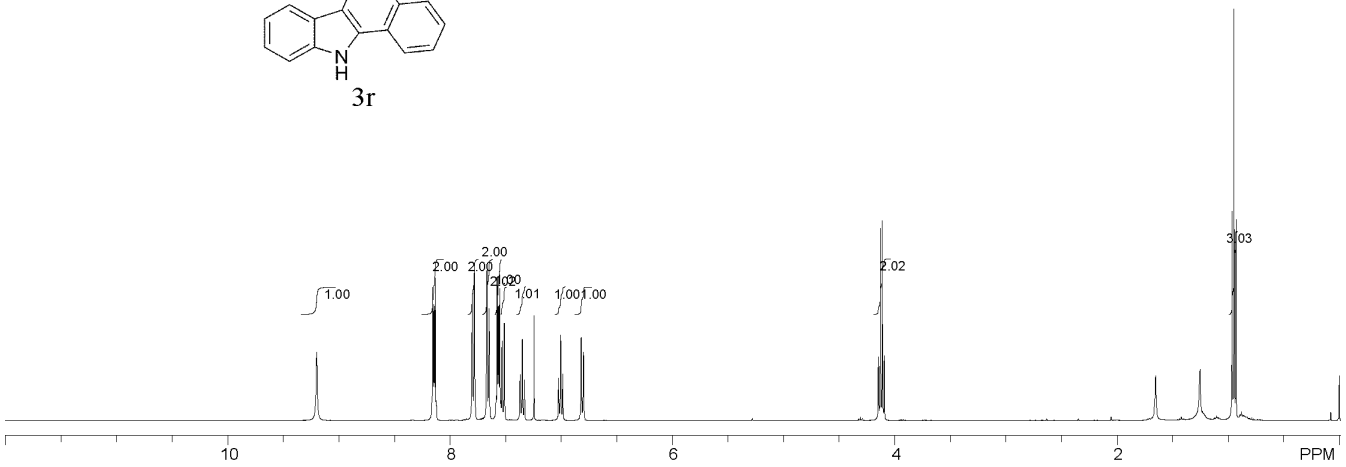
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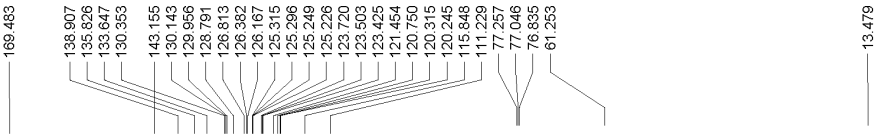
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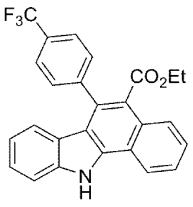
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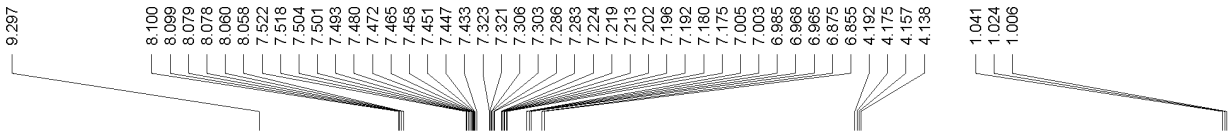
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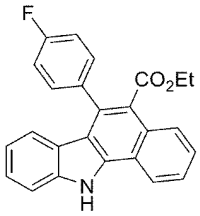
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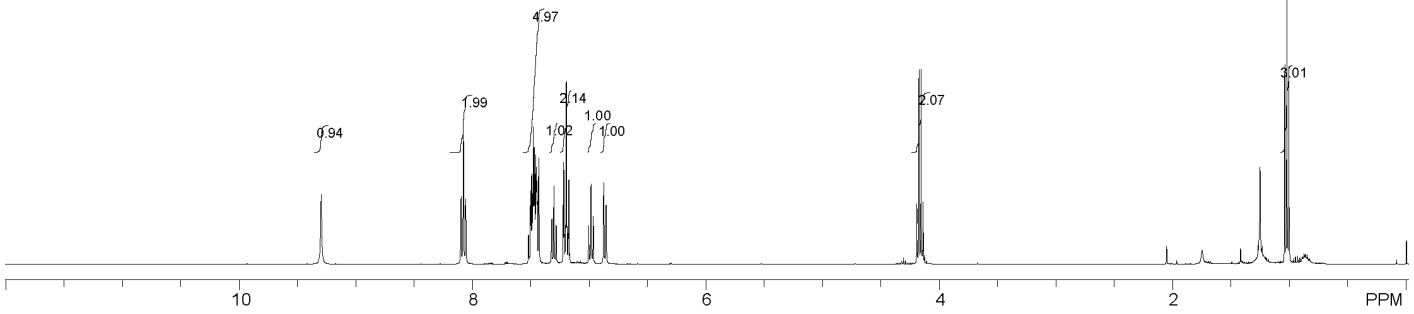
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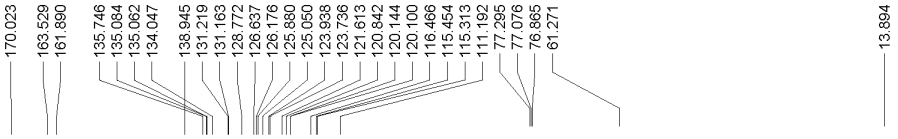
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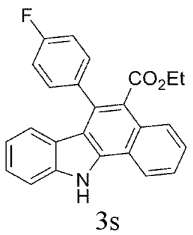
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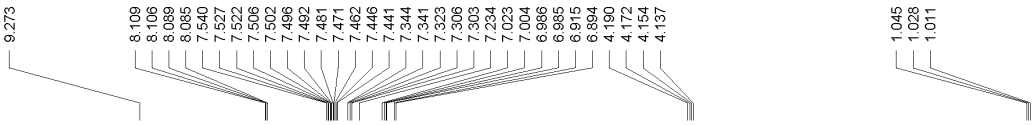
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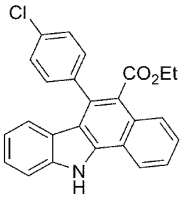
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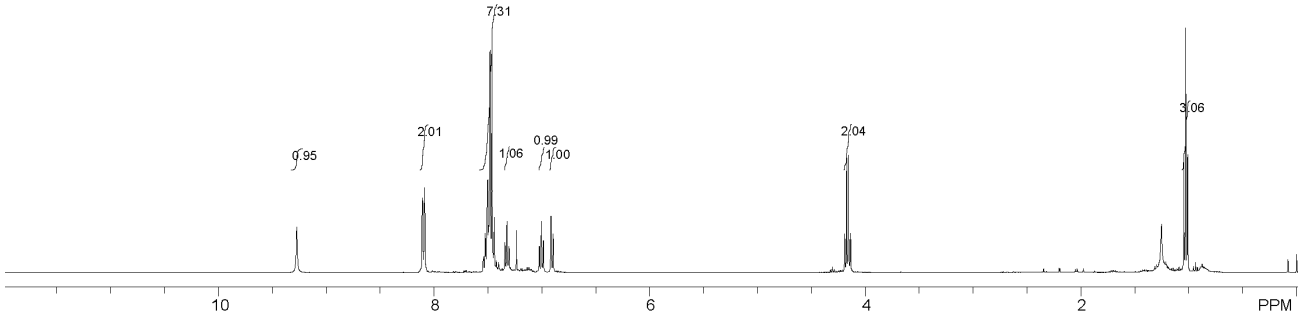
3t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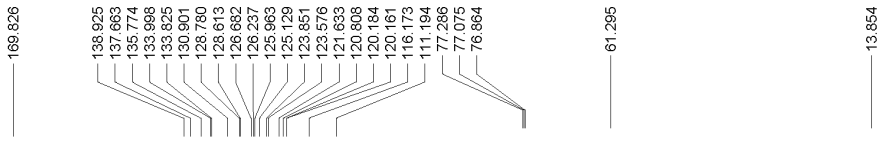
PPM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125.129
123.851
123.576
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120.161
116.173
111.194
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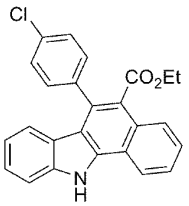
77.075
76.864
61.295
13.854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N
H

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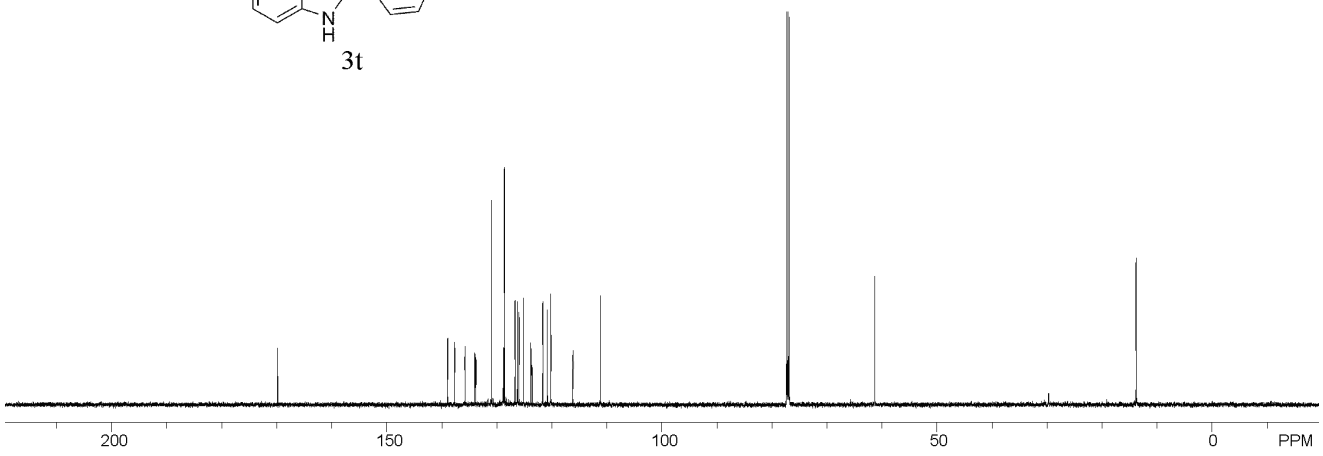
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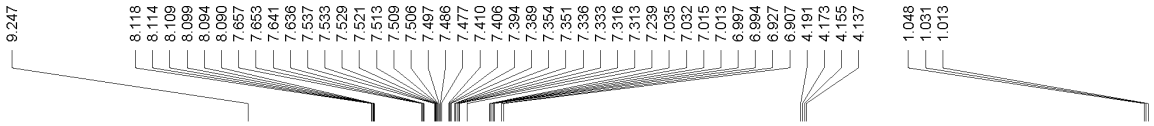
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8.090
7.657
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7.641
7.636
7.537
7.533
7.529
7.521
7.513
7.509
7.506
7.497
7.486
7.477
7.410
7.406
7.394
7.389
7.354
7.351
7.336
7.333
7.316
7.313
7.239
7.035
7.032
7.015
7.013
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4.173
4.155
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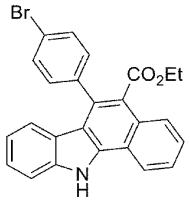
1.031
1.013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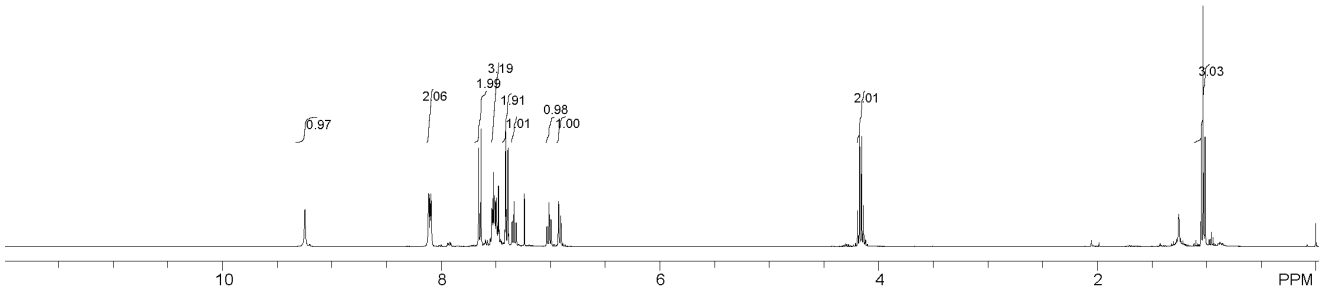
CO2Et
N
H

3u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3.03
10
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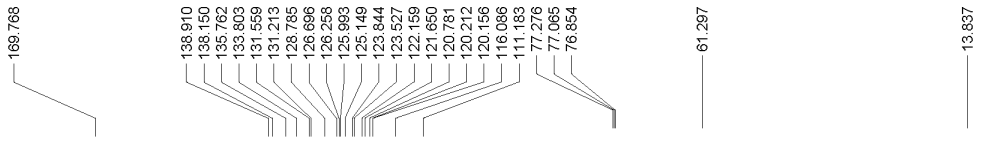
2
PPM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128.785
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126.258
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123.844
123.527
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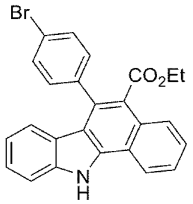
76.854
61.297
13.837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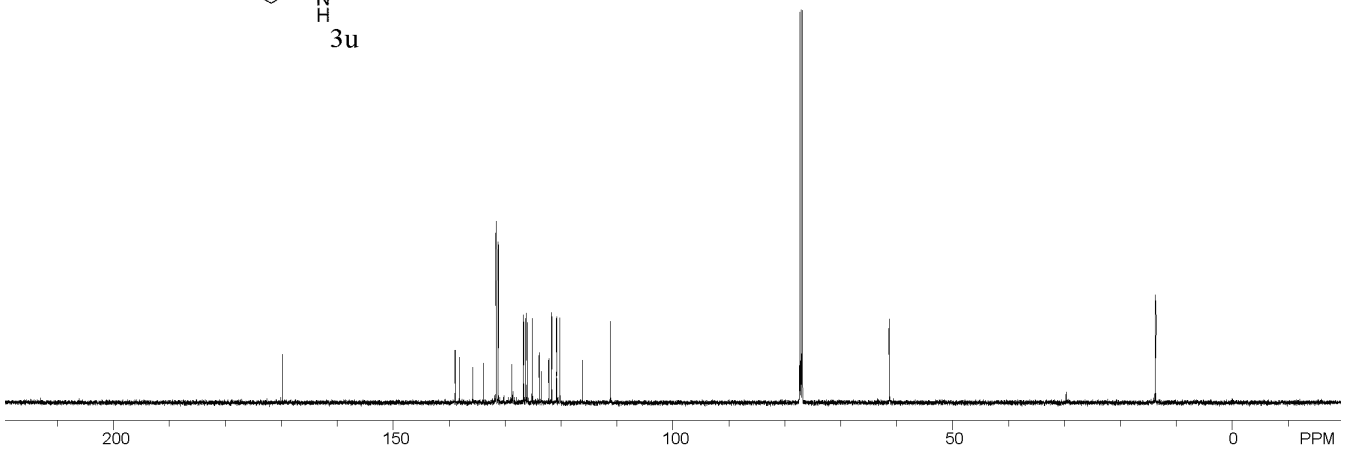
3u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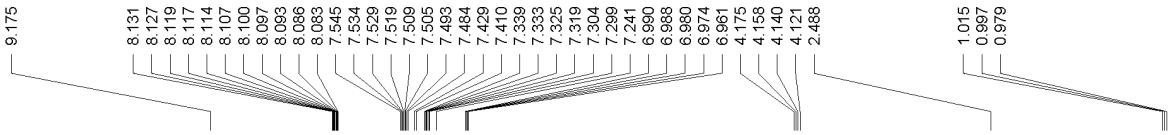
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8.114
8.107
8.100
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8.093
8.086
8.083
7.545
7.534
7.529
7.519
7.509
7.505
7.493
7.484
7.429
7.410
7.339
7.333
7.325
7.319
7.304
7.299
7.241
6.990
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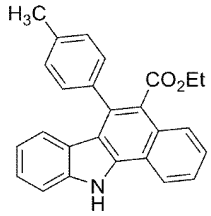
4.121
2.488
1.015
0.997
0.979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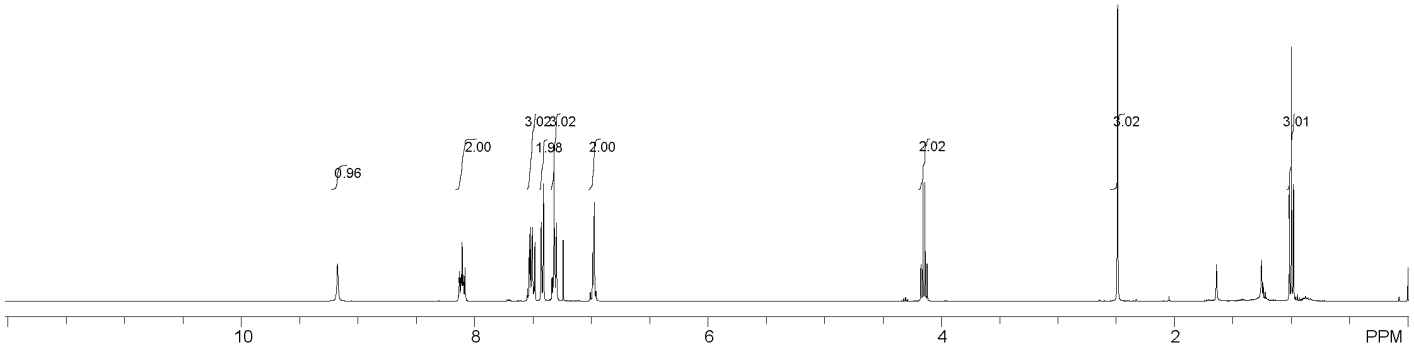
CO2Et
N
H

3v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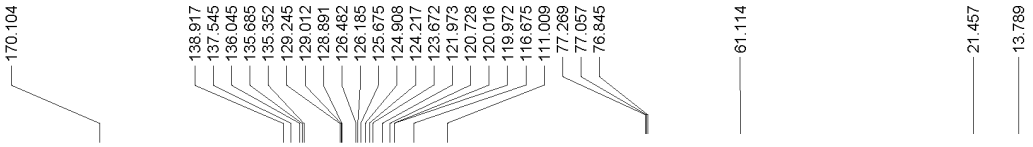
2.00
2.02
3.02
3.01
10
8
6
4
2
PPM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136.045
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135.352
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129.012
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126.185
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124.217
123.672
121.973
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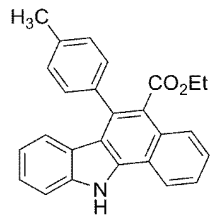
76.845
61.114
21.457
13.789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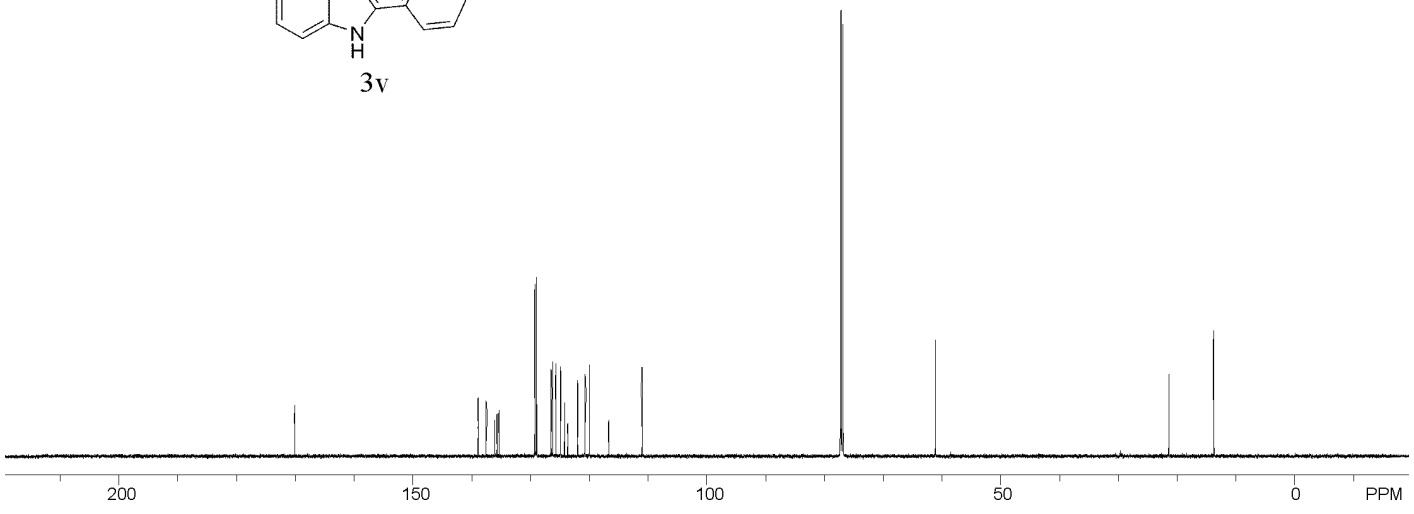
CO2Et
N
H

3v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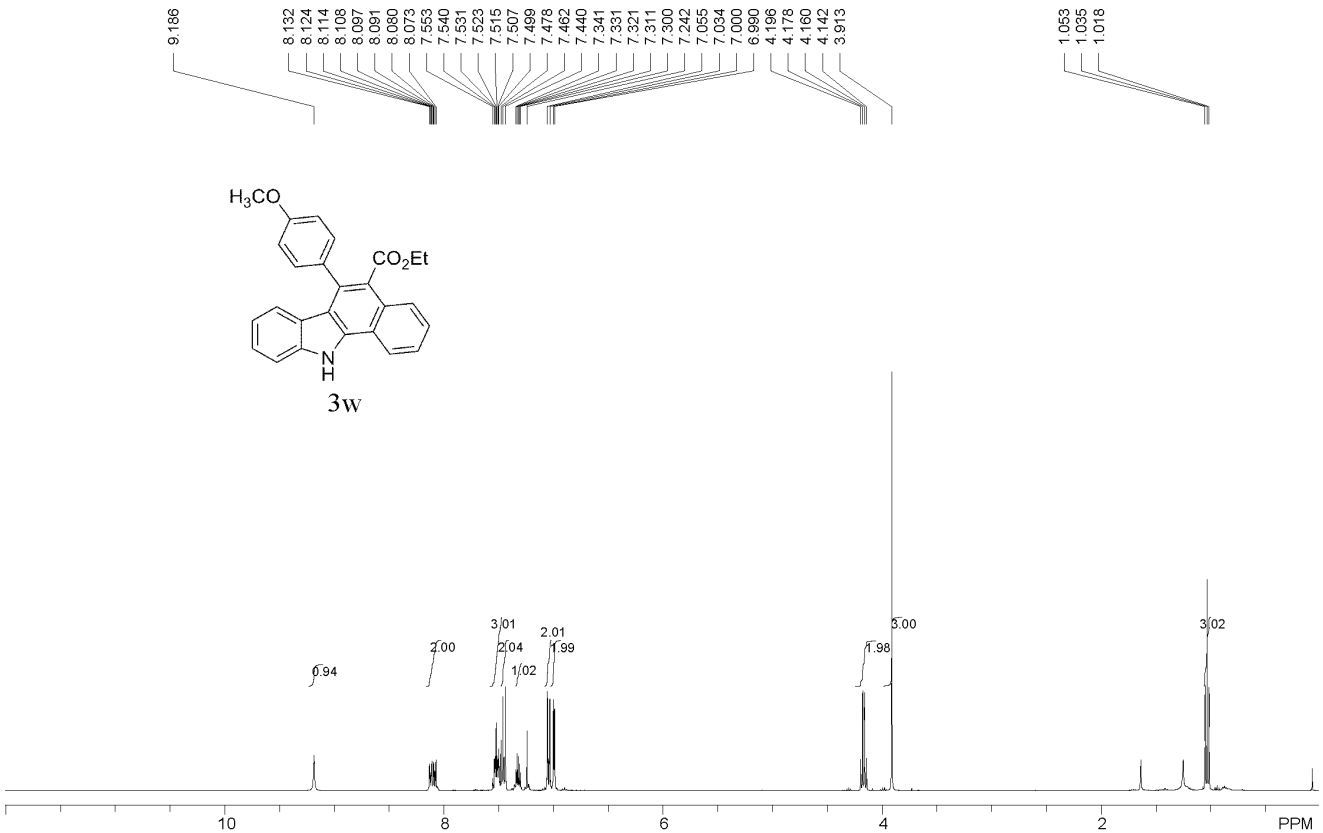
100
50
0
PPM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8.097
8.091
8.080
8.073
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7.540
7.531
7.523
7.515
7.507
7.499
7.478
7.462
7.440
7.341
7.331
7.321
7.311
7.300
7.242
7.055
7.034
7.000
6.990
4.196
4.178
4.160
4.142
3.913
1.053
1.035
1.018
H3CO
CO2Et
N
H
3w
0.94
2.00
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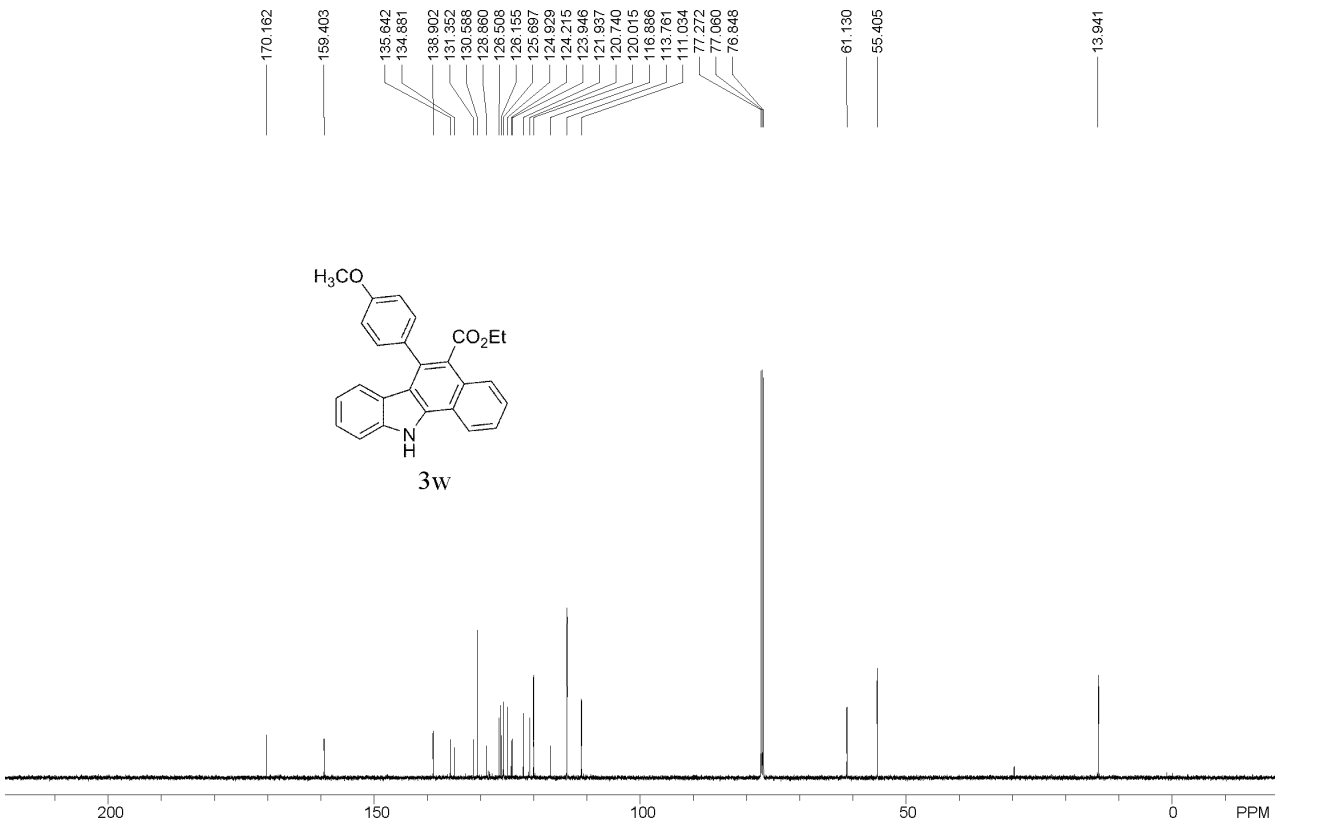
2.04
1.02
2.01
1.99
1.98
3.00
3.02
10
8
6
4
2
PPM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130.588
128.860
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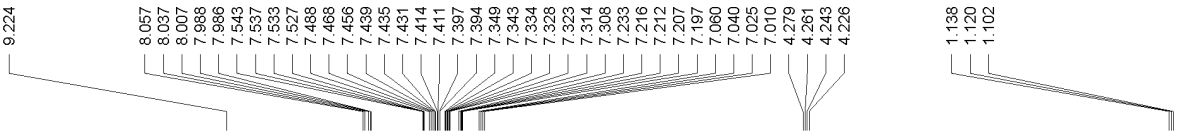
126.155
125.697
124.929
124.215
123.846
121.937
120.740
120.015
116.886
113.761
111.034
77.272
77.060
76.848
61.130
55.405
13.941
H3CO
CO2Et
N
H
3w
200
150
100
50
0
PPM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8.007
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7.537
7.533
7.527
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7.468
7.456
7.439
7.435
7.431
7.414
7.411
7.397
7.394
7.349
7.343
7.334
7.328
7.323
7.314
7.308
7.233
7.216
7.212
7.207
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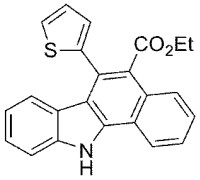
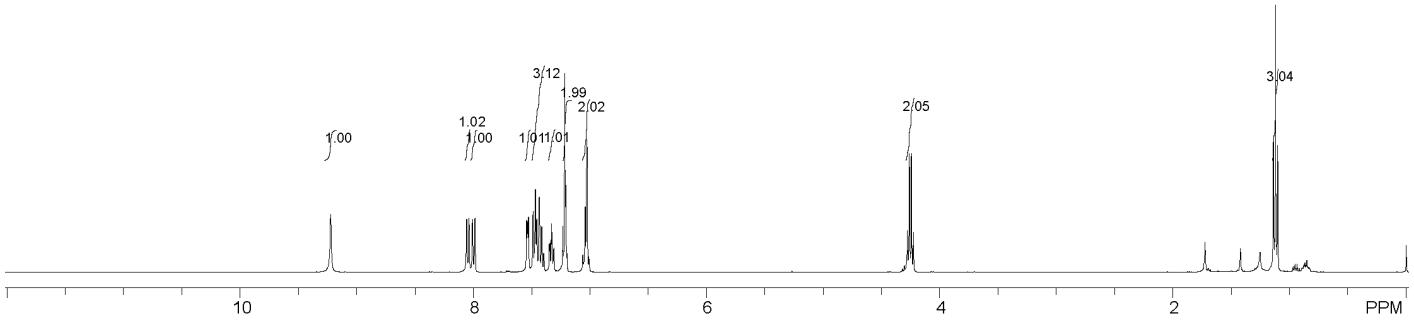
1.102


S
CO2Et
N
H

3x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1.01
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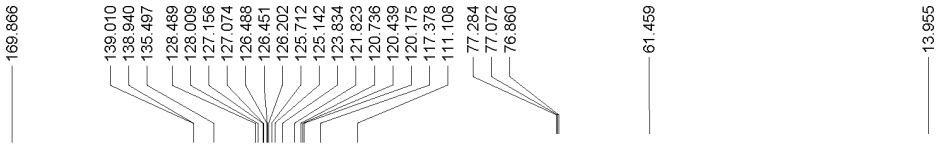
2.02
2.05
3.04
10
8
6
4
2
PPM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125.712
125.142
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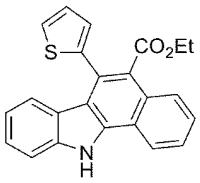
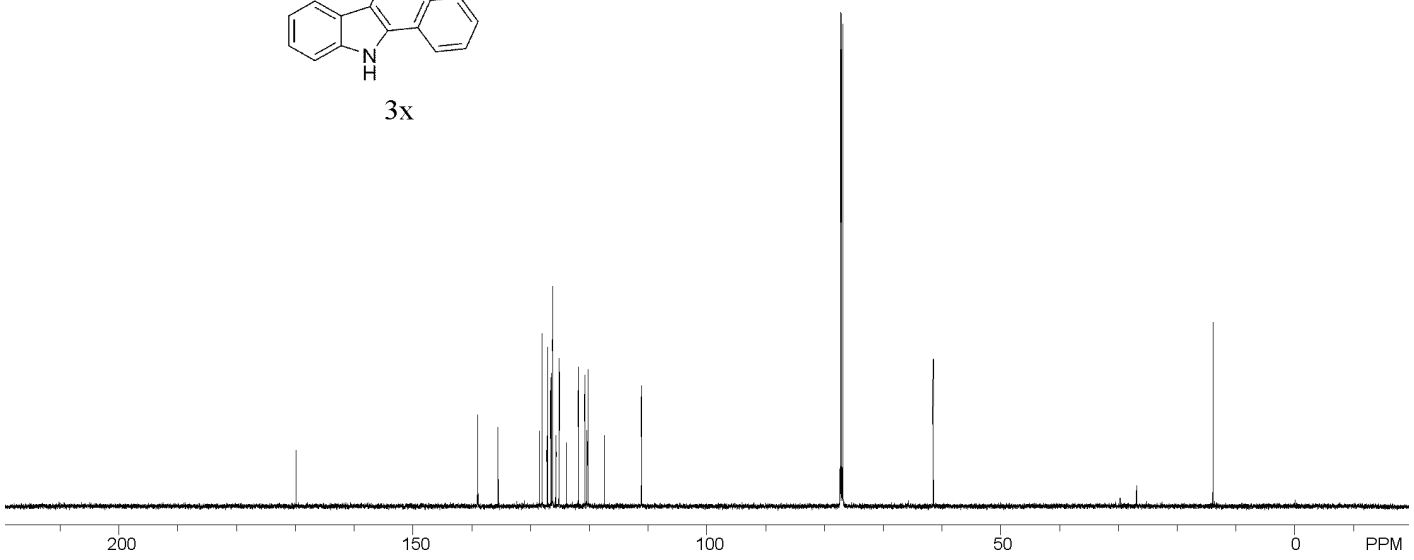
77.284
77.072
76.860
61.459
13.955


S
CO2Et
N
H

3x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100
50
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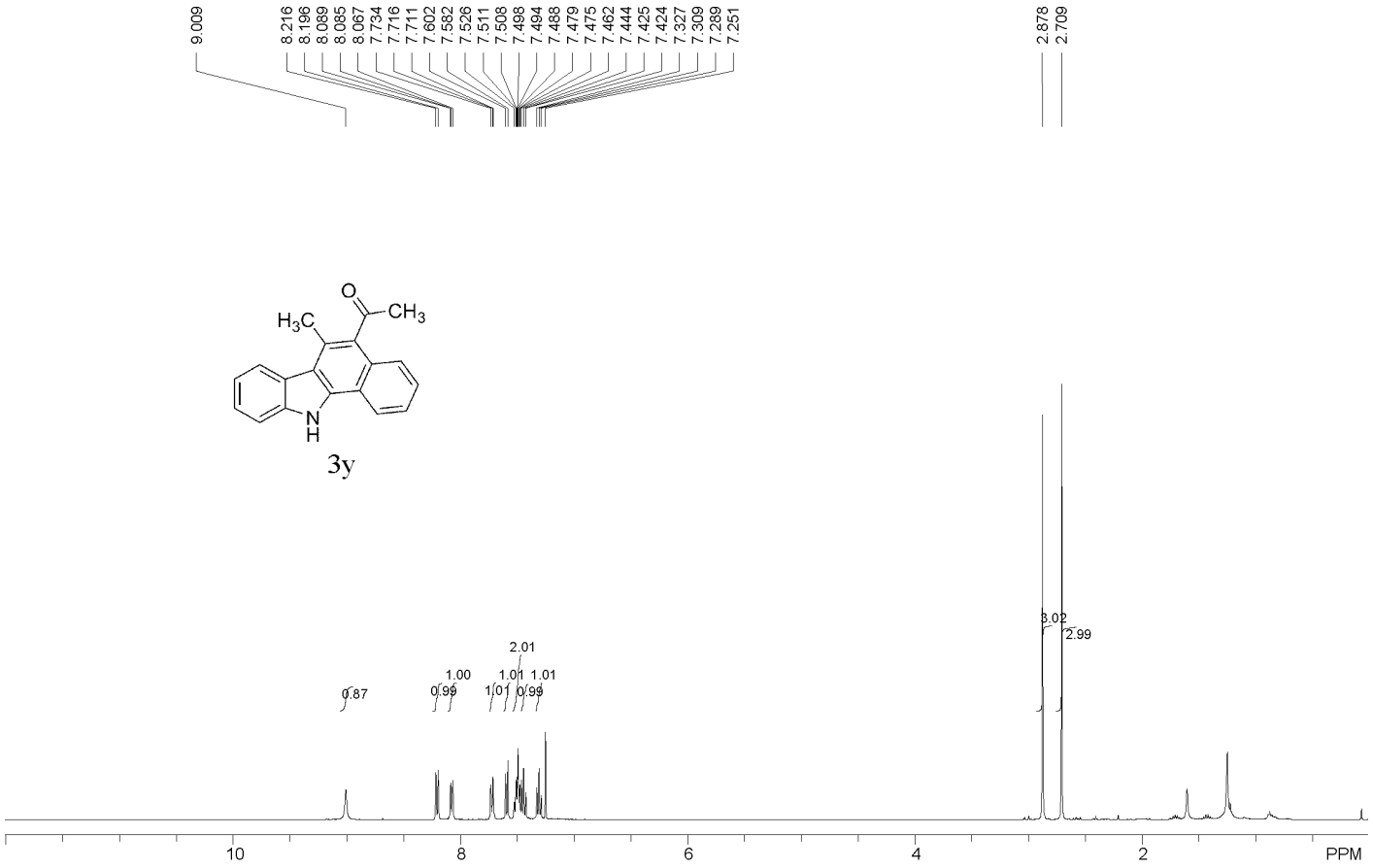
PPM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7.602
7.582
7.526
7.511
7.508
7.498
7.494
7.488
7.479
7.475
7.462
7.444
7.425
7.424
7.327
7.309
7.289
7.251
2.878
2.709
O
CH3
H3C
N
H
3y
0.87
1.00
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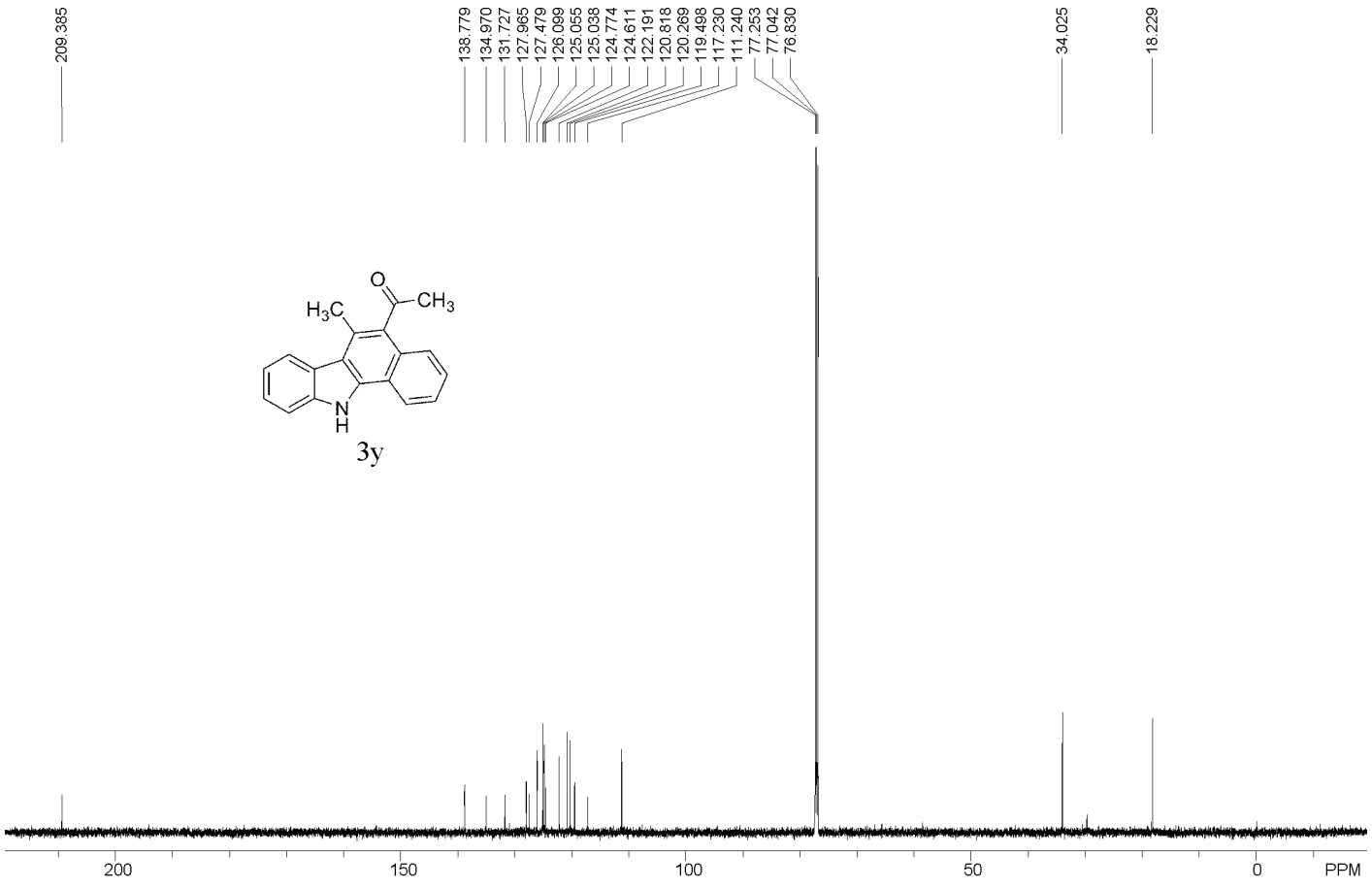
1.01
1.01
1.01
0.99
3.02
2.99
10
8
6
4
2
PPM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127.479
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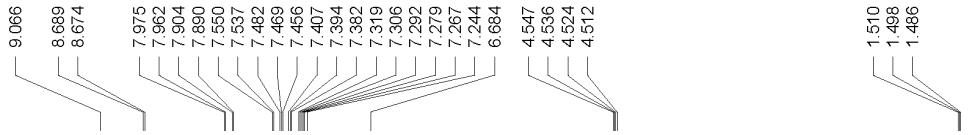
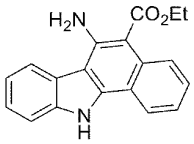
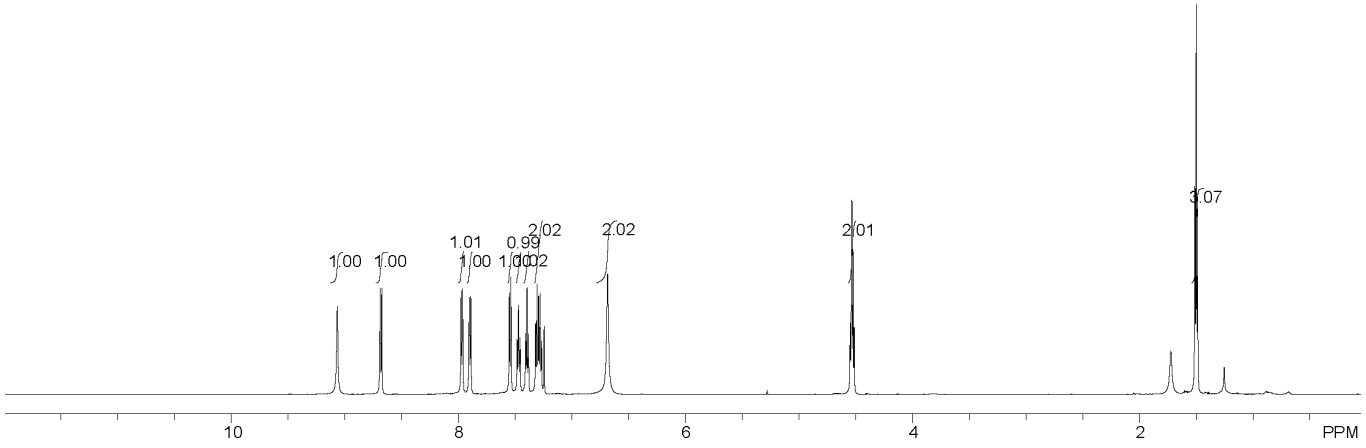
124.774
124.611
122.191
120.818
120.269
119.498
117.230
111.240
77.253
77.042
76.830
34.025
18.229
O
CH3
H3C
N
H
3y
200
150
100
50
0
PPM

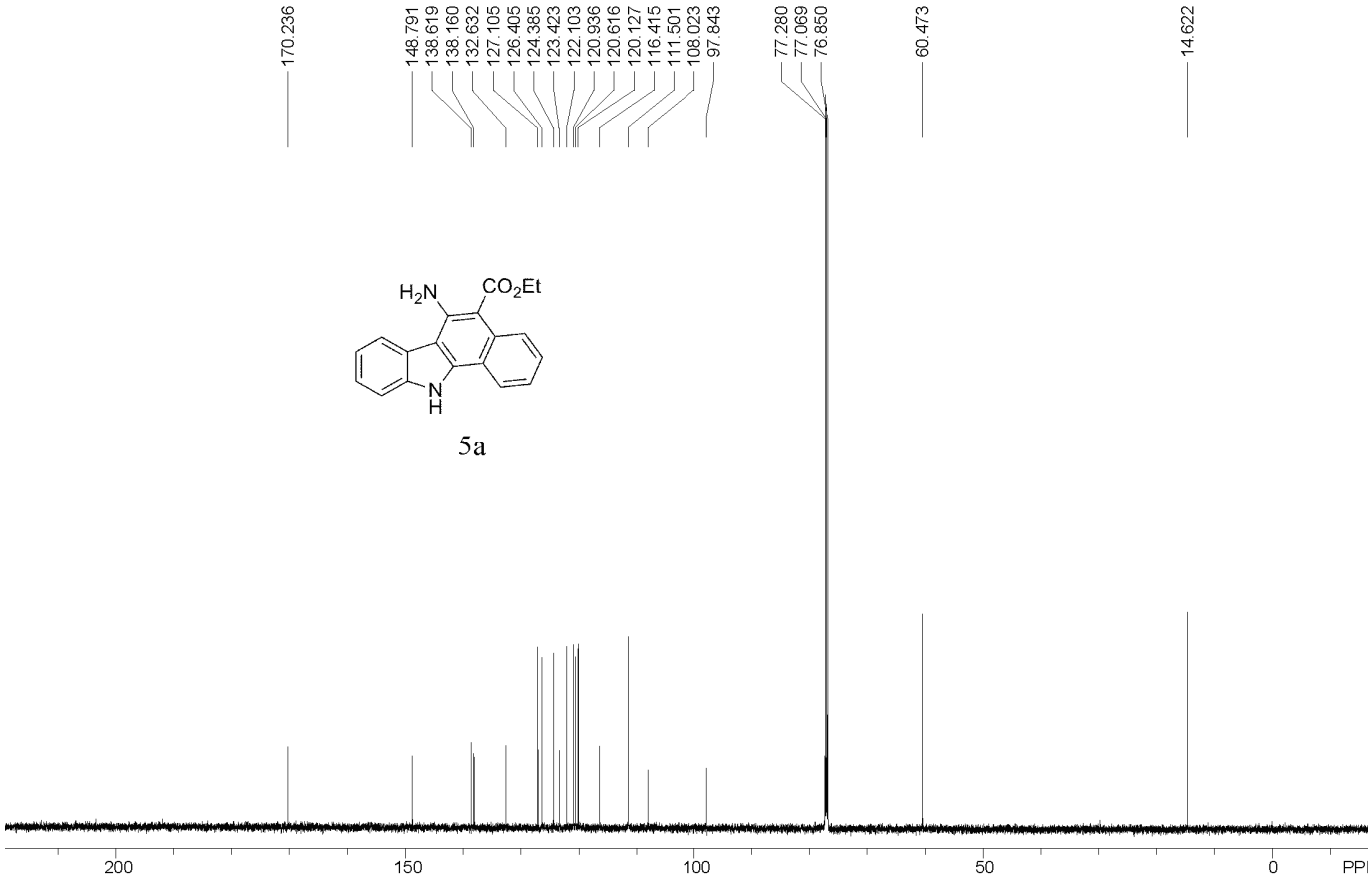
V. Copies of ^{1}H and ^{13}C NMR spectra of 5a-5h



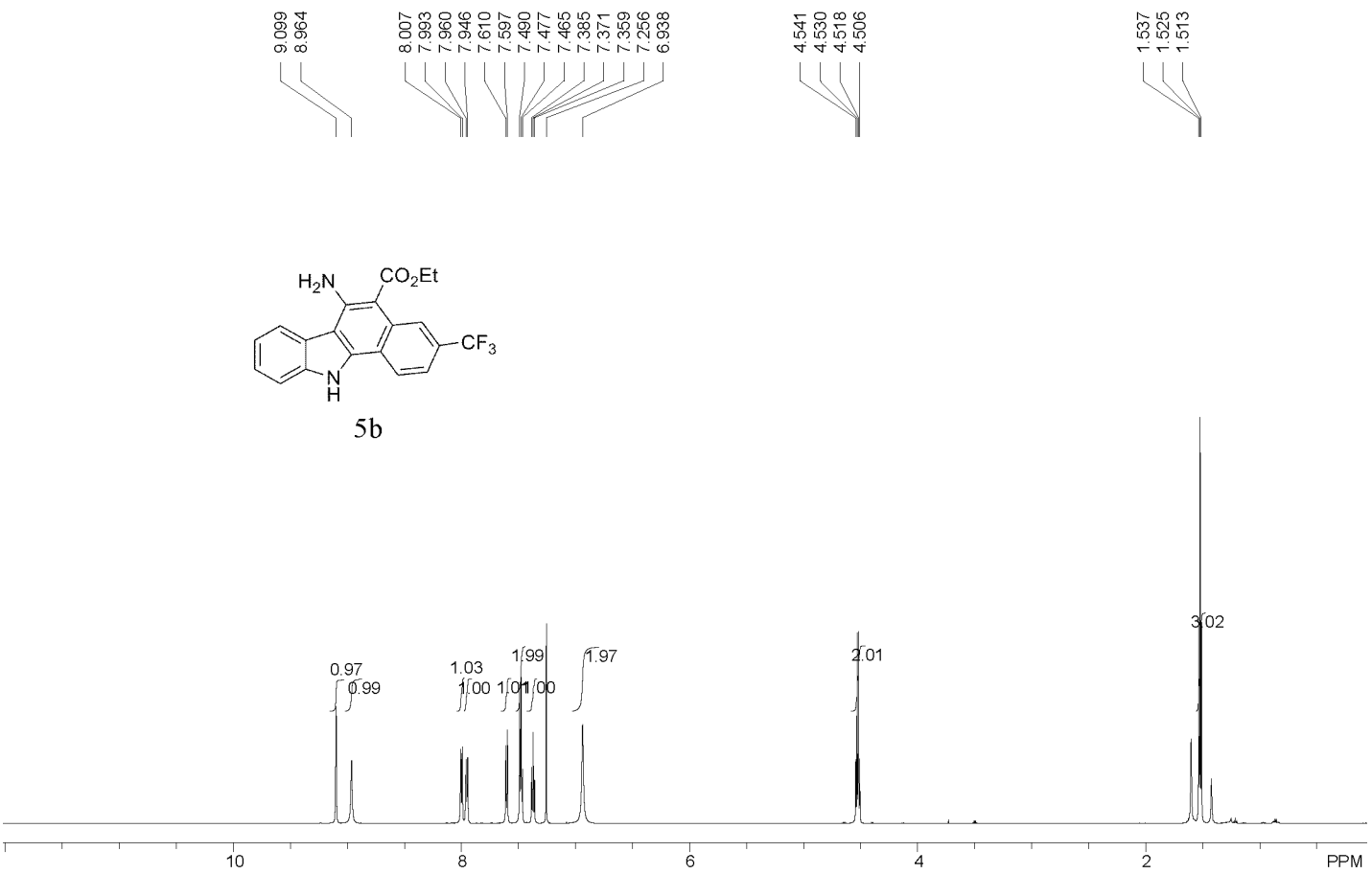


5a





5a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7.597
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7.477
7.465
7.385
7.371
7.359
7.256
6.938
4.541
4.530
4.518
4.506
1.537
1.525
1.513
H2N
CO2Et
CF3
N
H
5b
0.97
0.99
1.03
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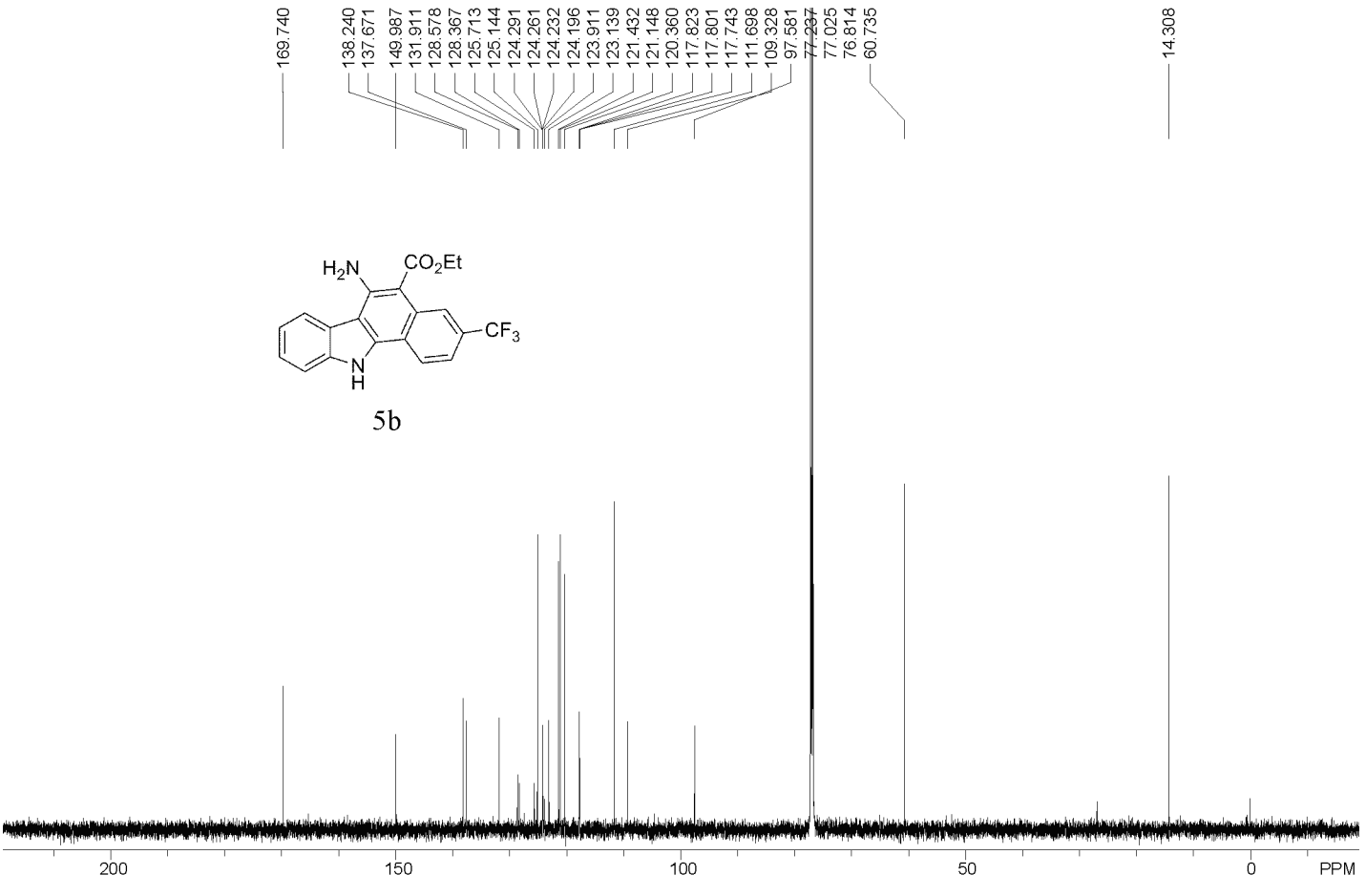
1.99
1.01
1.00
1.97
2.01
3.02
10
8
6
4
2
PPM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125.713
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124.291
124.261
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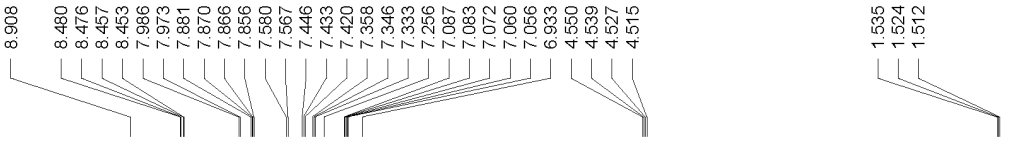
124.196
123.911
123.139
121.432
121.148
120.360
117.823
117.801
117.743
111.698
109.328
97.581
77.297
77.025
76.814
60.735
14.308
H2N
CO2Et
CF3
N
H
5b
200
150
100
50
0
PPM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7.881
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7.856
7.580
7.567
7.446
7.433
7.420
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7.346
7.333
7.256
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4.527
4.515
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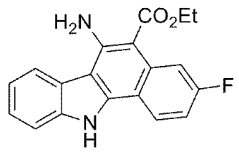
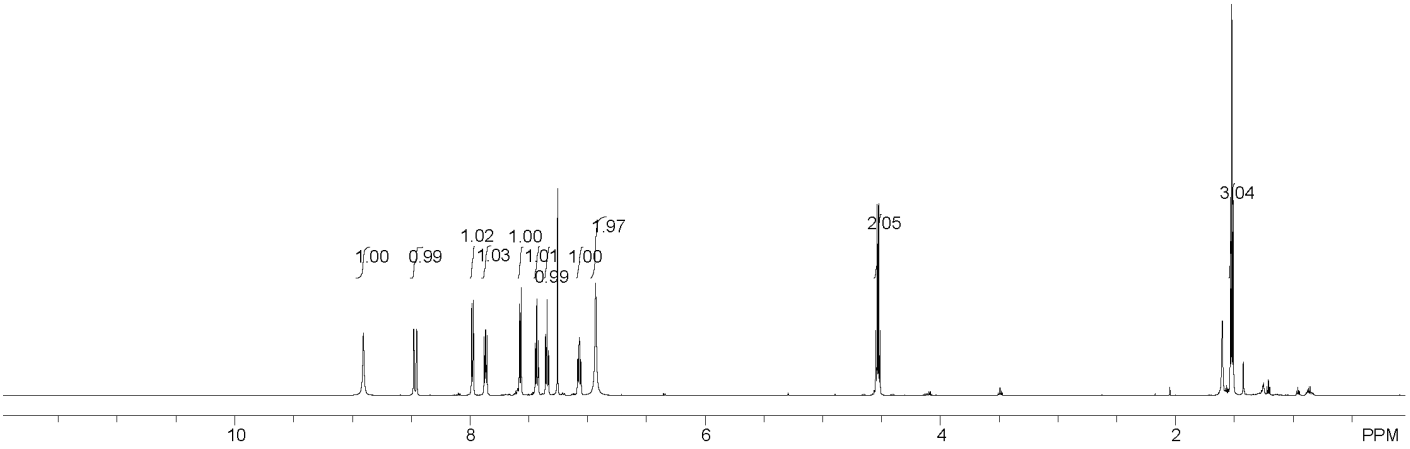
1.524
1.512


H2N
CO2Et
F
N
H

5c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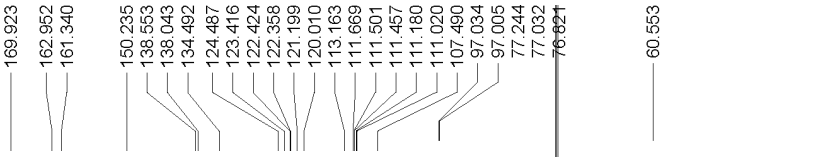
1.01
0.99
1.00
1.97
2.05
3.04
10
8
6
4
2
PPM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123.416
122.424
122.358
121.199
120.010
113.163
111.669
111.501
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111.020
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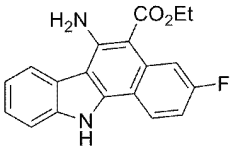
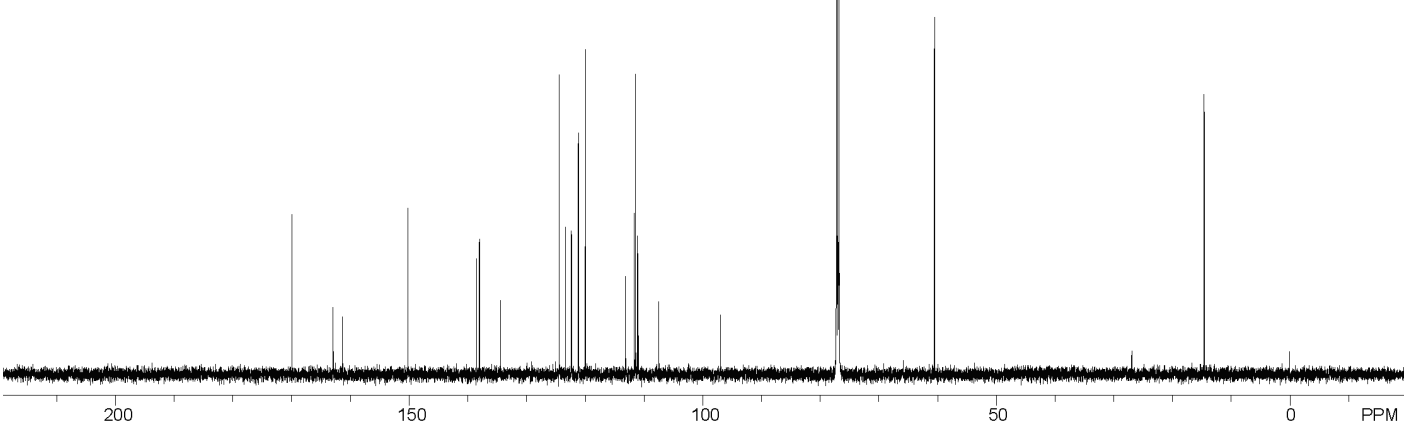
97.034
97.005
77.244
77.032
76.821
60.553
14.578


H2N
CO2Et
F
N
H

5c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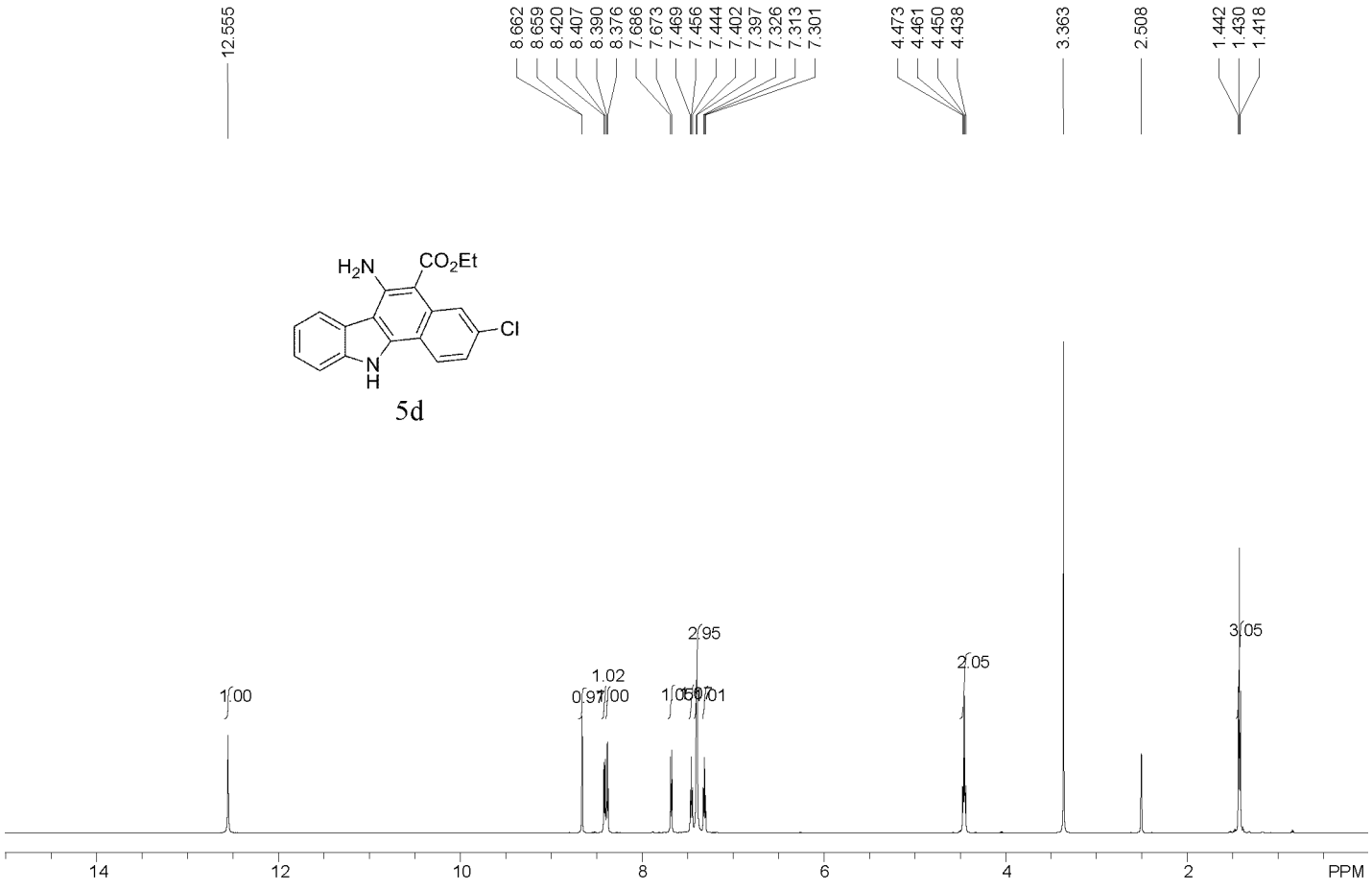
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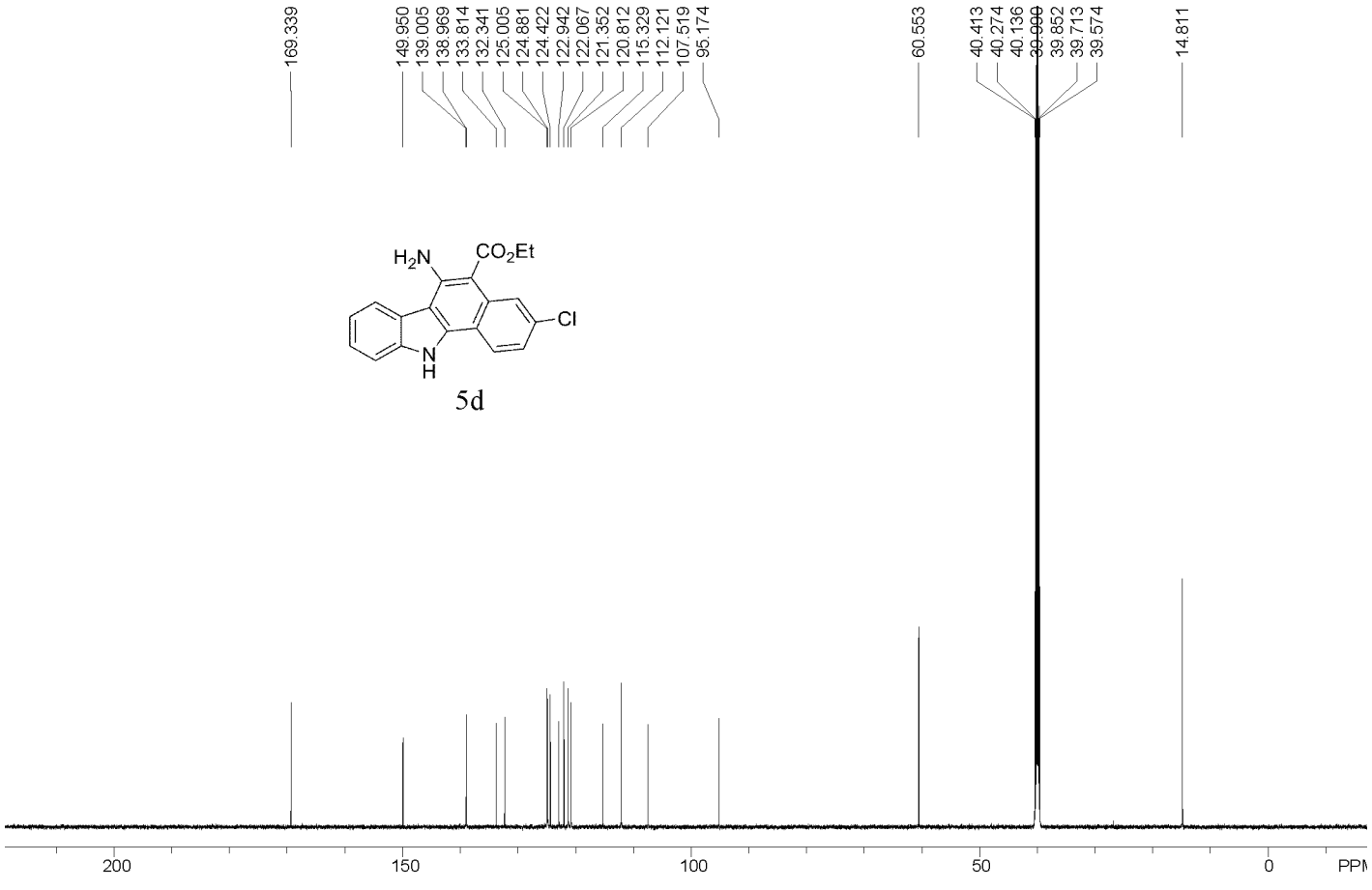
7.402
7.397
7.326
7.313
7.301
4.473
4.461
4.450
4.438
3.363
2.508
1.442
1.430
1.418
H2N
CO2Et
Cl
N
H
5d
1.00
1.02
0.97
1.00
2.95
1.05
1.01
2.05
3.05
14
12
10
8
6
4
2
PPM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132.341
125.005
124.881
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121.352
120.812
115.329
112.121
107.519
95.174
60.553
40.413
40.274
40.136
39.852
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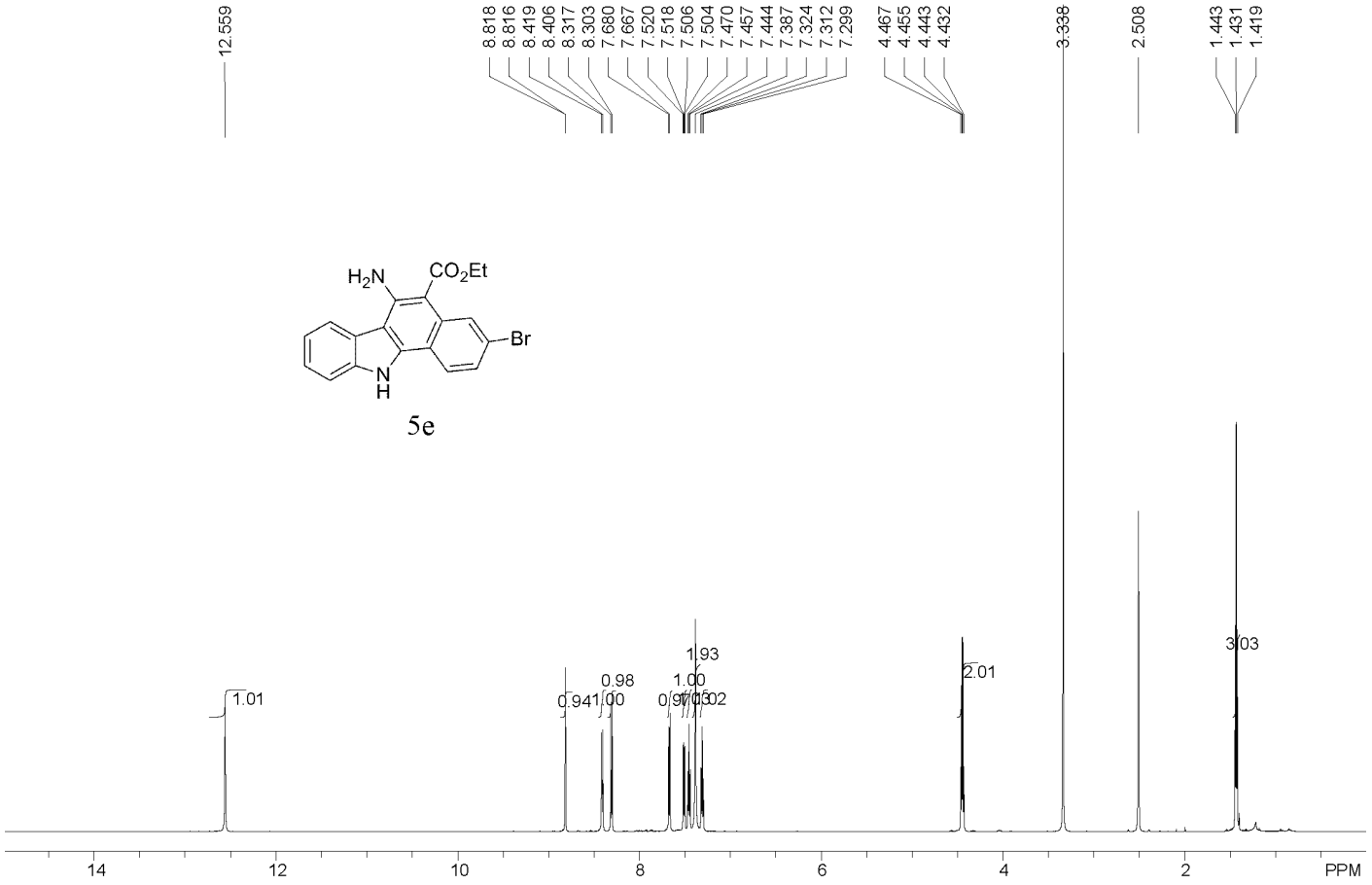
14.811
H2N
CO2Et
Cl
N
H
5d
200
150
100
50
0
PPM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7.504
7.470
7.457
7.444
7.387
7.324
7.312
7.299
4.467
4.455
4.443
4.432
3.338
2.508
1.443
1.431
1.419
H2N
CO2Et
Br
N
H
5e
1.01
0.94
1.00
0.98
1.00
1.93
1.02
2.01
3.03
14
12
10
8
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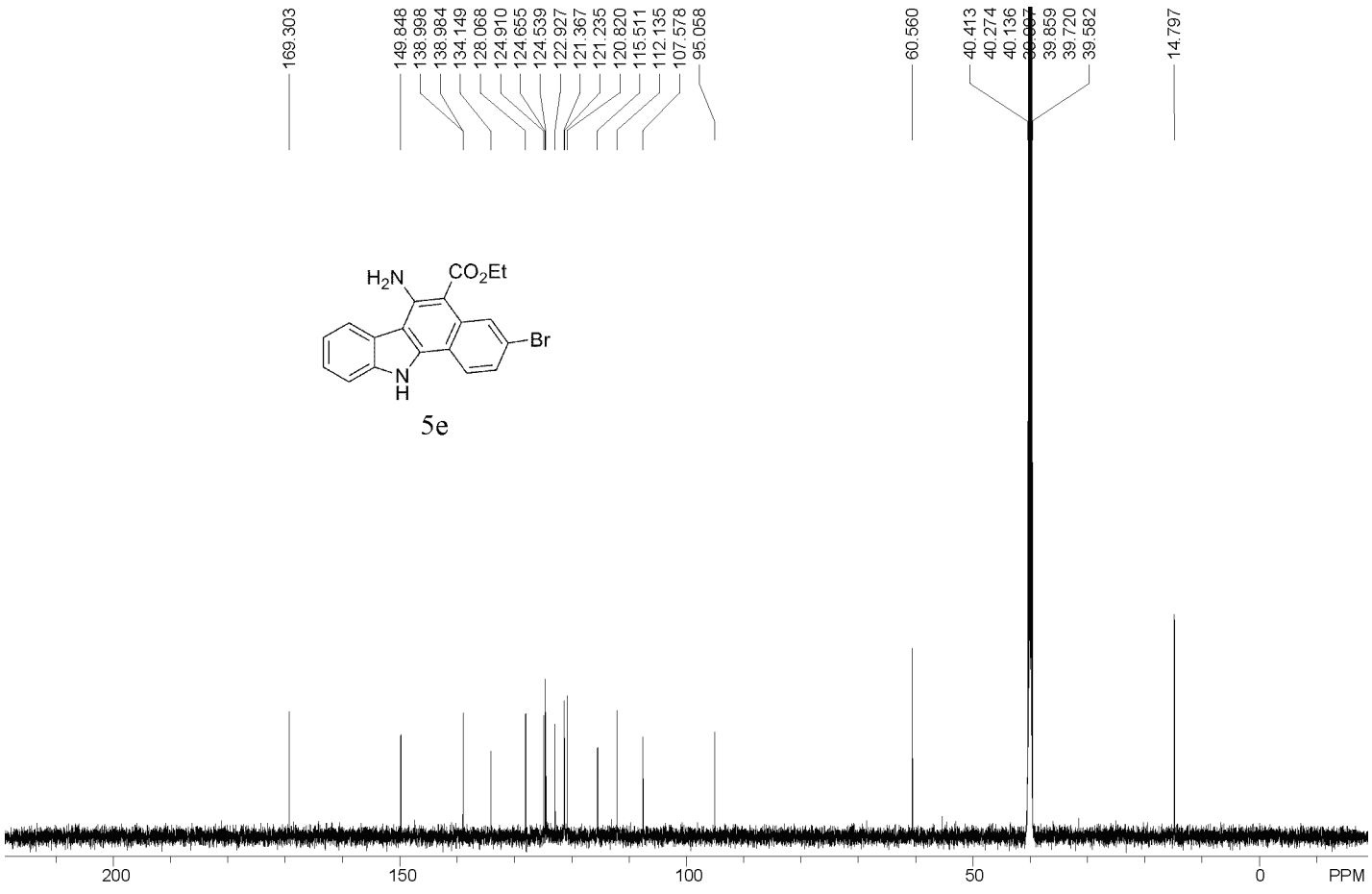
4
2
PPM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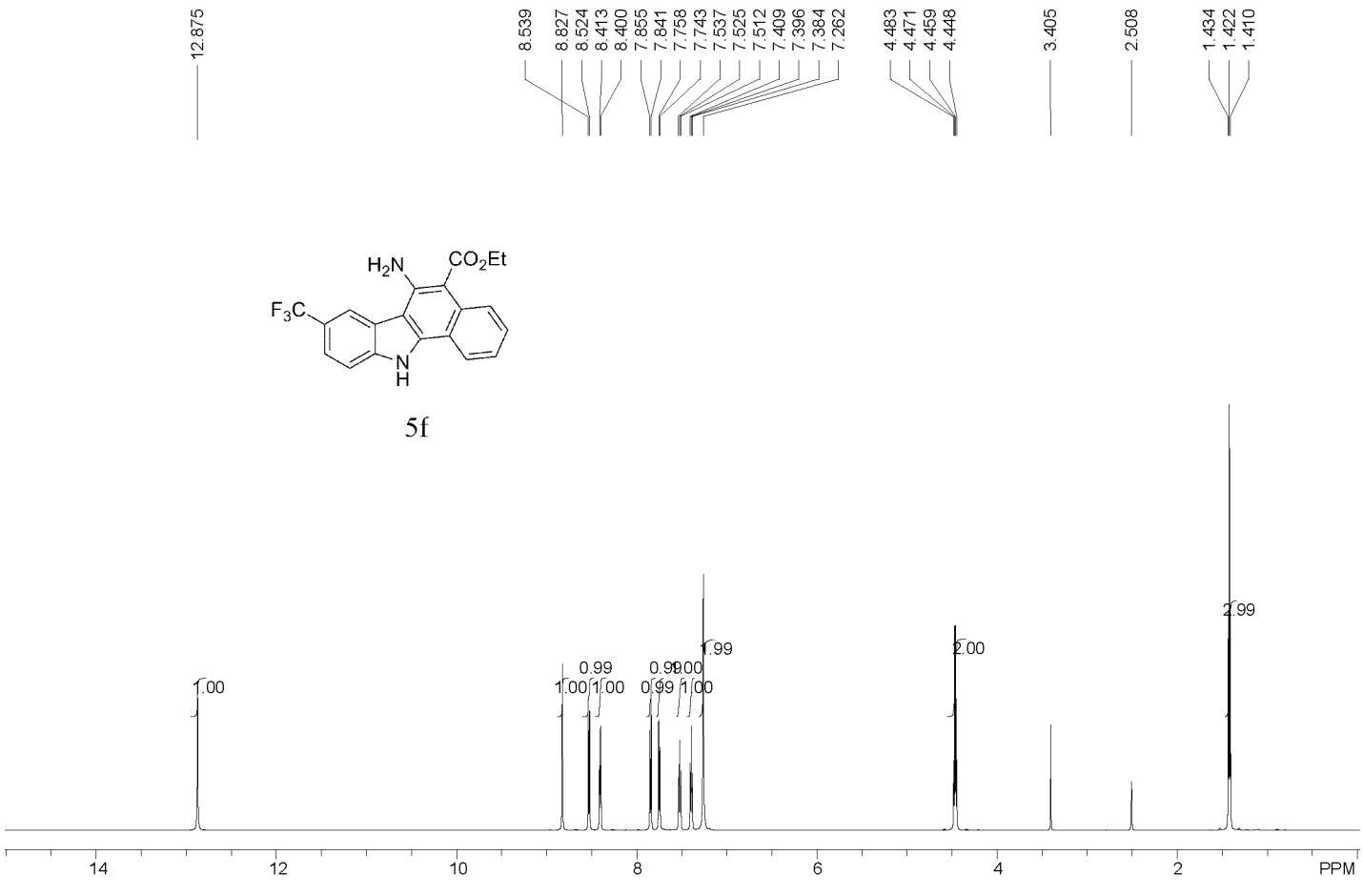
121.235
120.820
115.511
112.135
107.578
95.058
60.560
40.413
40.274
40.136
39.859
39.720
39.582
14.797
H2N
CO2Et
Br
N
H
5e
200
150
100
50
0
PPM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8.400
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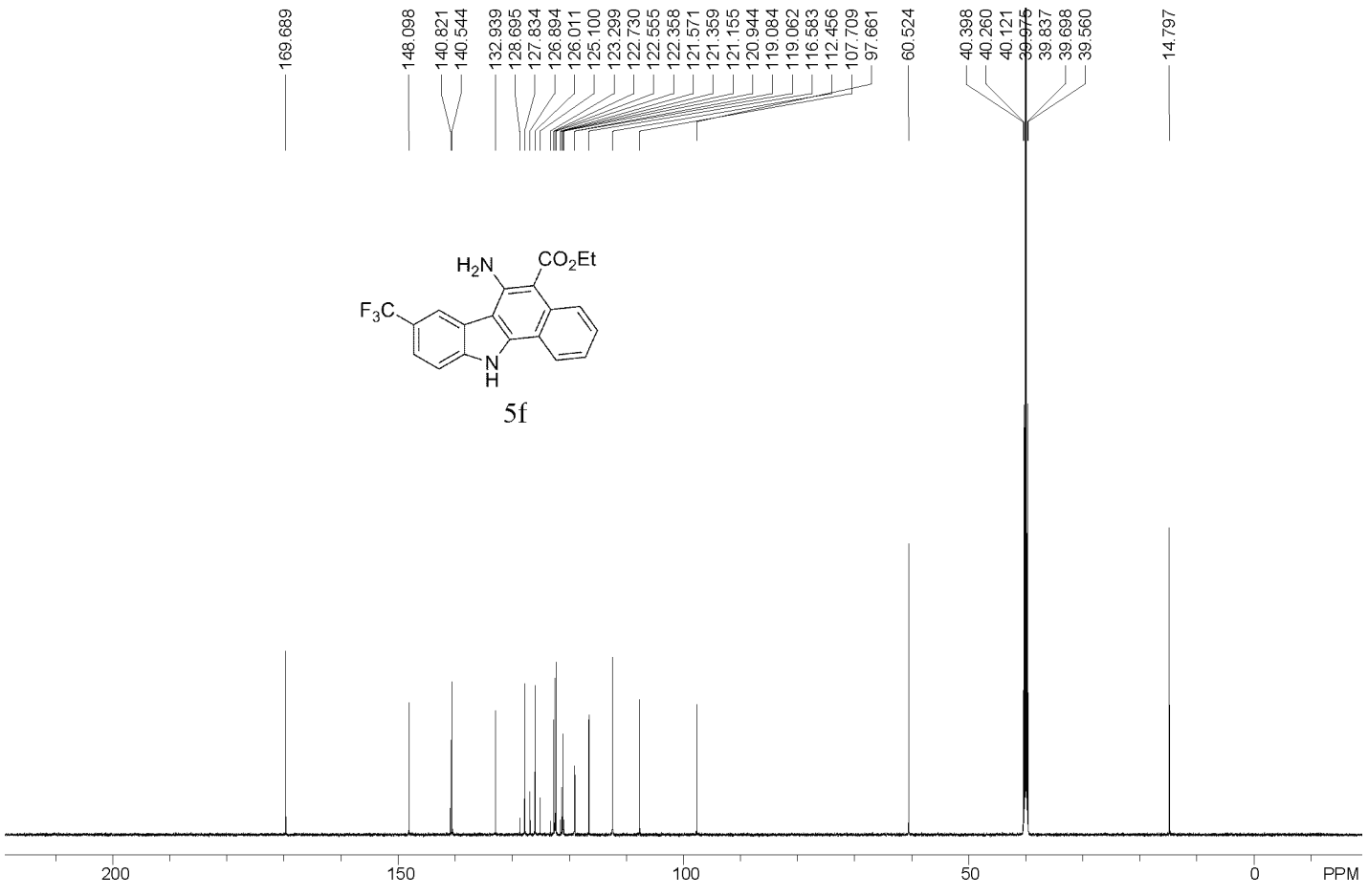
7.512
7.409
7.396
7.384
7.262
4.483
4.471
4.459
4.448
3.405
2.508
1.434
1.422
1.410
H2N
CO2Et
F3C
N
H
1.00
0.99
1.00
1.00
0.99
0.98
1.00
1.00
1.99
2.00
2.99
14
12
10
8
6
4
2
PPM

5f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122.358
121.571
121.359
121.155
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119.062
116.583
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107.709
97.661
60.524
40.398
40.260
40.121
39.975
39.837
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14.797
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CO2Et
F3C
N
H
200
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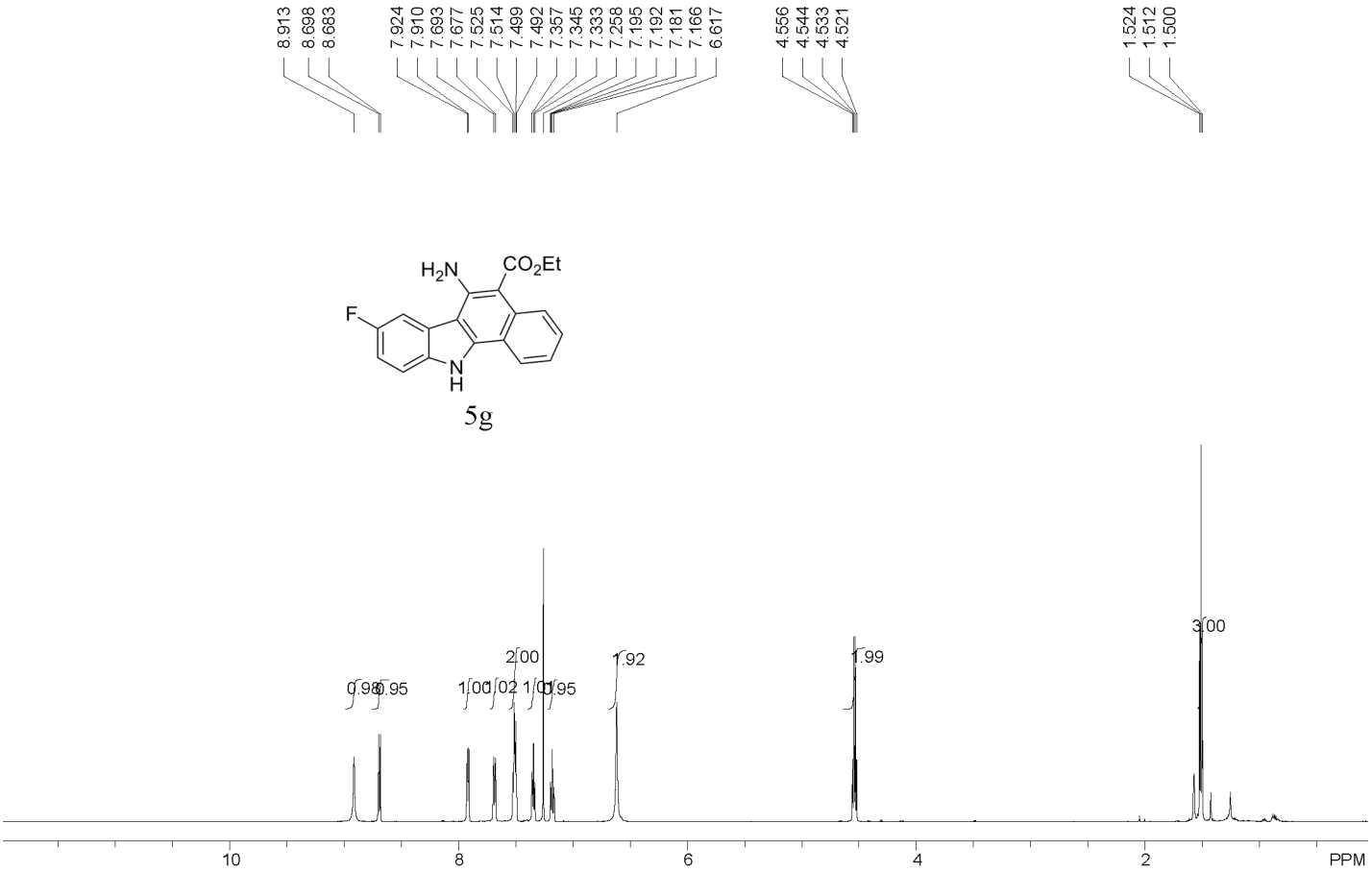
100
50
0
PPM

5f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7.345
7.333
7.258
7.195
7.192
7.181
7.166
6.617
4.556
4.544
4.533
4.521
1.524
1.512
1.500
H2N
CO2Et
F
N
H
5g
0.98
0.95
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2.00
1.01
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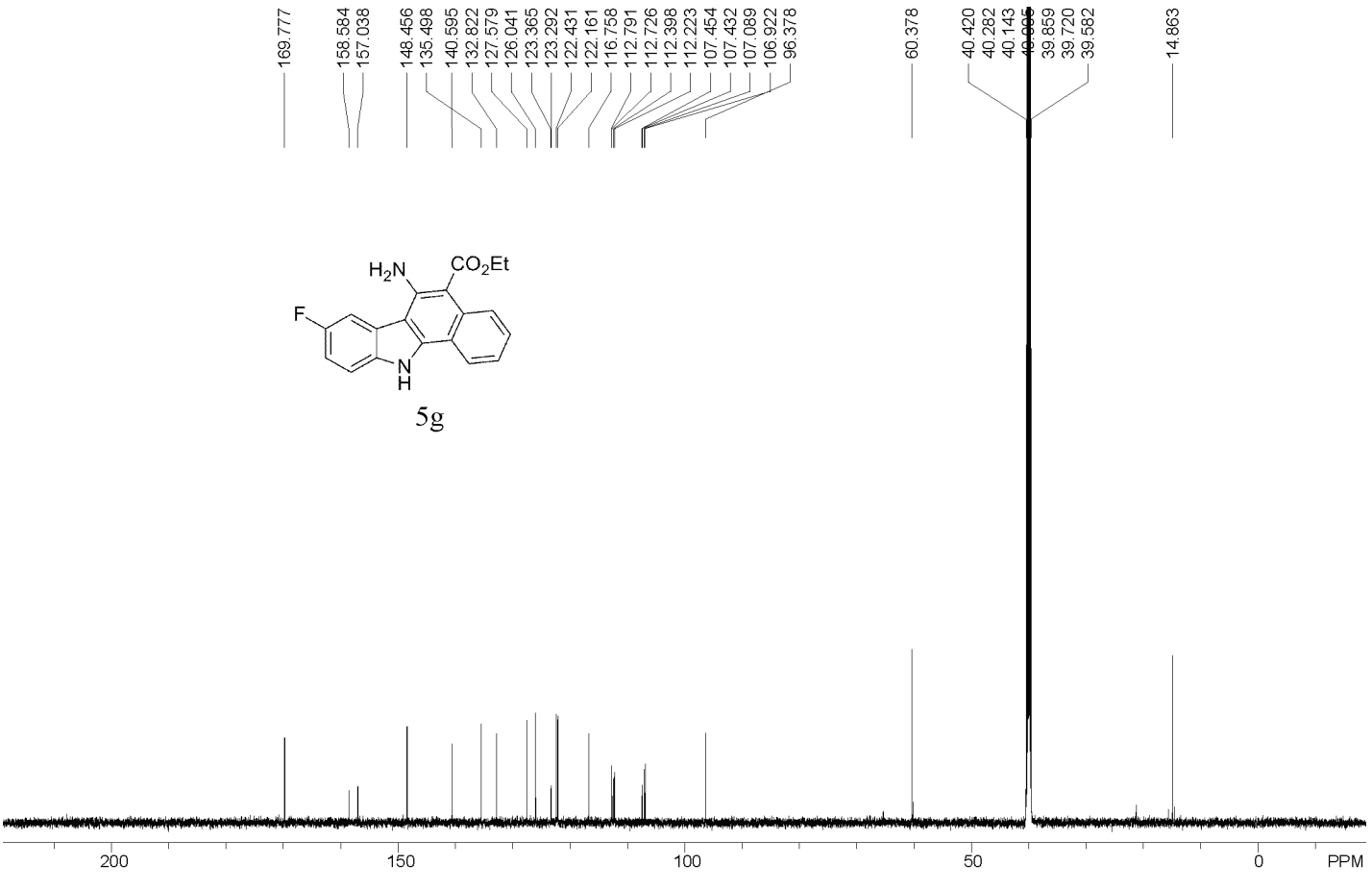
1.99
3.00
10
8
6
4
2
PPM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112.791
112.726
112.398
112.223
107.454
107.432
107.089
106.922
96.378
60.378
40.420
40.282
40.143
39.859
39.720
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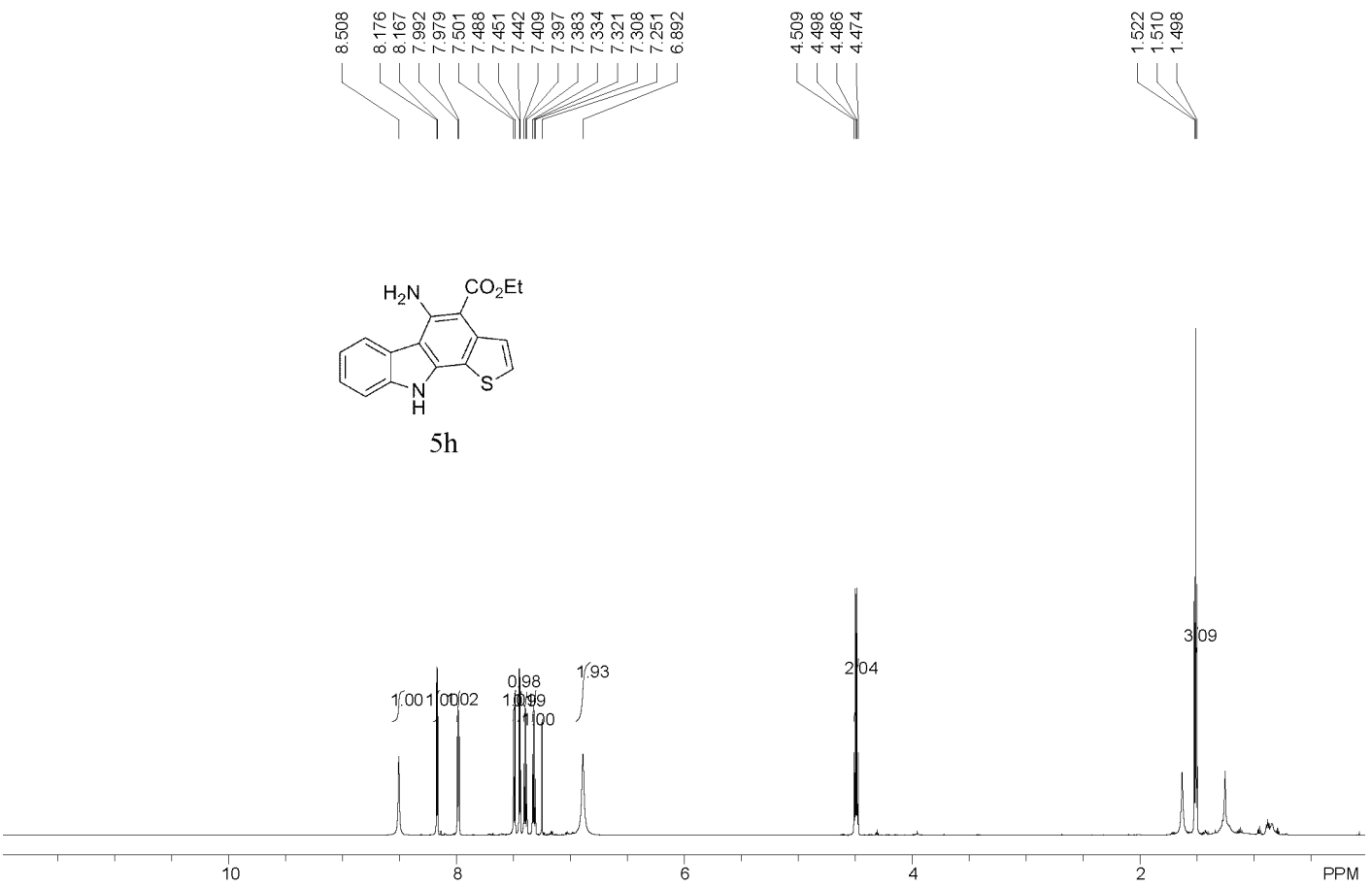
14.863
H2N
CO2Et
F
N
H
5g
200
150
100
50
0
PPM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7.488
7.451
7.442
7.409
7.397
7.383
7.334
7.321
7.308
7.251
6.892
4.509
4.498
4.486
4.474
1.522
1.510
1.498
H2N
CO2Et
N
H
S
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1.00
1.00
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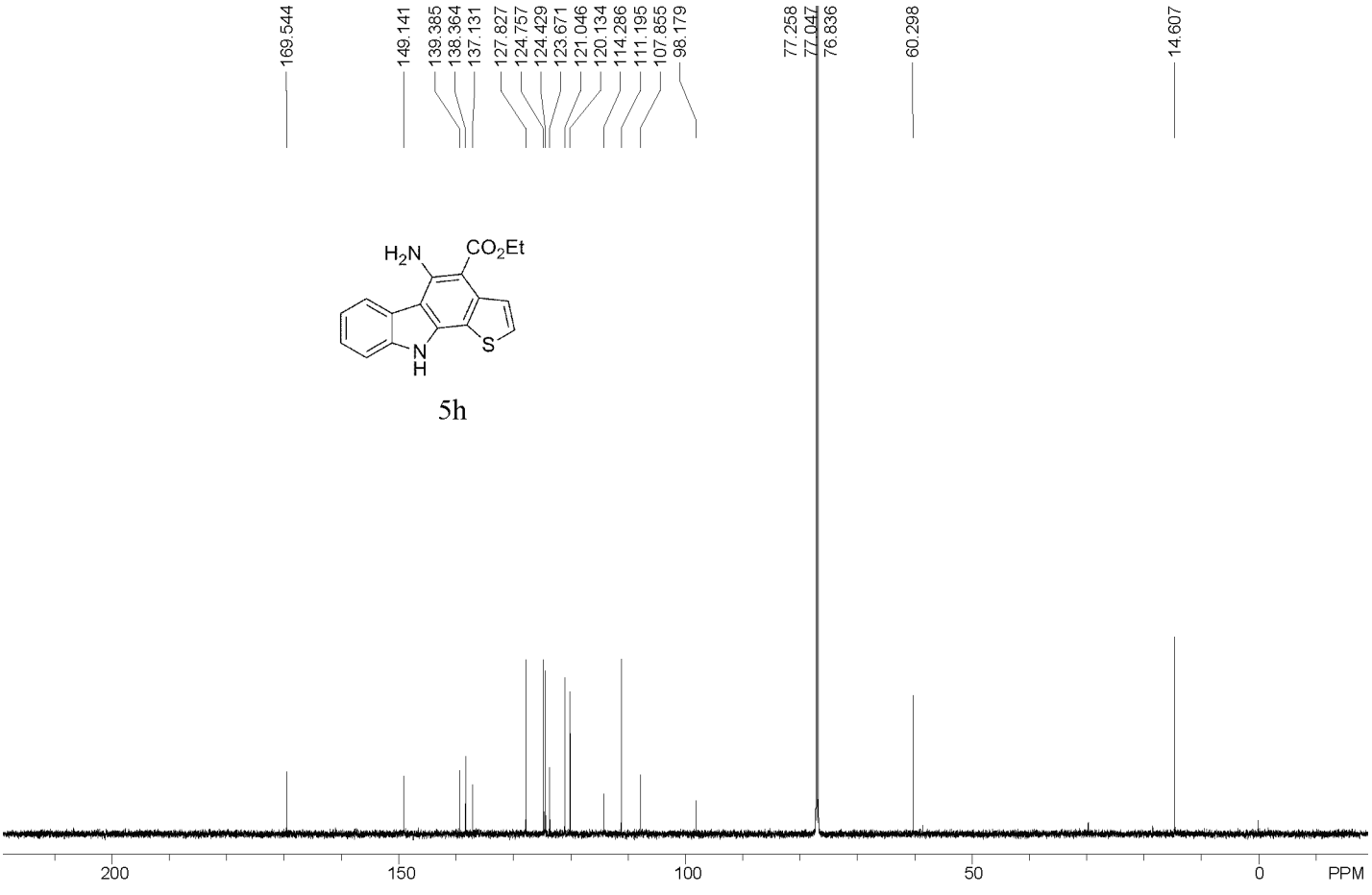
3.09
10
8
6
4
2
PPM

5h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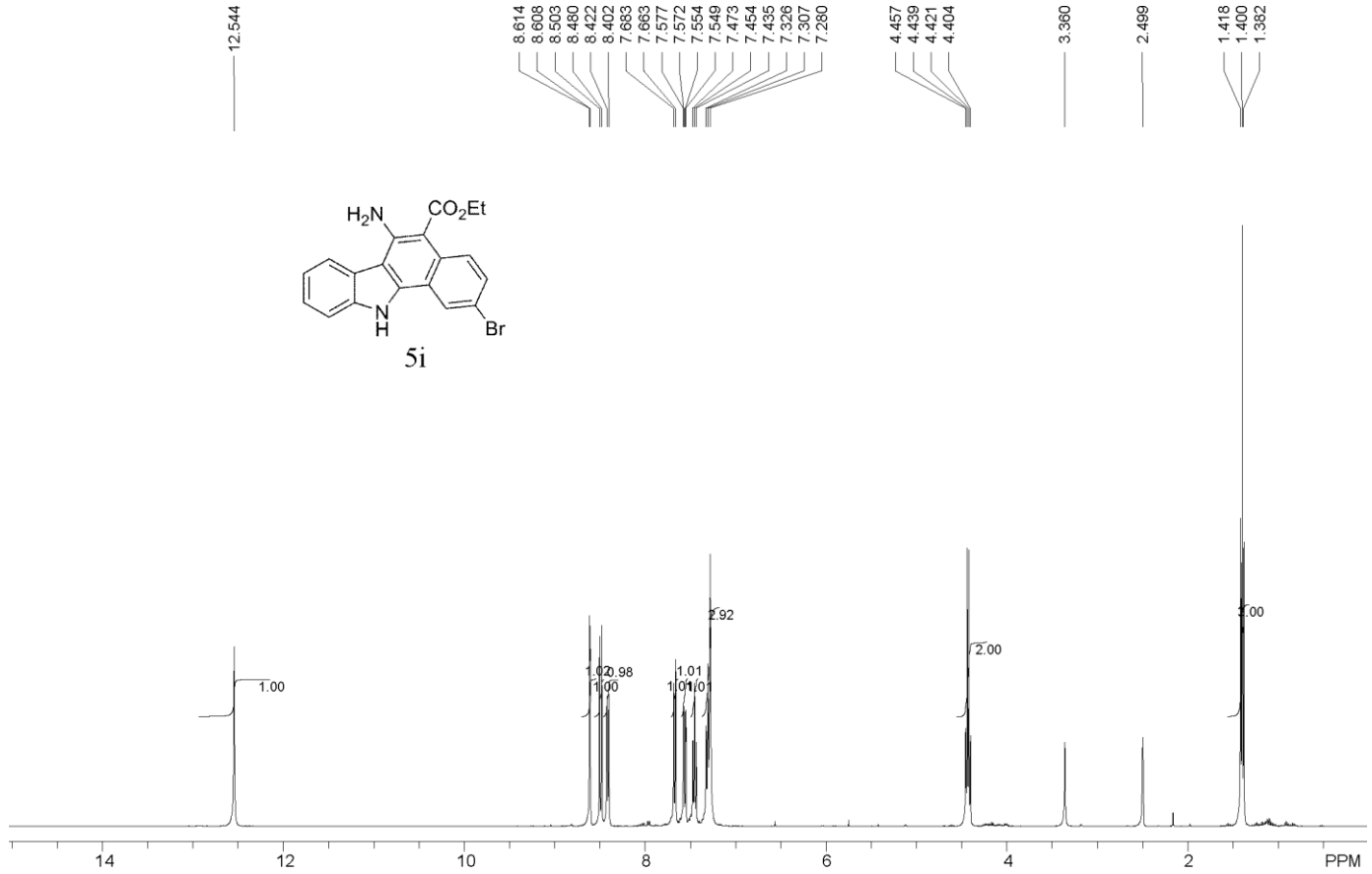
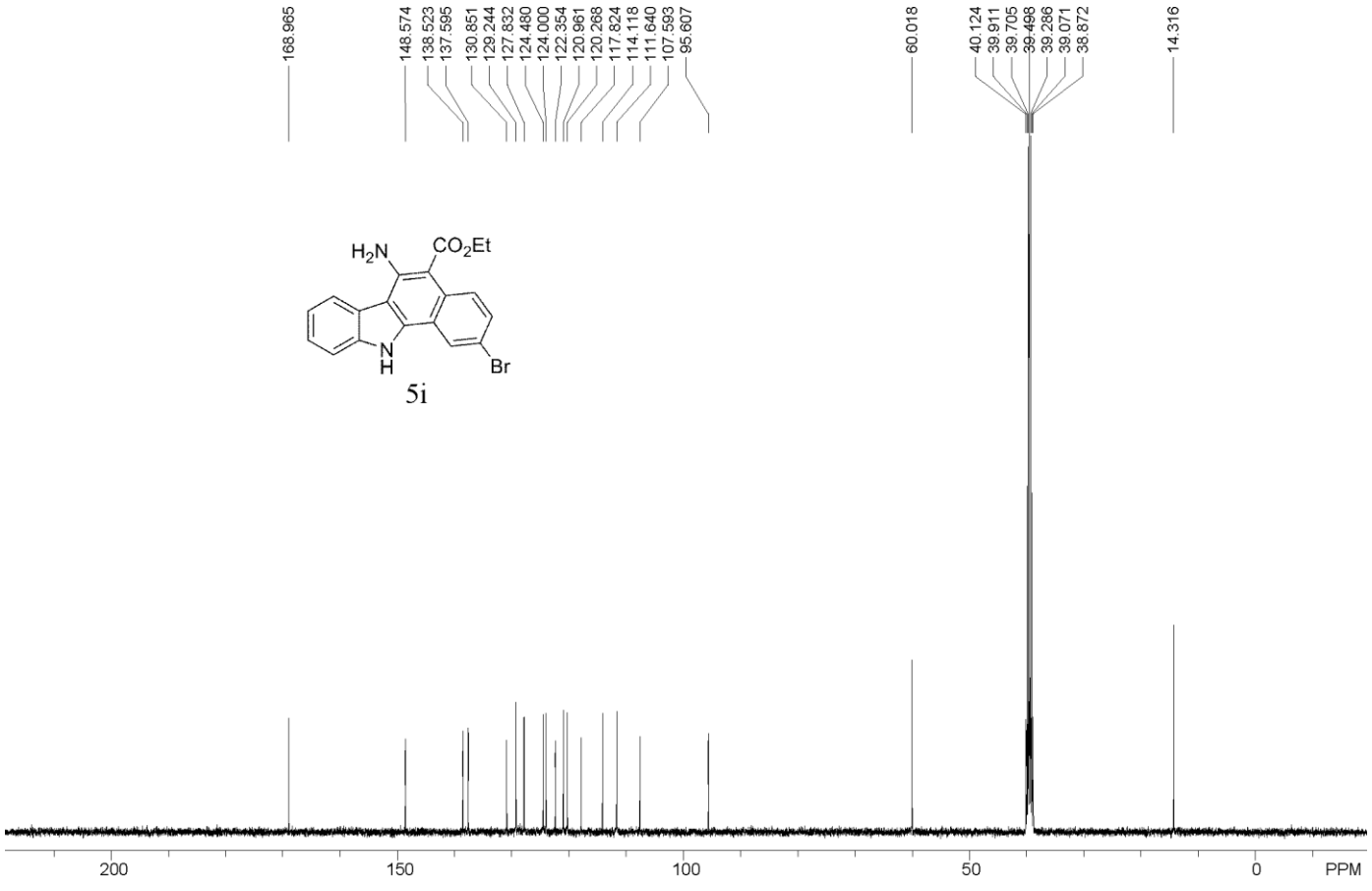
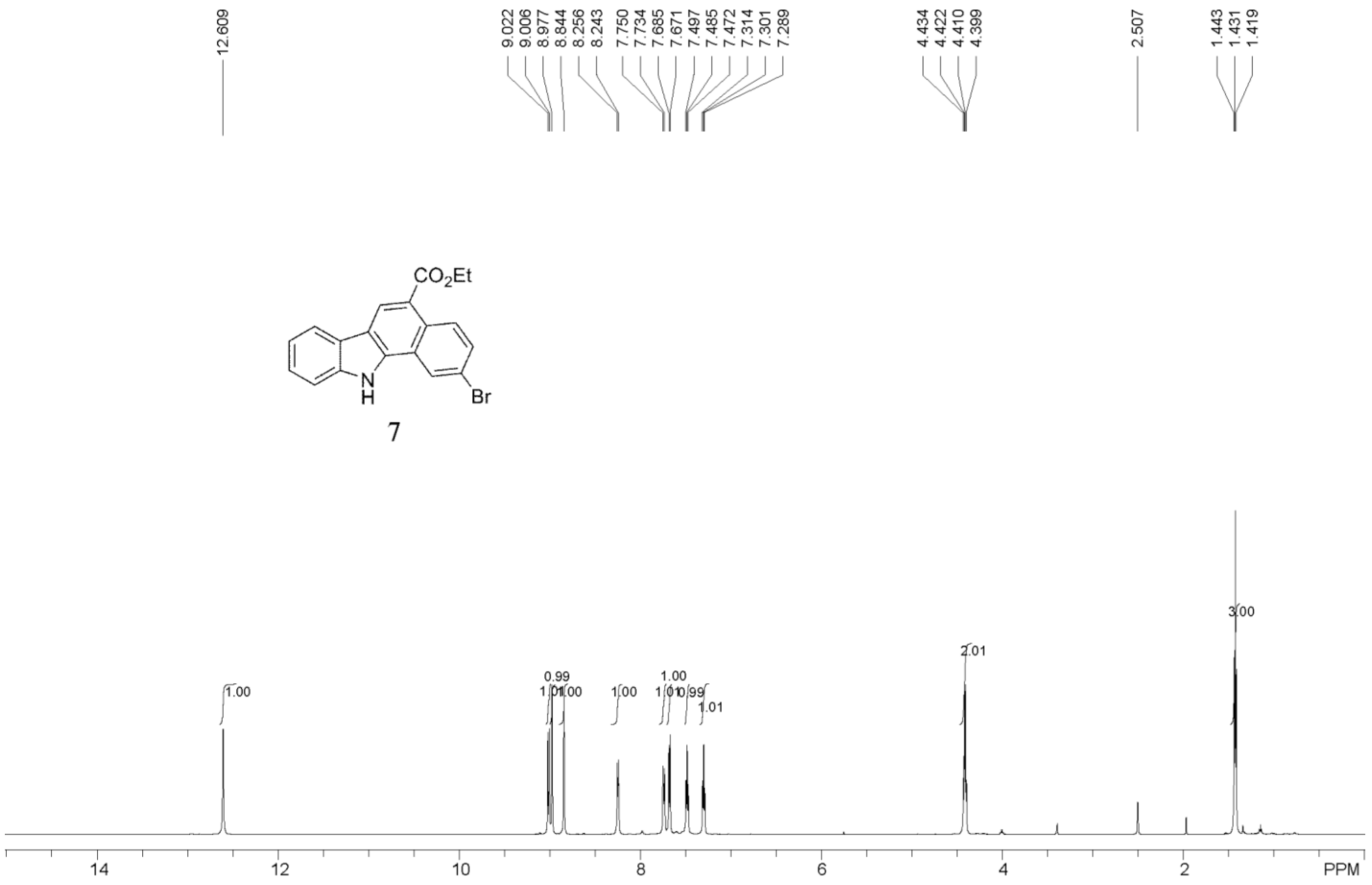
137.131
127.827
124.757
124.429
123.671
121.046
120.134
114.286
111.195
107.855
98.179
77.258
77.047
76.836
60.298
14.607
H2N
CO2Et
N
H
S
200
150
100
50
0
PPM

5h

VI. Copies of ^{1}H and ^{13}C NMR spectra of 5i, 7 and 8



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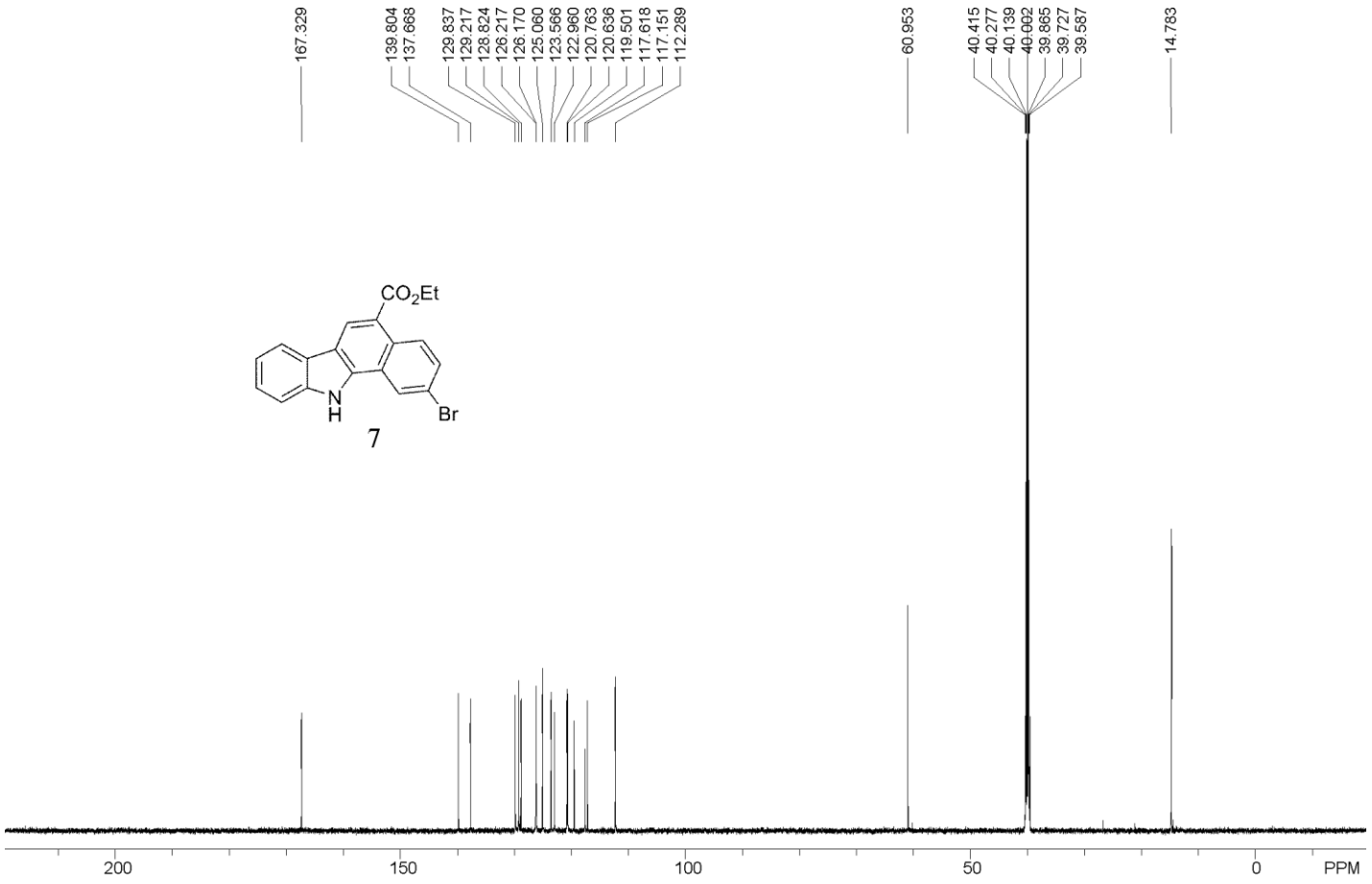
7.497
7.485
7.472
7.314
7.301
7.289
4.434
4.422
4.410
4.399
2.507
1.443
1.431
1.419
CO2Et
N
H
Br
7
1.00
0.99
1.01
1.00
1.00
1.00
1.01
0.99
1.01
2.01
3.00
14
12
10
8
6
4
2
PPM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126.170
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123.566
122.960
120.763
120.636
119.501
117.618
117.151
112.289
60.953
40.415
40.277
40.139
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39.587
14.783
CO2Et
N
H
Br
7
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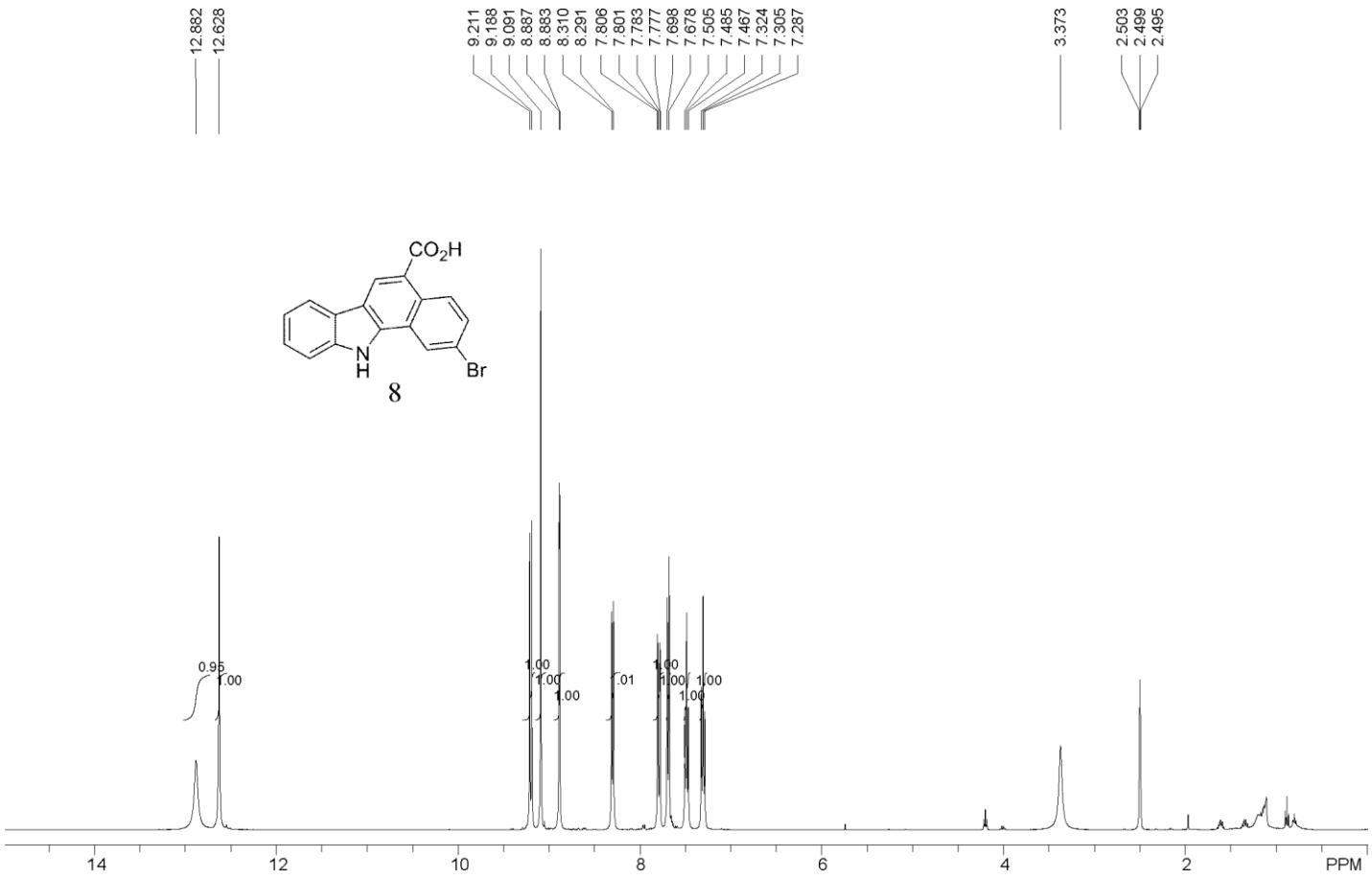
50
0
PPM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7.777
7.698
7.678
7.505
7.485
7.467
7.324
7.305
7.287
3.373
2.503
2.499
2.495
CO2H
N
H
Br
8
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1.00
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12
10
8
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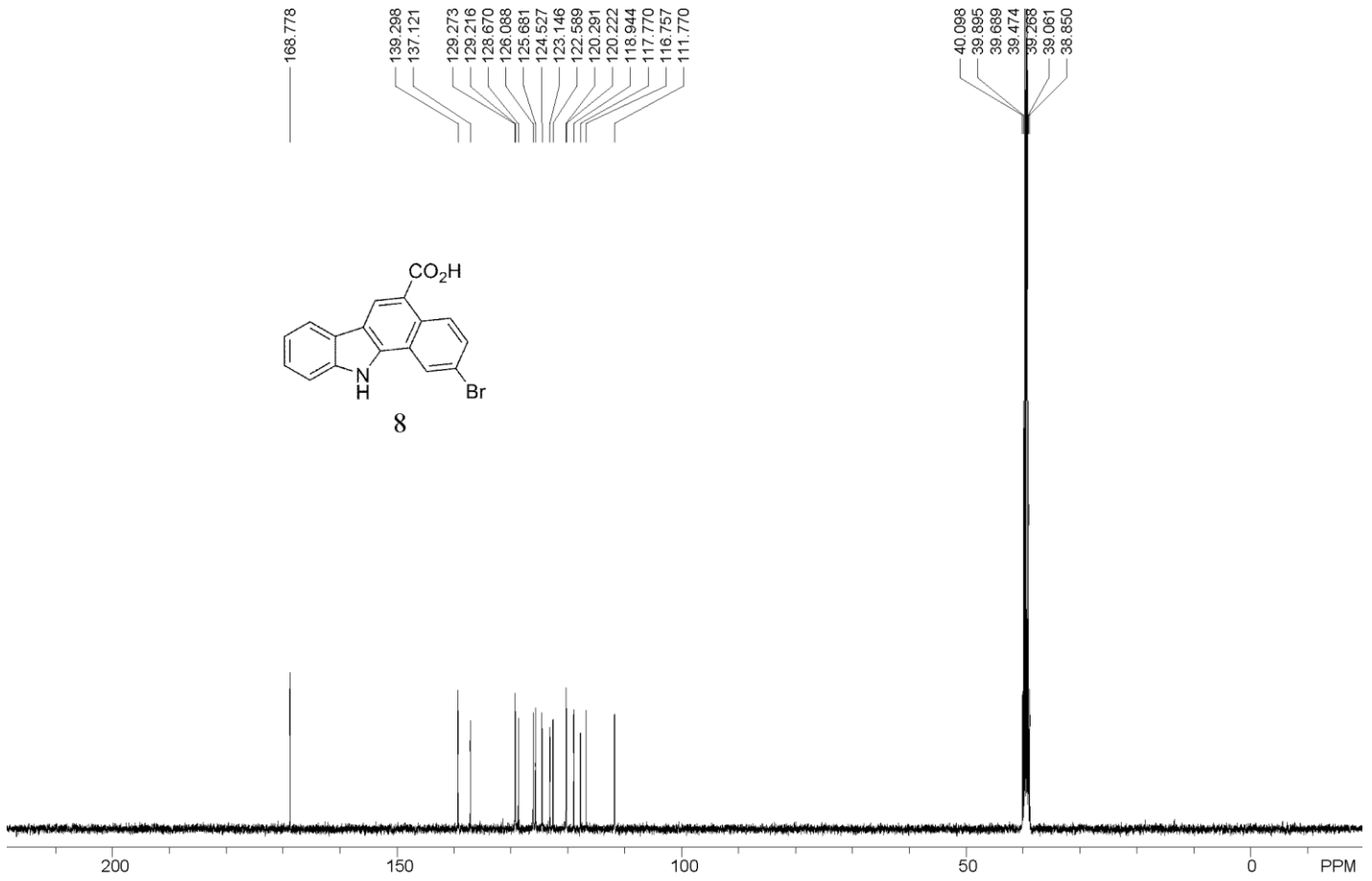
4
2
PPM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120.222
118.944
117.770
116.757
111.770
40.098
39.895
39.689
39.474
39.268
39.061
38.850
CO2H
N
H
Br
8
200
150
100
50
0
PPM

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(2) Y. Jiang, V. Z. Y. Khong, E. Lourdusamy and C.-M. Park, *Chem. Commun.*, 2012, **48**, 3133.

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(4) B. Li, B. Zhang, X. Zhang and X. Fan, *J. Org. Chem.*, 2016, **81**, 9530.

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