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Supporting Information

Ruthenium-Catalyzed *α*-Carbonyl Sulfoxonium Ylides Annulations with Aryl Substituted Pyrazoles *via* C–H/N–H Bond Functionalizations

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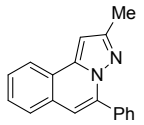
I. General Information

All reagents and solvents used in this work were obtained from commercial sources and were used without further purification. Thin-layer chromatography (TLC) was performed on silica gel GF254 (0.25 mm thickness) plates and visualized under UV light. Organic solutions were concentrated under reduced pressure at 40 °C (water bath temperature) using a Büchi rotary evaporator, unless otherwise noted. Column chromatography was performed on silica gel (200-300 mesh). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded with Bruker Avance III Ascend 500 (500 MHz, 126 MHz and 471 MHz respectively) and Avance III HD (400 MHz, 101 MHz and 376 MHz respectively) spectrometers. NMR spectra are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quarter, m = multiplet, br = broad), coupling (*J*) constant and integration. Melting points were measured on a digital Electrothermal 9100 apparatus. The high resolution mass spectra (HR-MS) data were recorded on Agilent 1290 Infinity LC & 6540 UHD Q-TOF mass spectrometer.

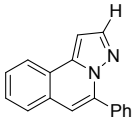
II. General Procedures for the Synthesis of 3

A suspension of 1*H*-pyrazoles **1** (0.10 mmol), sulfoxonium ylides **2** (0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $AgSbF_6$ (6.9 mg, 20 mol %) and $PhCO_2H$ (6.1 mg, 0.05 mmol) in EtOH (1.0 mL) was stirred at 140 °C for 20 h under an ambient atmosphere of N_2. After completion, the reaction mixture was diluted with saturated brine and extracted with EtOAc (3 x 25 mL). The combined organic layers were dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the crude product was purified by column chromatography on silica gel (n-hexane/EtOAc: 20/1~10/1) to yield the corresponding products.



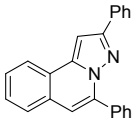
3aa: 84% yield

2-Methyl-5-phenylpyrazolo[5,1-*a*]isoquinoline (3aa): known compound[1], 21.6 mg, 84% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 6.7, 2.5 Hz, 1H), 7.95 – 7.91 (m, 2H), 7.73 – 7.69 (m, 1H), 7.55 – 7.46 (m, 5H), 6.96 (s, 1H), 6.88 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5, 140.2, 138.3, 134.0, 129.4, 129.3, 129.2, 128.3, 127.7, 127.0, 127.0, 123.7, 123.4, 111.6, 97.5, 14.3.



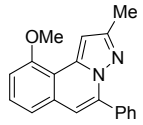
3ba: 80% yield

5-Phenylpyrazolo[5,1-*a*]isoquinoline (3ba): known compound[2], 19.5 mg, 80% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 8.0, 1.1 Hz, 1H), 8.01 (d, *J* = 2.1 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.76 (dd, *J* = 6.9, 2.1 Hz, 1H), 7.61 – 7.48 (m, 5H), 7.10 (d, *J* = 2.1 Hz, 1H), 7.06 (s, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8, 139.3, 138.5, 133.9, 129.4, 129.3, 129.2, 128.4, 128.0, 127.4, 127.2, 124.1, 123.5, 112.6, 97.8.



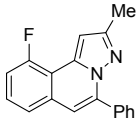
3ca: 77% yield

2,5-Diphenylpyrazolo[5,1-*a*]isoquinoline (3ca): known compound[3], 24.7 mg, 77% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 – 8.13 (m, 1H), 8.08 – 8.03 (m, 2H), 8.04 – 8.100(m, 2H), 7.77 – 7.72 (m, 1H), 7.61 – 7.49 (m, 5H), 7.46 – 7.40 (m, 2H), 7.41 (s, 1H), 7.38 – 7.32 (m, 1H), 7.08 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 140.7, 138.4, 133.7, 133.4, 129.6, 129.3, 129.2, 128.6, 128.2, 128.1, 127.9, 127.3, 127.2, 126.4, 123.9, 123.5, 112.5, 94.8.



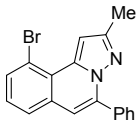
3da: 68% yield

10-Methoxy-2-methyl-5-phenylpyrazolo[5,1-*a*]isoquinoline (3da): unknown compound, 19.6 mg, 68% yield, yellow solid, mp: 105-106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 1H), 7.94 – 7.90 (m, 2H), 7.53 – 7.47 (m, 3H), 7.15 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.10 (d, *J* = 2.5 Hz, 1H), 6.89 (s, 1H), 6.75 (s, 1H), 3.93 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 150.7, 140.3, 138.7, 134.0, 130.8, 129.4, 129.2, 128.3, 125.1, 117.9, 117.0, 111.3, 107.8, 96.4, 55.4, 14.3. HRMS (ESI) m/z: calcd for $C_{19}H_{17}N_2O$ $[M+H]^+$: 289.1341, found: 289.1347.



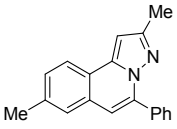
3ea: 60% yield

10-Fluoro-2-methyl-5-phenylpyrazolo[5,1-*a*]isoquinoline (3ea): unknown compound, 16.6 mg, 60% yield, yellow solid, mp: 99-101 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 2H), 7.55 – 7.43 (m, 5H), 7.26 – 7.22 (m, 1H), 7.06 (d, *J* = 4.6 Hz, 1H), 6.95 (d, *J* = 2.0 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3 (d, *J* = 252.2 Hz), 151.0, 139.3, 135.2 (d, *J* = 2.5 Hz), 133.7, 131.5 (d, *J* = 4.1 Hz), 129.4, 128.3, 128.0 (d, *J* = 8.6 Hz), 122.4 (d, *J* = 3.8 Hz), 113.4 (d, *J* = 15.0 Hz), 112.6 (d, *J* = 20.3 Hz), 110.8 (d, *J* = 2.8 Hz), 102.2 (d, *J* = 9.8 Hz),14.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.3. HRMS (ESI) m/z: calcd for $C_{18}H_{14}FN_2$ $[M+H]^+$: 277.1141, found: 277.1145.



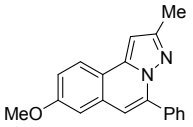
3fa: 61% yield

10-Bromo-5-phenylpyrazolo[5,1-*a*]isoquinoline (3fa): unknown compound, 20.6 mg, 61% yield, yellow solid, mp: 164-166 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 2H), 7.86 (s, 1H), 7.83 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.66 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.54 – 7.47 (m, 3H), 7.33 (t, *J* = 7.8 Hz, 1H), 6.93 (s, 1H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1, 139.0, 138.3, 133.7, 132.7, 132.1, 129.5, 129.4, 128.3, 127.8, 126.7, 123.3, 119.2, 111.7, 103.4, 14.3. HRMS (ESI) m/z: calcd for $C_{18}H_{14}BrN_2$ $[M+H]^+$: 337.0340, found: 337.0336.



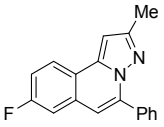
3ga: 82% yield

2,8-Dimethyl-5-phenylpyrazolo[5,1-*a*]isoquinoline (3ga): known compound[1], 22.3 mg, 82% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.96 – 7.92 (m, 2H), 7.55 – 7.48 (m, 4H), 7.38 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.92 (s, 1H), 6.84 (s, 1H), 2.56 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.47, 140.3, 138.2, 137.7, 134.1, 129.4, 129.4, 129.1, 128.7, 128.3, 126.7, 123.3, 121.5, 111.4, 97.0, 21.6, 14.3.



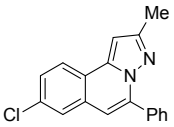
3ha: 83% yield

8-Methoxy-2-methyl-5-phenylpyrazolo[5,1-*a*]isoquinoline (3ha): unknown compound, 23.9 mg, 83% yield, yellow solid, mp: 111-112 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 1H), 7.94 – 7.91 (m, 2H), 7.53 – 7.47 (m, 3H), 7.15 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.10 (d, *J* = 2.5 Hz, 1H), 6.89 (s, 1H), 6.75 (s, 1H), 3.93 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 150.7, 140.3, 138.7, 134.0, 130.8, 129.4, 129.2, 128.3, 125.1, 117.9, 117.0, 111.3, 107.8, 96.4, 55.4, 14.3. HRMS (ESI) m/z: calcd for $C_{19}H_{17}N_2O$ $[M+H]^+$: 289.1341, found: 289.1347.



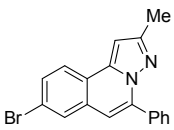
3ia: 72% yield

8-Fluoro-2-methyl-5-phenylpyrazolo[5,1-*a*]isoquinoline (3ia): known compound[1], 19.9 mg, 72% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.8, 5.4 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.54 – 7.47 (m, 3H), 7.36 (dd, *J* = 9.4, 2.5 Hz, 1H), 7.28 – 7.23 (m, 1H), 6.90 (s, 1H), 6.82 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.95 (d, *J* = 247.2 Hz), 150.9, 139.6 (d, *J* = 69.6 Hz), 133.6, 130.9 (d, *J* = 9.4 Hz), 129.5, 129.4, 128.3, 125.7, 125.7, 120.3 (d, *J* = 2.0 Hz), 115.7 (d, *J* = 23.9 Hz), 111.7 (d, *J* = 21.6 Hz), 110.8 (d, *J* = 3.6 Hz), 97.3, 14.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -112.7.



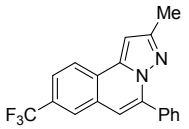
3ja: 76% yield

8-Chloro-2-methyl-5-phenylpyrazolo[5,1-*a*]isoquinoline (3ja): unknown compound, 22.2 mg, 76% yield, yellow solid, mp: 152-153 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.6 Hz, 1H), 7.92 – 7.89 (m, 2H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.54 – 7.47 (m, 4H), 6.87 (s, 1H), 6.85 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.0, 139.7, 139.4, 133.6, 133.4, 130.4, 129.5, 129.4, 128.4, 127.4, 126.2, 124.9, 122.0, 110.4, 97.8, 14.3. HRMS (ESI) m/z: calcd for $C_{18}H_{14}ClN_2$ $[M+H]^+$: 293.0846, found: 293.0849.



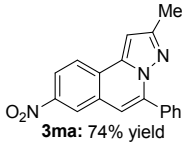
3ka: 78% yield

8-Bromo-2-methyl-5-phenylpyrazolo[5,1-*a*]isoquinoline (3ka): unknown compound, 26.3 mg, 78% yield, yellow solid, mp: 178-179 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.89 (m, 3H), 7.86 (d, *J* = 1.9 Hz, 1H), 7.62 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.55 – 7.48 (m, 3H), 6.86 (s, 2H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.0, 139.7, 139.4, 133.5, 130.8, 130.1, 129.5, 129.4, 129.3, 128.4, 125.0, 122.3, 121.5, 110.3, 97.9, 14.3. HRMS (ESI) m/z: calcd for $C_{18}H_{14}BrN_2$ $[M+H]^+$: 337.0340, found: 337.0344.



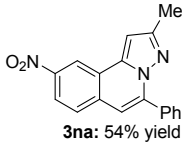
3la: 75% yield

2-Methyl-5-phenyl-8-(trifluoromethyl)pyrazolo[5,1-*a*]isoquinoline (3la): unknown compound, 24.5 mg, 75% yield, yellow solid, mp: 128-129 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 8.4, 0.4 Hz, 1H), 7.99 (s, 1H), 7.94 – 7.90 (m, 2H), 7.73 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.01 (s, 1H), 6.96 (s, 1H), 2.54 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.1, 139.6, 139.4, 133.4, 129.6, 129.4, 128.9, 128.9 (q, *J* = 39.1 Hz), 128.4, 125.6, 124.3 (q, *J* = 4.1 Hz), 124.2, 124.1 (q, *J* = 273.4 Hz), 123.1 (q, *J* = 3.5 Hz), 111.0, 98.8, 14.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ –62.4. HRMS (ESI) m/z: calcd for $C_{19}H_{14}F_3N_2$ $[M+H]^+$: 327.1109, found: 327.1103.



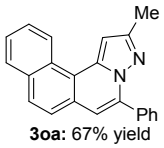
3ma: 74% yield

2-Methyl-8-nitro-5-phenylpyrazolo[5,1-*a*]isoquinoline: (3ma): unknown compound, 22.4 mg, 74% yield, yellow solid, mp: 133-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.33 (d, *J* = 8.9 Hz, 1H), 8.17 (d, *J* = 8.7 Hz, 1H), 7.93-7.91 (m, 2H), 7.55-7.53 (m, 3H), 7.07 (s, 1H), 7.03 (s, 1H), 2.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6, 146.6, 140.4, 139.0, 132.9, 129.9, 129.4, 129.1, 128.5, 127.4, 124.6, 122.8, 121.1, 111.0, 99.9, 14.3. HRMS (ESI) m/z: calcd for $C_{18}H_{14}N_3O_2$ $[M+H]^+$: 304.1086, found: 304.1091.



3na: 54% yield

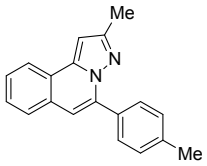
2-Methyl-9-nitro-5-phenylpyrazolo[5,1-*a*]isoquinoline: (3na): unknown compound, 16.4 mg, 54% yield, yellow solid, mp: 128-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 1.9 Hz, 1H), 8.30 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.96-7.93 (m, 2H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.55 (dd, *J* = 5.1, 1.7 Hz, 3H), 7.02 (d, *J* = 5.9 Hz, 2H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 145.8, 141.7, 139.6, 133.6, 132.9, 130.1, 129.4, 128.4, 128.0, 123.2, 121.8, 119.5, 110.2, 99.3, 14.3. HRMS (ESI) m/z: calcd for $C_{18}H_{14}N_3O_2$ $[M+H]^+$: 304.1086, found: 304.1091.



3oa: 67% yield

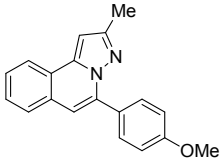
2-Methyl-5-phenylbenzo[*h*]pyrazolo[5,1-*a*]isoquinoline: (3oa): unknown compound, 20.7 mg, 67% yield, yellow solid, mp: 124-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 8.5 Hz, 1H), 8.02 – 7.98 (m, 3H), 7.92 (d, *J* = 8.5

Hz, 1H), 7.79 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.66 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.58 – 7.51 (m, 3H), 7.43 (s, 1H), 7.15 (s, 1H), 2.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 139.1, 138.8, 134.1, 132.8, 129.5, 129.3, 129.1, 129.0, 128.8, 128.3, 127.3, 126.1, 125.7, 125.4, 124.9, 119.6, 112.6, 101.1, 14.4. HRMS (ESI) m/z: calcd for $C_{22}H_{17}N_2$ $[M+H]^+$: 309.1392, found: 309.1398.



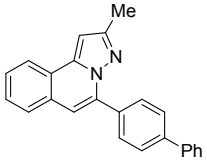
3ab: 82% yield

2-Methyl-5-(p-tolyl)pyrazolo[5,1-*a*]isoquinoline: (3ab): unknown compound, 22.3 mg, 82% yield, yellow solid, mp: 97-99 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 1H), 7.83 (d, *J* = 1.6 Hz, 1H), 7.82 (d, *J* = 1.7 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.54 – 7.49 (m, 2H), 7.34 (s, 1H), 7.32 (s, 1H), 6.94 (s, 1H), 6.87 (s, 1H), 2.52 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5, 140.2, 139.2, 138.4, 131.1, 129.3, 129.1, 129.0, 127.6, 126.9, 126.9, 123.6, 123.4, 111.2, 97.5, 21.4, 14.3. HRMS (ESI) m/z: calcd for $C_{19}H_{17}N_2$ $[M+H]^+$: 273.1392, found: 273.1396.



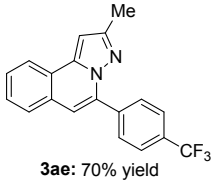
3ac: 87% yield

5-(4-Methoxyphenyl)-2-methylpyrazolo[5,1-*a*]isoquinoline: (3ac): known compound[1], 25.1 mg, 87% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 8.02 (m, 1H), 7.92 – 7.88 (m, 2H), 7.70 – 7.68 (m, 1H), 7.54 – 7.48 (m, 2H), 7.07 – 7.02 (m, 2H), 6.93 (s, 1H), 6.87 (s, 1H), 3.89 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 150.4, 140.2, 138.0, 130.8, 129.4, 127.6, 126.8, 126.8, 126.4, 123.4, 123.4, 113.7, 110.9, 97.5, 55.4, 14.3.



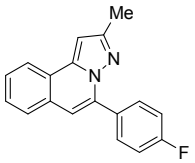
3ad: 80% yield

5-([1,1'-Biphenyl]-4-yl)-2-methylpyrazolo[5,1-*a*]isoquinoline: (3ad): unknown compound, 26.7 mg, 80% yield, yellow solid, mp: 142-143 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 8.06 (m, 1H), 8.05 – 8.01 (m, 2H), 7.76 – 7.71 (m, 3H), 7.68 – 7.66 (m, 2H), 7.56 – 7.51 (m, 2H), 7.51 – 7.47 (m, 2H), 7.42 – 7.36 (m, 1H), 7.03 (s, 1H), 6.90 (s, 1H), 2.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 142.0, 140.8, 140.2, 137.9, 132.9, 129.8, 129.3, 128.8, 127.7, 127.5, 127.3, 127.2, 127.1, 127.0, 123.7, 123.5, 111.6, 97.6, 14.4. HRMS (ESI) m/z: calcd for $C_{24}H_{19}N_2$ $[M+H]^+$: 335.1548, found: 335.1551.



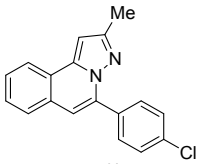
3ae: 70% yield

2-Methyl-5-(4-(trifluoromethyl)phenyl)pyrazolo[5,1-*a*]isoquinoline: (3ae): unknown compound, 22.8 mg, 70% yield, yellow solid, mp: 121-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.05 (m, 3H), 7.79 (s, 1H), 7.77 (s, 1H), 7.75 – 7.71 (m, 1H), 7.60 – 7.52 (m, 2H), 6.99 (s, 1H), 6.89 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8, 140.2, 137.4, 136.8, 131.0 (q, J = 32.4 Hz), 129.8, 128.9, 127.9, 127.6, 127.2, 125.3 (q, J = 3.8 Hz), 123.9, 123.5, 123.0 (q, J = 273.4 Hz), 112.3, 97.8, 14.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.7. HRMS (ESI) m/z: calcd for $C_{19}H_{14}F_3N_2$ $[M+H]^+$: 327.1109, found: 327.1105.



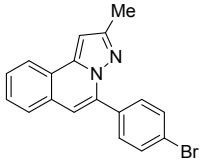
3af: 71% yield

5-(4-Fluorophenyl)-2-methylpyrazolo[5,1-*a*]isoquinoline: (3af): known compound[1], 19.6 mg, 71% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 1H), 7.95 – 7.90 (m, 2H), 7.71 – 7.69 (m, 1H), 7.54 – 7.52 (m, 2H), 7.22 – 7.18 (m, 2H), 6.93 (s, 1H), 6.88 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2 (d, J = 248.9 Hz), 150.6, 140.2, 137.2, 131.4 (d, J = 8.3 Hz), 130.0 (d, J = 3.4 Hz), 129.2, 127.8, 127.2, 127.0, 123.7, 123.5, 115.3 (d, J = 21.7 Hz), 111.5, 97.6, 14.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.9.



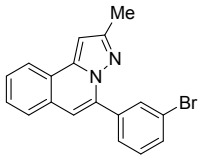
3ag: 73% yield

5-(4-Chlorophenyl)-2-methylpyrazolo[5,1-*a*]isoquinoline: (3ag): known compound[1], 21.4 mg, 73% yield, yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.03 (m, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.73 – 7.68 (m, 1H), 7.55 – 7.52 (m, 2H), 7.51 – 7.48 (m, 2H), 6.95 (s, 1H), 6.88 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 140.2, 137.1, 135.1, 132.4, 130.8, 129.1, 128.6, 127.8, 127.3, 127.1, 123.7, 123.5, 111.6, 97.7, 14.3.



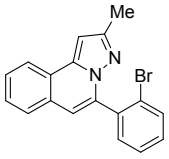
3ah: 76% yield

5-(4-Bromophenyl)-2-methylpyrazolo[5,1-*a*]isoquinoline: (3ah): unknown compound, 25.6 mg, 76% yield, yellow solid, mp: 167-168 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 7.6 Hz, 1H), 7.83 – 7.80 (m, 2H), 7.71 (d, J = 7.3 Hz, 1H), 7.65 – 7.62 (m, 2H), 7.57 – 7.50 (m, 2H), 6.95 (s, 1H), 6.88 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 140.2, 137.1, 132.8, 131.5, 131.0, 129.1, 128.8, 127.8, 127.3, 127.1, 123.7, 123.5, 111.6, 97.7, 14.3. HRMS (ESI) m/z: calcd for $C_{18}H_{14}BrN_2$ $[M+H]^+$: 337.0340, found: 337.0343.



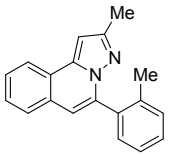
3ai: 73% yield

5-(3-Bromophenyl)-2-methylpyrazolo[5,1-*a*]isoquinoline: (3ai): unknown compound, 24.6 mg, 73% yield, yellow solid, mp: 156-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H), 7.91 – 7.86 (m, 1H), 7.73 – 7.67 (m, 1H), 7.61 (ddd, *J* = 8.0, 1.9, 1.0 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.39 (t, *J* = 7.9 Hz, 1H), 6.94 (s, 1H), 6.87 (s, 1H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 140.1, 136.6, 135.9, 132.2, 132.1, 129.7, 129.0, 128.1, 127.8, 127.4, 127.1, 123.8, 123.4, 122.3, 112.0, 97.7, 14.3. HRMS (ESI) m/z: calcd for $C_{18}H_{14}BrN_2$ $[M+H]^+$: 337.0340, found: 337.0345.



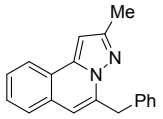
3aj: 60% yield

5-(2-Bromophenyl)-2-methylpyrazolo[5,1-*a*]isoquinoline: (3aj): unknown compound, 20.2 mg, 60% yield, yellow solid, mp: 138-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.07 (m, 1H), 7.77 – 7.70 (m, 2H), 7.61 – 7.51 (m, 3H), 7.47 (td, *J* = 7.5, 1.1 Hz, 1H), 7.37 (td, *J* = 7.9, 1.7 Hz, 1H), 6.89 (s, 1H), 6.88 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 139.5, 136.9, 135.5, 133.0, 131.8, 130.5, 128.8, 127.6, 127.4, 127.3, 127.1, 124.3, 124.0, 123.5, 112.3, 97.6, 14.4. HRMS (ESI) m/z: calcd for $C_{18}H_{14}BrN_2$ $[M+H]^+$: 337.0340, found: 337.0338.



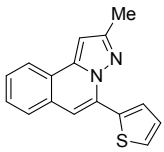
3ak: 70% yield

2-Methyl-5-(*o*-tolyl)pyrazolo[5,1-*a*]isoquinoline: (3ak): unknown compound, 19.1 mg, 70% yield, yellow solid, mp: 81-82 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.70 (dd, *J* = 6.9, 2.2 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.42 (m, 2H), 7.35 – 7.31 (m, 2H), 6.86 (s, 1H), 6.83 (s, 1H), 2.47 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.9, 139.6, 138.4, 138.0, 134.2, 130.1, 130.1, 129.3, 129.1, 127.6, 127.0, 126.9, 125.8, 123.8, 123.5, 111.7, 97.4, 19.8, 14.4. HRMS (ESI) m/z: calcd for $C_{19}H_{17}N_2$ $[M+H]^+$: 273.1392, found: 273.1393.



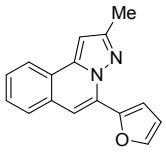
3al: 74% yield

5-Benzyl-2-methylpyrazolo[5,1-*a*]isoquinoline: (3al): known compound[1], 20.2 mg, 74% yield, yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.5 Hz, 1H), 7.55 – 7.52 (m, 1H), 7.49 – 7.42 (m, 2H), 7.42 – 7.36 (m, 4H), 7.34 – 7.30 (m, 1H), 6.85 (s, 1H), 6.42 (s, 1H), 4.50 (s, 2H), 2.58 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.3, 139.6, 138.6, 137.0, 129.9, 129.1, 128.6, 127.5, 126.8, 126.6, 126.5, 123.3, 123.1, 109.7, 97.6, 36.8, 14.2.



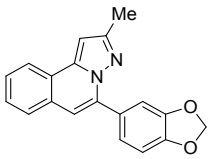
3am: 81% yield

2-Methyl-5-(thiophen-2-yl)pyrazolo[5,1-*a*]isoquinoline: (3am): unknown compound, 21.4 mg, 81% yield, yellow solid, mp: 73-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 3.7, 1.0 Hz, 1H), 8.08 – 8.02 (m, 1H), 7.73 (dt, *J* = 7.2, 3.4 Hz, 1H), 7.53 – 7.50 (m, 3H), 7.33 (s, 1H), 7.20 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.89 (s, 1H), 2.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 140.1, 134.6, 132.0, 129.0, 128.5, 127.9, 127.8, 127.0, 127.0, 126.9, 123.4, 123.2, 109.4, 97.6, 14.3. HRMS (ESI) m/z: calcd for $C_{16}H_{13}N_2S$ $[M+H]^+$: 265.0799, found: 265.0795.



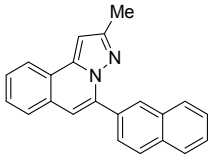
3an: 83% yield

5-(Furan-2-yl)-2-methylpyrazolo[5,1-*a*]isoquinoline: (3an): unknown compound, 20.6 mg, 83% yield, yellow solid, mp: 65-67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 1H), 8.02 (d, *J* = 3.4 Hz, 1H), 7.83 – 7.77 (m, 1H), 7.63 – 7.62 (m, 1H), 7.58 (s, 1H), 7.57 – 7.51 (m, 2H), 6.90 (s, 1H), 6.67 (dd, *J* = 3.4, 1.8 Hz, 1H), 2.63 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 146.4, 142.9, 140.2, 128.8, 128.4, 127.7, 127.3, 127.0, 123.4, 123.1, 114.3, 112.1, 107.5, 97.3, 14.3. HRMS (ESI) m/z: calcd for $C_{16}H_{13}N_2O$ $[M+H]^+$: 249.1028, found: 249.1032.



3ao: 66% yield

5-(Benzo[*d*][1,3]dioxol-5-yl)-2-methylpyrazolo[5,1-*a*]isoquinoline: (3ao): unknown compound, 20.0 mg, 66% yield, yellow solid, mp: 103-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 1H), 7.71 – 7.65 (m, 1H), 7.53 – 7.47 (m, 3H), 7.38 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.92 (s, 1H), 6.86 (s, 1H), 6.05 (s, 2H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 148.4, 147.4, 140.2, 137.8, 134.6, 129.2, 127.7, 127.7, 126.9, 126.9, 123.5, 123.4, 111.1, 110.1, 108.3, 101.3, 97.5, 14.3. HRMS (ESI) m/z: calcd for $C_{19}H_{15}N_2O_2$ $[M+H]^+$: 303.1134, found: 303.1138.

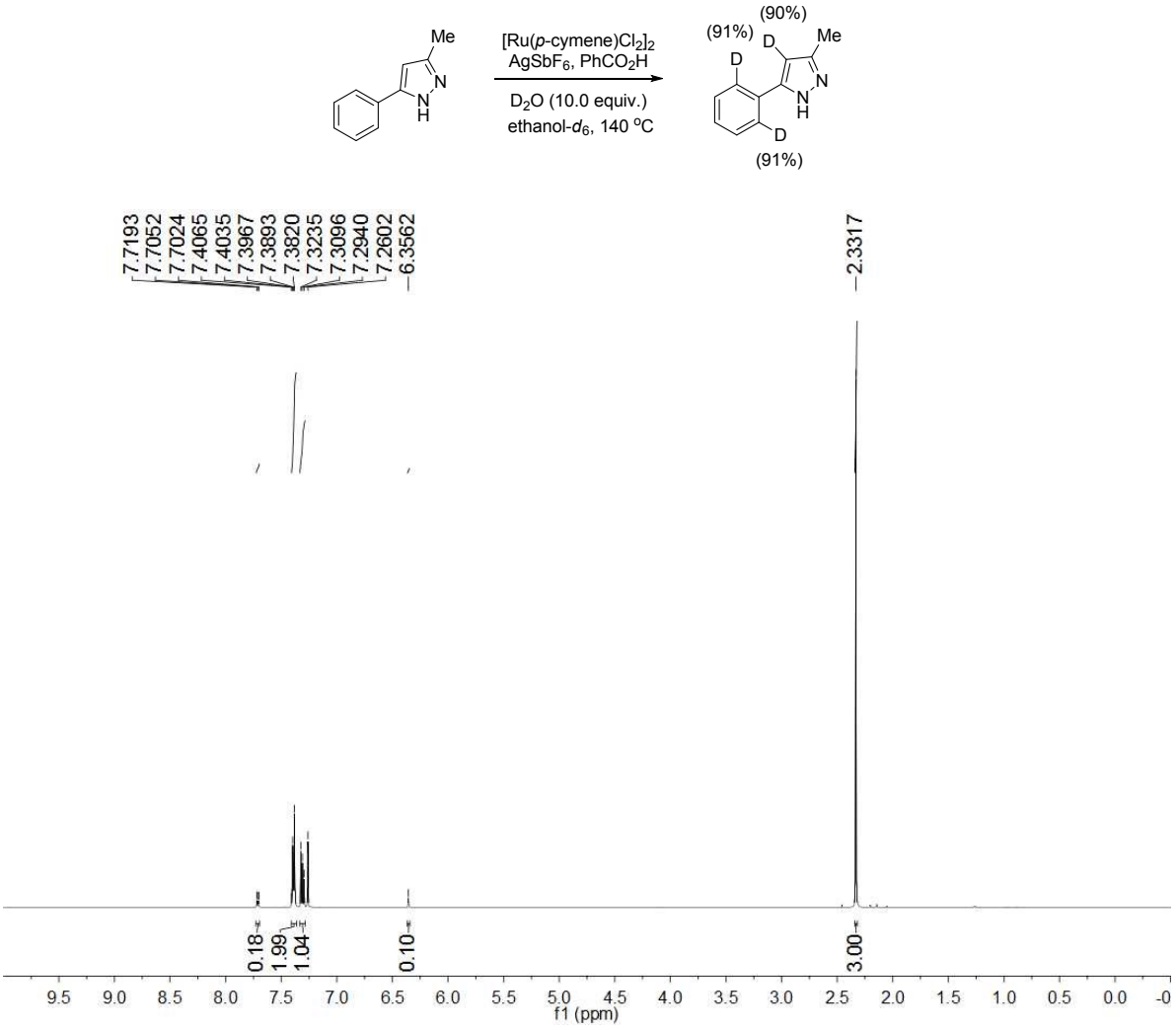


3ap: 78% yield

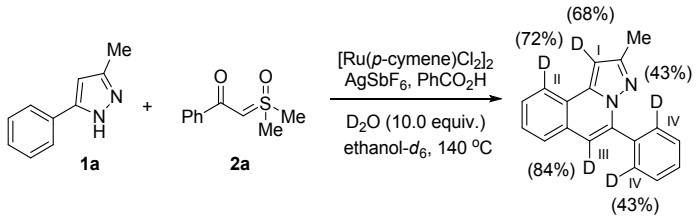
2-Methyl-5-(naphthalen-2-yl)pyrazolo[5,1-*a*]isoquinoline: (3ap): unknown compound, 24.1 mg, 78% yield, yellow solid, mp: 116-117 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.09 (d, *J* = 7.1 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.98 – 7.90 (m, 3H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.57 – 7.50 (m, 4H), 7.08 (s, 1H), 6.91 (s, 1H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 140.2, 138.3, 133.7, 133.3, 131.6, 129.3, 128.8, 128.5, 127.7, 127.7, 127.6, 127.1, 127.1, 127.0, 126.7, 126.2, 123.7, 123.5, 112.0, 97.6, 14.3. HRMS (ESI) m/z: calcd for $C_{22}H_{17}N_2$ $[M+H]^+$: 309.1392, found: 309.1392.

III. Mechanistic Studies

H/D Exchange Experiments. Under N_2, a suspension of 1*H*-pyrazoles **1a** (0.10 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $AgSbF_6$ (6.9 mg, 20 mol %), D_2O (18 μL, 1.0 mmol), and $PhCO_2H$ (6.1 mg, 0.05 mmol) in ethanol-d_6 (1.0 mL) was stirred at 140 °C for 20 h. At ambient temperature, the reaction mixture was diluted with saturated brine and extracted with EtOAc (3 x 25 mL). The combined organic layers were dried over Na_2SO_4. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford a white solid product, which was characterized by ^1H NMR spectroscopy.



A suspension of 1*H*-pyrazoles **1** (0.10 mmol), sulfoxonium ylides **2** (0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $AgSbF_6$ (6.9 mg, 20 mol %), D_2O (18 μL, 1.0 mmol), and $PhCO_2H$ (6.1 mg, 0.05 mmol) in ethanol-d_6 (1.0 mL) was stirred at 140 °C for 20 h under an ambient atmosphere of N_2. At ambient temperature, the reaction mixture was diluted with saturated brine and extracted with EtOAc (3 x 25 mL). The combined organic layers were dried over Na_2SO_4. After filtration and evaporation of the solvents *in vacuo*, the crude product was purified by column chromatography on silica gel (n-hexane/EtOAc: 20/1~10/1) to yield the corresponding product.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+
O
O
Ph
S
Me
Me
2a
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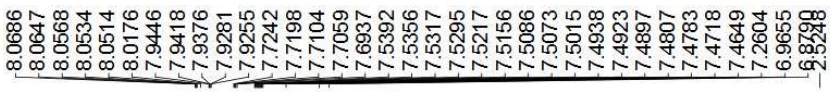
D2O (10.0 equiv.)
ethanol-d6, 140 °C
(68%)
(72%)
D
I
Me
D
II
N
(43%)
N
D
IV
(84%)
D
III
D
IV
(43%)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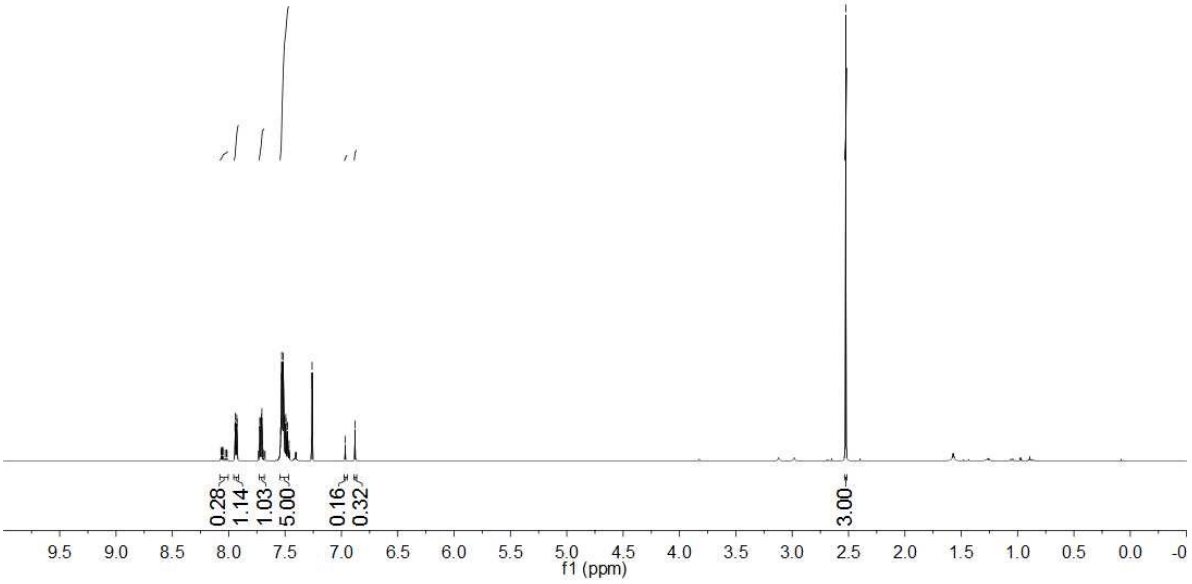
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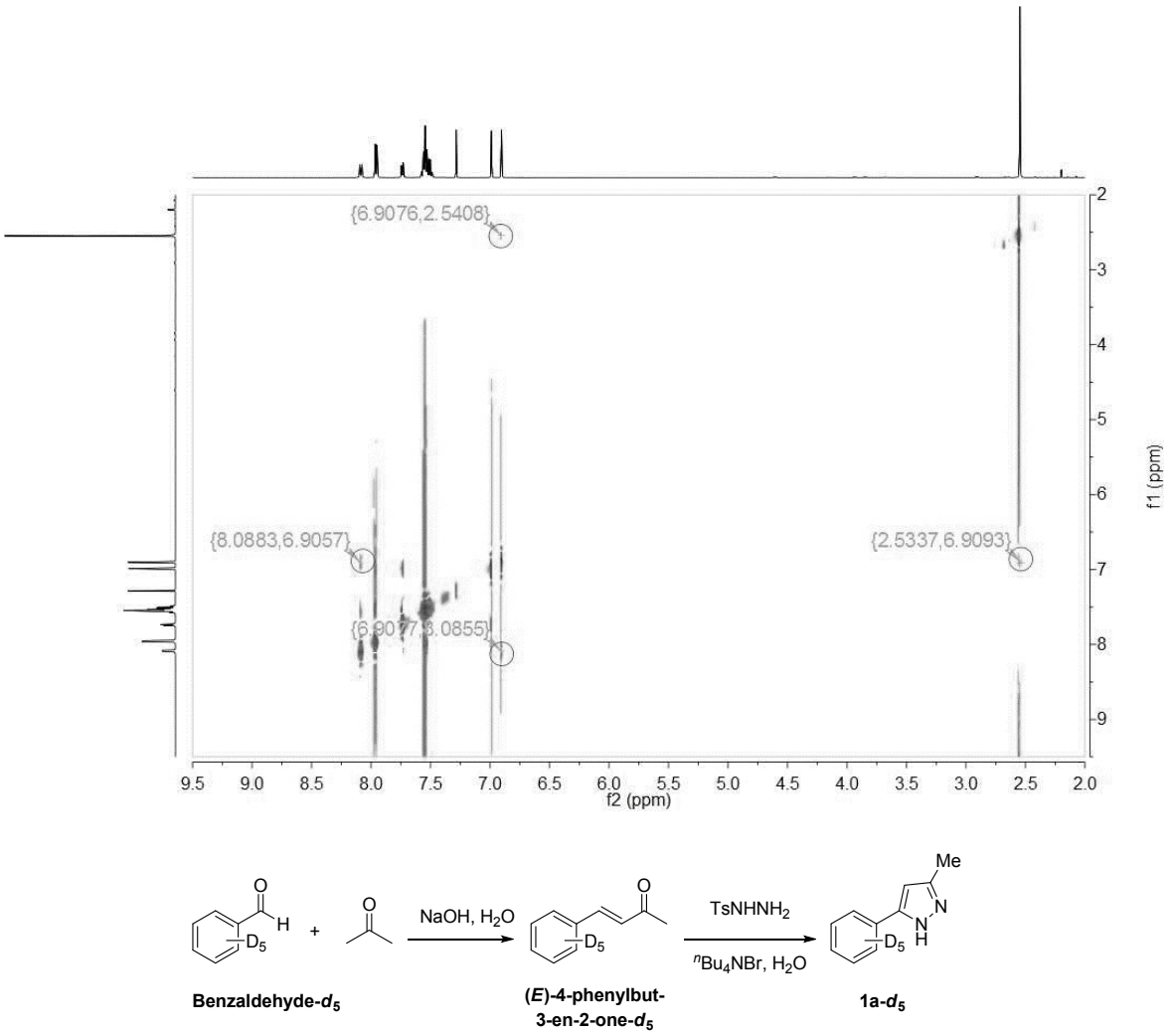
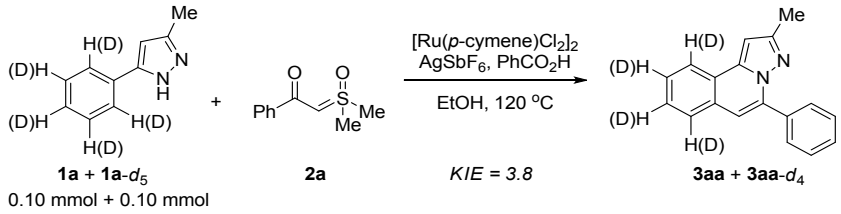


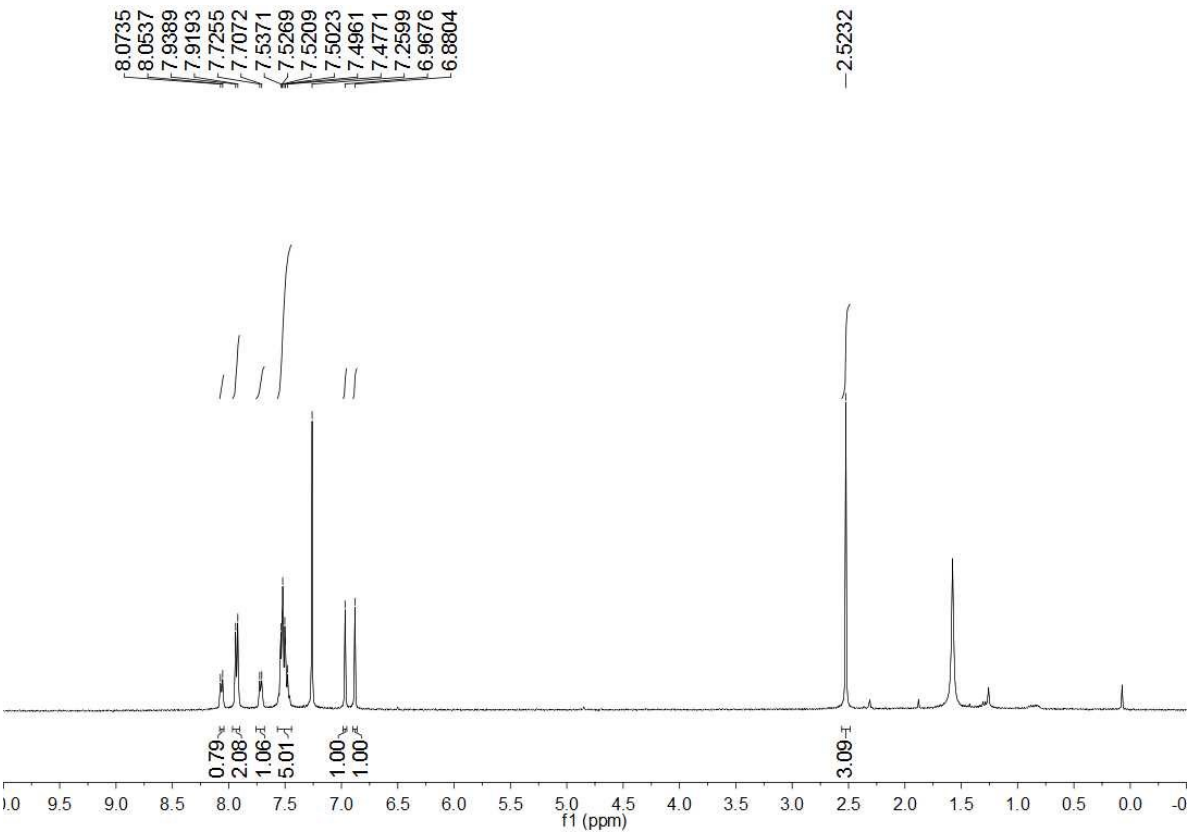
(*E*)-4-phenylbut-3-en-2-one-d_5 was synthesized according to the known method.[4] Benzaldehyde-d_5 (10 mmol, 1.0 equiv.) was suspended in a mixture of acetone/water (2 mL/2 mL), and 1% aqueous solution of sodium hydroxide (5 mL) was slowly added to the reaction mixture. The reaction mixture was heated to 65 °C and stirred until no benzaldehyde-d_5 was detected by TLC. The reaction mixture was cooled to ambient temperature, a mixture of water (10 mL) and toluene (10 mL) was added to the flask. The organic phase was separated, washed with brine. The combined organic layer was dried with $MgSO_4$ and concentrated to dryness, and the residue was purified by flash chromatography on silica gel to give the product (75% yield). **(*E*)-4-phenylbut-3-en-2-one-d_5:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 16.3 Hz, 1H), 6.72 (d, J = 16.3 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 143.1, 134.0, 130.0, 129.8, 129.5, 128.5, 128.2, 128.0, 127.9, 127.6, 127.4, 126.9, 27.28.

1a-d_5 was synthesized according to the known method.[5] **(*E*)-4-phenylbut-3-en-2-one-d_5** (5.0 mmol, 1 equiv), tosyl hydrazide (6.0 mmol, 1.2 equiv), NaOH (1.5 equiv), ^{n}Bu$_4$NBr (1.5 equiv), and 5 mL H_2O were added to a Schlenk tube, under N_2. The reaction mixture was heated to 80 °C and stirred for 10 h. The reaction mixture was then allowed to cool to ambient temperature, and diluted with 15 mL of ethyl acetate, and washed with brine (15 mL), water (15 mL), and then the organic layer was dried over Na_2SO_4. After concentrated *in vacuo*, the crude product was purified

by column chromatography to give the product (60% yield). **1a-d_5:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35 (s, 1H), 2.32 (d, J = 0.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.4, 128.3, 128.1, 127.8, 125.5, 125.3, 125.1, 102.0, 11.5.

Kinetic Isotope Effect Experiments. Two pressure tubes were separately charged with **1a** (0.10 mmol) and **1a-d_5** (0.1 mmol), and to each tube was added sulfoxonium ylides **2** (0.20 mmol), $[RuCl_2(p\text{-cymene})]_2$ (3.1 mg, 5.0 mol %), $AgSbF_6$ (6.9 mg, 20 mol %), $PhCO_2H$ (6.1 mg, 0.05 mmol), and EtOH (1.5 mL) under N_2. The two reaction mixtures were stirred side by side in an oil bath preheated at 120 °C for 30 min. After that, the reaction was quenched in an ice bath and n-hexane was rapidly added to each tube. The two mixtures were combined and the solvent was removed under vacuum and the residue was purified by silica gel chromatography using n-hexane/EtOAc: 20/1~10/1 to yield the product **3aa** and **3aa-d_4** as white solid (20.0 mg, 8% yield). The KIE value was determined to be k_H/k_D = 3.8 on the basis of ^{1}H NMR analysis.

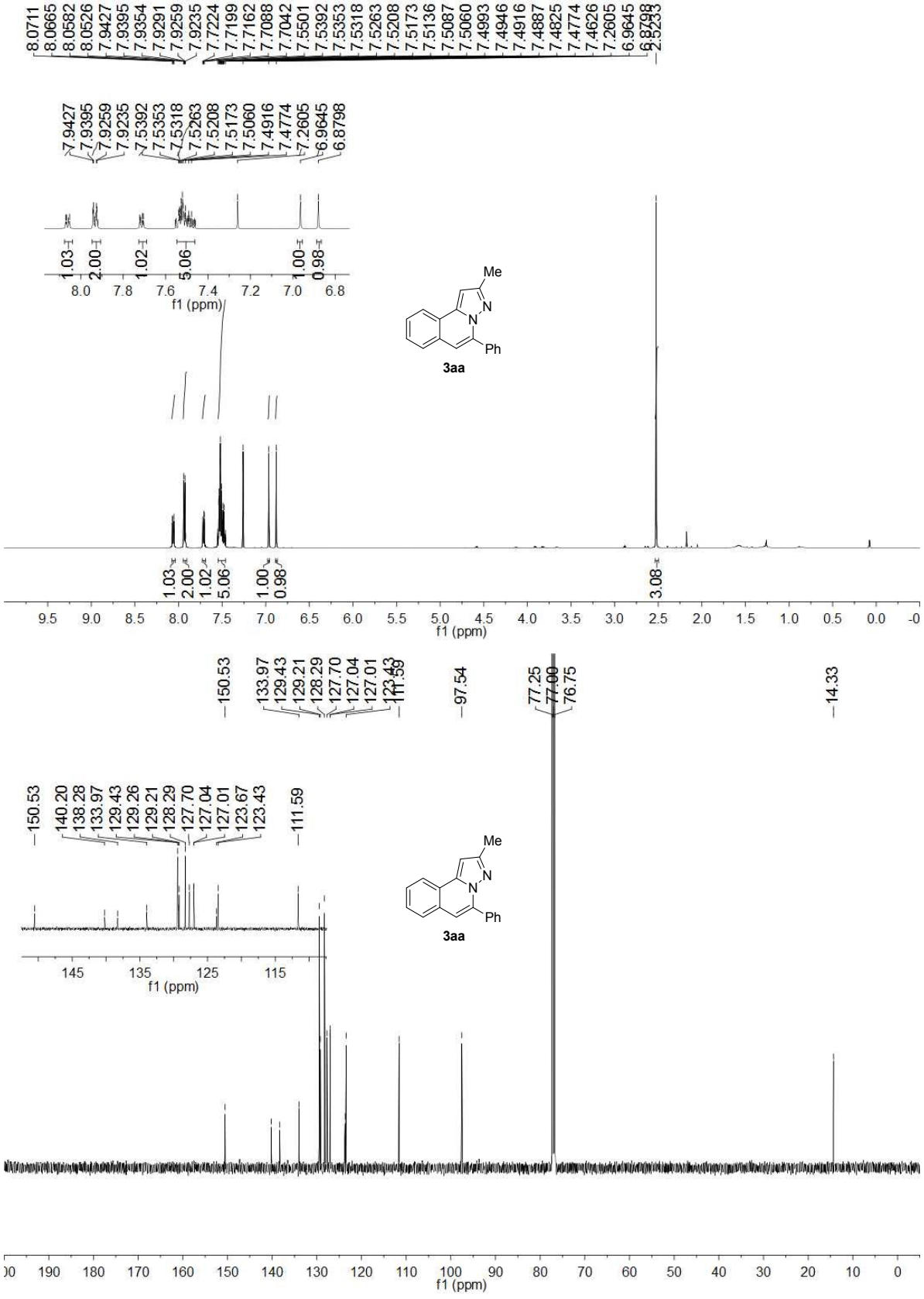


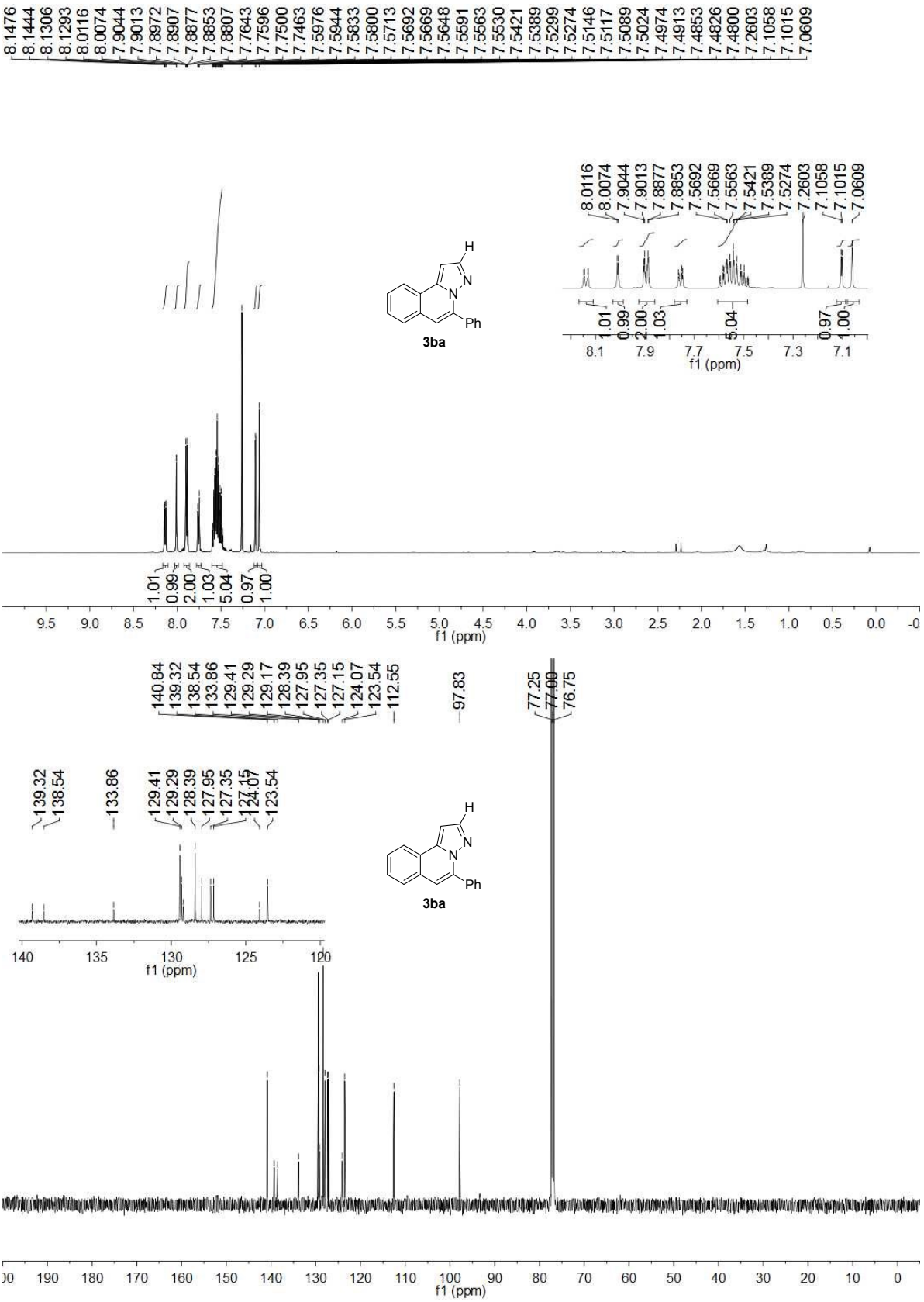


IV. References

1. X. Fan, M. Yan, Y. Wang, X. Zhang, *J. Org. Chem.*, **2015**, *80*, 10536-10547.
2. S. Li, J. Wu, *Org. Lett.,* **2011**, *13*, 712-715.
3. Y. Yang, H. Ren, D. Wang, F. Shi, C. Wu, *RSC Adv.*, **2013**, *3*, 10434-10441.
4. a) R. Shi, F. Liao, H. Niu, A. Lei, *Org. Chem. Front*., **2018**, *5*, 1957-1961; b) H.-Y. Hao, Y.-J. Mao, Z.-Y. Xu, S.-J. Lou, D.-Q. Xu, *Org. Lett*., **2020**, *22*, 2396-2402.
5. J. Wen, Y. Fu, R.-Y. Zhang, J. Zhang, S.-Y. Chen, X.-Q. Yu, *Tetrahedron*, **2011**, *67*, 9618-9621.

V. Spectral Data for Representative Compounds

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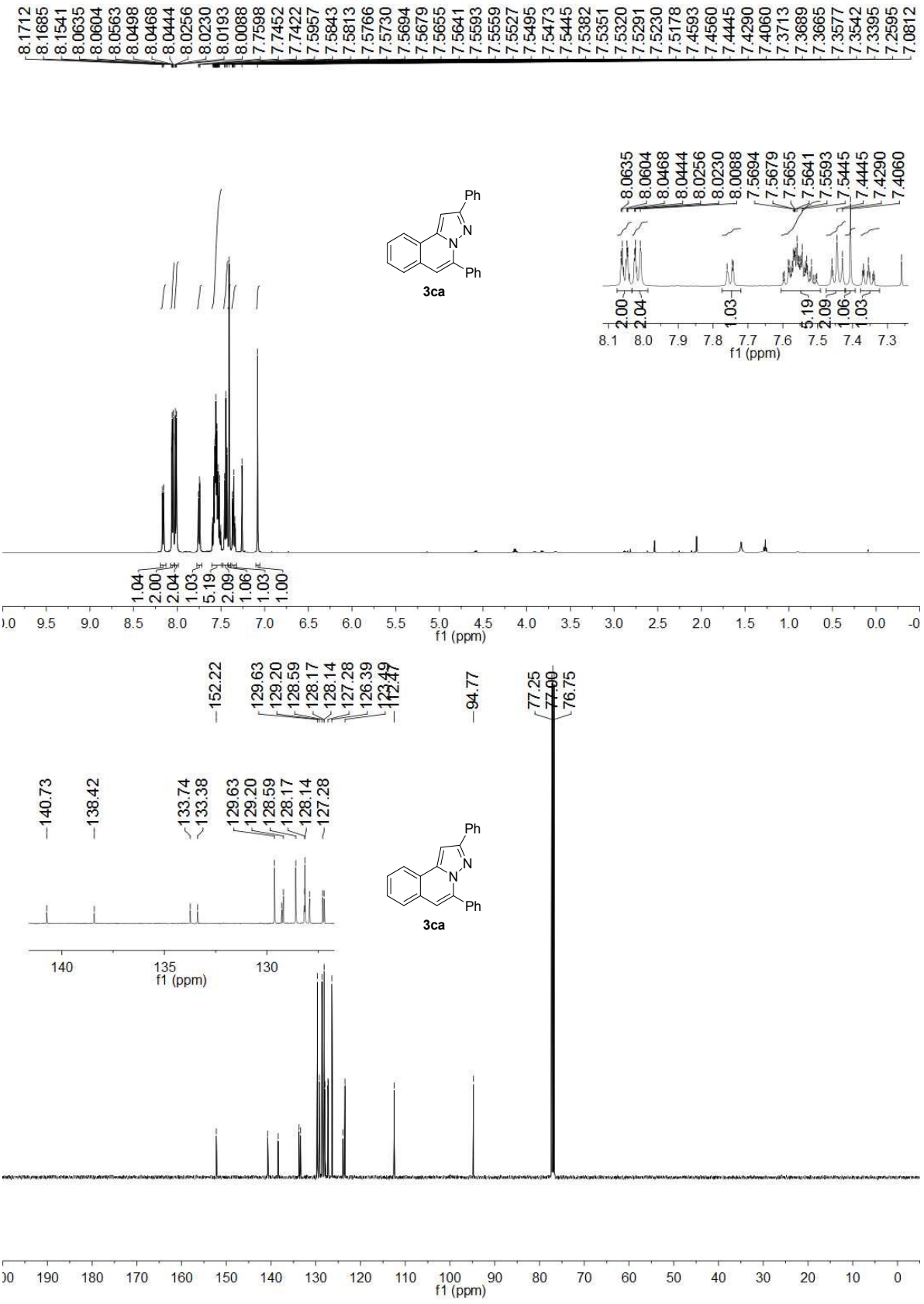
f1 (ppm)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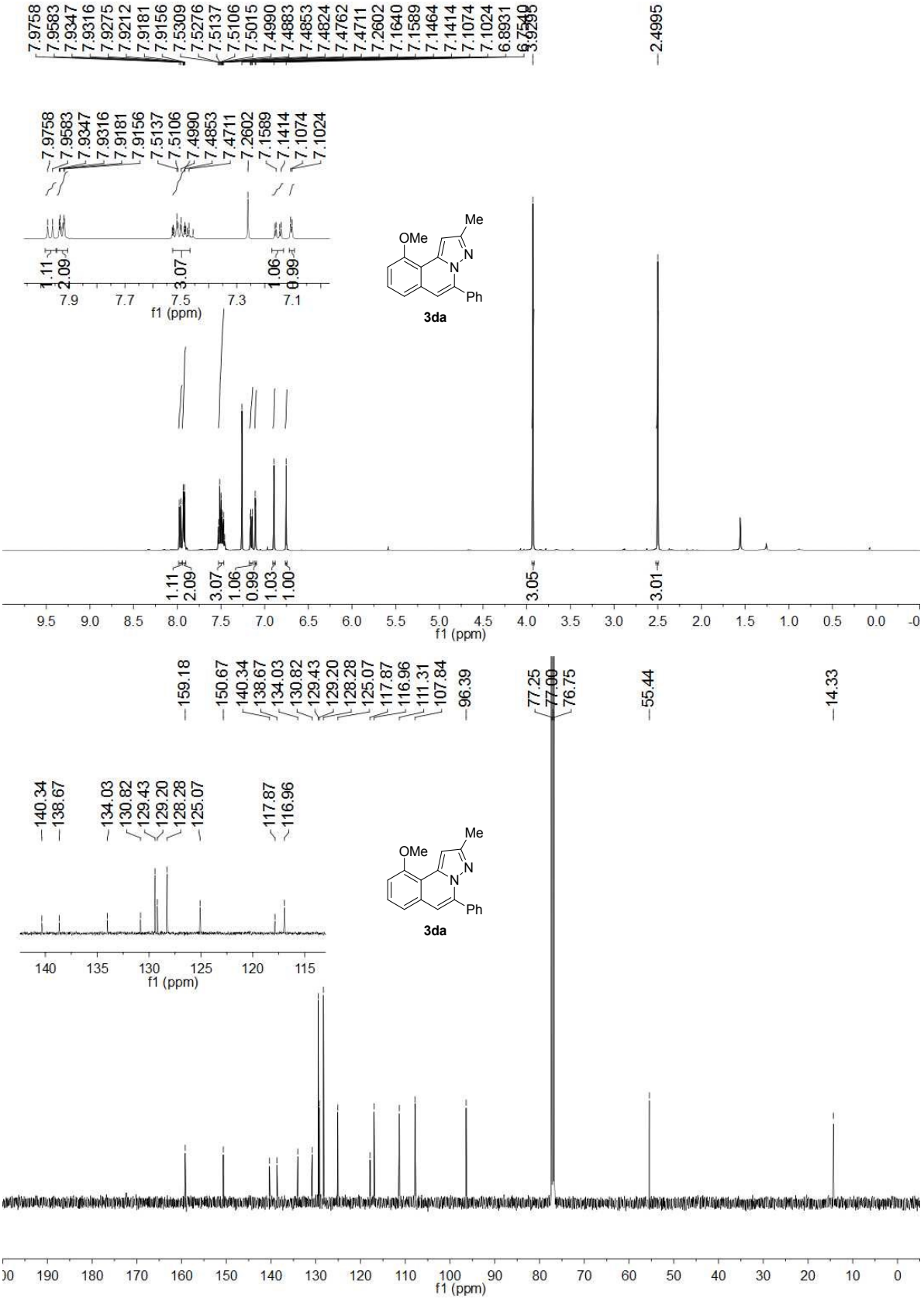
f1 (ppm)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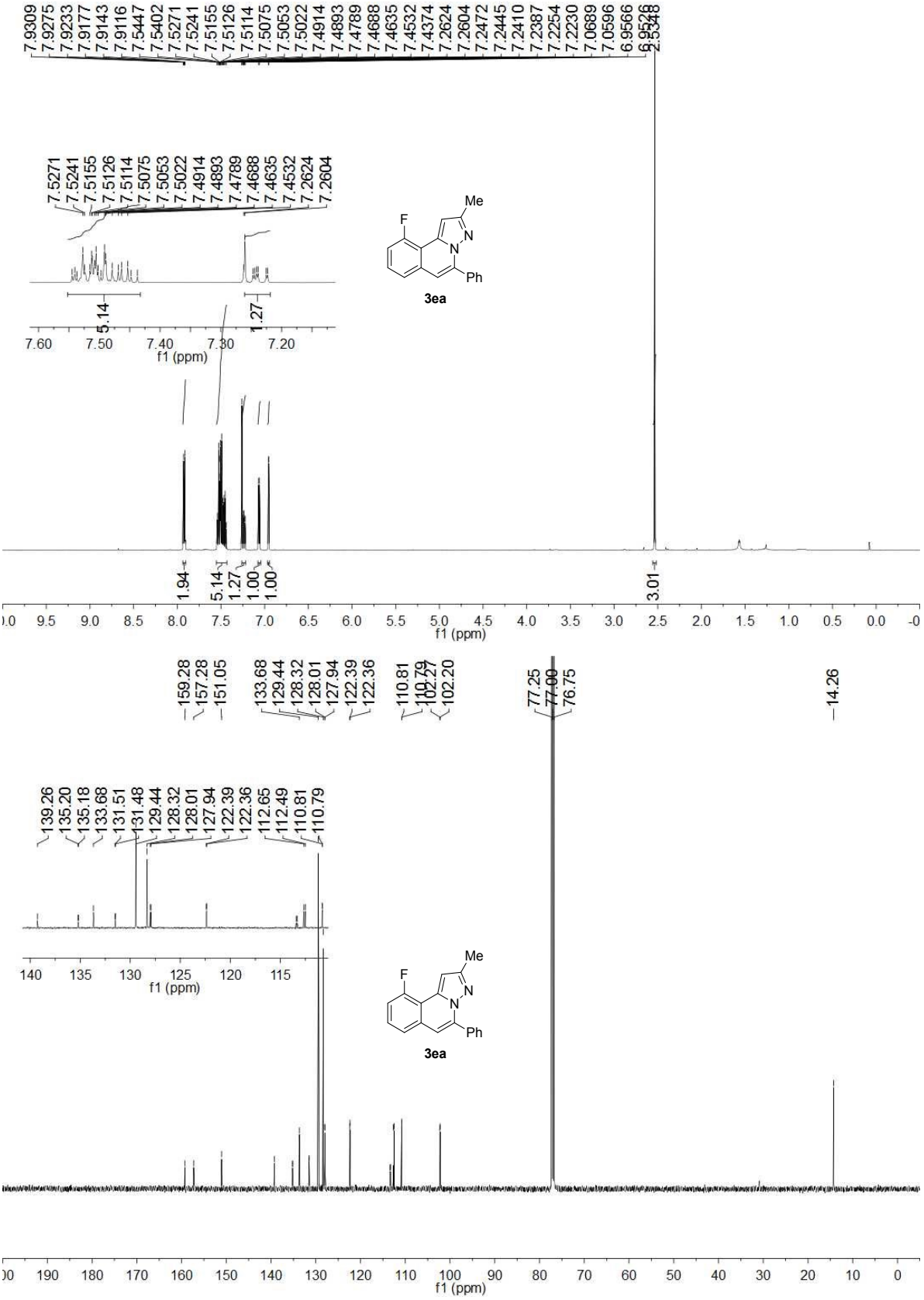
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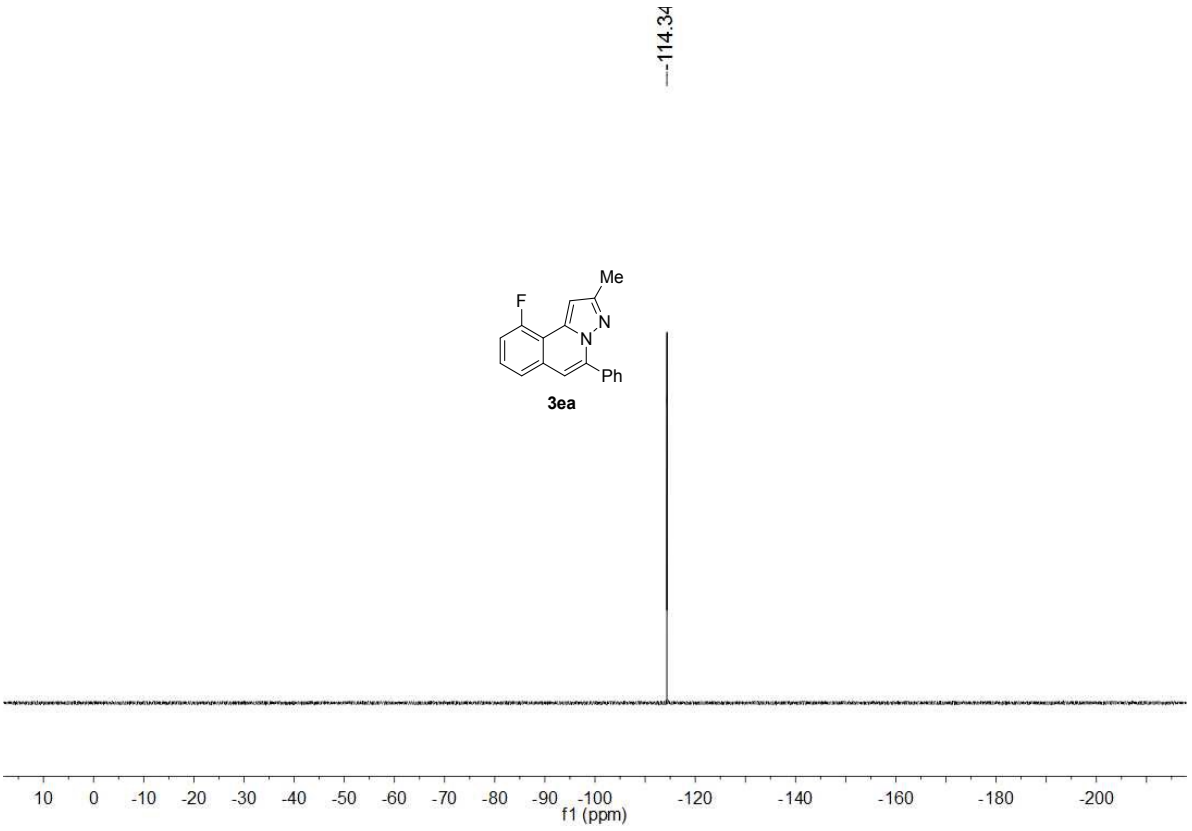
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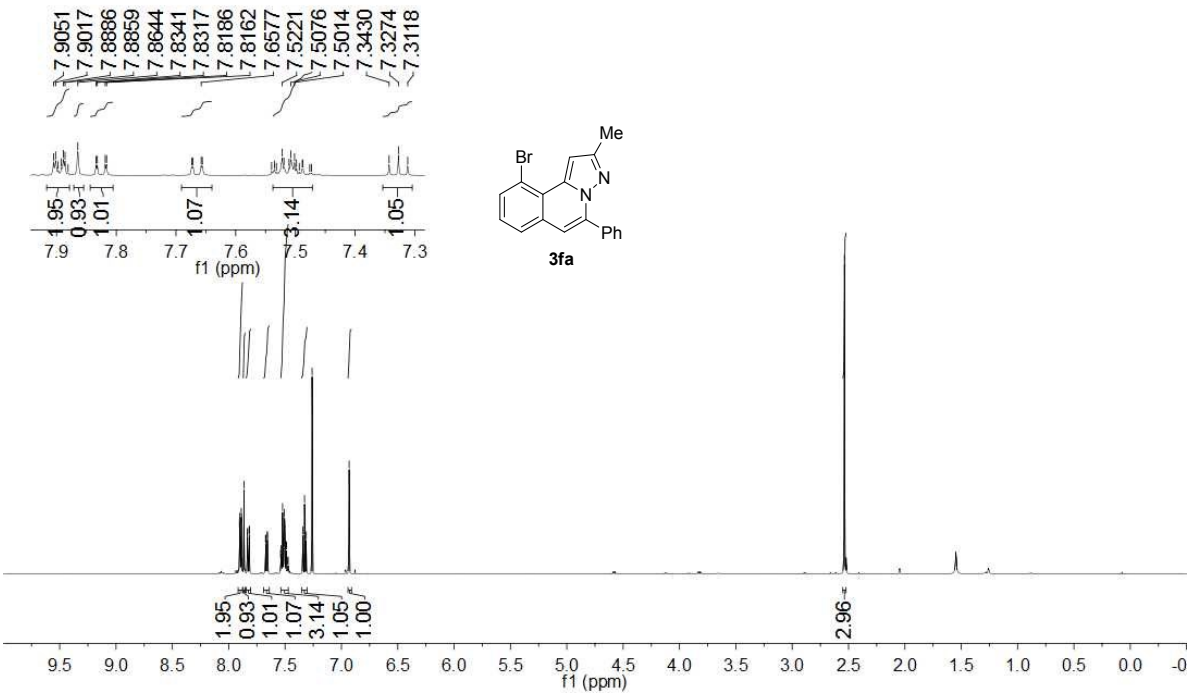
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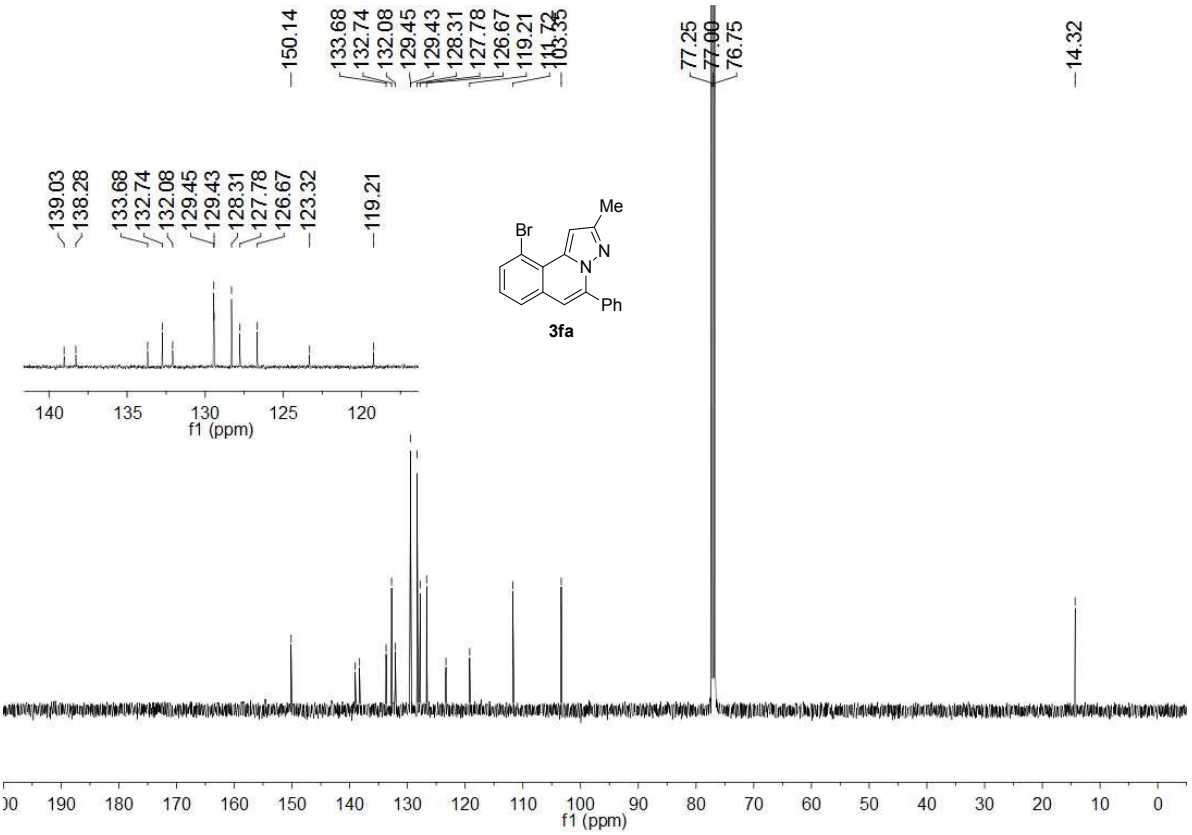
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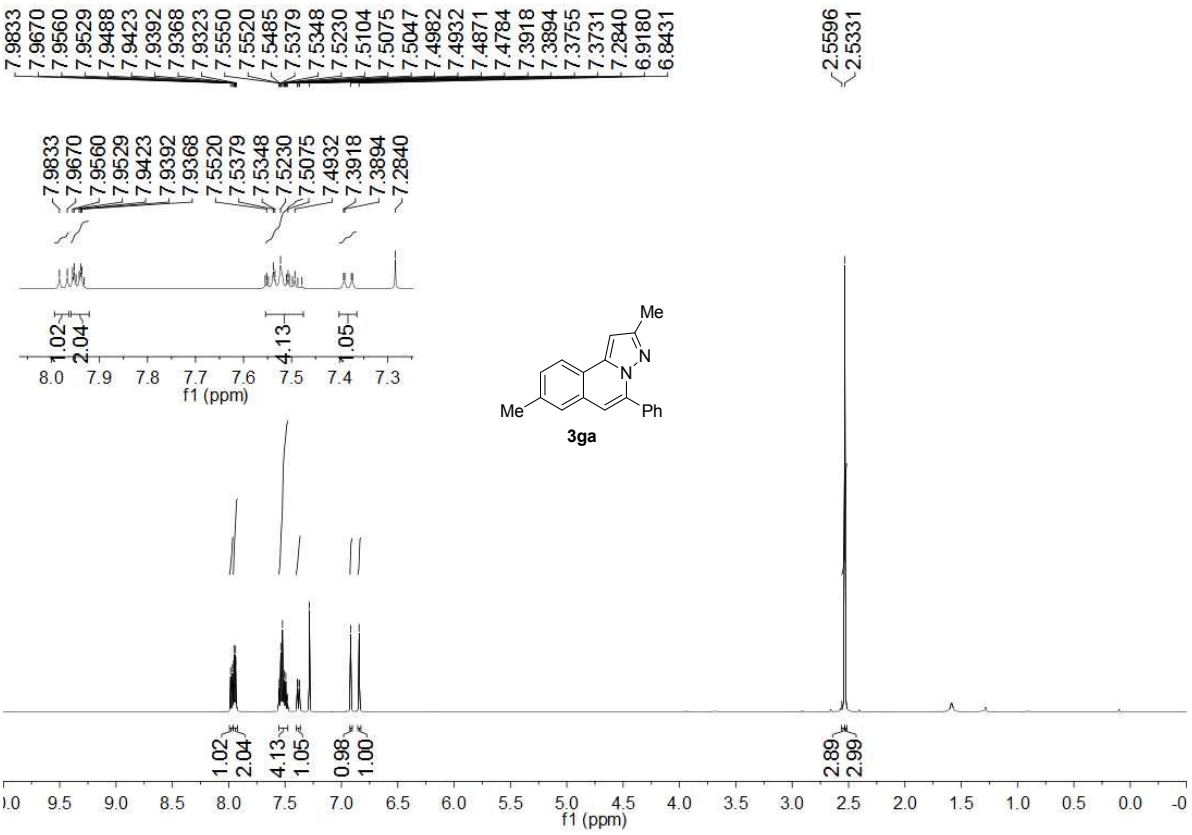
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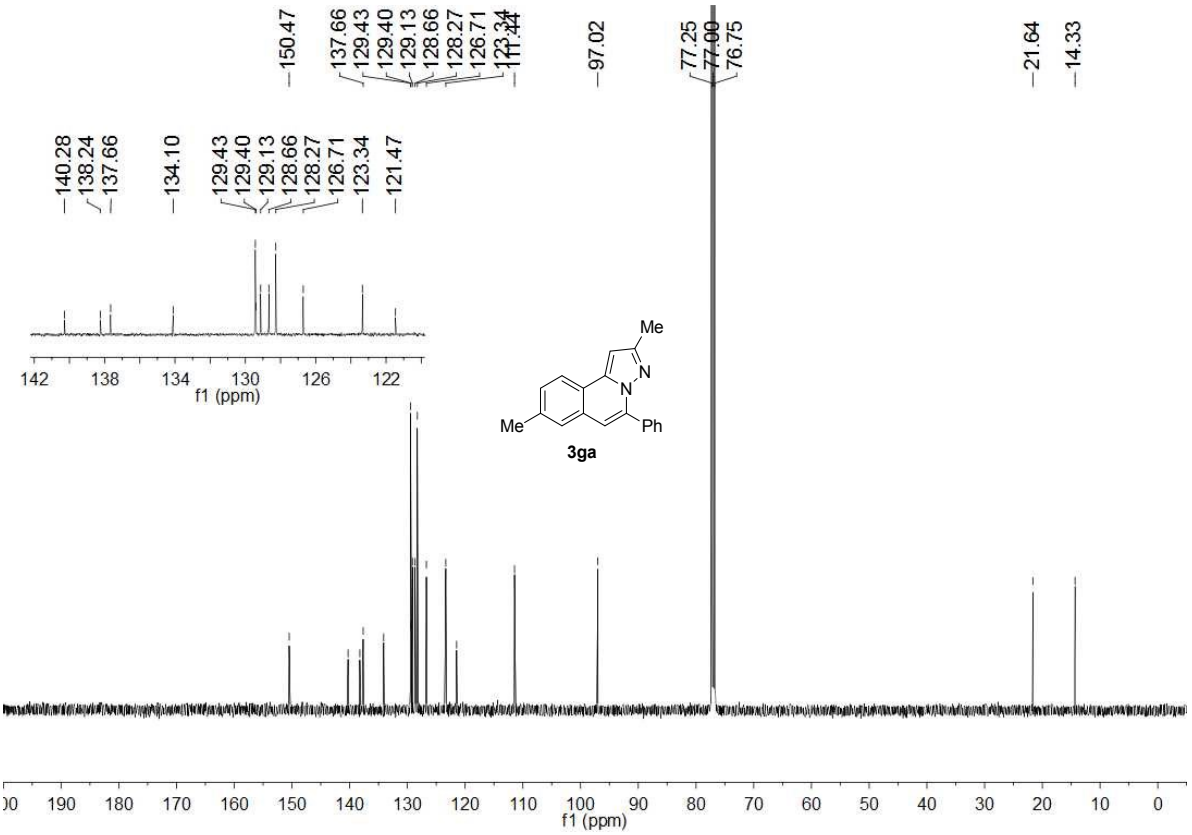
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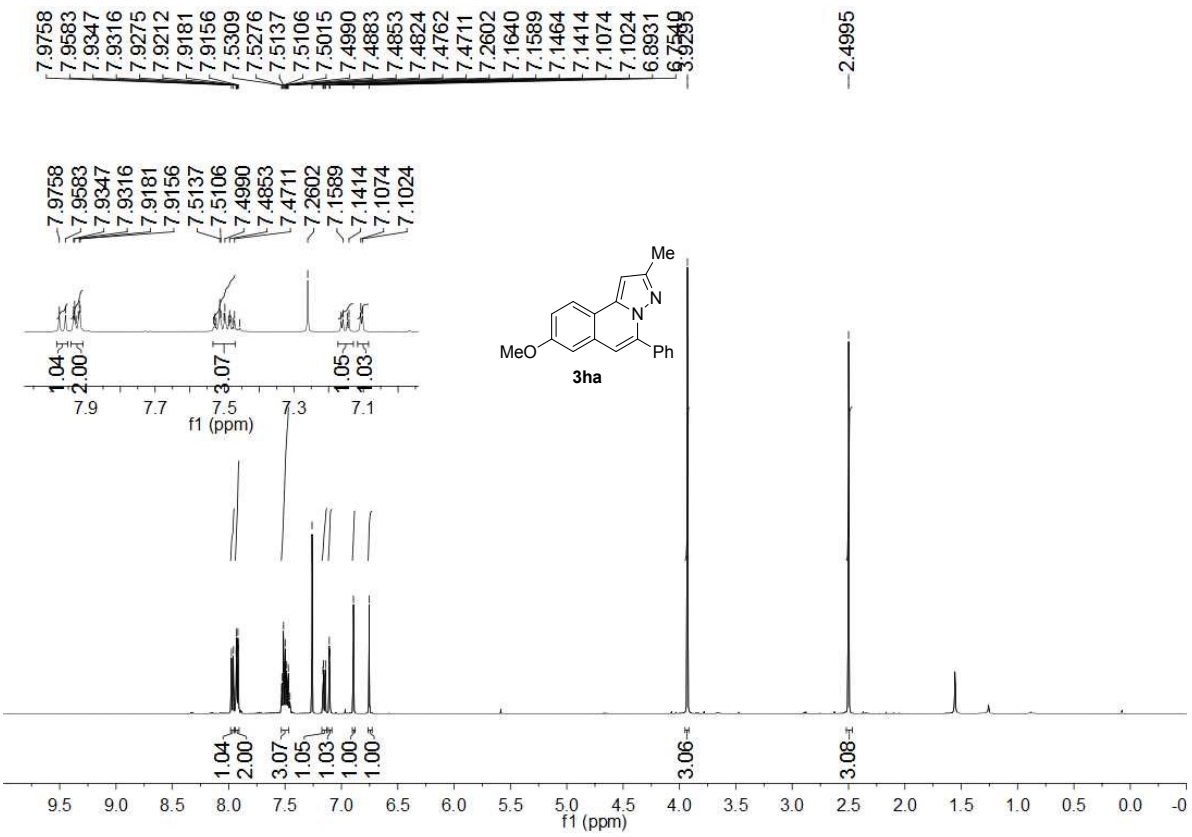
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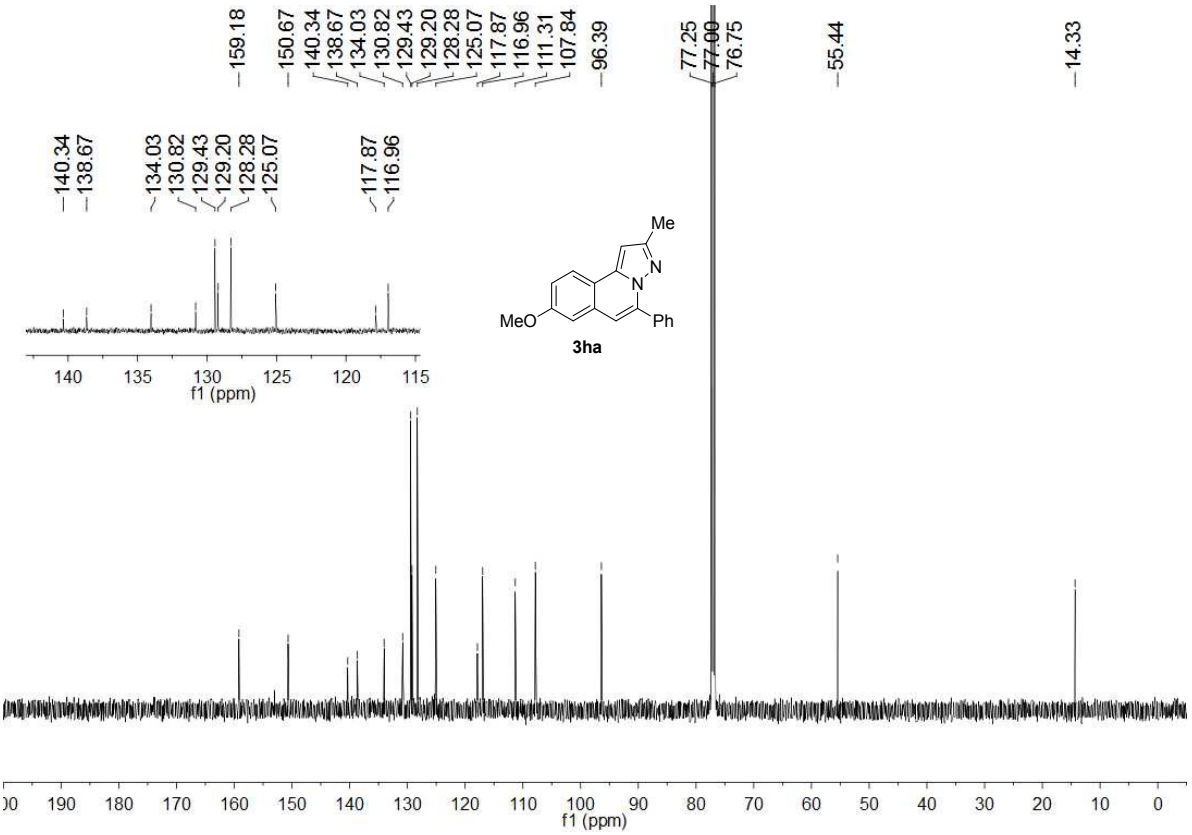
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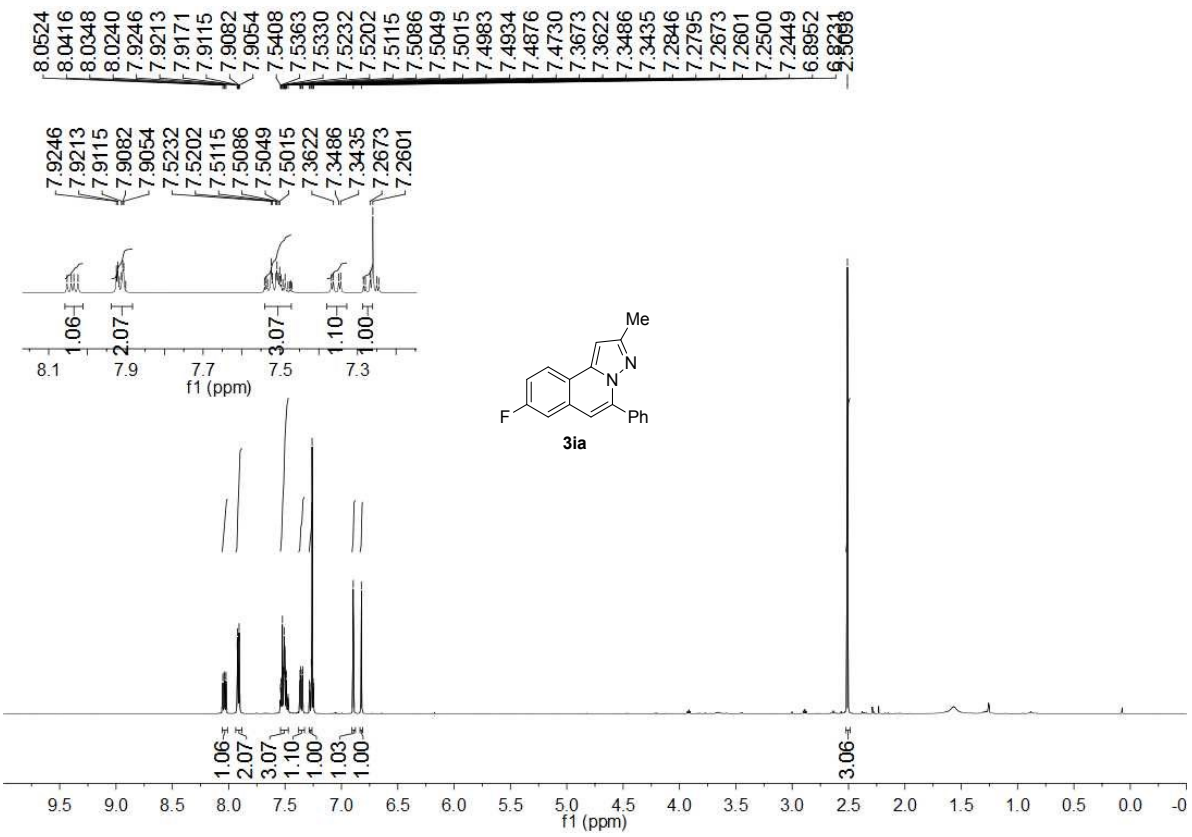
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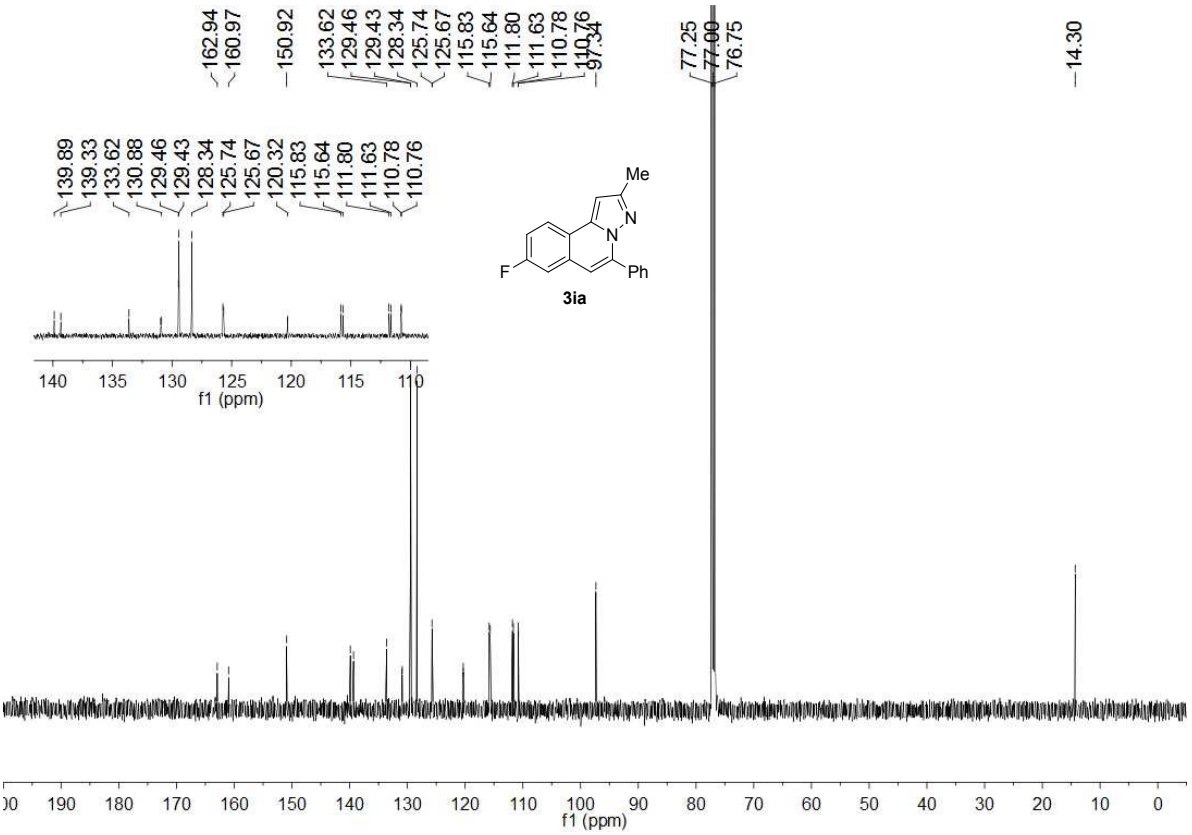
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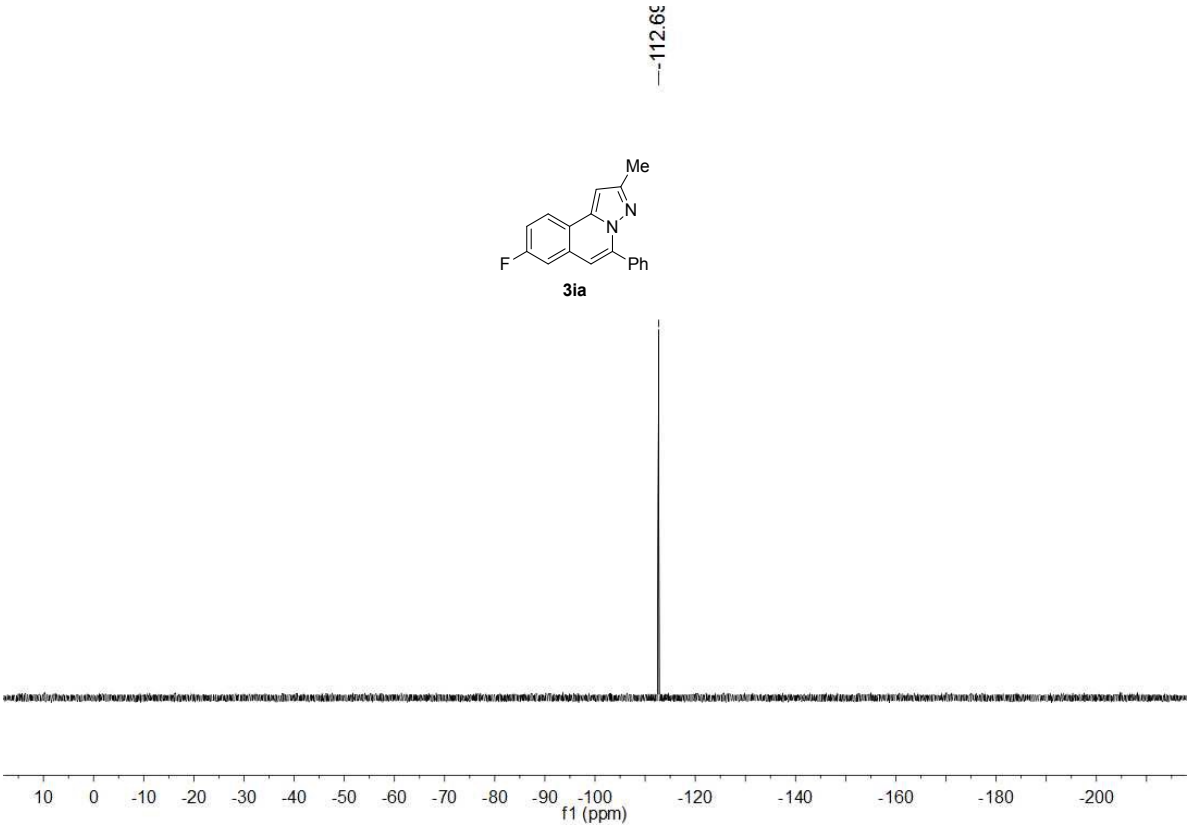
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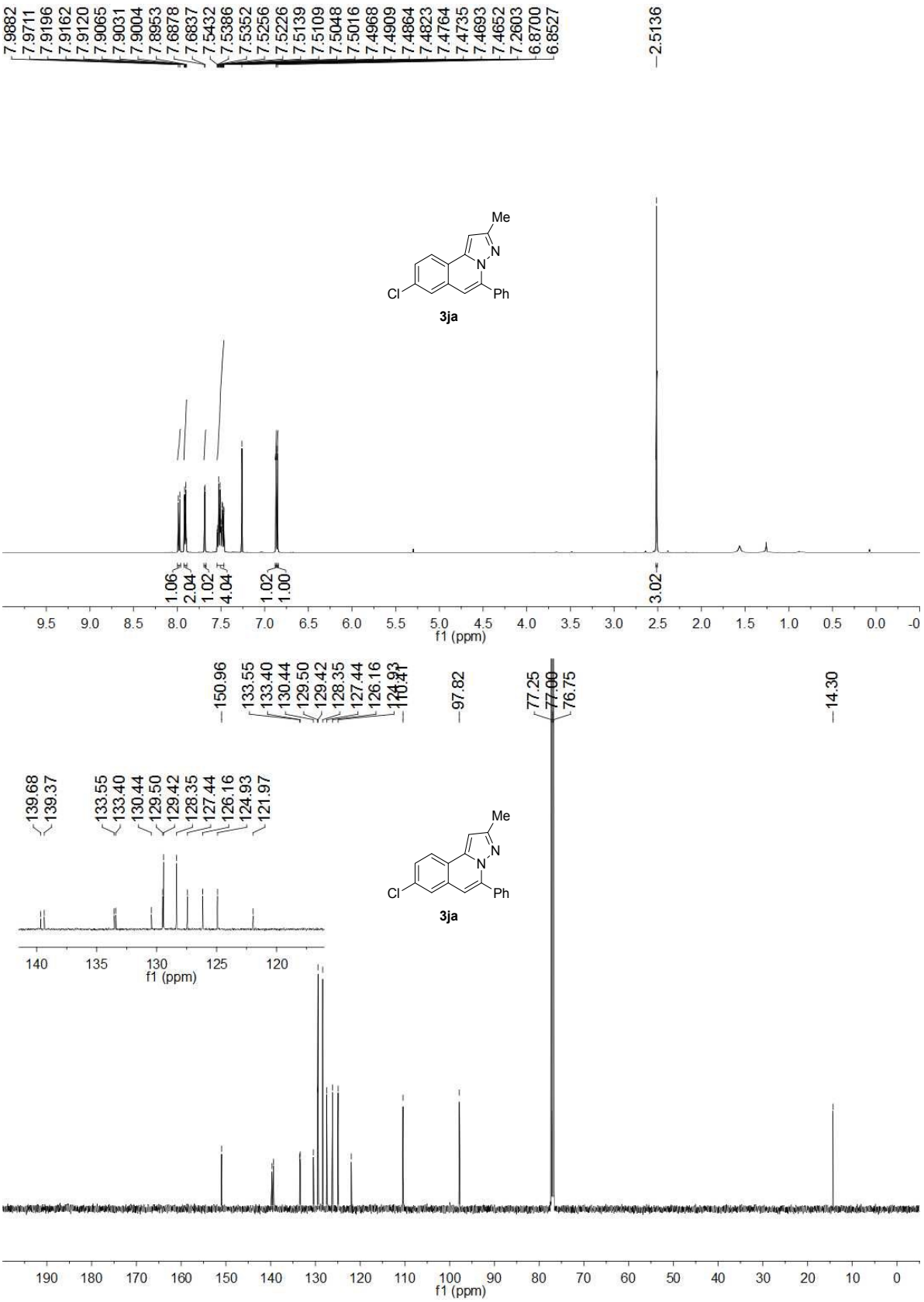
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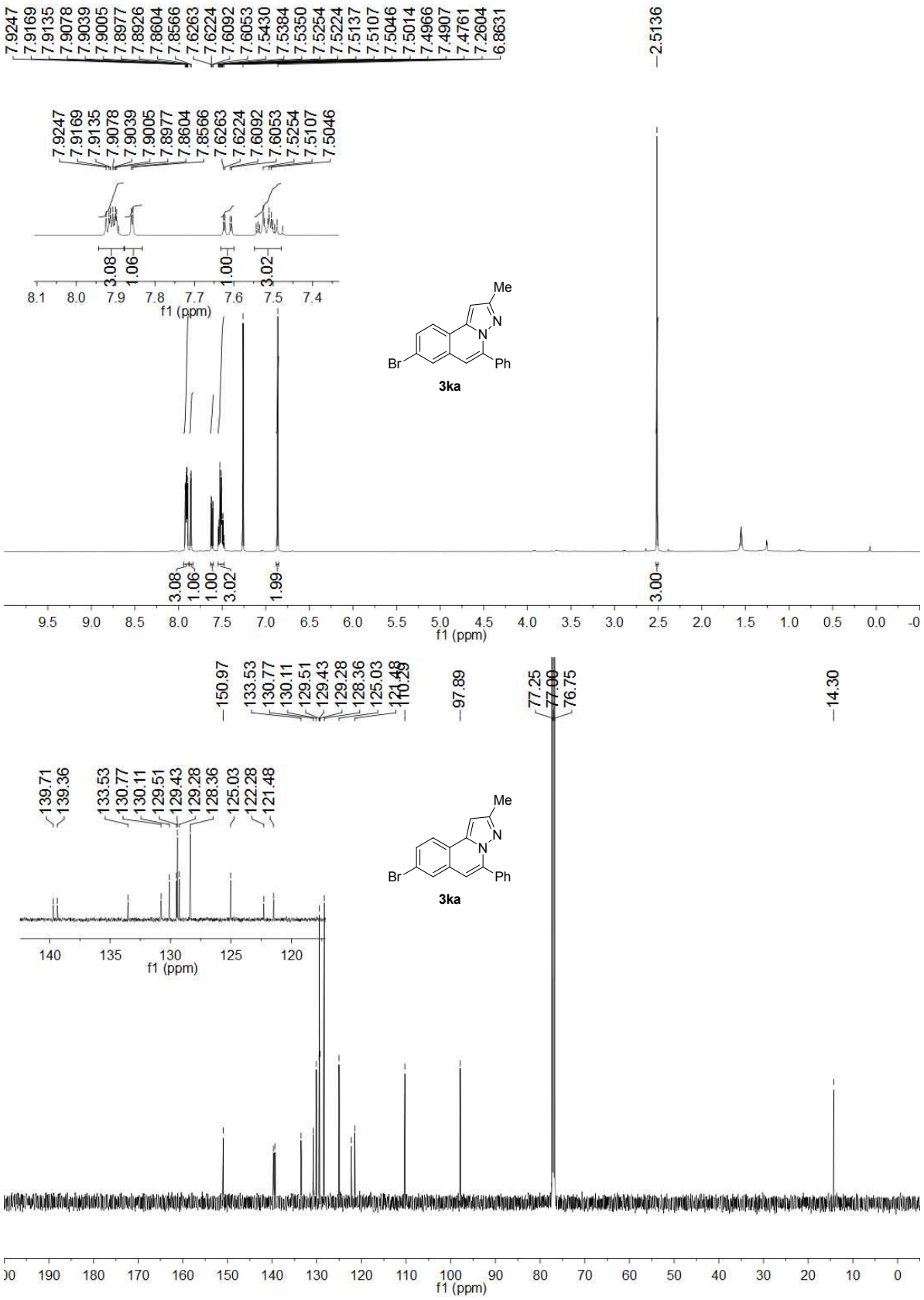
f1 (ppm)
f1 (ppm)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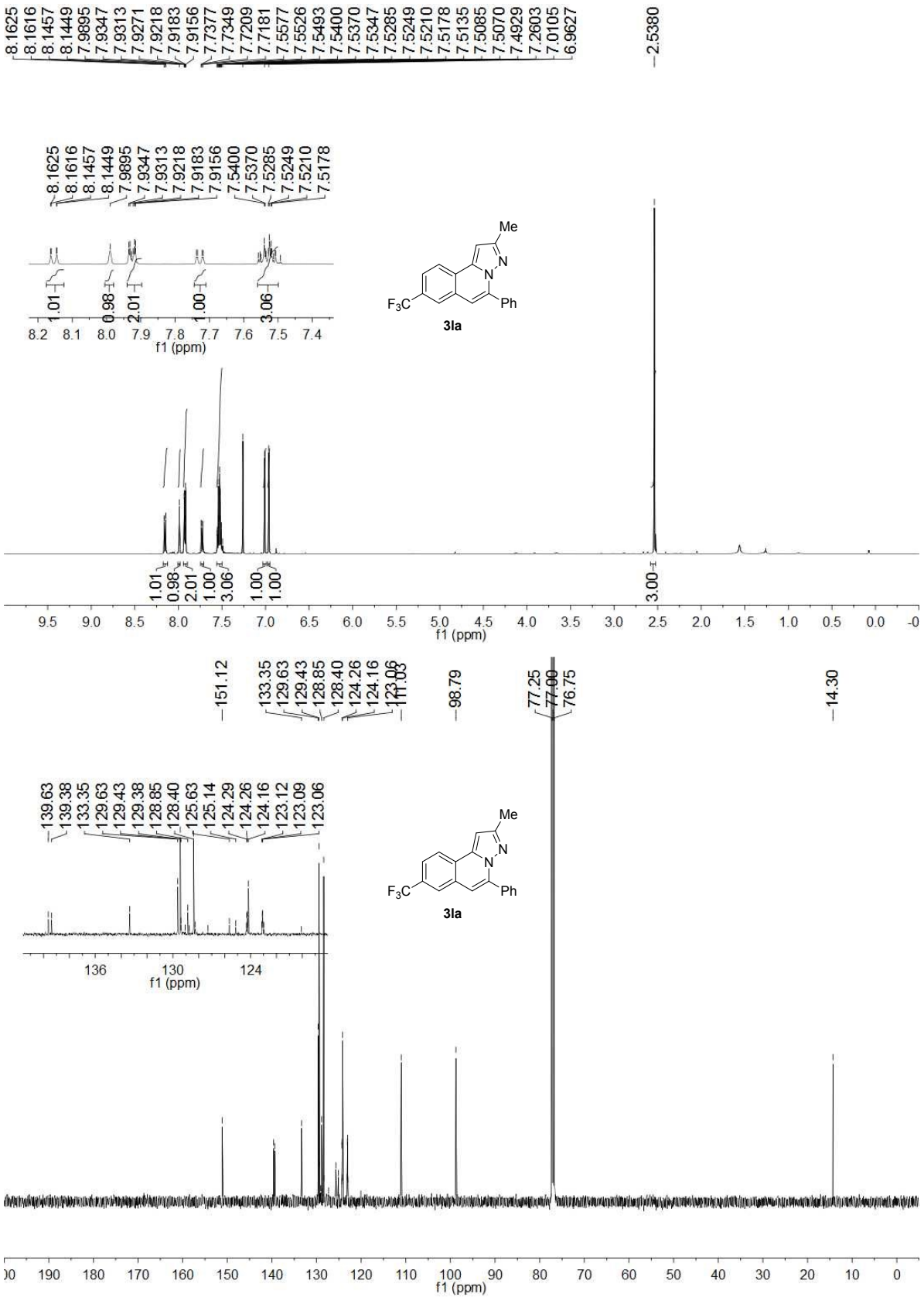
7.9169
7.9135
7.9078
7.9039
7.9005
7.8977
7.8926
7.8604
7.8566
7.6263
7.6224
7.6092
7.6053
7.5430
7.5384
7.5350
7.5254
7.5224
7.5137
7.5107
7.5046
7.5014
7.4966
7.4907
7.4761
7.2604
6.8631
2.5136
3.08
1.06
1.00
3.02
1.99
3.00
f1 (ppm)
Me
N
N
Br
Ph
3ka
150.97
133.53
130.77
130.11
129.51
129.43
129.28
128.36
125.03
122.28
121.48
97.89
77.25
77.00
76.75
14.30
139.71
139.36
f1 (ppm)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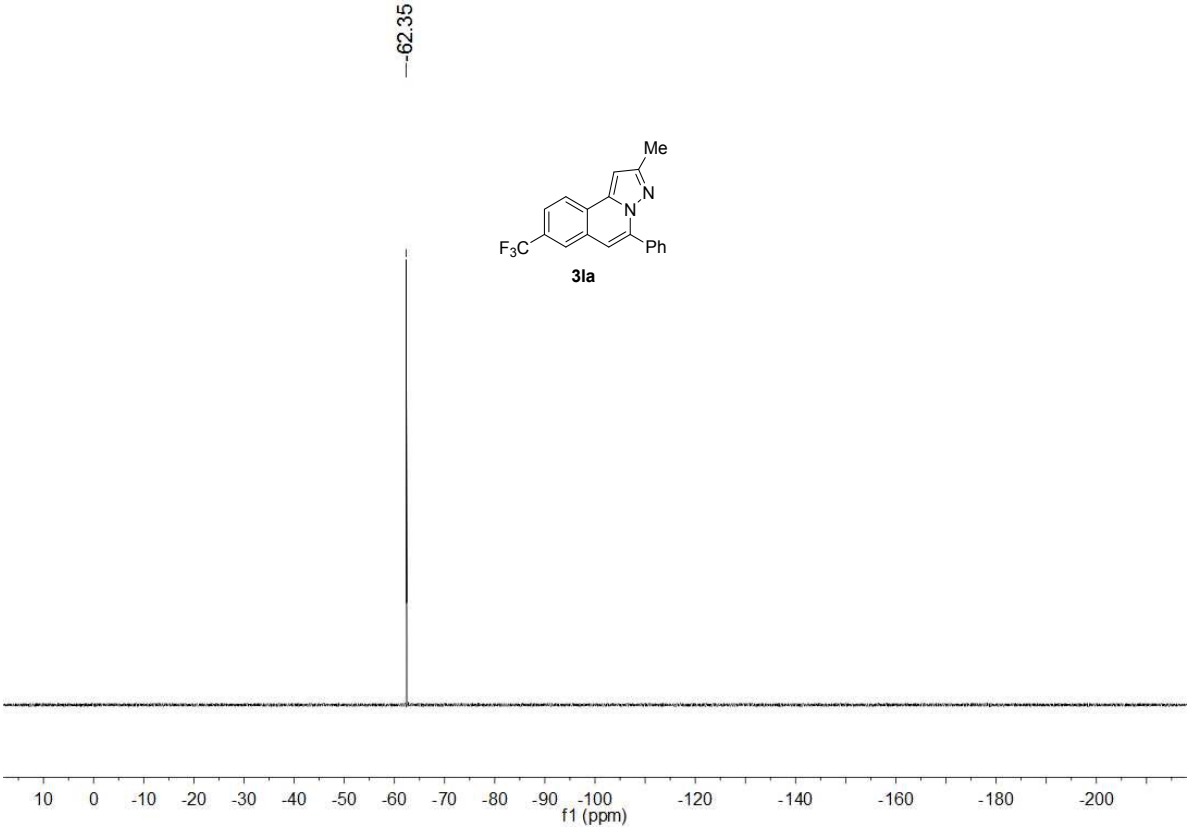
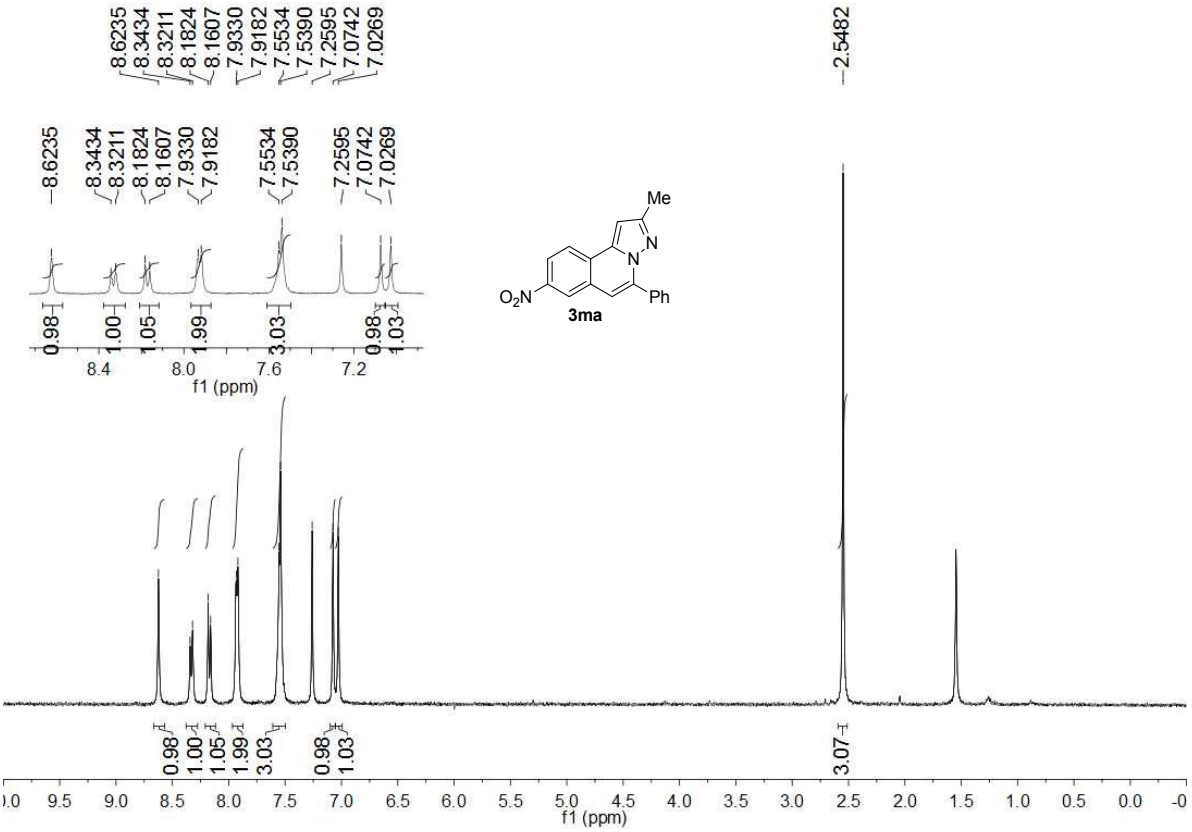
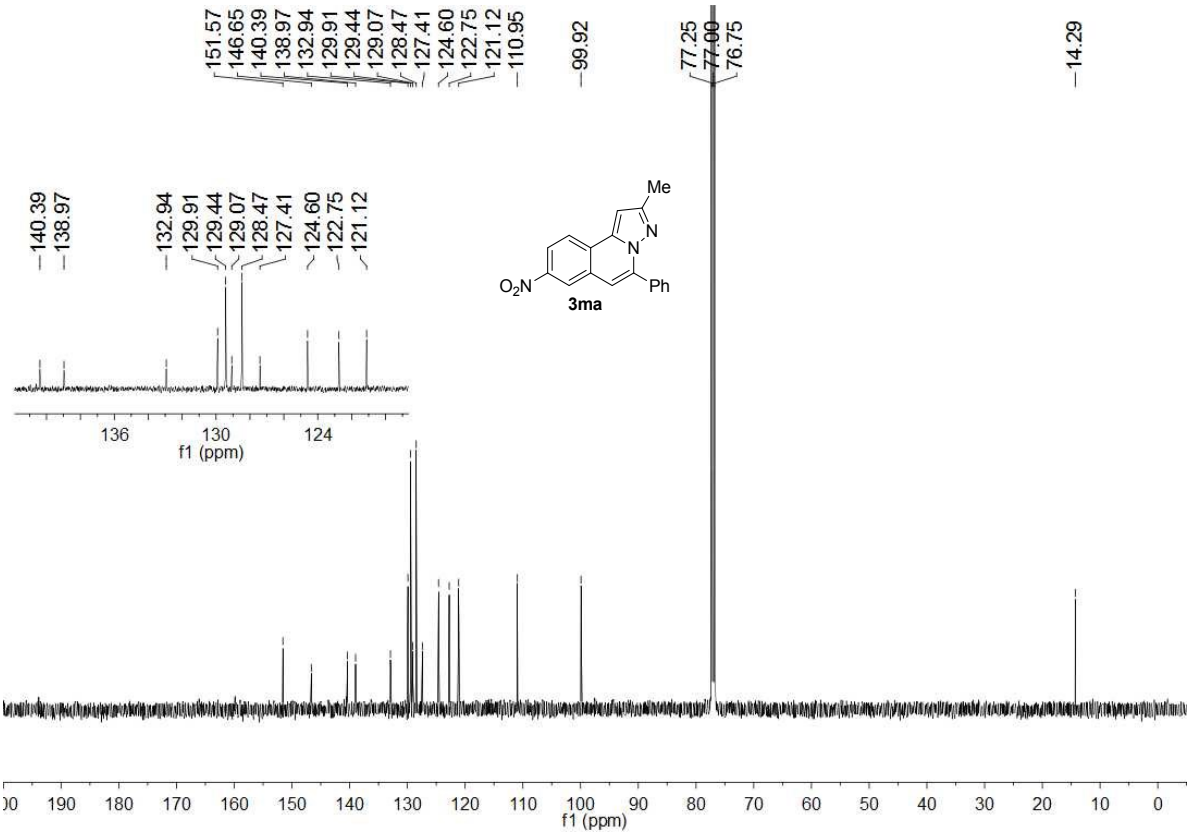
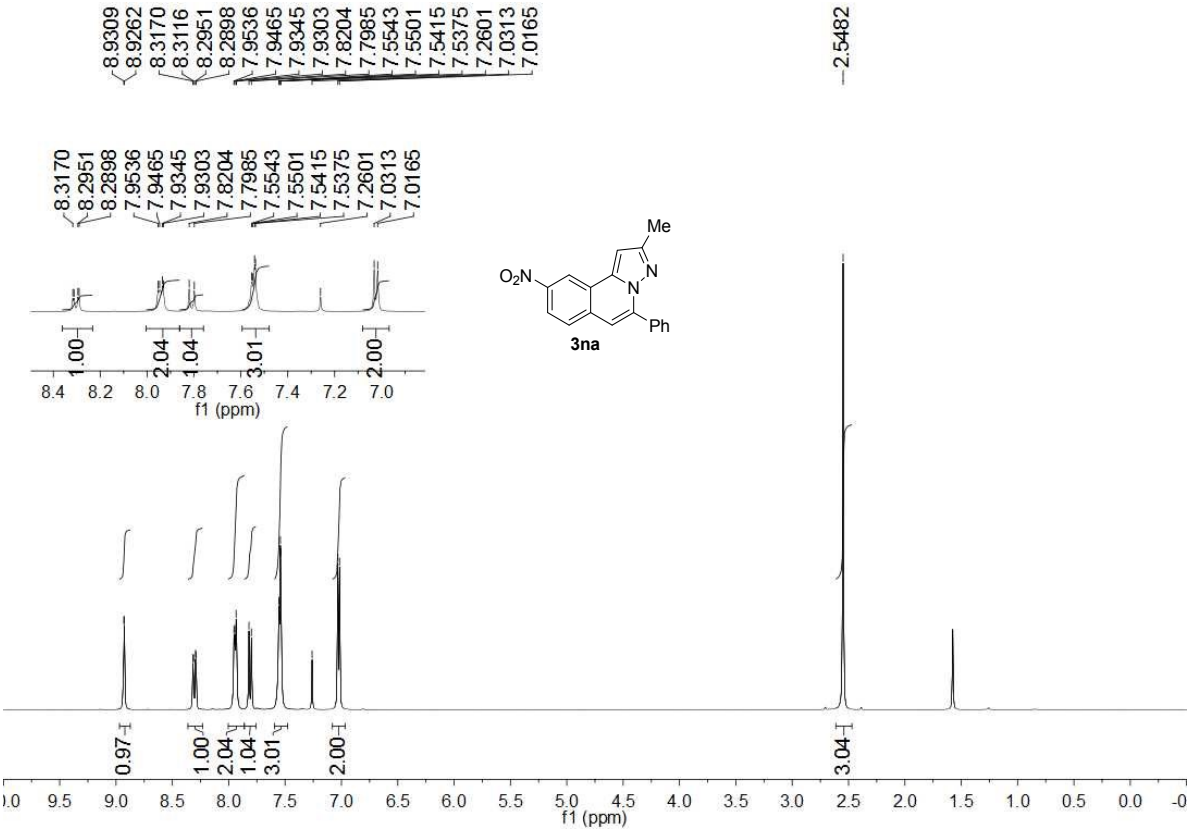
8.1616
8.1457
8.1449
7.9895
7.9347
7.9313
7.9271
7.9218
7.9183
7.9156
7.7377
7.7349
7.7209
7.7181
7.5577
7.5526
7.5493
7.5400
7.5370
7.5347
7.5285
7.5249
7.5210
7.5178
7.5135
7.5085
7.5070
7.4929
7.2603
7.0105
6.9627
2.5380
1.01
0.98
2.01
1.00
3.06
1.00
1.00
3.00
f1 (ppm)
Me
N
N
F3C
Ph
3la
151.12
133.35
129.63
129.43
128.85
128.40
124.26
124.16
123.06
111.03
98.79
77.25
77.00
76.75
14.30
139.63
139.38
133.35
129.63
129.43
129.38
128.85
128.40
125.63
125.14
124.29
124.26
124.16
123.12
123.09
123.06
136
130
124
f1 (ppm)


-62.35
Me
N
N
F3C
Ph
3la
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


8.6235
8.3434
8.3211
8.1824
8.1607
7.9330
7.9182
7.5534
7.5390
7.2595
7.0742
7.0269
-2.5482
Me
N
N
O2N
Ph
3ma
0.98
1.00
1.05
1.99
3.03
0.98
1.03
3.07
8.4
8.0
7.6
7.2
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


151.57
146.65
140.39
138.97
132.94
129.91
129.44
129.07
128.47
127.41
124.60
122.75
121.12
110.95
99.92
77.25
77.00
76.75
14.29
Me
N
N
O2N
Ph
3ma
f1 (ppm)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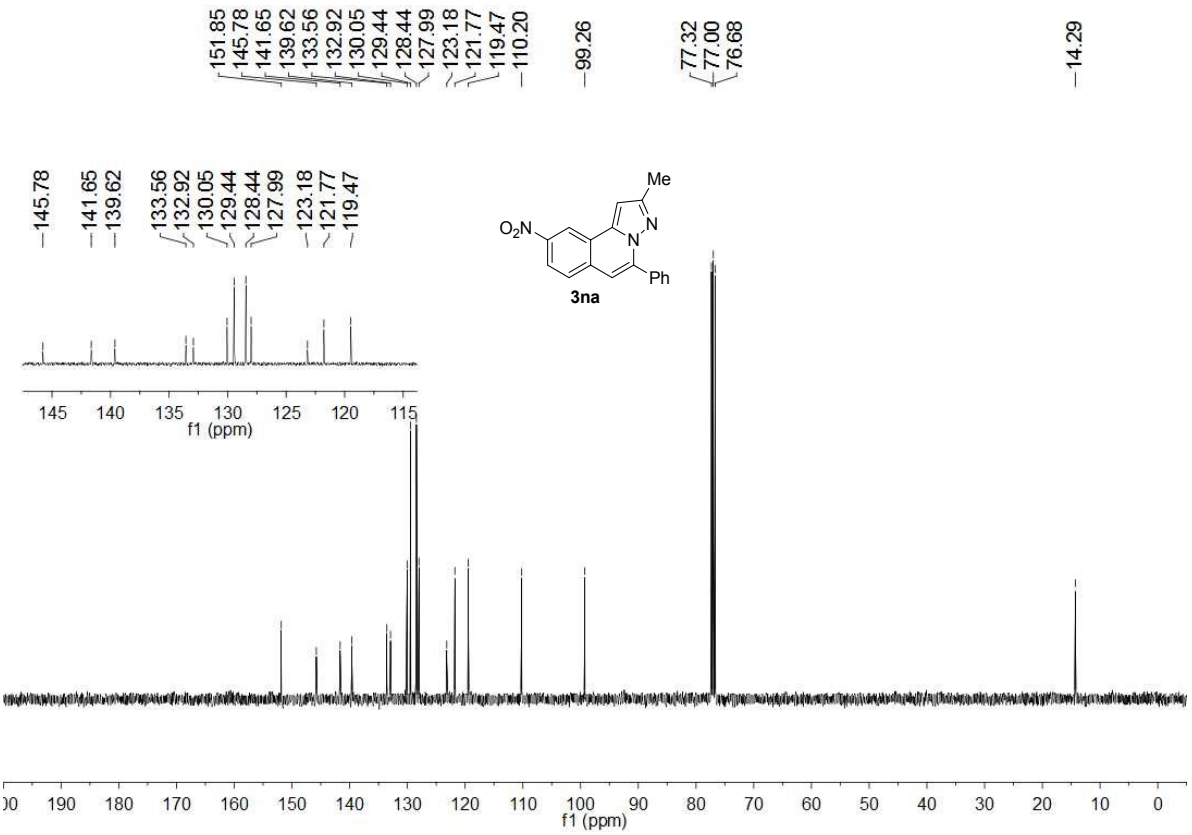
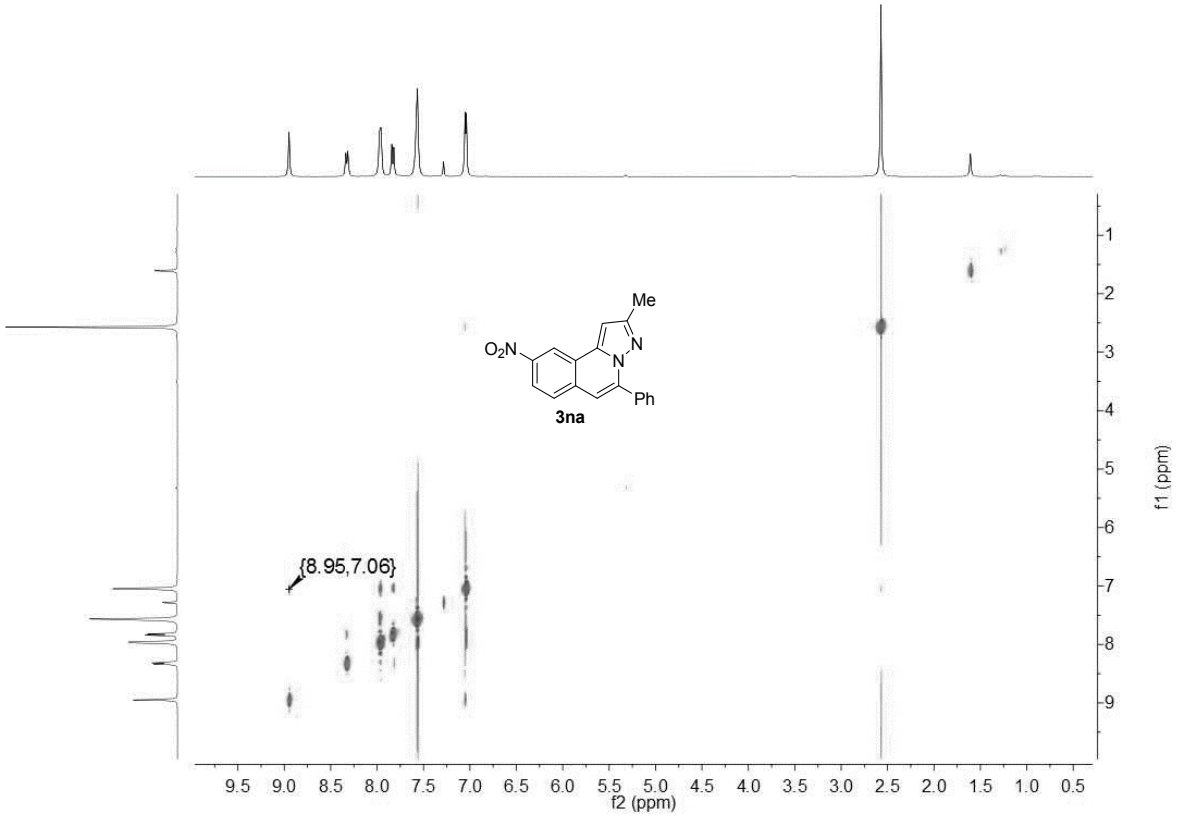
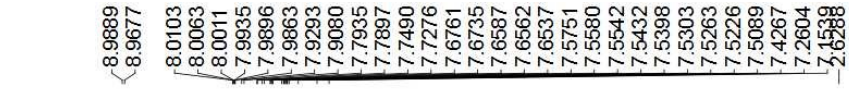
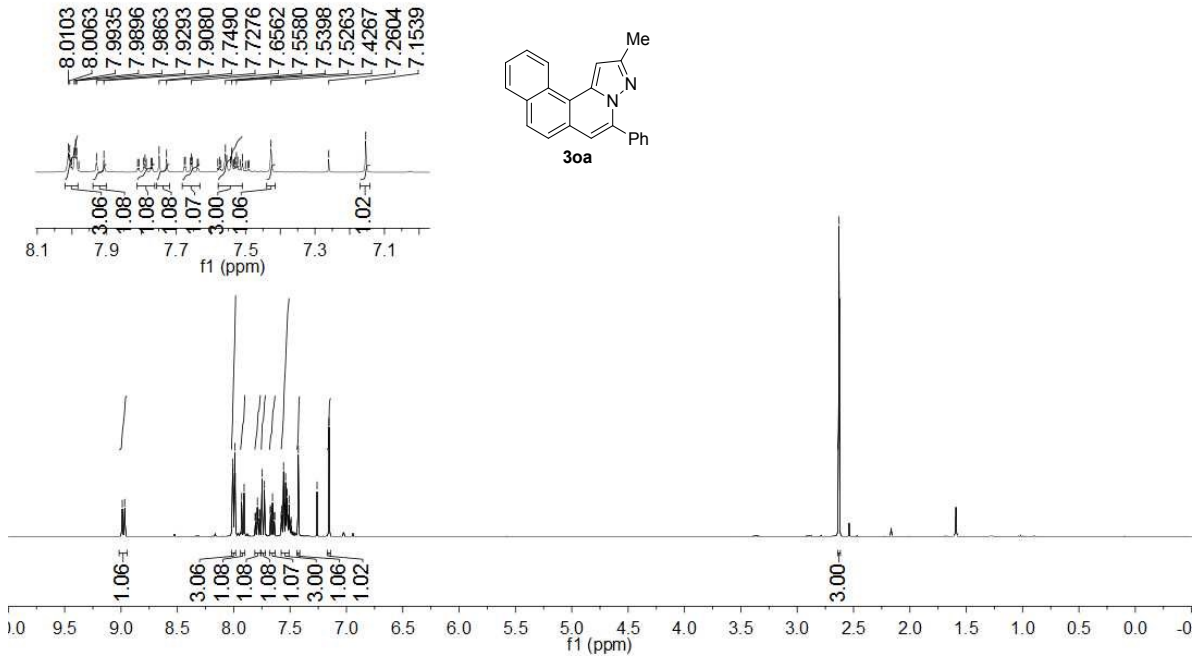
8.9262
8.3170
8.3116
8.2951
8.2898
7.9536
7.9465
7.9345
7.9303
7.8204
7.7985
7.5543
7.5501
7.5415
7.5375
7.2601
7.0313
7.0165
2.5482
1.00
2.04
1.04
3.01
2.00
0.97
1.00
2.04
1.04
3.01
2.00
3.04
Me
N
N
O2N
Ph
3na
f1 (ppm)


151.85
145.78
141.65
139.62
133.56
132.92
130.05
129.44
128.44
127.99
123.18
121.77
119.47
110.20
99.26
77.32
77.00
76.68
14.29
Me
O_2N
N
N
Ph
3na
f1 (ppm)


Me
O_2N
N
N
Ph
3na
{8.95,7.06}
f2 (ppm)
f1 (ppm)


8.9889
8.9677
8.0103
8.0063
8.0011
7.9935
7.9896
7.9863
7.9293
7.9080
7.7935
7.7897
7.7490
7.7276
7.6761
7.6735
7.6587
7.6562
7.6537
7.5751
7.5580
7.5542
7.5432
7.5398
7.5303
7.5263
7.5226
7.5089
7.4267
7.2604
2.6288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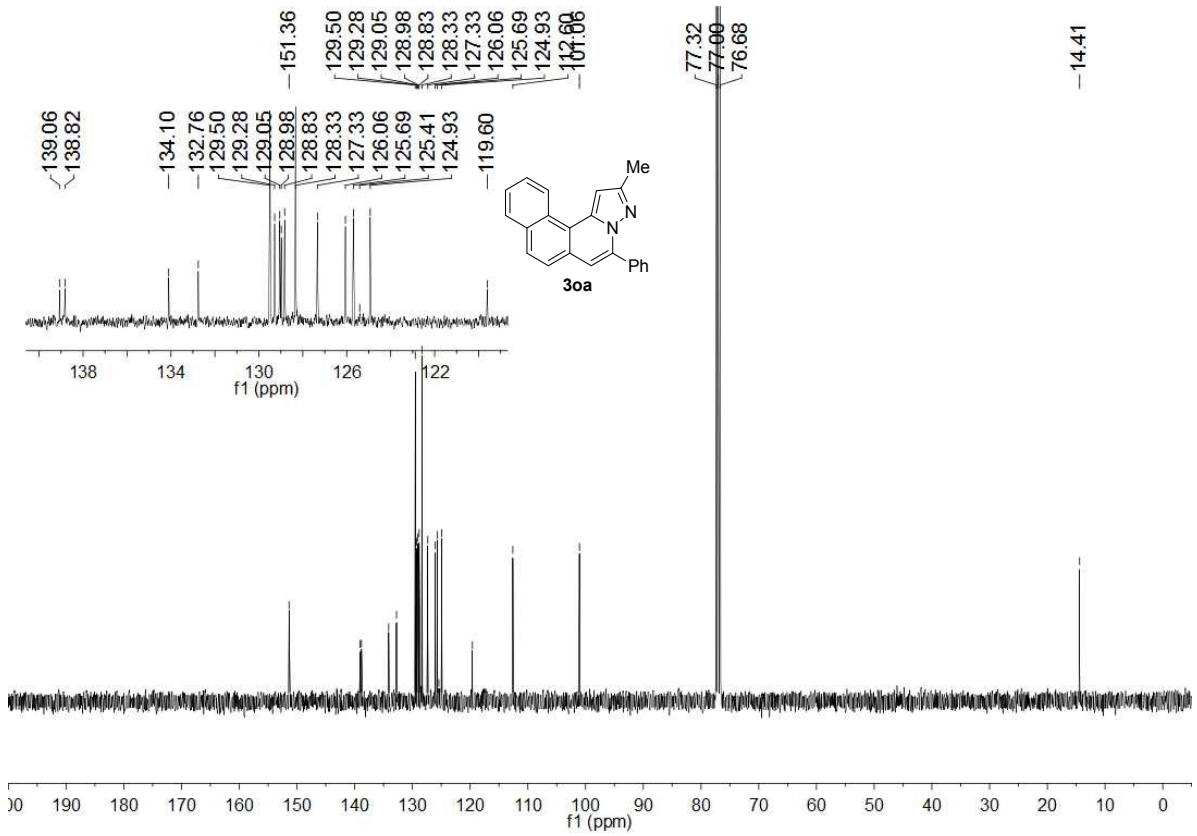
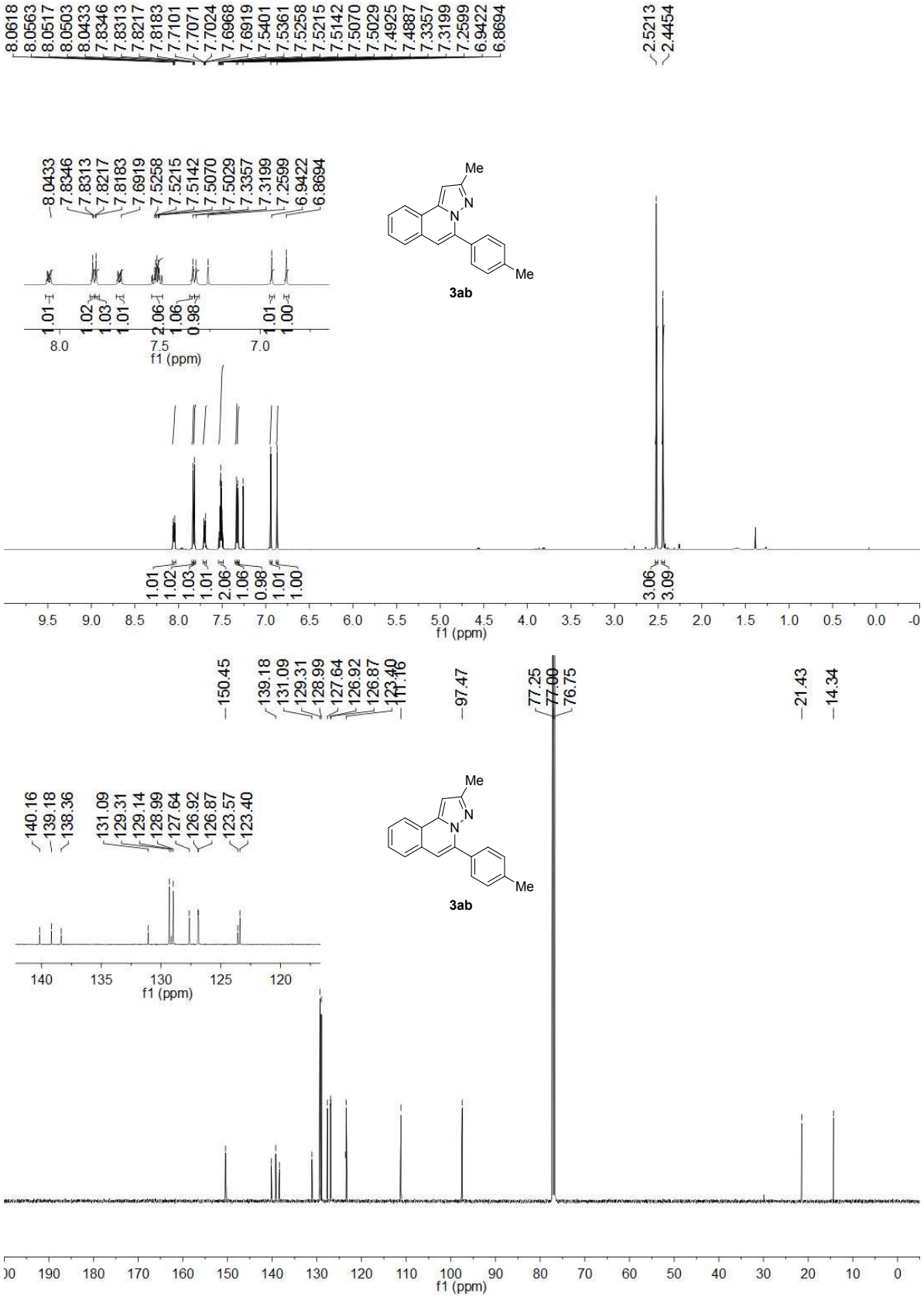
8.0063
7.9935
7.9896
7.9863
7.9293
7.9080
7.7490
7.7276
7.6562
7.5580
7.5398
7.5263
7.4267
7.2604
7.1539
Me
N
N
Ph
3oa
3.06
1.08
1.08
1.08
1.07
3.00
1.06
1.02
8.1
7.9
7.7
7.5
7.3
7.1
f1 (ppm)
1.06
3.06
1.08
1.08
1.08
1.07
3.00
1.06
1.02
3.00
f1 (ppm)


151.36
129.50
129.28
129.05
128.98
128.83
128.33
127.33
126.06
125.69
124.93
112.60
101.66
77.32
77.00
76.68
14.41
139.06
138.82
134.10
132.76
129.50
129.28
129.05
128.98
128.83
128.33
127.33
126.06
125.69
125.41
124.93
119.60
Me
N
N
Ph
3oa
138
134
130
126
122
f1 (ppm)
f1 (ppm)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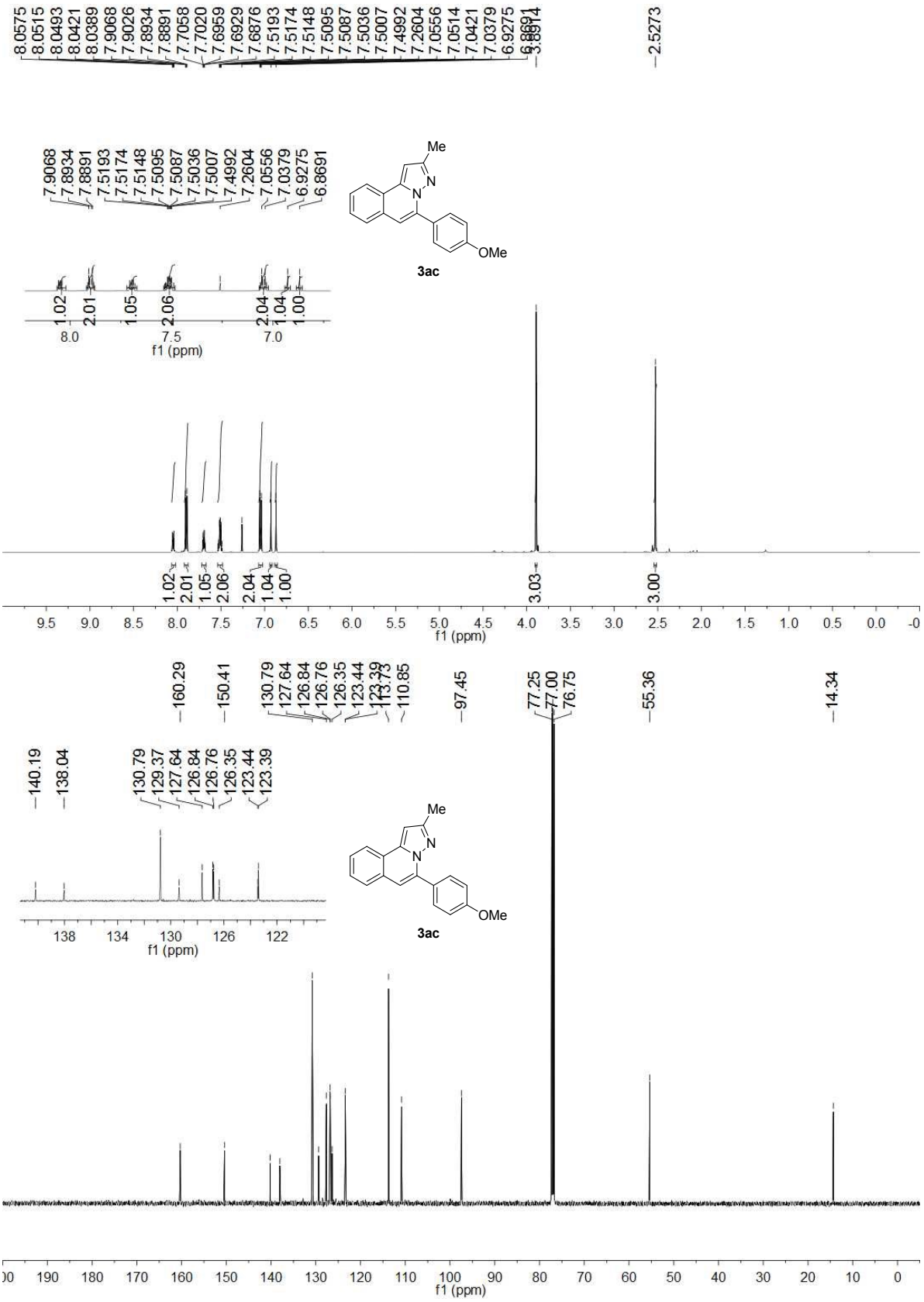
8.0563
8.0517
8.0503
8.0433
7.8346
7.8313
7.8217
7.8183
7.7101
7.7071
7.7024
7.6968
7.6919
7.5401
7.5361
7.5258
7.5215
7.5142
7.5070
7.5029
7.4925
7.4887
7.3357
7.3199
7.2599
6.9422
6.8694
2.5213
2.4454
Me
N
N
Me
3ab
1.01
1.02
1.03
1.01
2.06
1.06
0.98
1.01
1.00
8.0
7.5
7.0
f1 (ppm)
3.06
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)
150.45
139.18
131.09
129.31
128.99
127.64
126.92
126.87
123.40
111.16
97.47
77.25
77.00
76.75
21.43
14.34
140.16
139.18
138.36
131.09
129.31
129.14
128.99
127.64
126.92
126.87
123.57
123.40
140
135
130
125
120
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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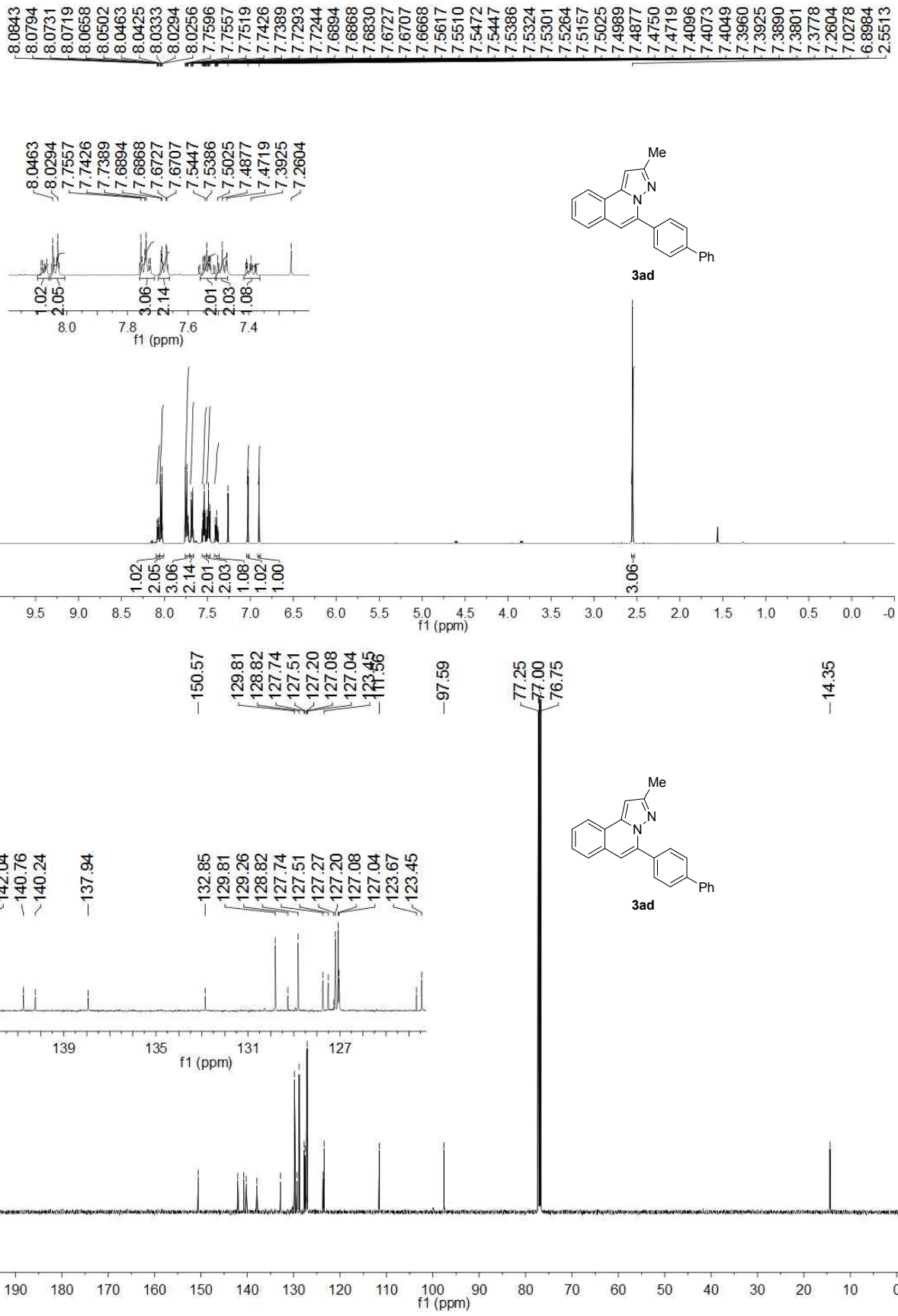
8.0515
8.0493
8.0421
8.0389
7.9068
7.9026
7.8934
7.8891
7.7058
7.7020
7.6959
7.6929
7.6876
7.5193
7.5174
7.5148
7.5095
7.5087
7.5036
7.5007
7.4992
7.2604
7.0556
7.0514
7.0421
7.0379
6.9275
3.8914
2.5273
Me
N
N
OMe
3ac
1.02
2.01
1.05
2.06
2.04
1.04
1.00
8.0
7.5
7.0
f1 (ppm)
3.03
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)
160.29
150.41
130.79
127.64
126.84
126.76
126.35
123.44
123.39
113.73
110.85
97.45
77.25
77.00
76.75
55.36
14.34
140.19
138.04
130.79
129.37
127.64
126.84
126.76
126.35
123.44
123.39
Me
N
N
OMe
3ac
138
134
130
126
122
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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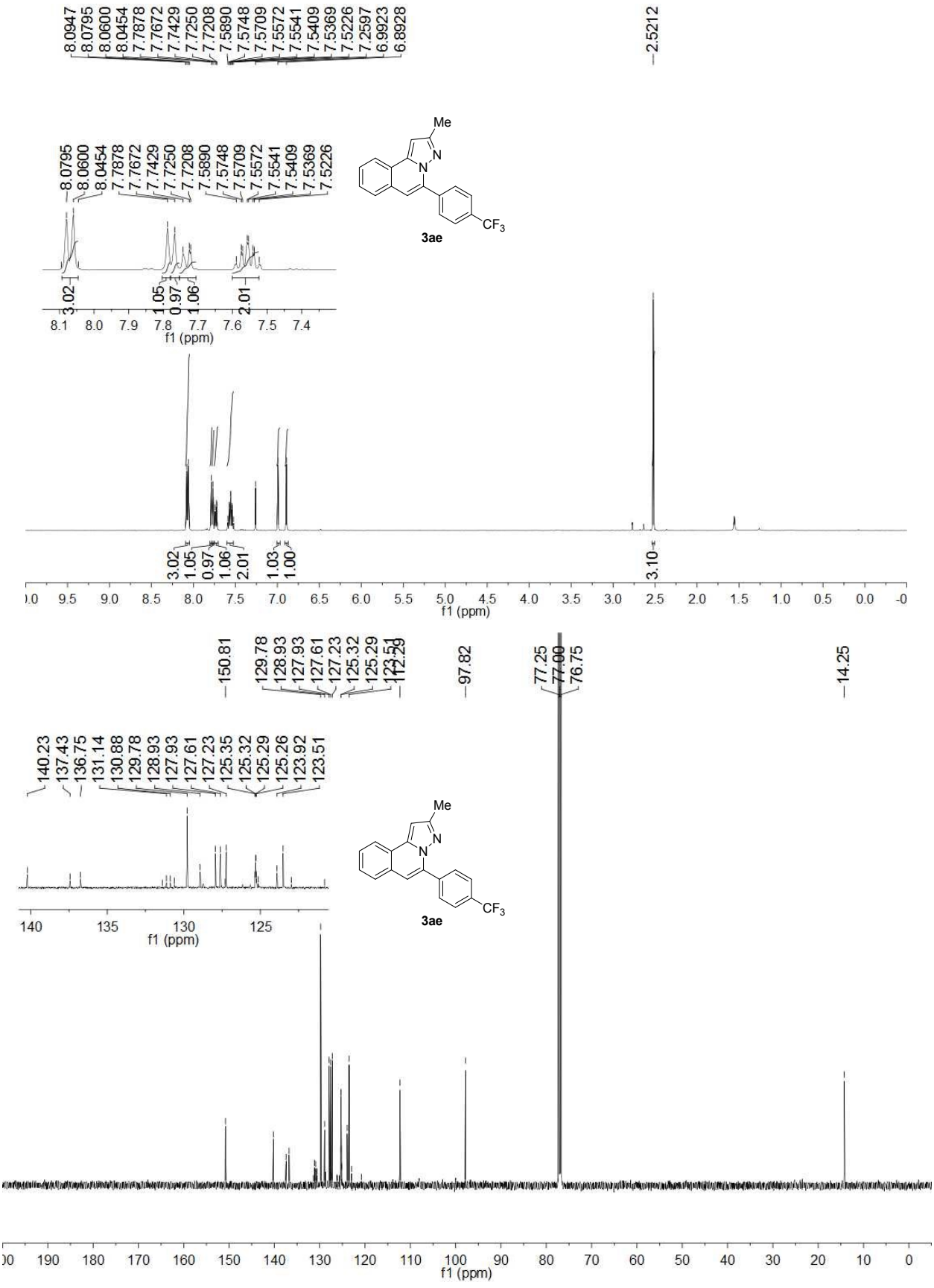
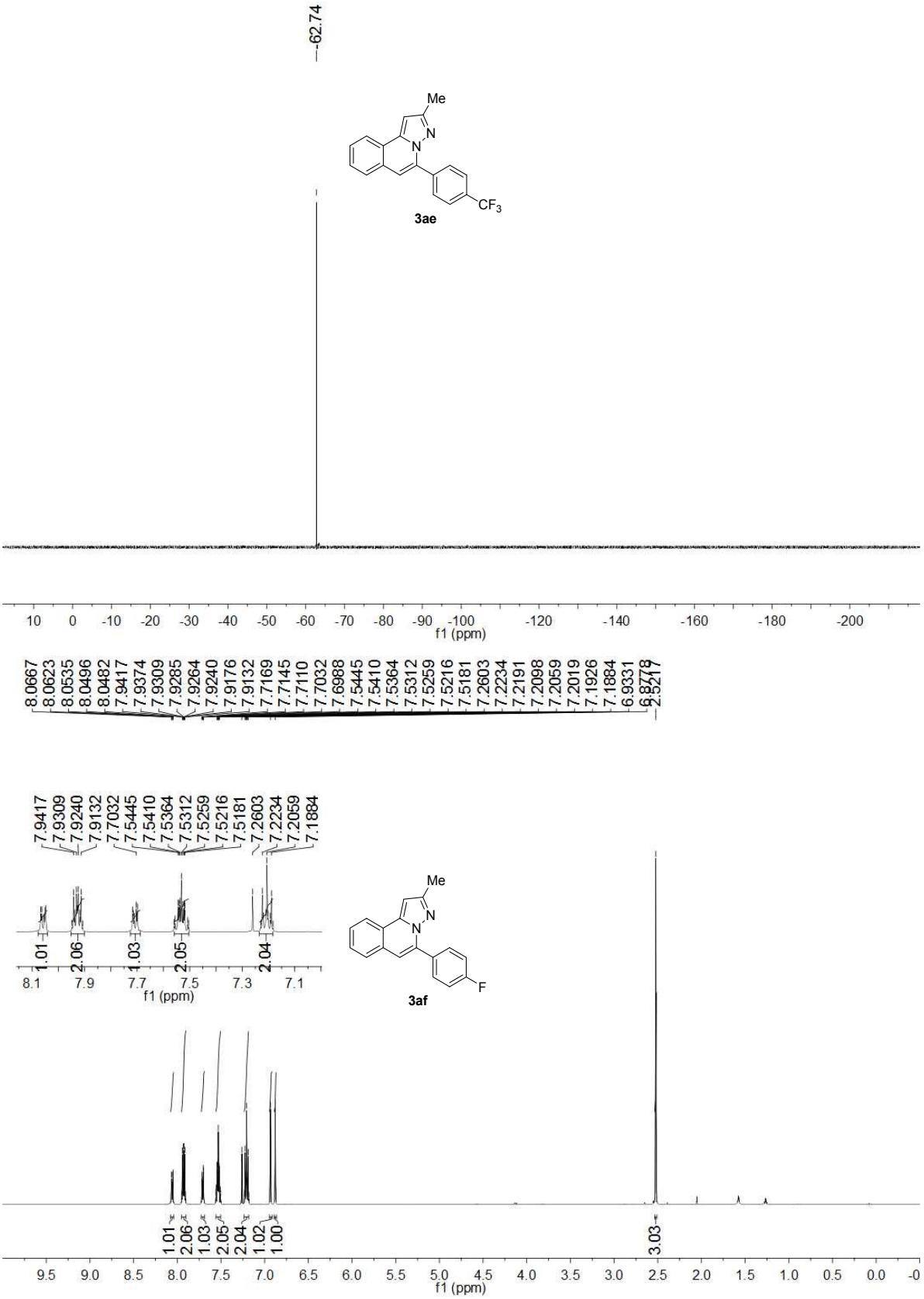
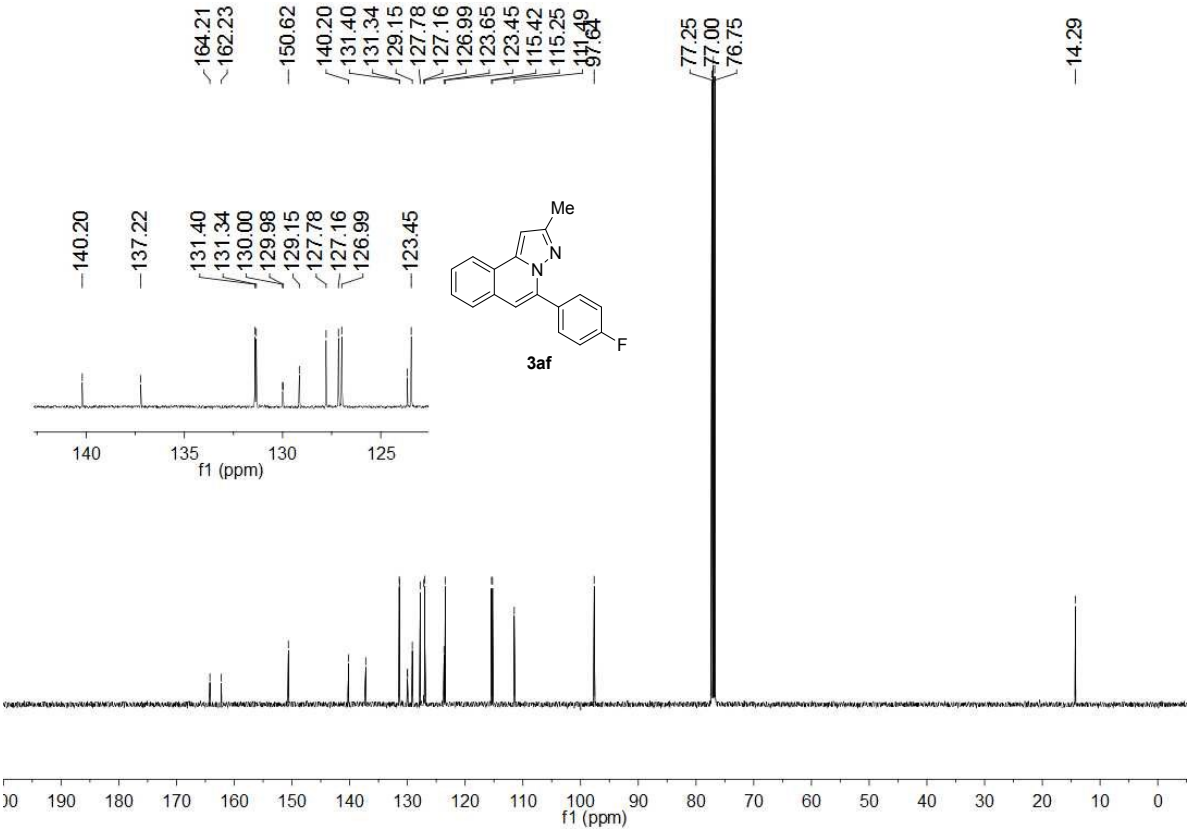
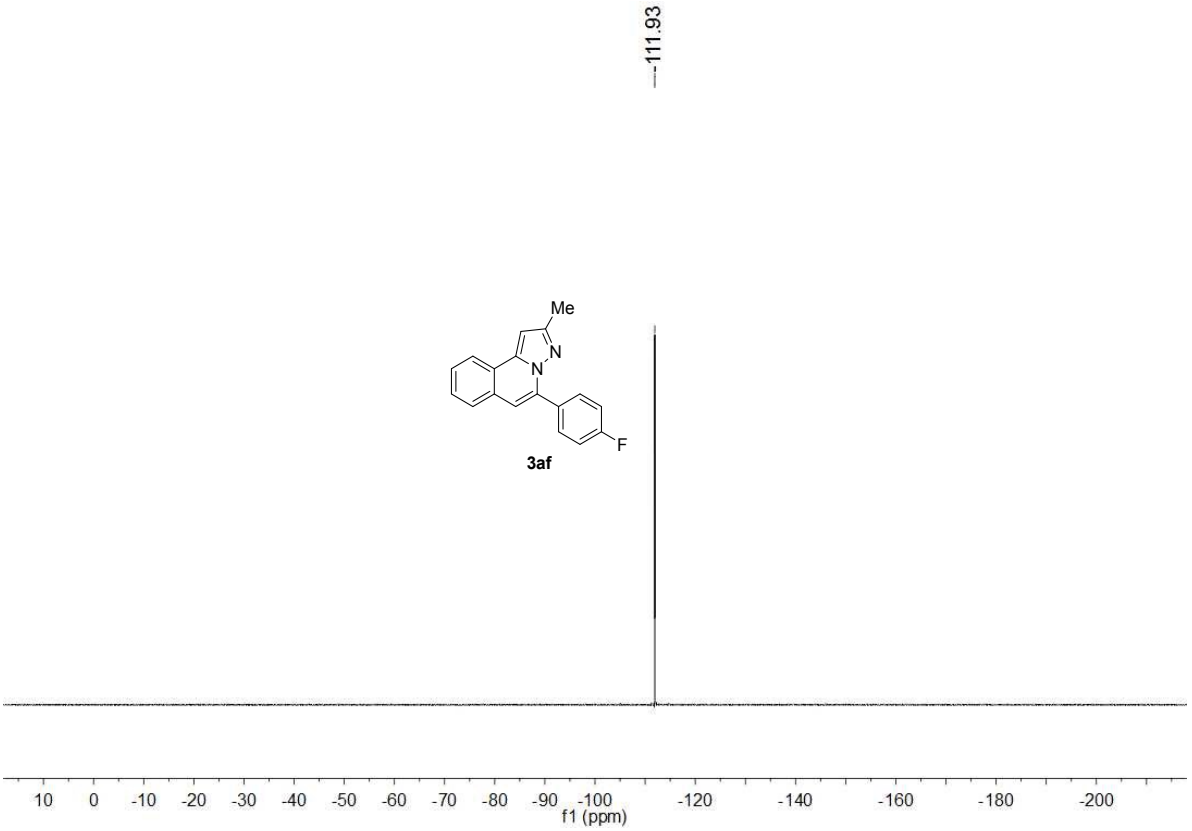
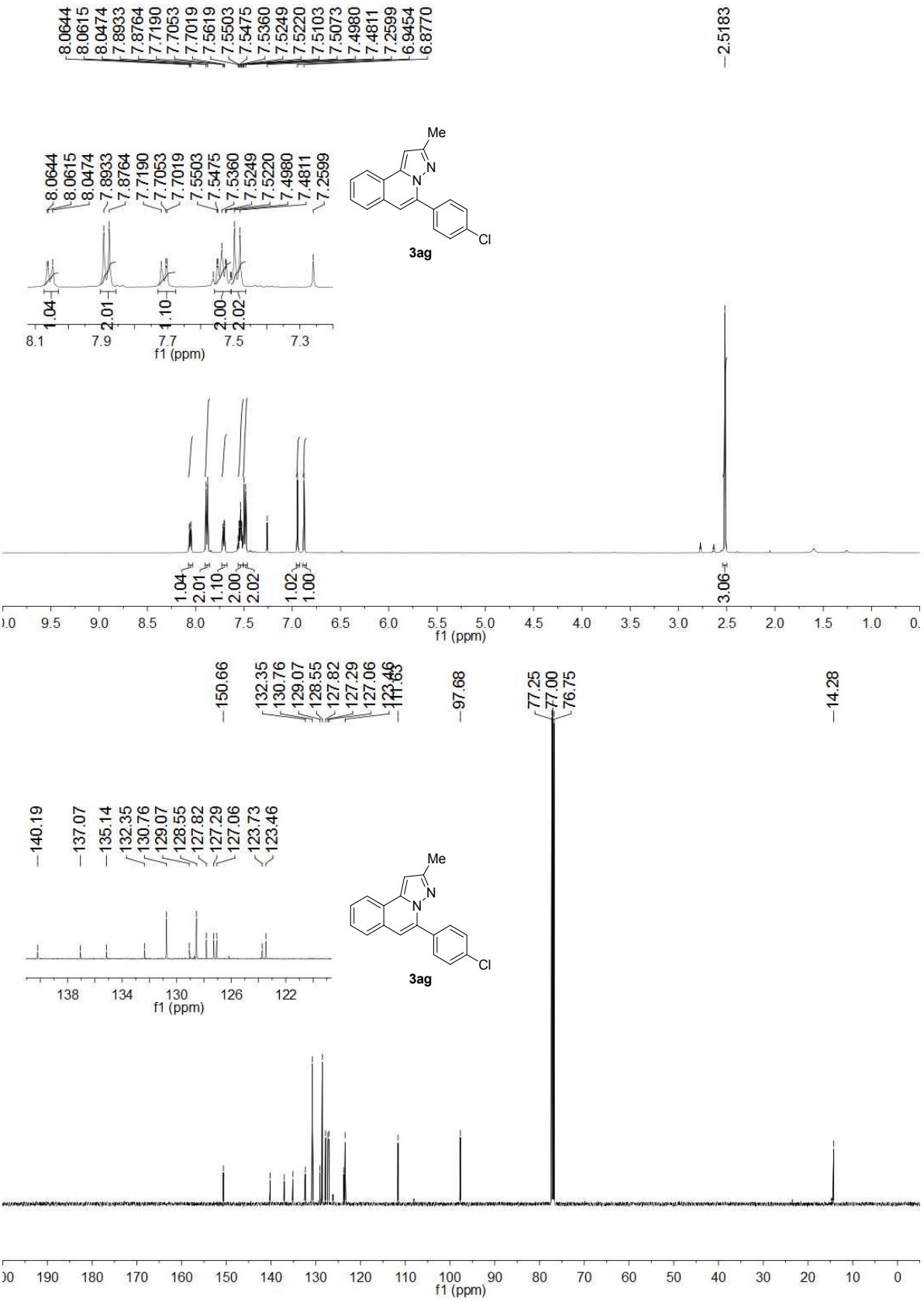
8.0719
8.0658
8.0502
8.0463
8.0425
8.0333
8.0294
8.0256
7.7596
7.7557
7.7519
7.7426
7.7389
7.7293
7.7244
7.6894
7.6868
7.6830
7.6727
7.6707
7.6668
7.5617
7.5510
7.5472
7.5447
7.5386
7.5324
7.5301
7.5264
7.5157
7.5025
7.4989
7.4877
7.4750
7.4719
7.4096
7.4073
7.4049
7.3960
7.3925
7.3890
7.3801
7.3778
7.2604
7.0278
6.8984
2.5513
Me
N
N
Ph
3ad
f1 (ppm)
150.57
129.81
128.82
127.74
127.51
127.20
127.08
127.04
123.45
111.56
97.59
77.25
77.00
76.75
14.35
142.04
140.76
140.24
137.94
132.85
129.81
129.26
128.82
127.74
127.51
127.27
127.20
127.08
127.04
123.67
123.45


8.0947
8.0795
8.0600
8.0454
7.7878
7.7672
7.7429
7.7250
7.7208
7.5890
7.5748
7.5709
7.5572
7.5541
7.5409
7.5369
7.5226
7.2597
6.9923
6.8928
2.5212
Me
N
N
CF3
3ae
3.02
1.05
0.97
1.06
2.01
1.03
1.00
3.10
f1 (ppm)
150.81
129.78
128.93
127.93
127.61
127.23
125.32
125.29
123.51
112.29
97.82
77.25
77.00
76.75
14.25
140.23
137.43
136.75
131.14
130.88
129.78
128.93
127.93
127.61
127.23
125.35
125.32
125.29
125.26
123.92
123.51
f1 (ppm)


-62.74
Me
N
N
CF3
3ae
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)
8.0667
8.0623
8.0535
8.0496
8.0482
7.9417
7.9374
7.9309
7.9285
7.9264
7.9240
7.9176
7.9132
7.7169
7.7145
7.7110
7.7032
7.6988
7.5445
7.5410
7.5364
7.5312
7.5259
7.5216
7.5181
7.2603
7.2234
7.2191
7.2098
7.2059
7.2019
7.1926
7.1884
6.9331
6.8779
2.5217
7.9417
7.9309
7.9240
7.9132
7.7032
7.5445
7.5410
7.5364
7.5312
7.5259
7.5216
7.5181
7.2603
7.2234
7.2059
7.1884
1.01
2.06
1.03
2.05
2.04
8.1 7.9 7.7 7.5 7.3 7.1
f1 (ppm)
Me
N
N
F
3af
1.01
2.06
1.03
2.05
2.04
1.02
1.00
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


164.21
162.23
150.62
140.20
131.40
131.34
129.15
127.78
127.16
126.99
123.65
123.45
115.42
115.25
111.49
97.64
77.25
77.00
76.75
14.29
140.20
137.22
131.40
131.34
130.00
129.98
129.15
127.78
127.16
126.99
123.45
Me
N
N
F
3af
140
135
130
125
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


111.93
Me
N
N
F
3af
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)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8.0474
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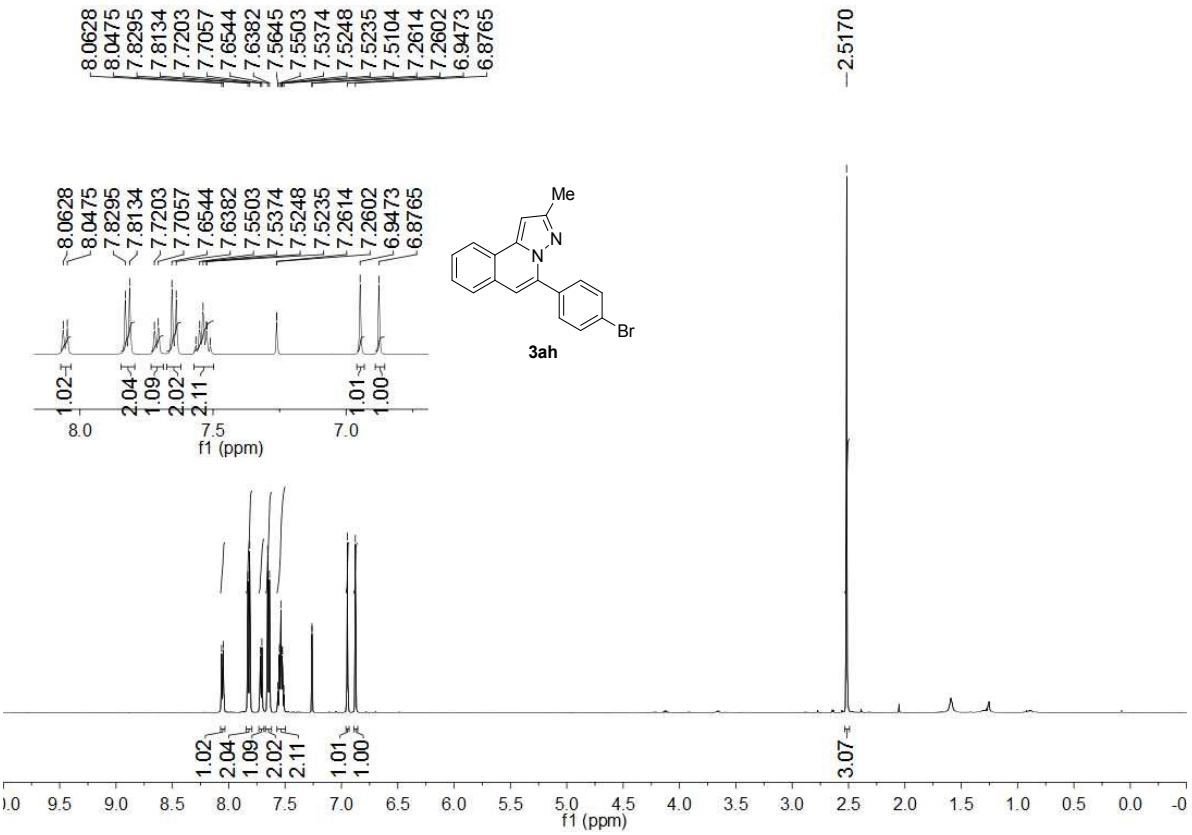
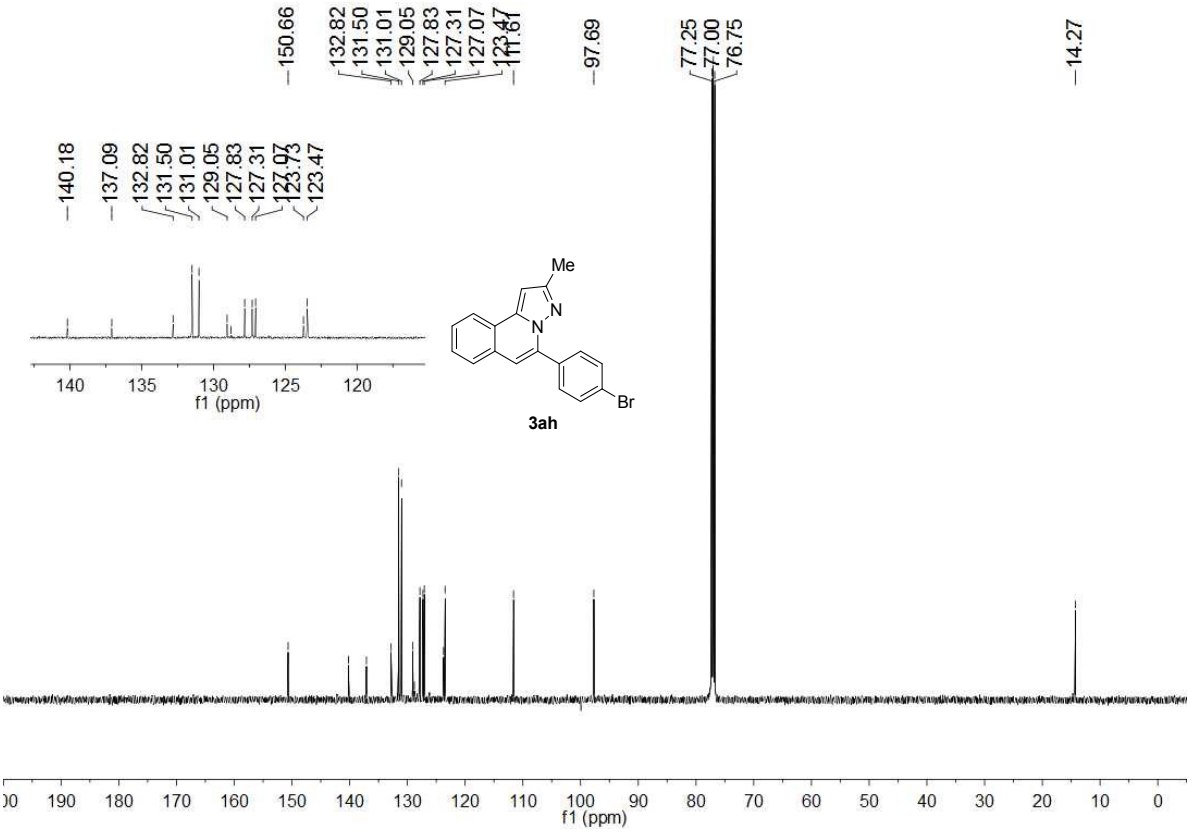
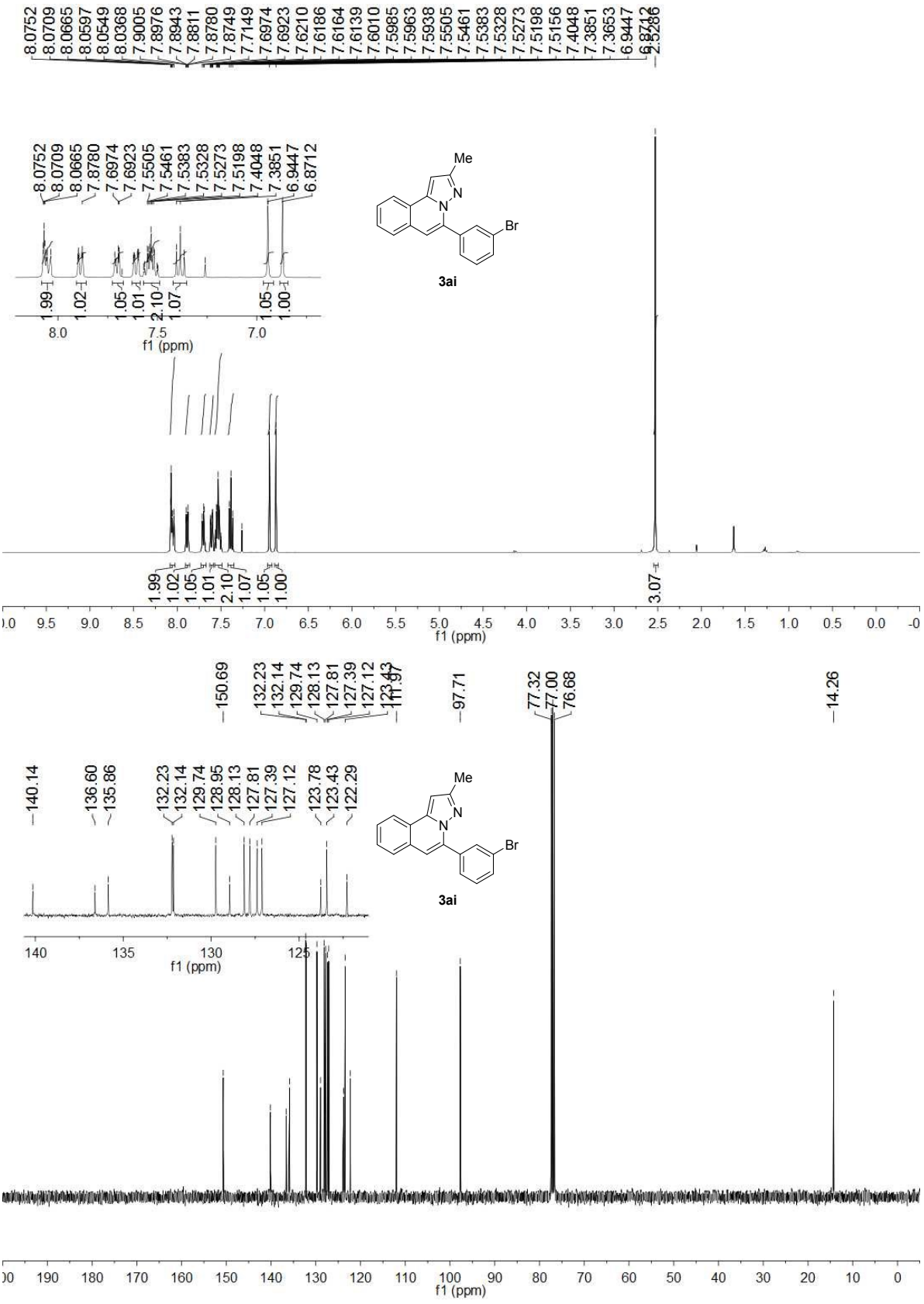
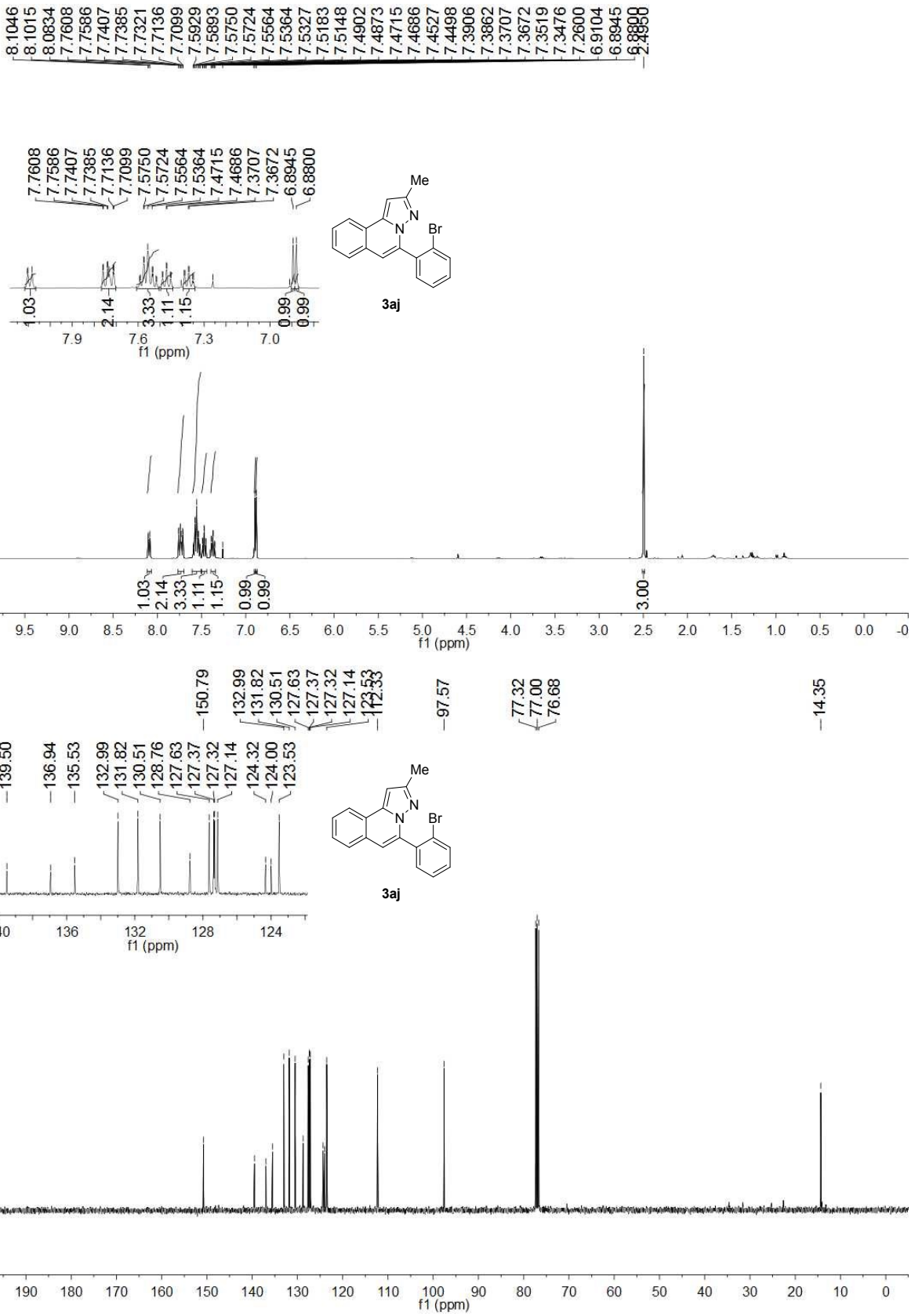
7.8764
7.7190
7.7053
7.7019
7.5619
7.5503
7.5475
7.5360
7.5249
7.5220
7.5103
7.5073
7.4980
7.4811
7.2599
6.9454
6.8770
2.5183
Me
N
N
Cl
3ag
1.04
2.01
1.10
2.00
2.02
1.02
1.00
3.06
f1 (ppm)
150.66
132.35
130.76
129.07
128.55
127.82
127.29
127.06
123.46
111.63
97.68
77.25
77.00
76.75
14.28
140.19
137.07
135.14
132.35
130.76
129.07
128.55
127.82
127.29
127.06
123.73
123.46
f1 (ppm)


8.0628
8.0475
8.8295
7.8134
7.7203
7.7057
7.6544
7.6382
7.5645
7.5503
7.5374
7.5248
7.5235
7.5104
7.2614
7.2602
6.9473
6.8765
2.5170
Me
N
N
Br
3ah
1.02
2.04
1.09
2.02
2.11
1.01
1.00
3.07
f1 (ppm)


150.66
132.82
131.50
131.01
129.05
127.83
127.31
127.07
123.47
111.81
97.69
77.25
77.00
76.75
14.27
140.18
137.09
Me
N
N
Br
3ah
f1 (ppm)


8.0752
8.0709
8.0665
8.0597
8.0549
8.0368
7.9005
7.8976
7.8943
7.8811
7.8780
7.8749
7.7149
7.6974
7.6923
7.6210
7.6186
7.6164
7.6139
7.6010
7.5985
7.5963
7.5938
7.5505
7.5461
7.5383
7.5328
7.5273
7.5198
7.5156
7.4048
7.3851
7.3653
6.9447
6.8712
2.5286
Me
N
N
Br
3ai
1.99
1.02
1.05
1.01
2.10
1.07
1.05
1.00
3.07
f1 (ppm)
150.69
140.14
136.60
135.86
132.23
132.14
129.74
128.95
128.13
127.81
127.39
127.12
123.78
123.43
122.29
111.97
97.71
77.32
77.00
76.68
14.26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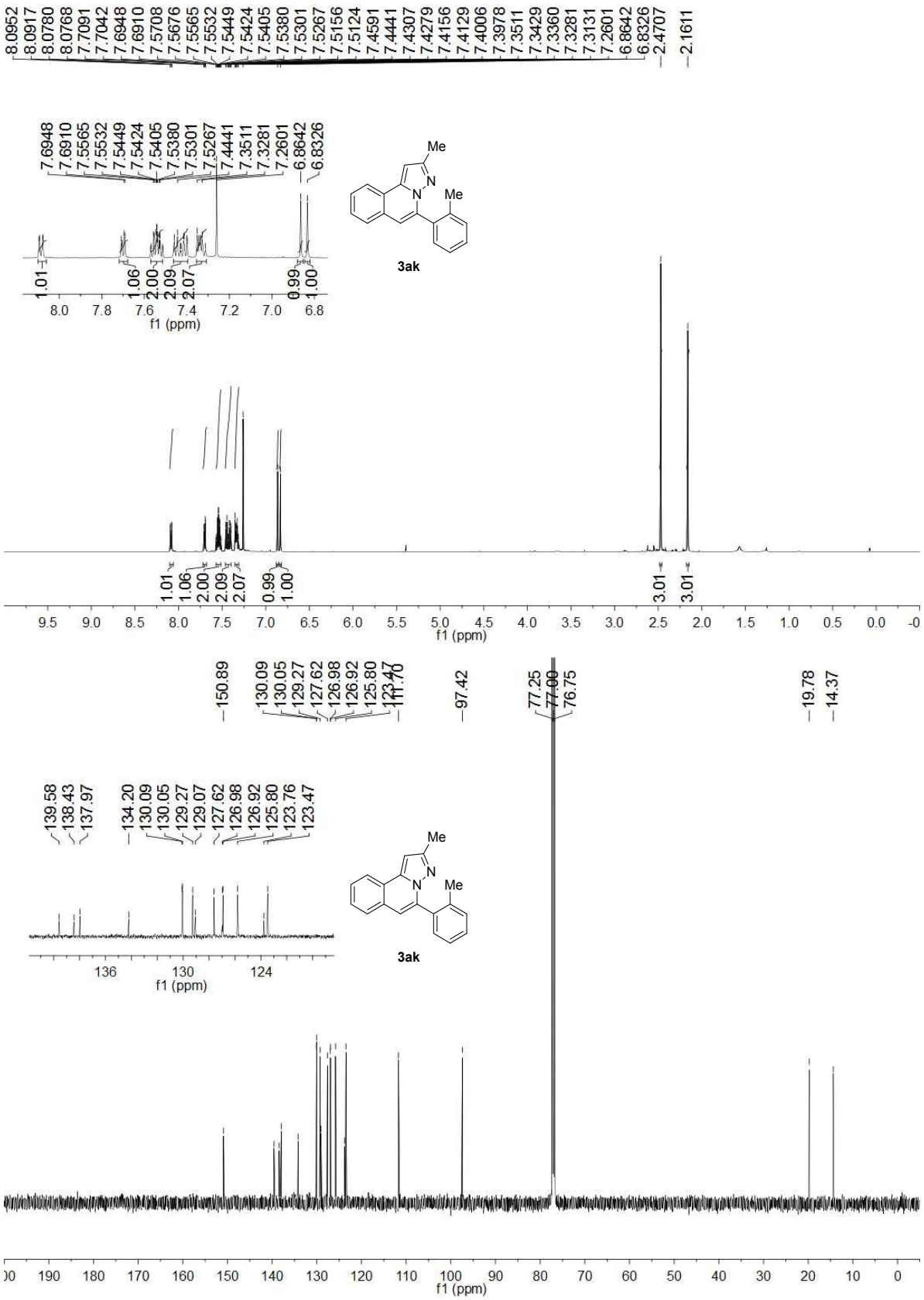
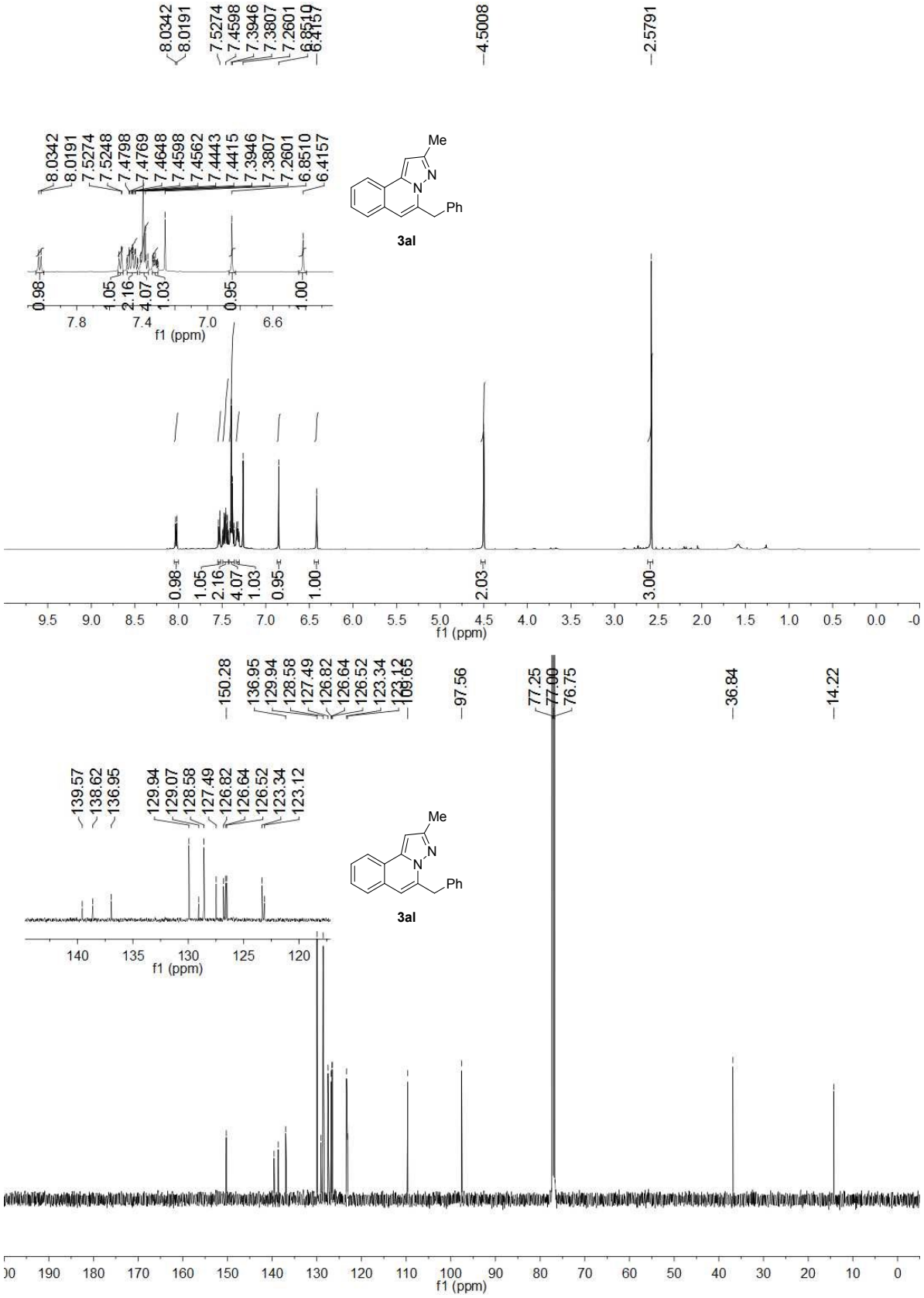
8.1015
8.0834
7.7608
7.7586
7.7407
7.7385
7.7321
7.7136
7.7099
7.5929
7.5893
7.5750
7.5724
7.5564
7.5364
7.5327
7.5183
7.5148
7.4902
7.4873
7.4715
7.4686
7.4527
7.4498
7.3906
7.3862
7.3707
7.3672
7.3519
7.3476
7.2600
6.9104
6.8945
6.8800
2.4950
Me
N
N
Br
3aj
1.03
2.14
3.33
1.11
1.15
0.99
0.99
3.00
f1 (ppm)
150.79
132.99
131.82
130.51
127.63
127.37
127.32
127.14
123.53
112.33
97.57
77.32
77.00
76.68
14.35
139.50
136.94
135.53
132.99
131.82
130.51
128.76
127.63
127.37
127.32
127.14
124.32
124.00
123.53
f1 (ppm)


8.0952
8.0917
8.0780
8.0768
7.7091
7.7042
7.6948
7.6910
7.5708
7.5676
7.5565
7.5532
7.5449
7.5424
7.5405
7.5380
7.5301
7.5267
7.5156
7.5124
7.4591
7.4441
7.4307
7.4279
7.4156
7.4129
7.4006
7.3978
7.3511
7.3429
7.3360
7.3281
7.3131
7.2601
6.8642
6.8326
2.4707
2.1611
Me
N
N
Me
3ak
1.01
1.06
2.00
2.09
2.07
0.99
1.00
3.01
3.01
f1 (ppm)
150.89
130.09
130.05
129.27
127.62
126.98
126.92
125.80
123.47
111.70
97.42
77.25
77.00
76.75
19.78
14.37
139.58
138.43
137.97
134.20
129.07
f1 (ppm)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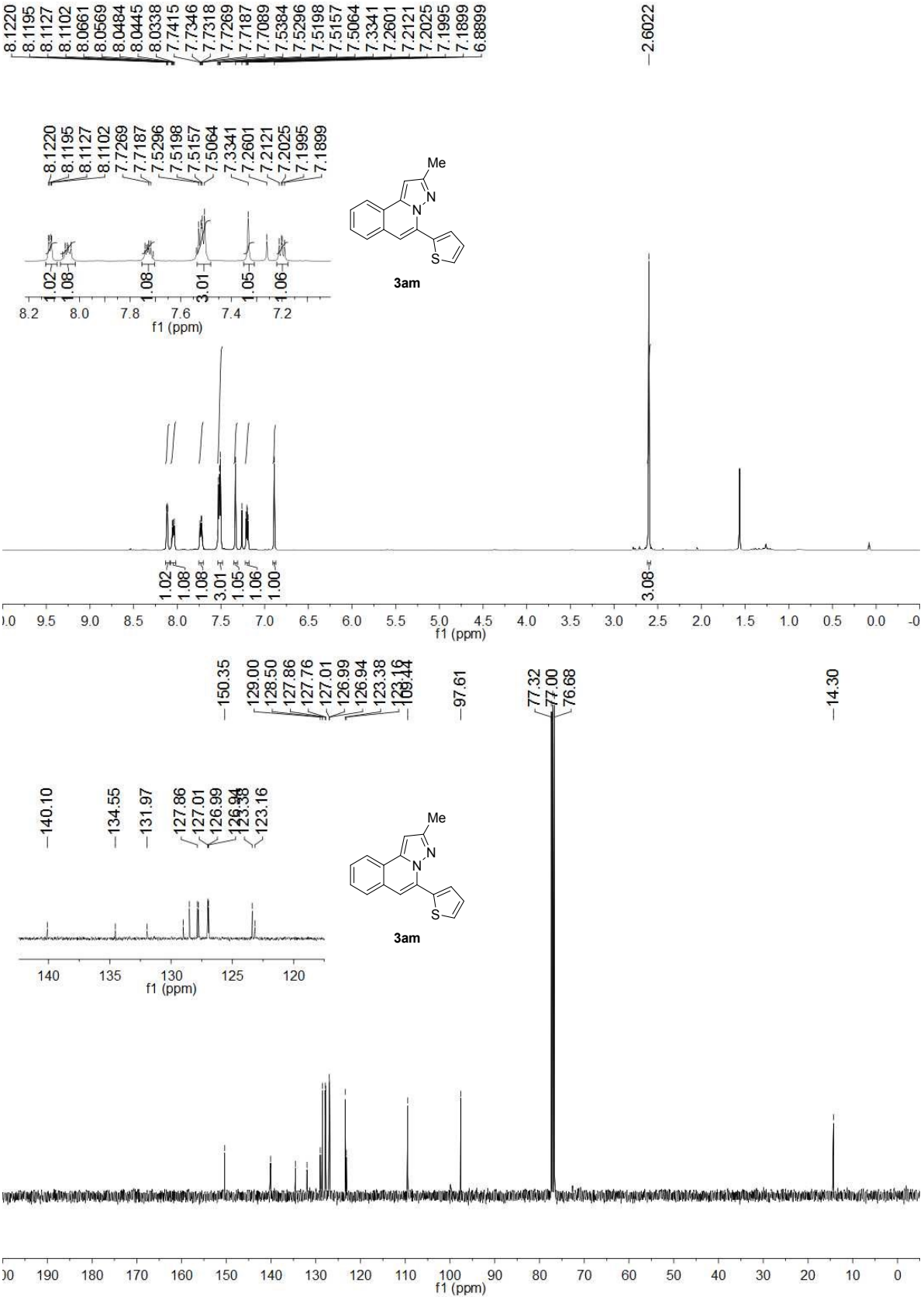
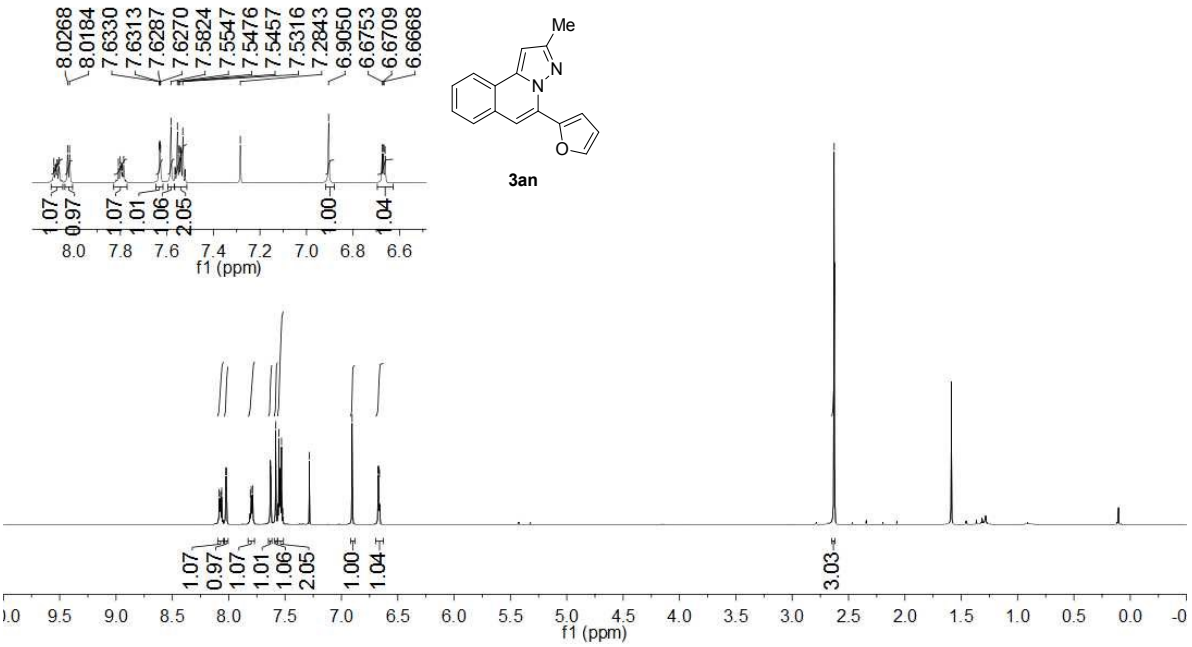
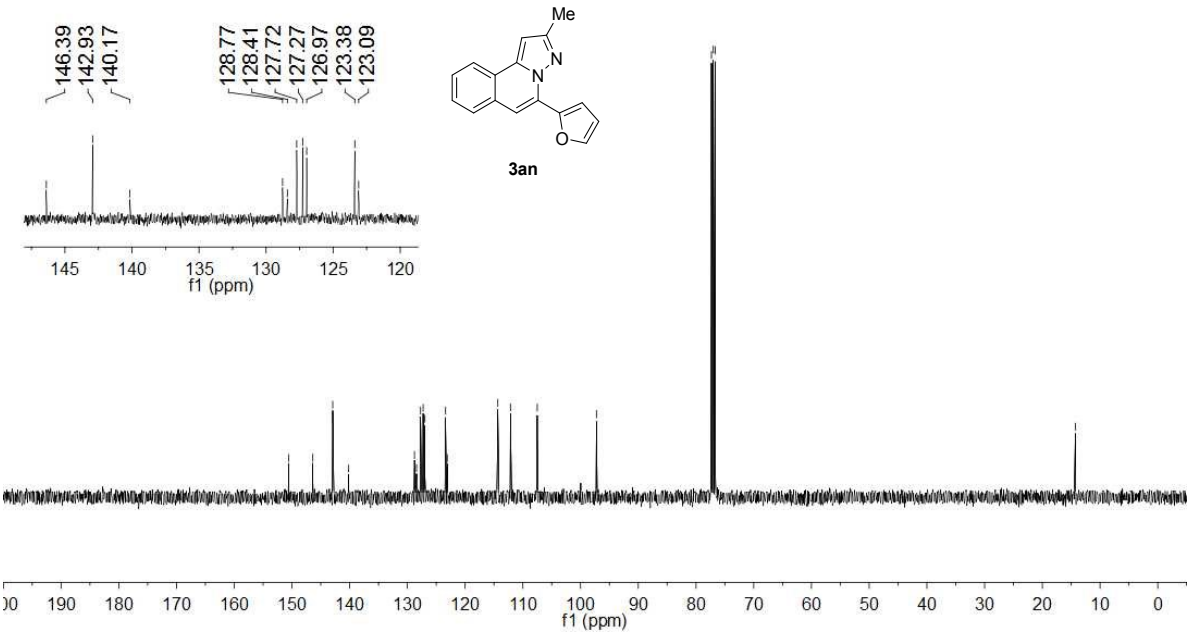
8.0191
7.5274
7.5248
7.4798
7.4769
7.4648
7.4598
7.4562
7.4443
7.4415
7.3946
7.3807
7.2601
6.8510
6.4157
4.5008
2.5791
Me
N
N
Ph
3al
0.98
1.05
2.16
4.07
1.03
0.95
1.00
2.03
3.00
f1 (ppm)
150.28
136.95
129.94
128.58
127.49
126.82
126.64
126.52
123.34
123.12
109.65
97.56
77.25
77.00
76.75
36.84
14.22
139.57
138.62
136.95
129.94
129.07
128.58
127.49
126.82
126.64
126.52
123.34
123.12
f1 (ppm)

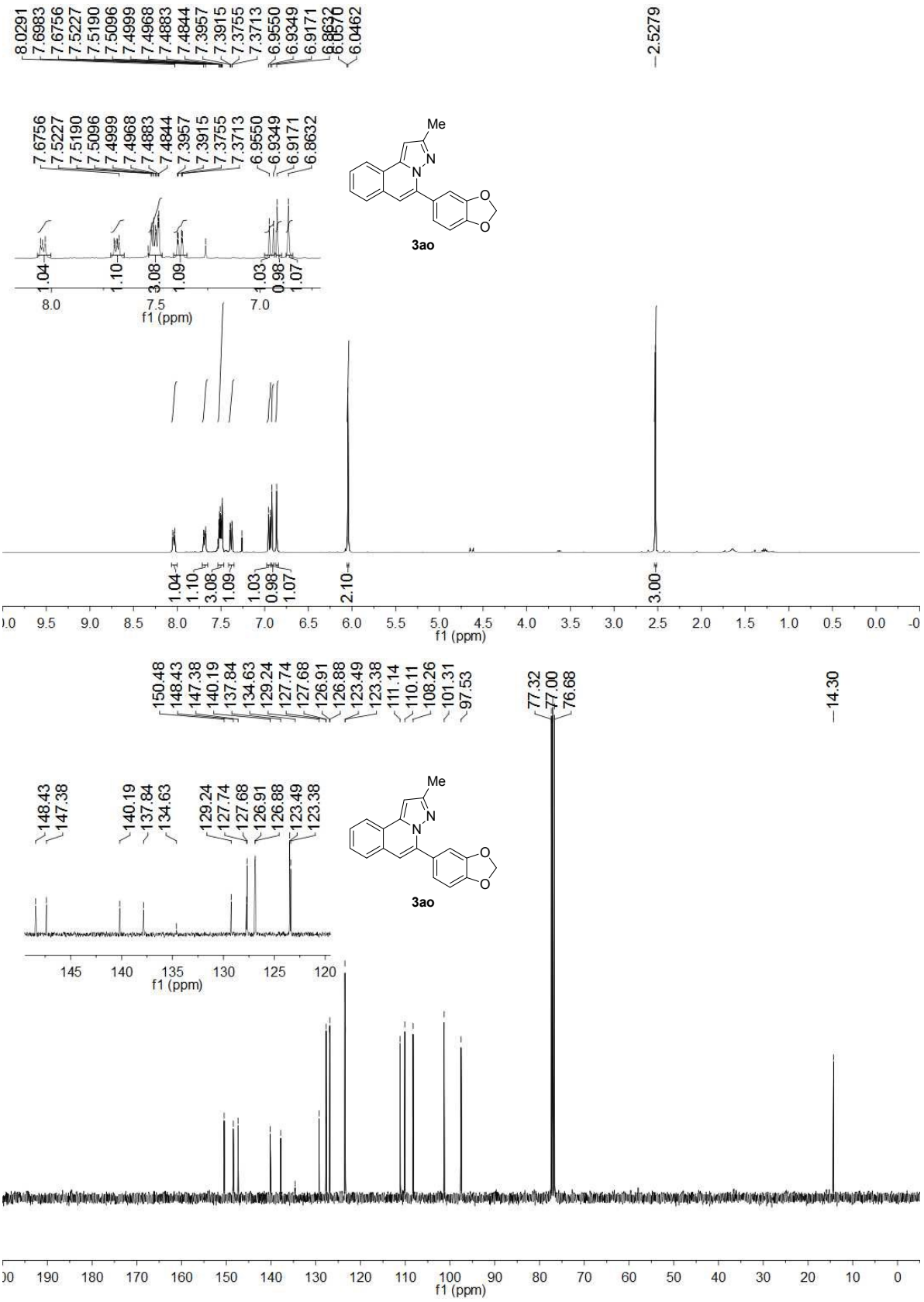

8.1220
8.1195
8.1127
8.1102
8.0661
8.0569
8.0484
8.0445
8.0338
7.7415
7.7346
7.7318
7.7269
7.7187
7.7089
7.5384
7.5296
7.5198
7.5157
7.5064
7.3341
7.2601
7.2121
7.2025
7.1995
7.1899
6.8899
2.6022
1.02
1.08
1.08
3.01
1.05
1.06
1.00
3.08
f1 (ppm)
Me
N
N
S
3am
150.35
129.00
128.50
127.86
127.76
127.01
126.99
126.94
123.38
123.16
109.44
97.61
77.32
77.00
76.68
14.30
140.10
134.55
131.97
f1 (ppm)


8.0856
8.0801
8.0781
8.0759
8.0714
8.0700
8.0624
8.0268
8.0184
7.8084
7.8004
7.7957
7.7917
7.7854
7.6330
7.6313
7.6287
7.6270
7.5824
7.5655
7.5635
7.5547
7.5476
7.5457
7.5407
7.5386
7.5316
7.5228
7.5207
7.2843
6.9050
6.6753
6.6709
6.6668
6.6623
2.6276


8.0268
8.0184
7.6330
7.6313
7.6287
7.6270
7.5824
7.5547
7.5476
7.5457
7.5316
7.2843
6.9050
6.6753
6.6709
6.6668
Me
N
N
O
3an
1.07
0.97
1.07
1.01
1.06
2.05
1.00
1.04
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6
f1 (ppm)
1.07
0.97
1.07
1.01
1.06
2.05
1.00
1.04
3.03
f1 (ppm)


150.56
146.39
142.93
140.17
128.77
127.72
127.27
126.97
123.38
123.09
112.14
107.50
97.25
77.32
77.00
76.68
14.29


146.39
142.93
140.17
128.77
128.41
127.72
127.27
126.97
123.38
123.09
Me
N
N
O
3an
145 140 135 130 125 120
f1 (ppm)
f1 (ppm)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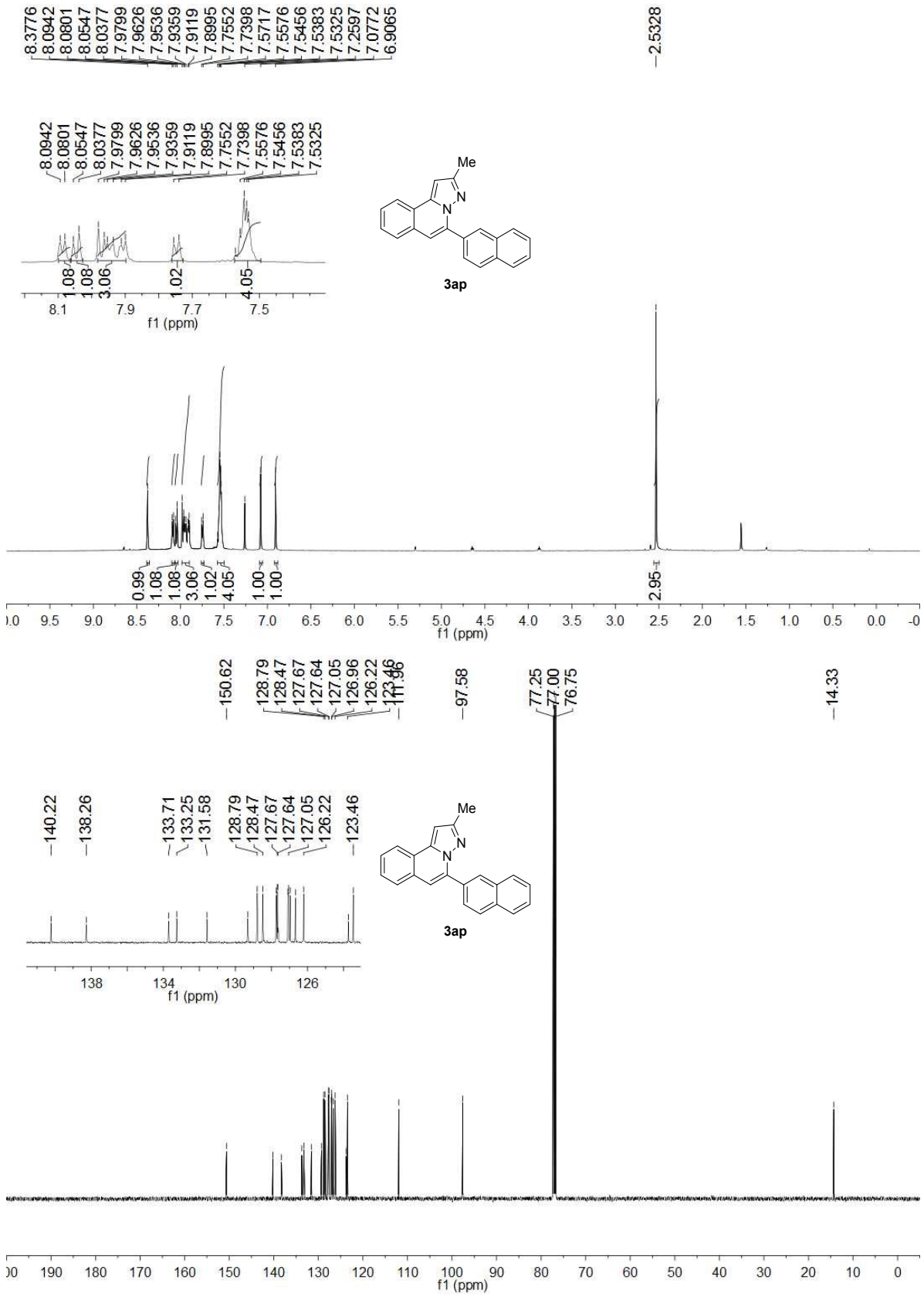
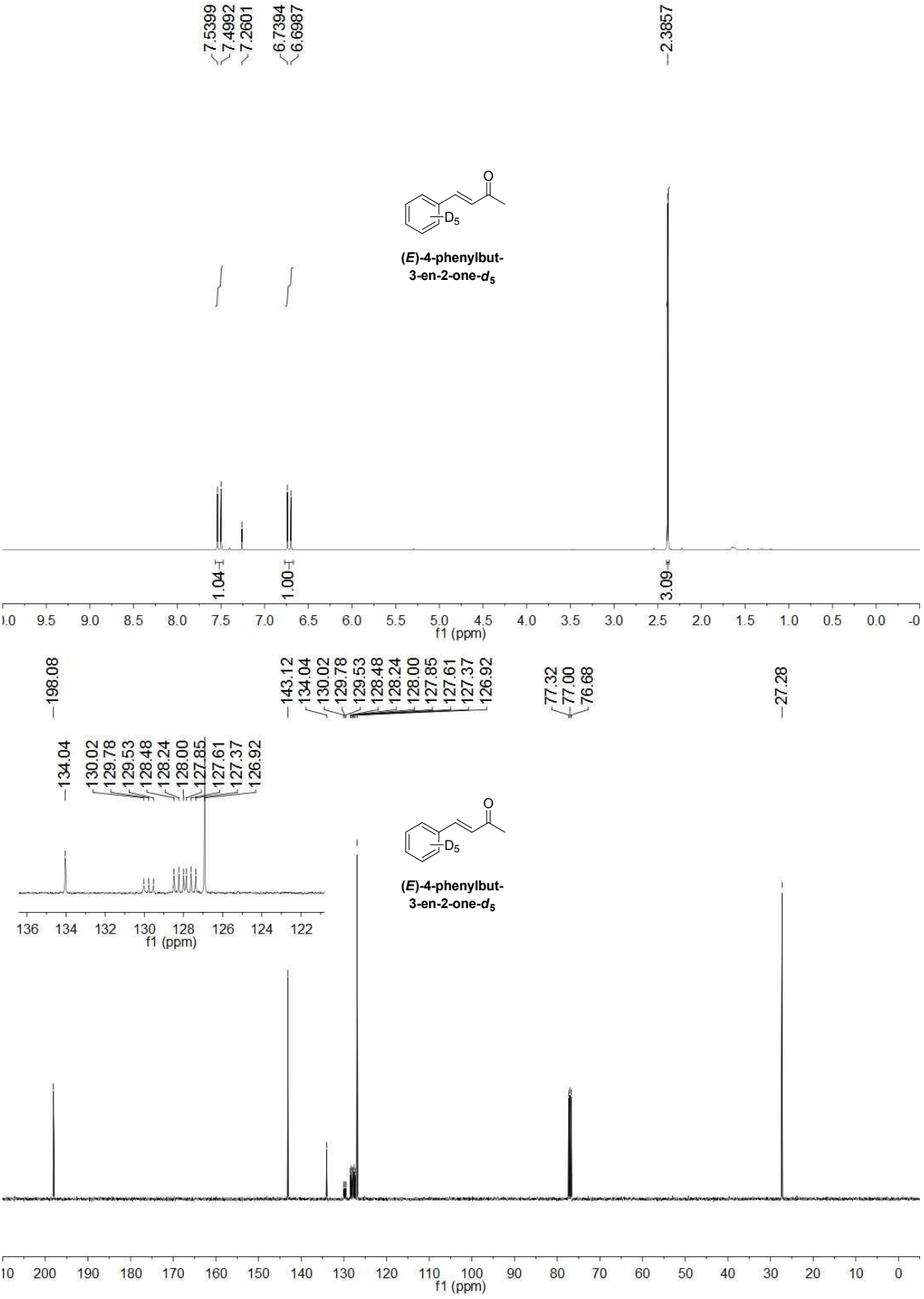
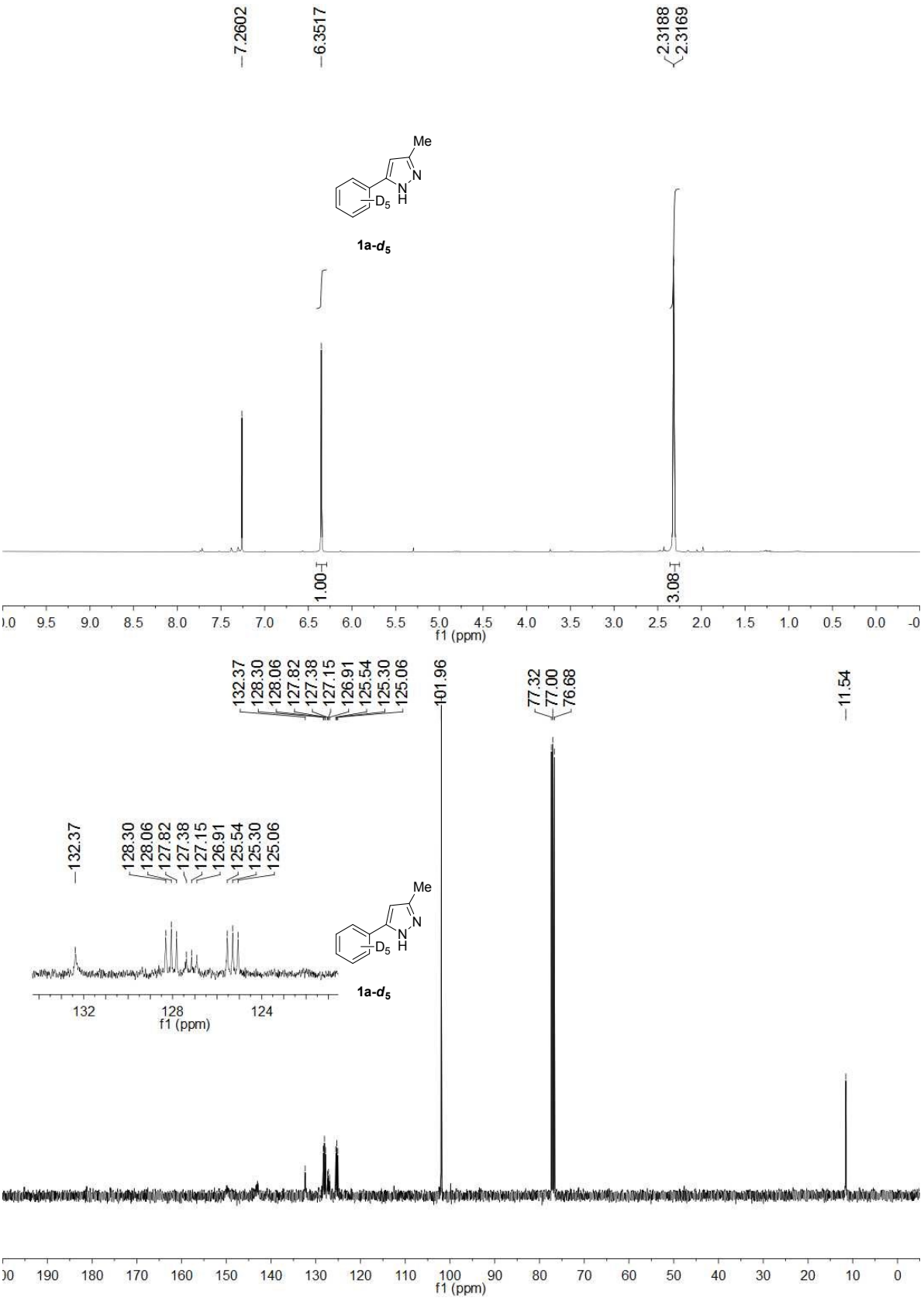
7.6756
7.5227
7.5190
7.5096
7.4999
7.4968
7.4883
7.4844
7.3957
7.3915
7.3755
7.3713
6.9550
6.9349
6.9171
6.8632
6.0576
6.0462
2.5279
Me
N
N
O
O
3ao
1.04
1.10
3.08
1.09
1.03
0.98
1.07
2.10
3.00
f1 (ppm)
150.48
148.43
147.38
140.19
137.84
134.63
129.24
127.74
127.68
126.91
126.88
123.49
123.38
111.14
110.11
108.26
101.31
97.53
77.32
77.00
76.68
14.30
f1 (ppm)


8.3776
8.0942
8.0801
8.0547
8.0377
7.9799
7.9626
7.9536
7.9359
7.9119
7.8995
7.7552
7.7398
7.5717
7.5576
7.5456
7.5383
7.5325
7.2597
7.0772
6.9065
2.5328
1.08
1.08
3.06
1.02
4.05
f1 (ppm)
Me
N
N
3ap
0.99
1.08
1.08
3.06
1.02
4.05
1.00
1.00
2.95
f1 (ppm)
150.62
128.79
128.47
127.67
127.64
127.05
126.96
126.22
123.46
111.96
97.58
77.25
77.00
76.75
14.33
140.22
138.26
133.71
133.25
131.58
128.79
128.47
127.67
127.64
127.05
126.22
123.46
f1 (ppm)
Me
N
N
3ap
f1 (ppm)


7.5399
7.4992
7.2601
6.7394
6.6987
2.3857
O
D5
(E)-4-phenylbut-3-en-2-one-d5
1.04
1.00
3.09
f1 (ppm)
198.08
143.12
134.04
130.02
129.78
129.53
128.48
128.24
128.00
127.85
127.61
127.37
126.92
77.32
77.00
76.68
27.28
f1 (ppm)


7.2602
6.3517
2.3188
2.3169
Me
N
N
H
D5
1a-d5
1.00
3.08
f1 (ppm)
132.37
128.30
128.06
127.82
127.38
127.15
126.91
125.54
125.30
125.06
101.96
77.32
77.00
76.68
11.54
132
128
124
f1 (ppm)