Electronic Supplementary Information for

A New Entry to Highly Functionalized Pyrroles via Cascade Reaction of α-Amino Esters and Alkynals

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1 General Remarks

^{1}H NMR spectra were recorded on a Bruker Mercury 400 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as (s = single, d = double, t = triple, q = quartet, m = multiple or unresolved, and brs = broad single). ^{13}C NMR spectra were recorded on a Bruker 100 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm. Commercially available reagents were used without further purification. Amino ester were prepared according to the literature procedure.[1] The alkynals **2a-c** and **2e-f** were prepared from the corresponding alkynes,[2a] **2d** and **2g-j** were prepared from the corresponding aldehydes.[2b]

2 General Procedure for Et_3N promoted cascade condensation/intramolecular cyclization/1,2-ester migration of α-amino acid esters hydrochloride and alkynals

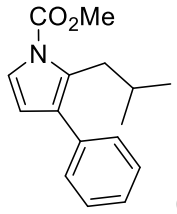
General Reaction Procedure:

To a 10 mL of round-bottom flask were added α-amino acid esters hydrochloride (1.2 mmol), DCM (4 mL) and Et_3N (1.5 mmol). The reaction mixture was stirred at 25 ºC for 5 min and then alkynal (1 mmol) was added in one portion. The cascade reaction was stirred in room temperature for 24 h (monitored by thin-layer chromatography or ^{1}H NMR spectroscopy).

General Workup Procedure:

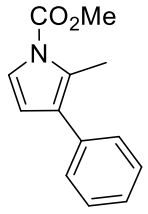
Saturated ammonium chloride solution (5 mL) was added to the mixture, the layers were separated, and the aqueous layer was extracted with DCM (5 mL x 2). The combined organic components were washed with saturated brine (5 mL), dried over with anhydrous Na_2SO_4, filtration and evaporated in vacuum. The residue was purified by column chromatography to give the desired product.

3 The Data of Characterization



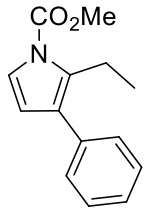
(**3a**)

methyl 2-isobutyl-3-phenyl-1H-pyrrole-1-carboxylate: Yield (83%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.27 (m, 3H), 6.72 (d, *J* = 12.8 Hz, 1H), 6.25 (d, *J* = 12.8 Hz, 1H), 3.72 (s, 3H), 2.26 (d, *J* = 7.2 Hz, 2H), 1.99 - 1.89 (m, 1H), 0.93 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.52, 150.59, 136.32, 133.24, 129.18, 127.92, 127.77, 115.70, 115.35, 60.19, 33.58, 27.96, 22.26. HRMS (ESI+) Calcd. For $C_{16}H_{19}NO_2Na$ ($[M+Na]^+$): 280.1308, found: 280.1307.



(**3b**)

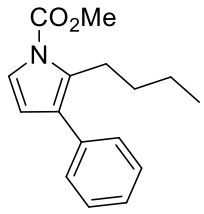
methyl 2-methyl-3-phenyl-1H-pyrrole-1-carboxylate: Yield (73%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.36 - 7.26 (m , 3H), 6.72 (d, *J* = 12.8 Hz, 1H), 6.23 (d, *J* = 12.8 Hz, 1H), 3.73 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.01, 150.53, 136.26, 133.34, 129.14, 127.93, 115.19, 112.01, 60.15, 9.93. HRMS (ESI+) Calcd. For $C_{13}H_{13}NO_2Na$ ($[M+Na]^+$): 238.0838, found: 238.0829.



(**3c**)

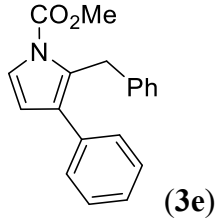
methyl 2-ethyl-3-phenyl-1H-pyrrole-1-carboxylate: Yield (65%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.28 (m, 3H), 6.73 (d, *J* = 12.8 Hz, 1H), 6.25 (d, *J* = 12.8 Hz, 1H), 3.73 (s, 3H), 2.43 (q, *J* = 7.6 Hz, 2H), 1.19 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz,

Chloroform-*d*) δ 153.45, 150.57, 136.27, 133.22, 129.14, 127.87, 127.72, 117.70, 115.25, 60.19, 17.97, 13.06. For $C_{14}H_{15}NO_2Na$ ($[M+Na]^+$): 252.0995, found: 252.0998.



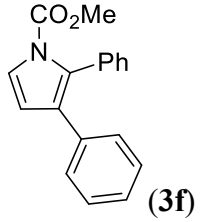
(**3d**)

methyl 2-butyl-3-phenyl-1H-pyrrole-1-carboxylate: Yield (71%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.35 - 7.25 (m, 3H), 6.71 (d, *J* = 12.8 Hz, 1H), 6.24 (d, *J* = 12.8 Hz, 1H), 3.71 (s, 3H), 2.39 (t, *J* = 7.6 Hz, 2H), 1.62 – 1.55 (m, 2H),1.40 – 1.31 (m , 2H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.87, 150.58, 133.19, 129.14, 127.86, 127.71, 116.49, 115.27, 60.17, 30.63, 24.15, 22.18, 13.77. For $C_{16}H_{19}NO_2Na$ ($[M+Na]^+$): 280.1308, found: 280.1305.



(**3e**)

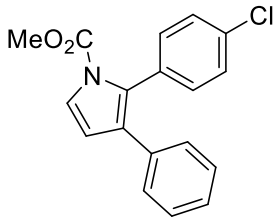
methyl 2-benzyl-3-phenyl-1H-pyrrole-1-carboxylate: Yield (85%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.28 (m, 6H), 7.26 – 7.14 (m, 2H), 6.71 (d, *J* = 12.8 Hz, 1H), 6.23 (d, *J* = 12.8 Hz, 1H), 3.75 (s, 2H), 3.70 (s, 3H);^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.20, 139.36, 136.22, 133.57, 129.20, 128.49, 128.37, 127.95, 127.75, 126.15, 115.23, 115.20, 60.11, 30.84. HRMS (ESI+) Calcd. For $C_{19}H_{17}ClNO_2Na$ ($[M+Na]^+$): 314.1151, found: 314.1159.



(**3f**)

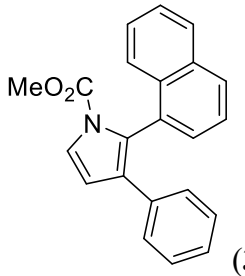
methyl 2,3-diphenyl-1H-pyrrole-1-carboxylate: Yield (64%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) 7.80 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.36 (m, 4H), 7.29 (m, 1H), 7.22

(d, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 12.8 Hz, 1H), 6.30 (d, *J* = 12.8 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.81, 150.22, 136.26, 134.11, 131.18, 129.27, 128.40, 128.03, 127.79, 126.25, 124.76, 114.87, 113.91, 59.27. HRMS (ESI+) Calcd. For $C_{18}H_{15}NO_2Na$ ([M+Na]$^+$): 300.0995, found: 300.0988.



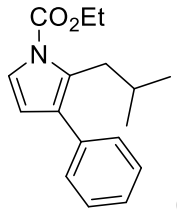
(**3g**)

methyl 2-(4-chlorophenyl)-3-phenyl-1H-pyrrole-1-carboxylate: Yield (62%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.34 (m, 5H), 6.80 (d, *J* = 12.8 Hz, 1H), 6.30 (d, *J* = 12.8 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.83, 150.18, 136.18, 134.36, 131.63, 129.24, 128.52, 128.09, 127.79, 126.87, 125.95, 114.67, 113.62, 77.32, 77.00, 76.68, 59.18. HRMS (ESI+) Calcd. For $C_{18}H_{14}ClNO_2Na$ ([M+Na]$^+$): 334.0605, found: 334.0612.



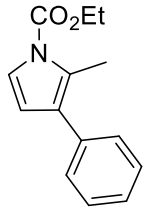
(**3h**)

methyl 2-(naphthalen-2-yl)-3-phenyl-1H-pyrrole-1-carboxylate: Yield (57%); white solid, m.p. 85-87 °C; $[\alpha]^{30}_D$ = -13.8 (*c* 0.39, CH_2Cl_2); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 (d, *J* = 9.2 Hz, 1H), 7.87 – 7.77 (m, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.37 (m, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 12.8 Hz, 1H), 6.39 (d, *J* = 12.8 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.72, 150.38, 136.24, 134.11, 133.85, 131.18, 129.35, 128.21, 128.07, 128.05, 127.91, 127.85, 126.88, 126.08, 125.93, 125.70, 125.13, 114.94, 114.78, 77.32, 77.00, 76.68, 59.57. HRMS (ESI+) Calcd. For $C_{22}H_{17}NO_2Na$ ([M+Na]$^+$): 350.1151, found: 350.1148.



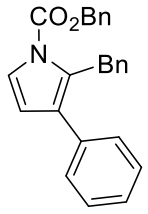
(**3j**)

ethyl 2-isobutyl-3-phenyl-1H-pyrrole-1-carboxylate: Yield (54%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.27 (m, 3H), 6.71 (d, *J* = 12.8 Hz, 1H), 6.25 (d, *J* = 12.8 Hz, 1H), 3.98 (q, *J* = 7.2 Hz, 2H), 2.26 (d, *J* = 7.2 Hz, 2H), 1.96 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 0.93 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.71, 150.78, 136.32, 133.22, 129.11, 127.87, 127.75, 116.76, 115.42, 69.53, 33.57, 27.93, 22.27, 14.94. HRMS (ESI+) Calcd. For $C_{17}H_{21}NO_2Na$([M+Na]$^+$): 294.1465, found: 294.1466.



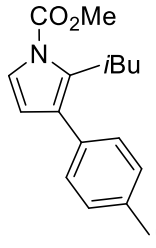
(**3k**)

ethyl 2-methyl-3-phenyl-1H-pyrrole-1-carboxylate: Yield (52%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.27 (m, 3H), 6.72 (d, *J* = 12.8 Hz, 1H), 6.23 (d, *J* = 12.8 Hz, 1H), 3.99 (q, *J* = 7.2 Hz, 2H), 2.05 (s, 3H), 1.25 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.18, 150.84, 136.28, 133.39, 129.12, 127.93, 127.81, 115.30, 113.34, 69.63, 14.91, 9.99. HRMS (ESI+) Calcd. For $C_{14}H_{15}NO_2Na$ ([M+Na]$^+$): 252.0995, found: 252.0990.



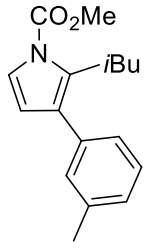
(**3l**)

benzyl 2-benzyl-3-phenyl-1H-pyrrole-1-carboxylate: Yield (77%); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.35 – 7.29 (m, 6H), 7.24 – 7.22 (m, 2H), 7.18 – 7.14 (m, 5H), 6.73 (d, *J* = 12.8 Hz, 1H), 6.24 (d, *J* = 12.8 Hz, 1H), 4.88 (s, 2H), 3.65 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.10, 151.27, 139.15, 136.34, 135.11, 133.89, 129.22, 128.72, 128.57, 128.57, 128.40, 128.31, 128.03, 127.84, 126.11, 117.19, 115.36, 75.35, 30.79.



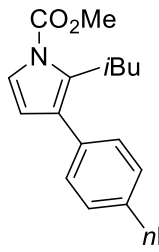
(**3m**)

methyl 2-isobutyl-3-(p-tolyl)-1H-pyrrole-1-carboxylate: Yield (77%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 12.8 Hz, 1H), 6.19 (d, *J* = 12.8 Hz, 1H), 3.77 (s, 3H), 2.36 (s, 3H), 2.28 (s, 2H), 1.99 – 1.89 (m, 1H), 0.94 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.45, 137.97, 133.32, 133.29, 129.26, 128.49, 115.82, 114.37, 60.36, 33.60, 27.95, 22.26, 21.32. HRMS (ESI+) Calcd. For $C_{17}H_{21}NO_2Na$ ($[M+Na]^+$): 294.1465, found: 294.1456.



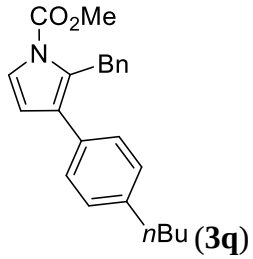
(**3n**)

methyl 2-isobutyl-3-(m-tolyl)-1H-pyrrole-1-carboxylate: Yield (65%), yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (s, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 12.8 Hz, 1H), 6.22 (d, *J* = 12.8 Hz, 1H), 3.74 (s, 3H), 2.35 (s, 3H), 2.26 (d, *J* = 7.2 Hz, 2H), 1.99 – 1.89 (m, 1H), 0.94 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.48, 150.64, 137.20, 136.13, 133.42, 129.74, 128.72, 127.65, 126.33, 115.69, 60.18, 33.55, 27.94, 22.24, 21.36. HRMS (ESI+) Calcd. For $C_{17}H_{21}NO_2Na$ ($[M+Na]^+$): 294.1465, found: 294.1455.



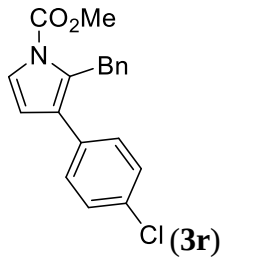
(**3p**)

methyl 3-(4-butylphenyl)-2-isobutyl-1H-pyrrole-1-carboxylate: Yield (74%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 12.8 Hz, 1H), 6.19 (d, *J* = 12.8 Hz, 1H), 3.76 (s, 3H), 2.61 (t, *J* = 8.0 Hz, 2H), 2.26 (d, *J* = 7.2 Hz, 2H), 1.94 (m, 1H), 1.62 – 1.54 (m, 2H), 1.39 – 1.31 (m, 2H), 0.93 (m, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.45, 150.82, 143.01, 133.58, 133.44, 129.24, 127.88, 115.73, 114.47, 60.27, 35.45, 33.60, 33.55, 27.97, 22.29, 22.27, 13.94. HRMS (ESI+) Calcd. For $C_{20}H_{27}NO_2Na$ ($[M+Na]^+$): 336.1934, found: 336.1942.



(**3q**)

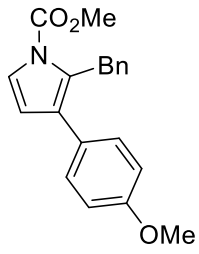
methyl 2-benzyl-3-(4-butylphenyl)-1H-pyrrole-1-carboxylate: Yield (84%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.26 (m, 4H), 7.25 – 7.20 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 12.8 Hz, 1H), 6.18 (d, *J* = 12.8 Hz, 1H), 3.75 (s, 2H), 3.74 (s, 3H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.59 (m, 2H), 1.35 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.07, 150.88, 142.97, 139.36, 133.68, 133.43, 129.24, 128.46, 128.31, 127.80, 126.08, 115.21, 114.24, 60.10, 35.39, 33.47, 30.82, 22.22, 13.88. HRMS (ESI+) Calcd. For $C_{23}H_{25}NO_2Na$ ($[M+Na]^+$): 370.1778, found: 370.1777.



(**3r**)

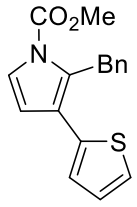
methyl 2-benzyl-3-(4-chlorophenyl)-1H-pyrrole-1-carboxylate: Yield (81%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.25 (m, 6H), 7.23 – 7.17 (m, 1H), 6.59 (d, *J* = 12.8 Hz, 1H), 6.22 (d, *J* = 12.8 Hz, 1H), 3.74 (m, 5H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ

154.21, 150.38, 139.22, 134.48, 132.02, 130.68, 128.46, 128.33, 127.88, 126.16, 115.55, 115.38, 60.18, 30.80. HRMS (ESI+) Calcd. For $C_{19}H_{16}ClNO_2Na$ ($[M+Na]^+$): 325.0870, found: 325.0875.



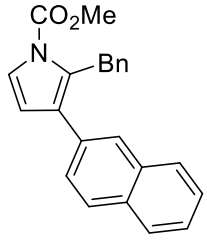
(**3s**)

methyl 2-benzyl-3-(4-methoxyphenyl)-1H-pyrrole-1-carboxylate: Yield (80%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.8 Hz, 2H), 7.33 – 7.17 (m, 5H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 12.8 Hz, 1H), 6.11 (d, *J* = 12.8 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.76 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.48, 154.04, 151.07, 139.40, 133.35, 131.04, 128.61, 128.51, 128.34, 126.12, 115.40, 113.14, 112.95, 60.36, 55.20, 30.88. HRMS (ESI+) Calcd. For $C_{20}H_{19}NO_2Na$ ($[M+Na]^+$): 321.1365, found: 321.1368.



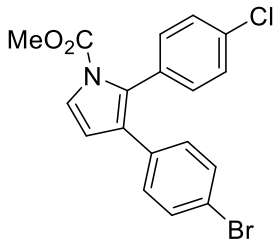
(**3t**)

methyl 2-benzyl-3-(thiophen-2-yl)-1H-pyrrole-1-carboxylate: Yield (72%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 3.2 Hz, 1H), 7.38 – 7.15 (m, 6H), 7.05 – 6.99 (m, *J* = 4.0 Hz 1H), 6.73 (d, *J* = 12.8 Hz, 1H), 6.05 (d, *J* = 12.8 Hz, 1H), 3.93 (s, 3H), 3.82 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.33, 150.76, 139.32, 138.94, 131.77, 128.58, 128.35, 127.99, 126.90, 126.14, 125.04, 116.19, 110.48, 60.69, 30.99. HRMS (ESI+) Calcd. For $C_{17}H_{15}NO_2SNa$ ($[M+Na]^+$): 320.0716, found: 320.0722.



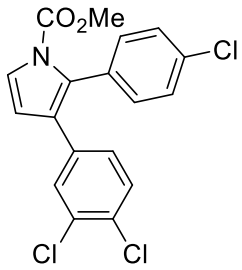
(**3u**)

methyl 2-benzyl-3-(naphthalen-2-yl)-1H-pyrrole-1-carboxylate: Yield (79%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.84 – 7.72 (m, 3H), 7.67 (d, *J* = 8.4 Hz, 1H),7.46 (t, *J* = 4.8 Hz, 2H), 7.30 (m, 4H), 7.21(m, 1H), 6.83 (d, *J* = 12.8 Hz, 1H), 6.30 (d, *J* = 12.8 Hz, 1H), 3.76 (s, 2H), 3.66 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.25, 150.80, 139.36, 133.49, 132.99, 132.93, 128.67, 128.52, 128.40, 128.16, 127.52, 127.19, 127.08, 126.23, 126.17, 126.04, 115.47, 115.26, 60.11, 30.88. HRMS (ESI+) Calcd. For $C_{23}H_{19}NO_2Na$ ([M+Na]$^+$): 364.1308, found: 364.1311.



(**3v**)

methyl 3-(4-bromophenyl)-2-(4-chlorophenyl)-1H-pyrrole-1-carboxylate: Yield (66%); yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) 7.71 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.36 – 7.32 (m, 4H), 6.78 (d, *J* = 13.2 Hz, 1H), 6.29 (d, *J* = 13.2 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.83, 150.18, 136.18, 134.36, 131.63, 129.24, 128.81, 128.52, 128.08, 127.79, 125.95, 114.67, 113.62, 59.66. HRMS (ESI+) Calcd. For $C_{18}H_{13}BrClNO_2Na$ ([M+Na]$^+$): 411.9710, found: 411.9719.

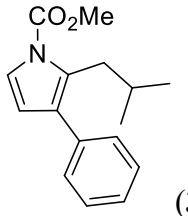


(**3w**)

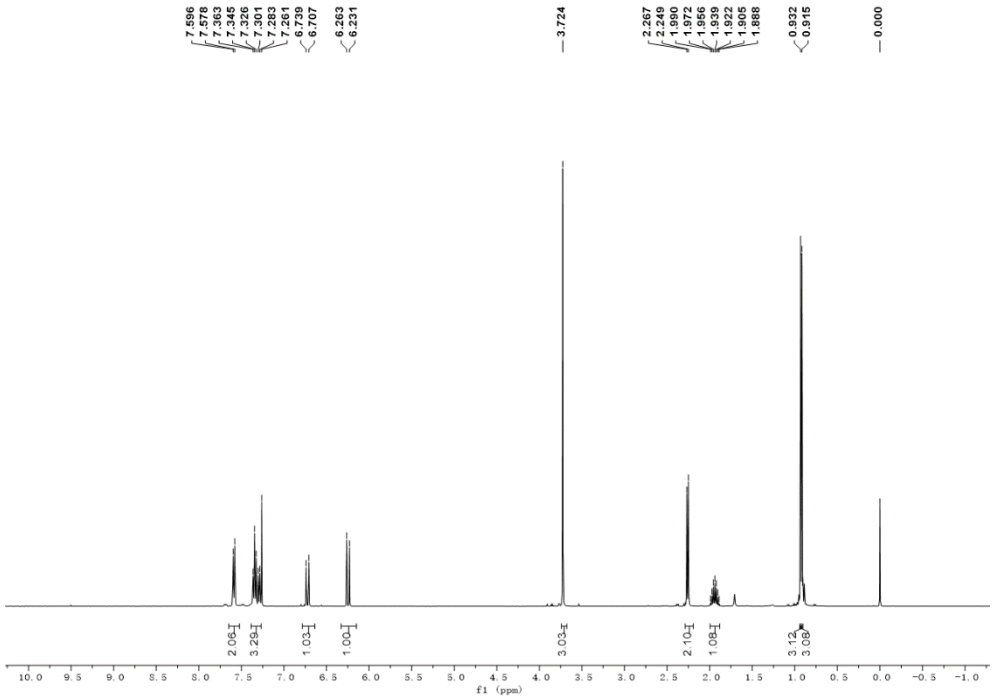
methyl 2-(4-chlorophenyl)-3-(3,4-dichlorophenyl)-1H-pyrrole-1-carboxylate: Yield (78%); white solid, m.p. 100-102 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.48 – 7.41 (m, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 12.8 Hz, 1H), 6.32 (d, *J* = 12.8 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.07, 149.61, 135.79, 132.03, 131.94,

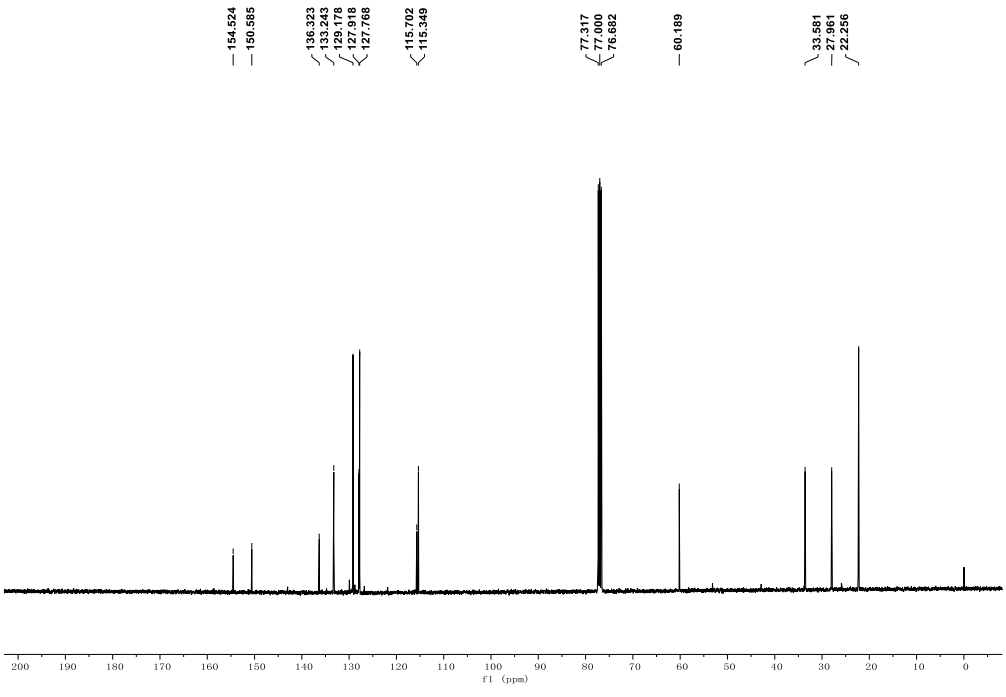
131.91, 131.25, 131.16, 129.75, 129.51, 129.17, 128.63, 126.05, 114.26, 59.44. HRMS (ESI+) Calcd. For $C_{18}H_{12}Cl_3NO_2Na$ ($[M+Na]^+$): 401.9826, found: 401.9820.

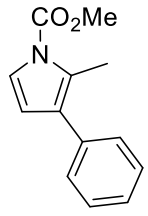
4 NMR Spectrum



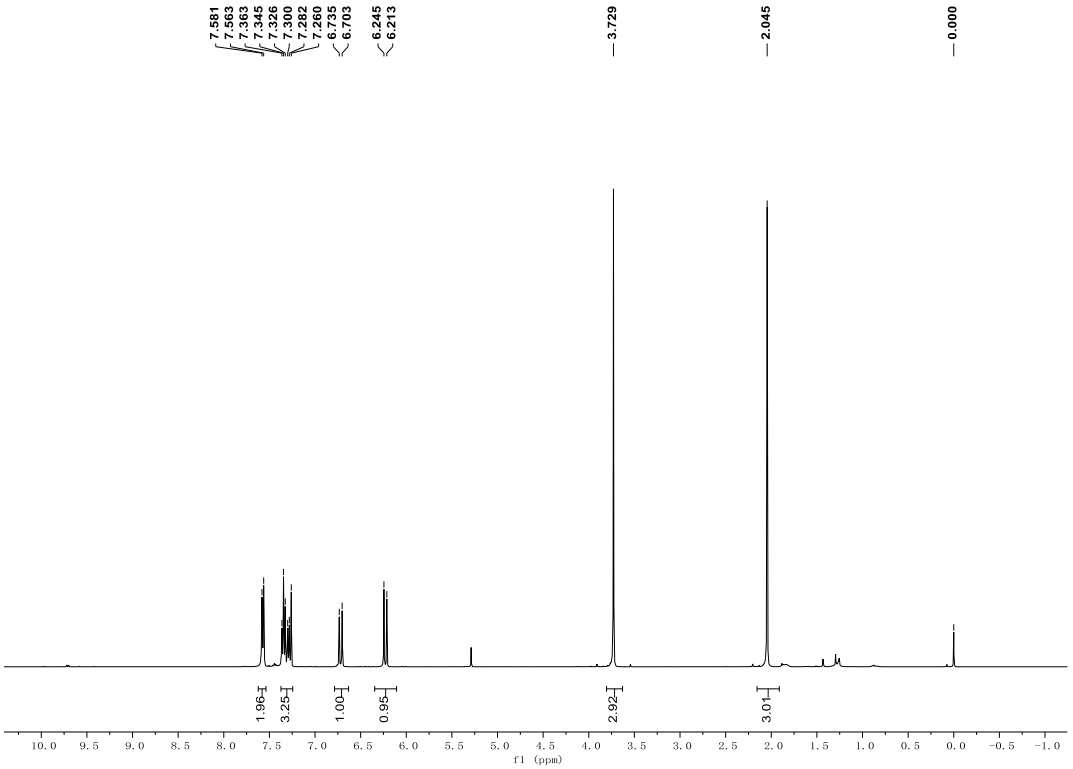
(**3a**)






CO2Me
N

(3b)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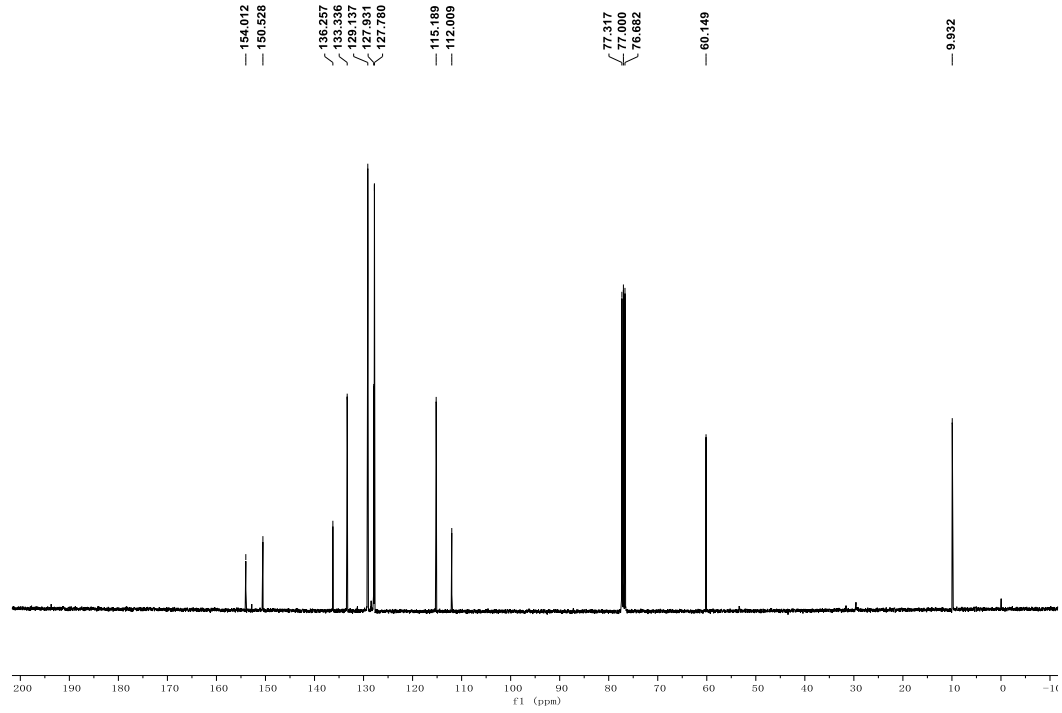
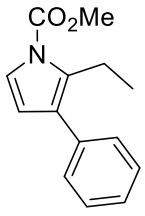
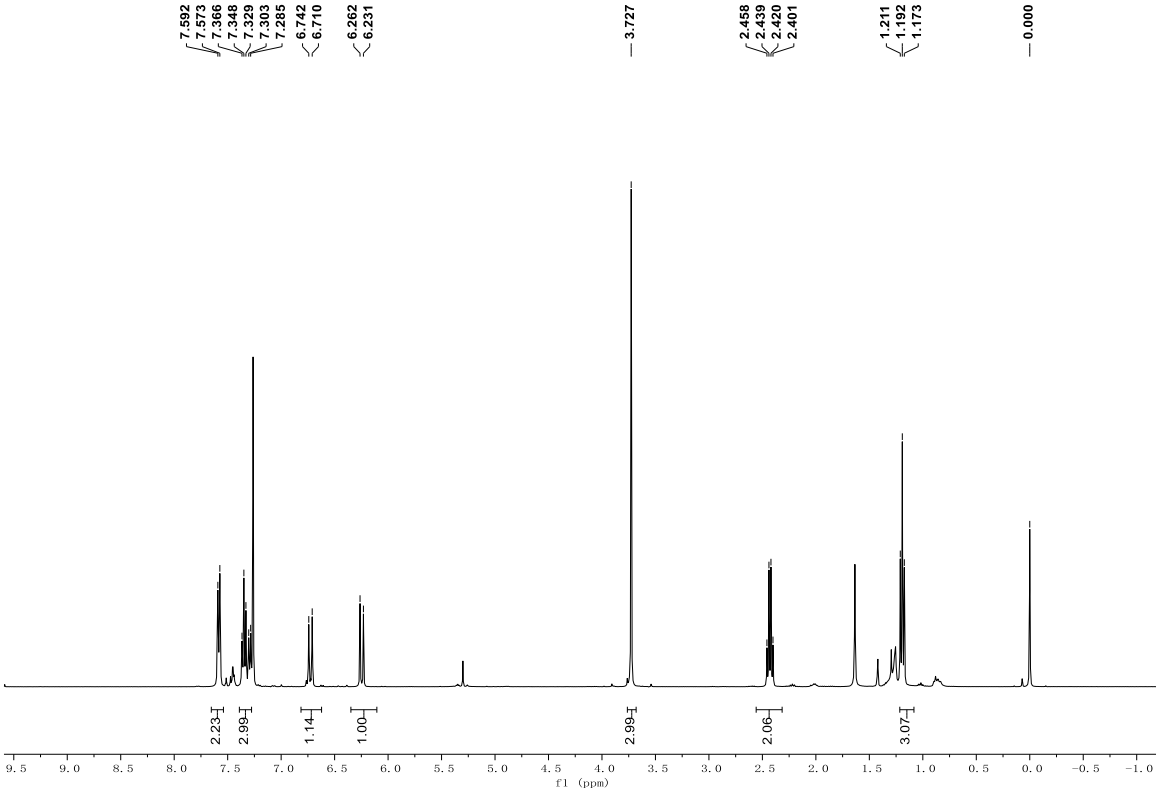
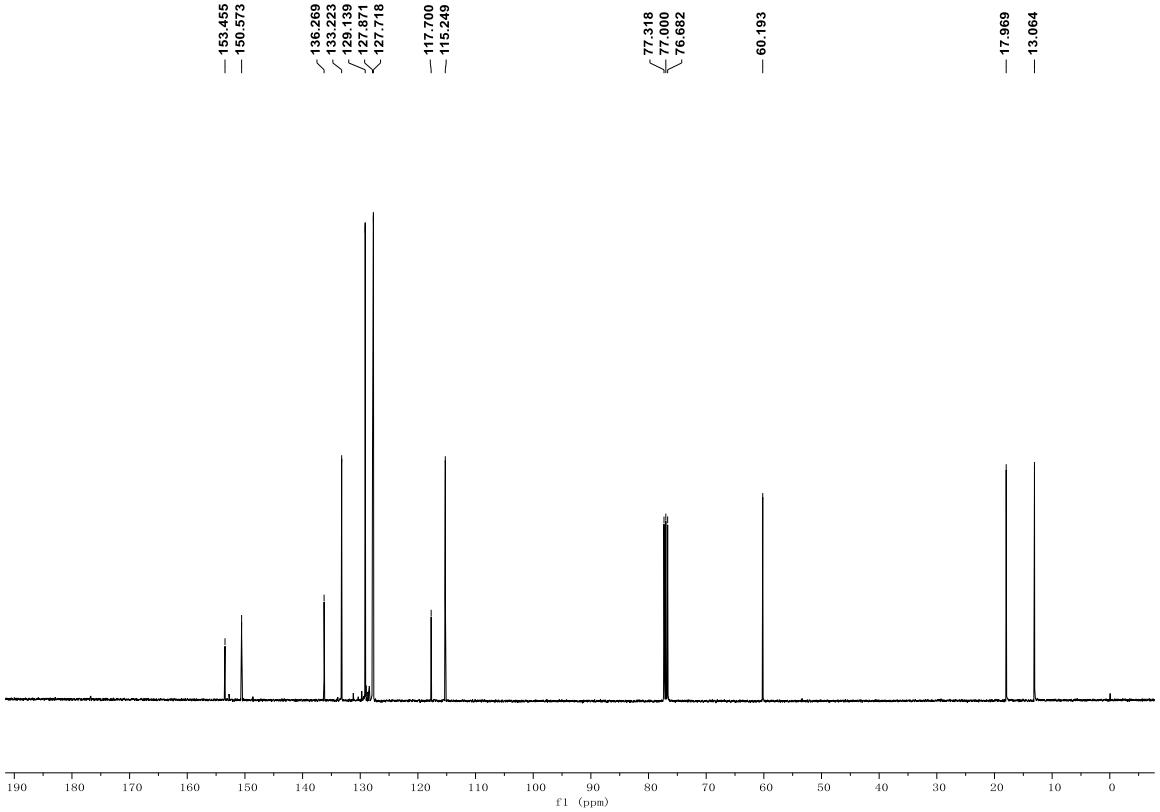
7.563
7.363
7.345
7.326
7.300
7.282
7.260
6.735
6.703
6.245
6.213
3.729
2.045
0.000
1.96
3.25
1.00
0.95
2.92
3.01
f1 (ppm)

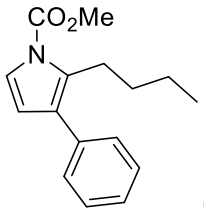

154.012
150.528
136.257
133.336
129.137
127.931
127.780
115.189
112.009
77.317
77.000
76.682
60.149
9.932
f1 (ppm)


CO2Me
N

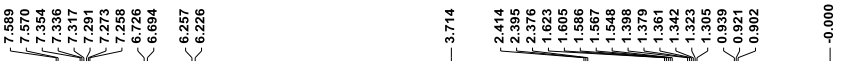
(3c)


7.592
7.573
7.366
7.348
7.329
7.303
7.285
6.742
6.710
6.262
6.231
3.727
2.458
2.439
2.420
2.401
1.211
1.192
1.173
0.000
2.23
2.99
1.14
1.00
2.99
2.06
3.07
f1 (ppm)


153.455
150.573
136.269
133.223
129.139
127.871
127.718
117.700
115.249
77.318
77.000
76.682
60.193
17.969
13.064
f1 (ppm)


CO2Me
N

(3d)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7.570
7.354
7.336
7.317
7.291
7.273
7.258
6.726
6.694
6.257
6.226
3.714
2.414
2.395
2.376
1.623
1.605
1.586
1.567
1.548
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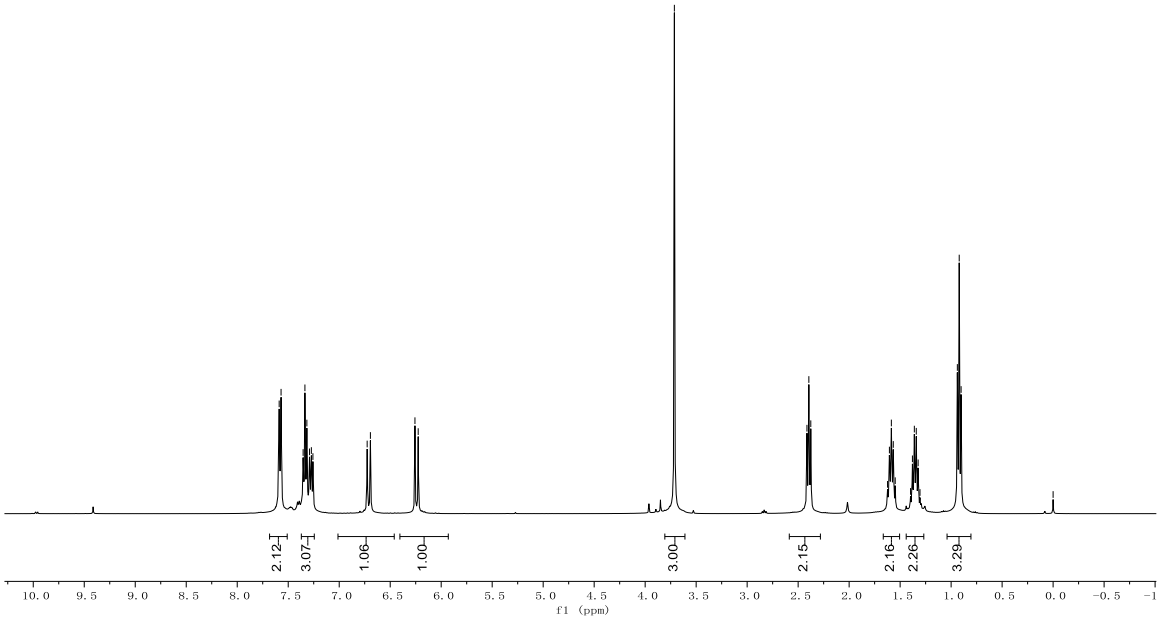
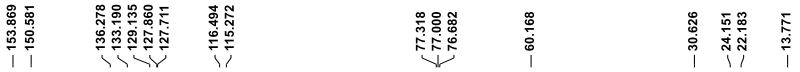
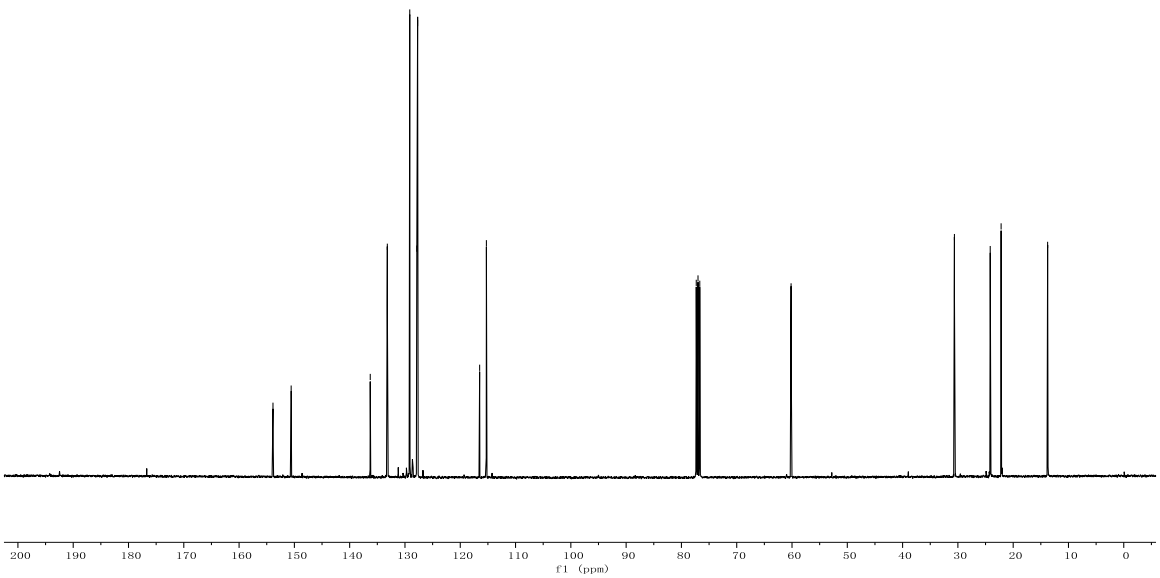
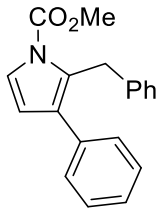
1.379
1.361
1.342
1.323
1.305
0.939
0.921
0.902
-0.000

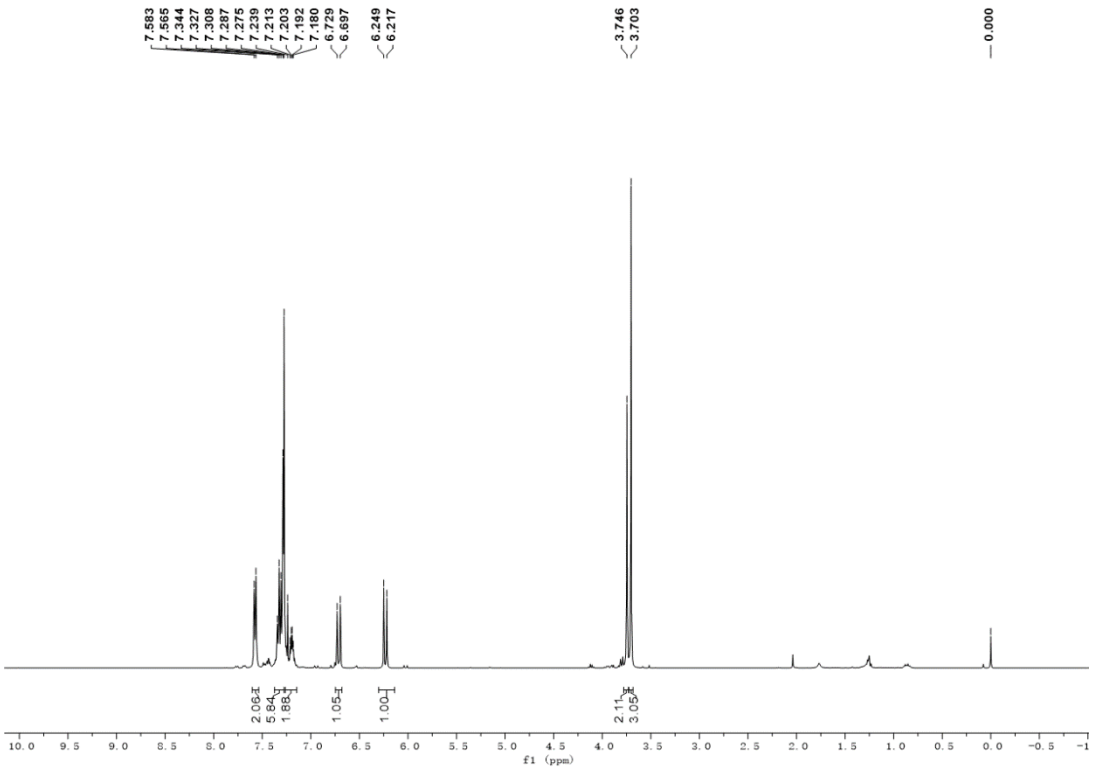

2.12
3.07
1.06
1.00
3.00
2.15
2.16
2.26
3.29
f1 (ppm)


153.869
150.581
136.278
133.190
129.135
127.860
127.711
116.494
115.272
77.318
77.000
76.682
60.168
30.626
24.151
22.183
13.771


f1 (ppm)


CO2Me
N
Ph

(**3e**)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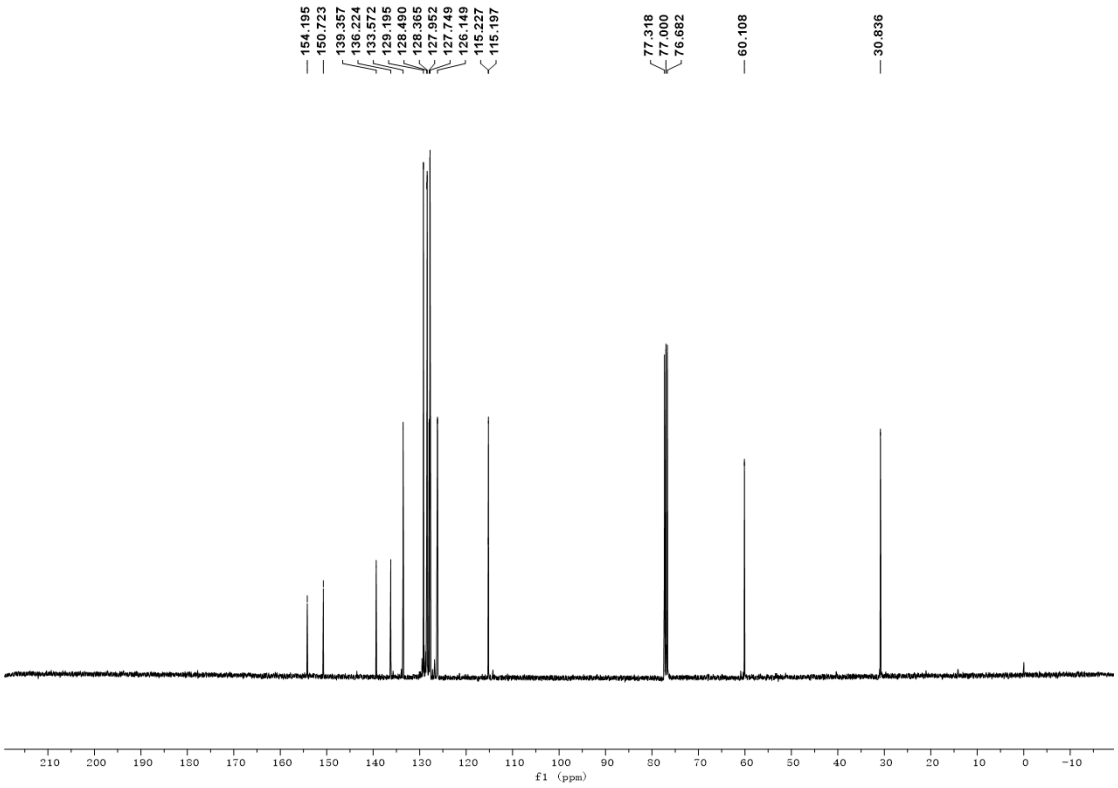
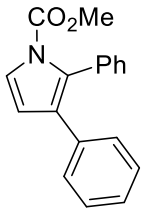
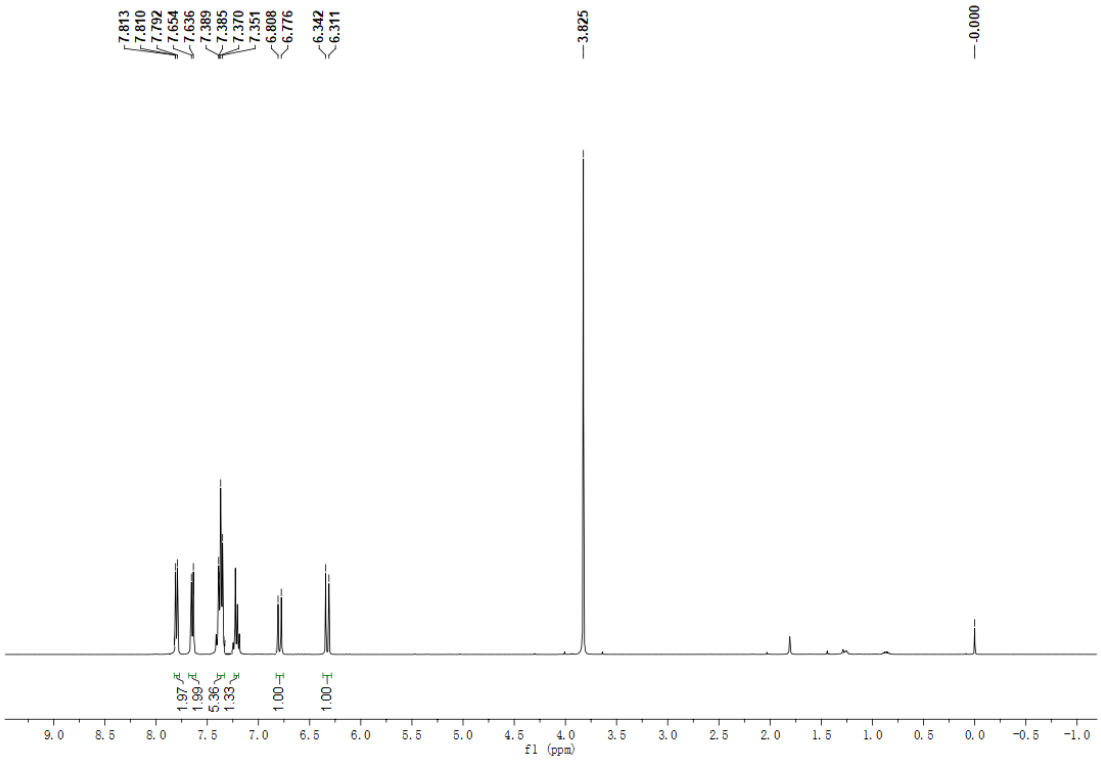
7.344
7.327
7.308
7.287
7.275
7.239
7.213
7.203
7.192
7.180
6.729
6.697
6.249
6.217
3.746
3.703
0.000
2.06
5.84
1.88
1.05
1.00
2.11
3.05
f1 (ppm)


154.195
150.723
139.357
136.224
133.572
129.195
128.490
128.365
127.952
127.749
126.149
115.227
115.197
77.318
77.000
76.682
60.108
30.836
f1 (ppm)


CO2Me
N
Ph

(3f)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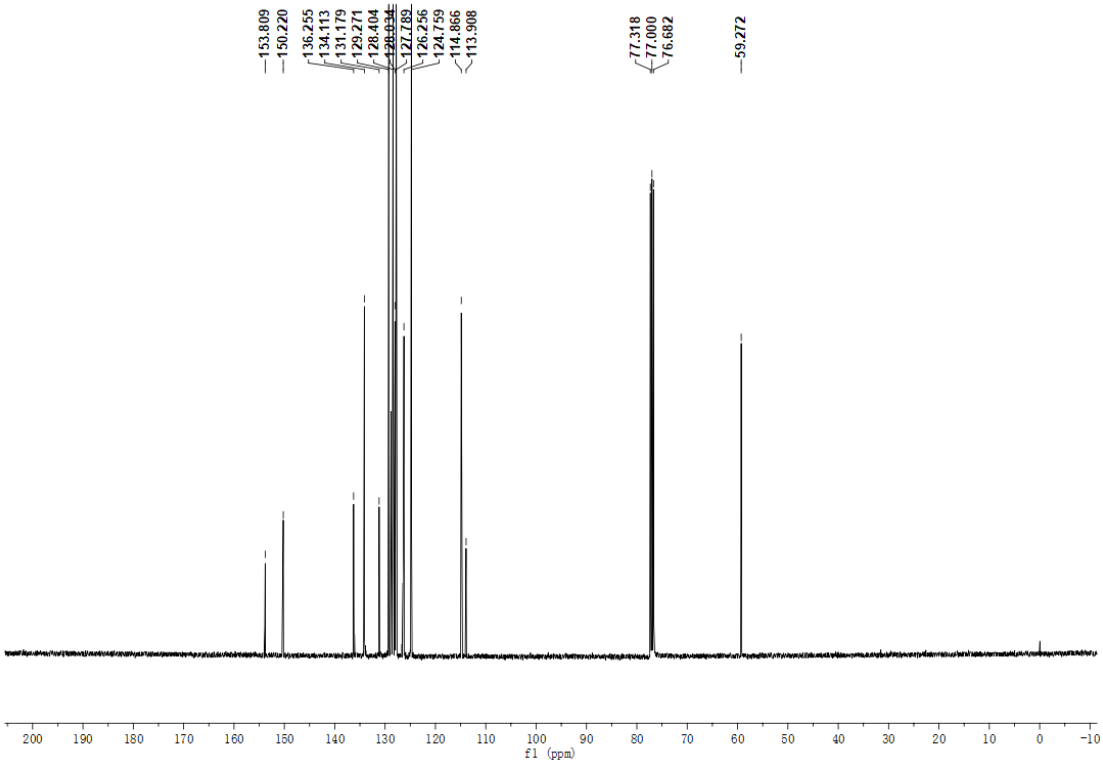
7.792
7.654
7.636
7.389
7.385
7.370
7.351
6.808
6.776
6.342
6.311
3.825
0.000
1.97
1.99
5.36
1.33
1.00
1.00
f1 (ppm)


153.809
150.220
136.255
134.113
131.179
129.271
128.404
127.789
126.256
124.759
114.866
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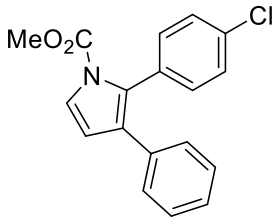
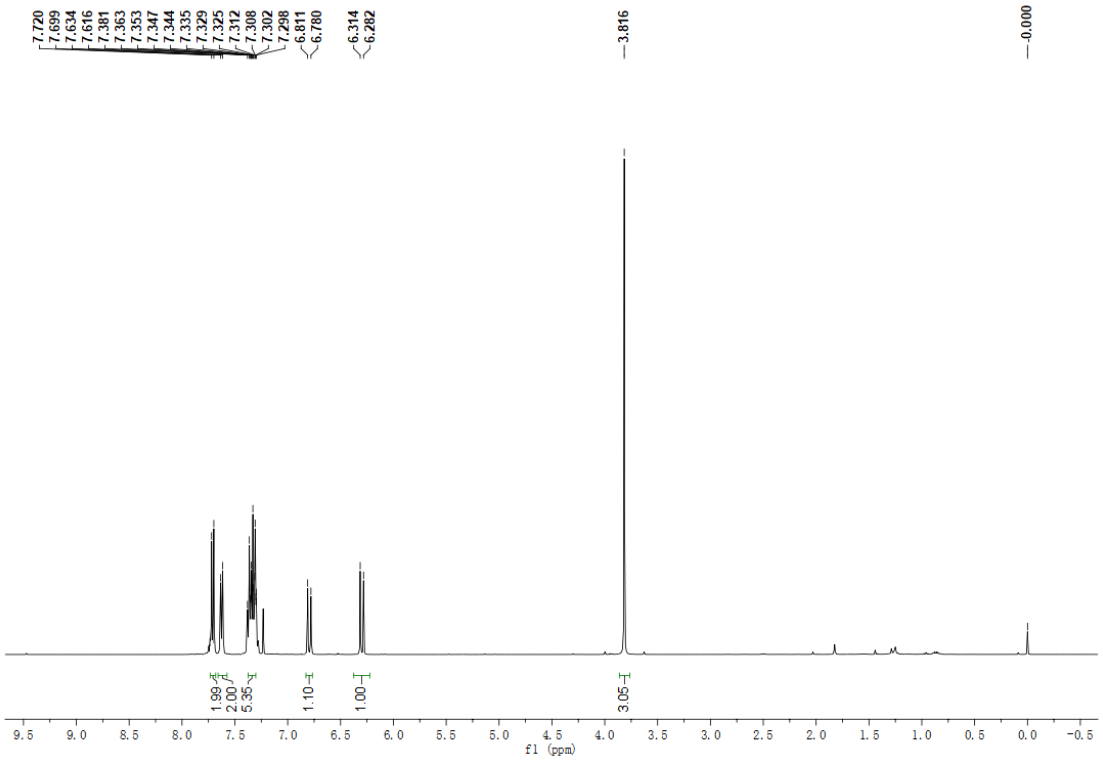
77.318
77.000
76.682
59.272
f1 (ppm)


MeO2C
N
Cl

(3g)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7.634
7.616
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7.363
7.353
7.347
7.344
7.335
7.329
7.325
7.312
7.308
7.302
7.298
6.811
6.780
6.314
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3.816
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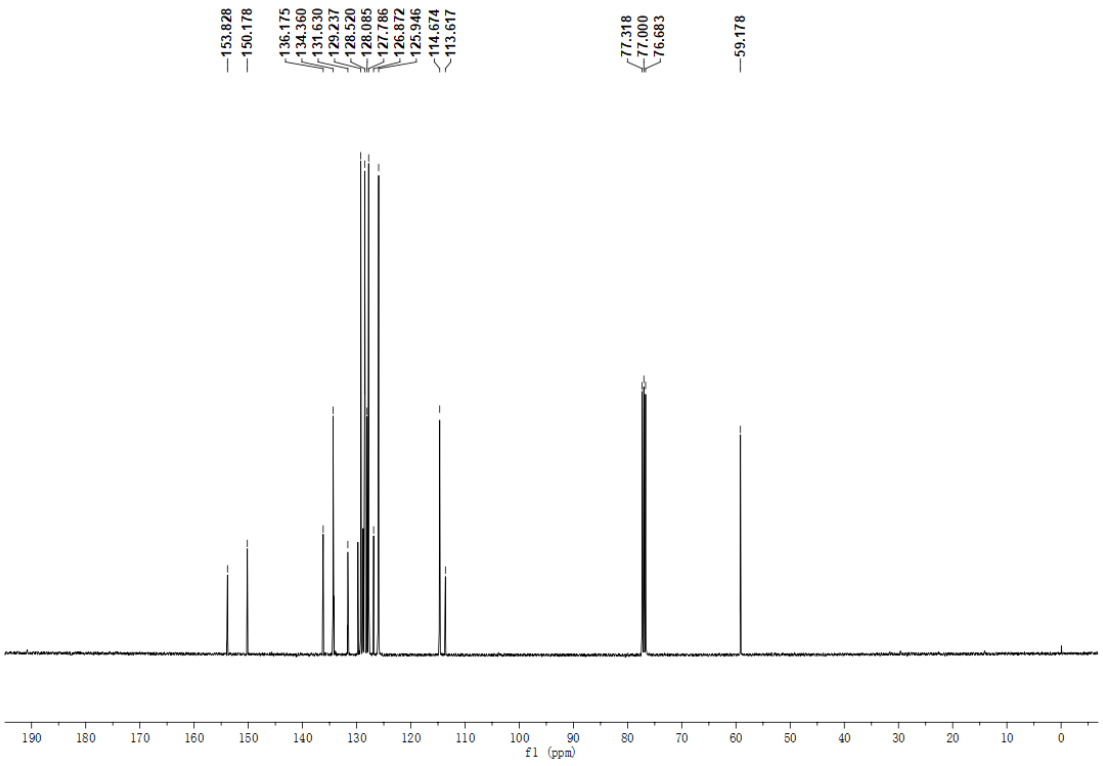
1.99
2.00
5.35
1.10
1.00
3.05
f1 (ppm)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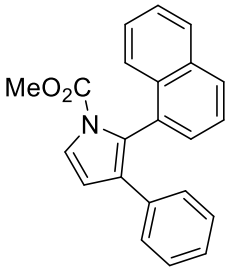
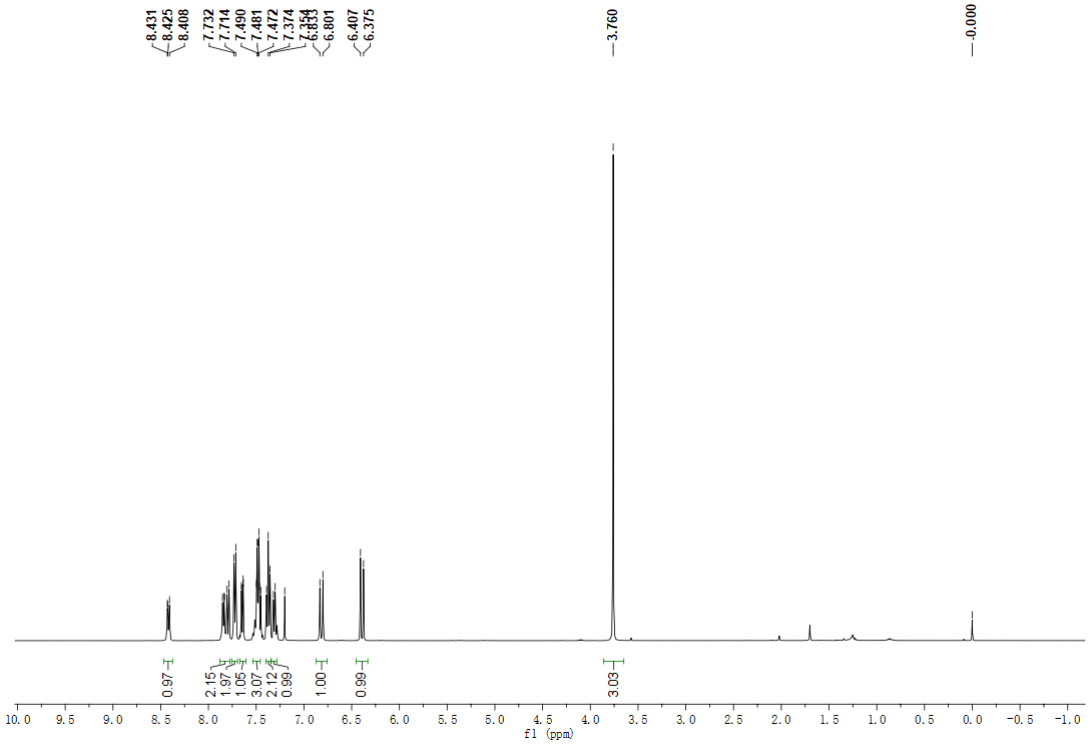
136.175
134.360
131.630
129.237
128.520
128.085
127.786
126.872
125.946
114.674
113.617
77.318
77.000
76.683
59.178
f1 (ppm)


MeO2C
N

(3h)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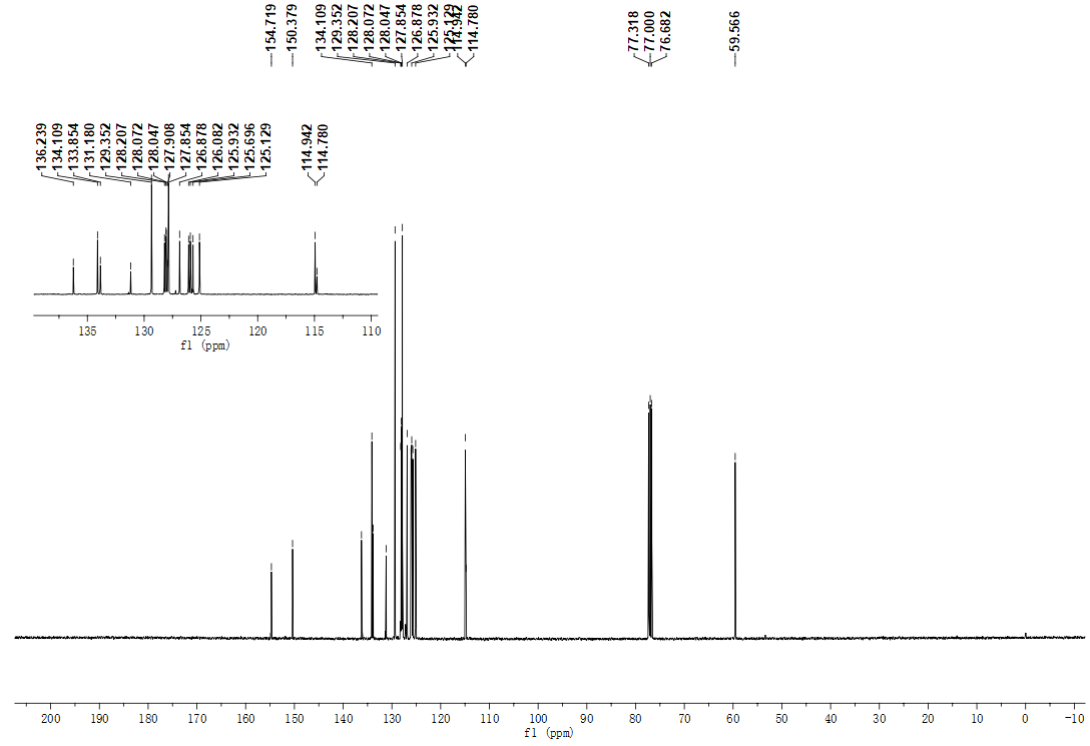
8.408
7.732
7.714
7.490
7.481
7.472
7.374
6.801
6.407
6.375
3.760
0.000
0.97
2.15
1.97
1.05
3.07
2.12
0.99
1.00
0.99
3.03
f1 (ppm)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134.109
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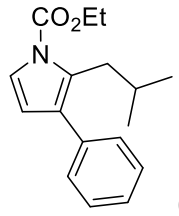
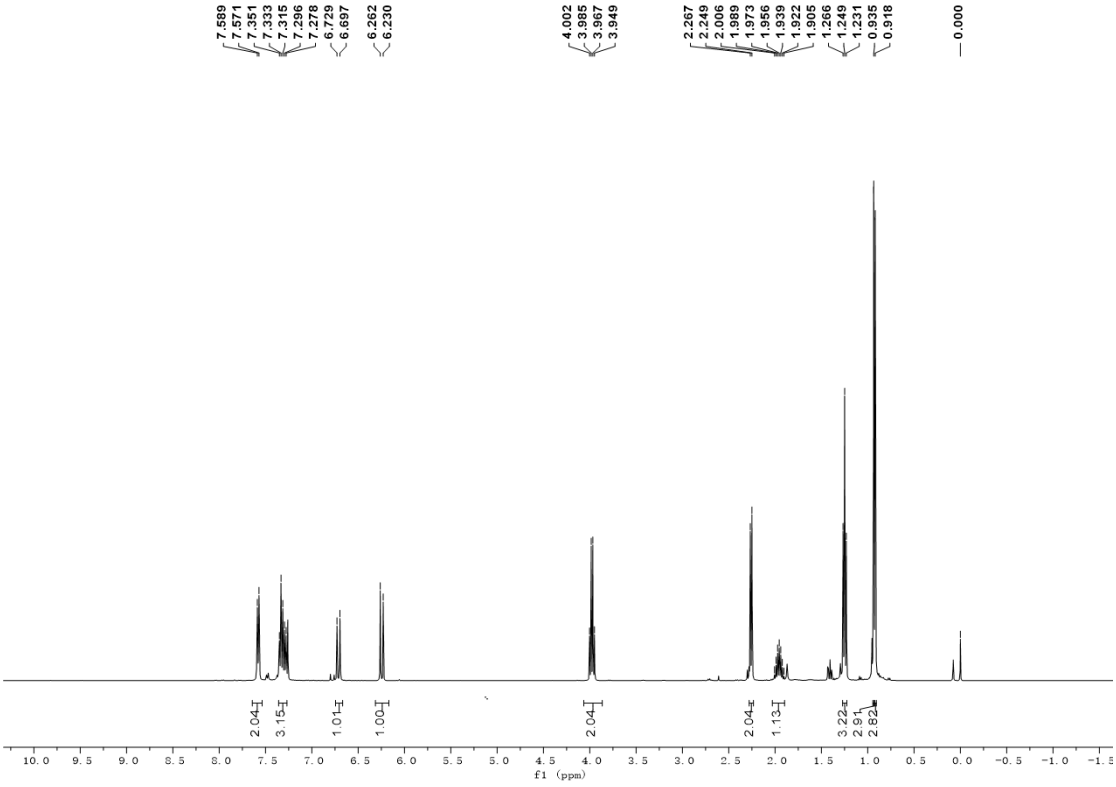
128.072
128.047
127.854
126.878
125.932
114.942
114.780
77.318
77.000
76.682
59.566
136.239
134.109
133.854
131.180
129.352
128.207
128.072
128.047
127.908
127.854
126.878
126.082
125.932
125.696
125.129
114.942
114.780
f1 (ppm)
f1 (ppm)


CO2Et
N

(3j)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7.333
7.315
7.296
7.278
6.729
6.697
6.262
6.230
4.002
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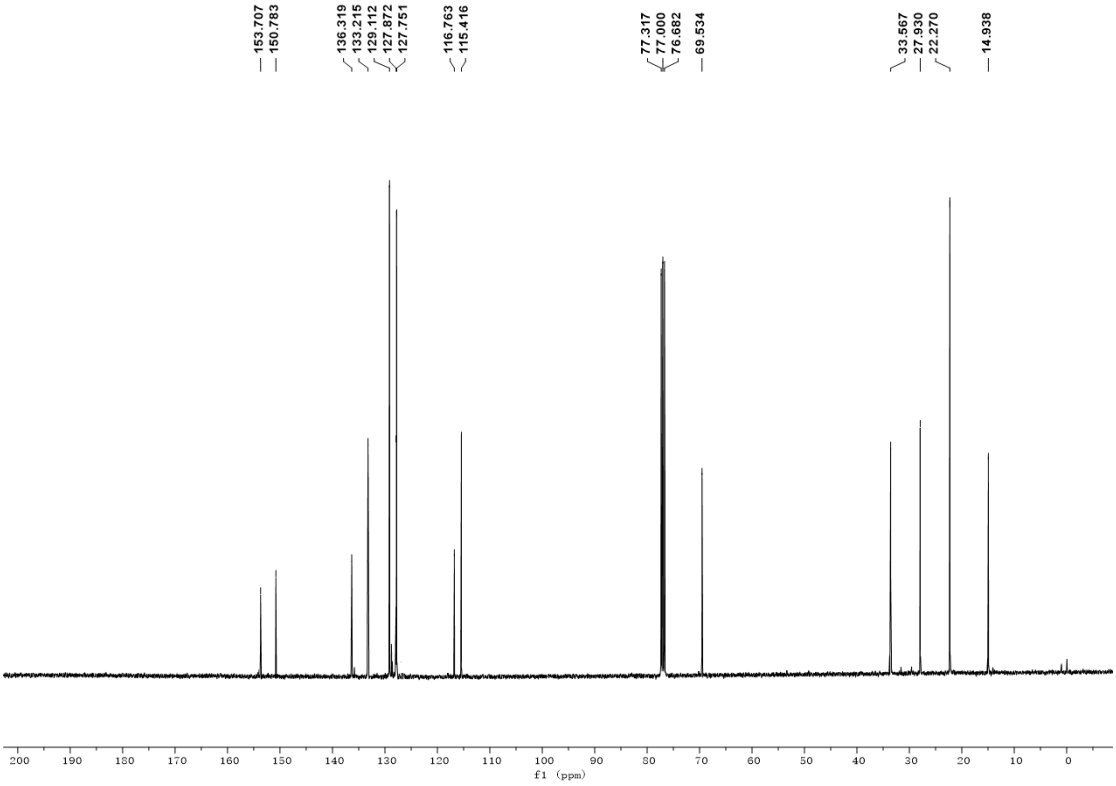
3.967
3.949
2.267
2.249
2.006
1.989
1.973
1.956
1.939
1.922
1.905
1.266
1.249
1.231
0.935
0.918
0.000
2.04
3.15
1.01
1.00
2.04
2.04
1.13
3.22
2.91
2.82
f1 (ppm)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133.215
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127.872
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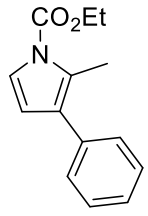
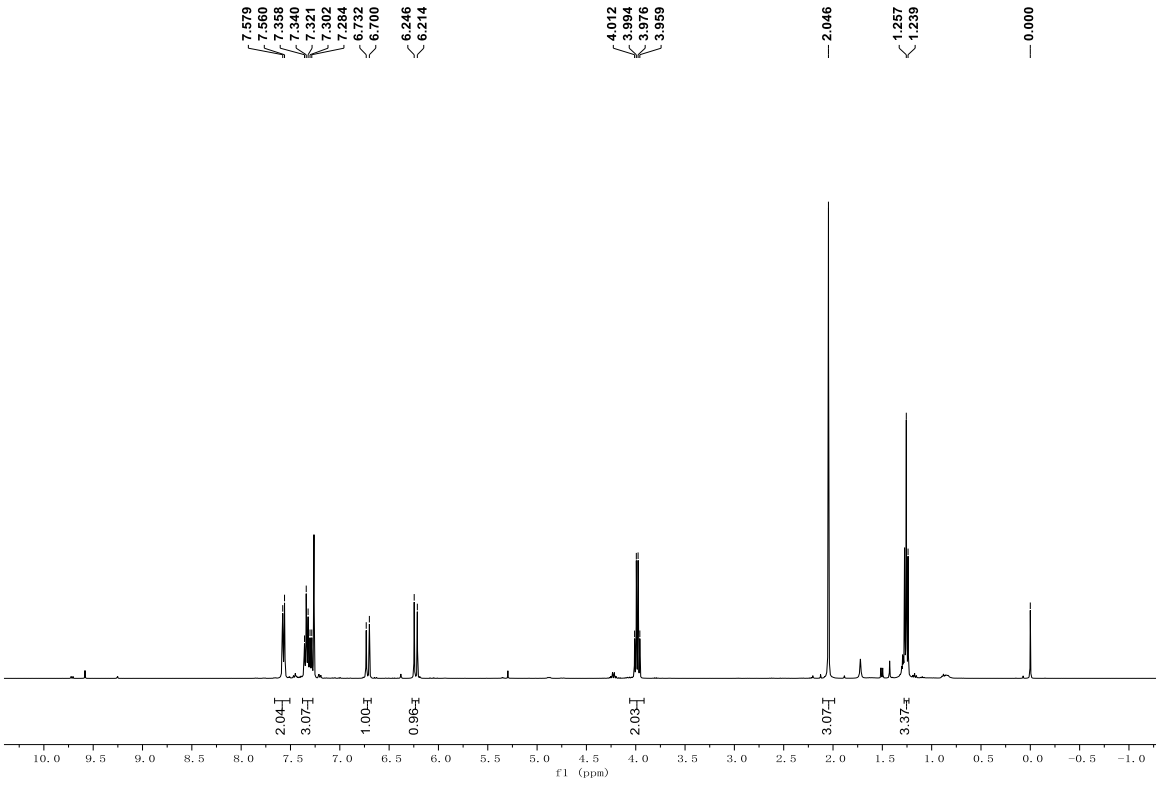
116.763
115.416
77.317
77.000
76.682
69.534
33.567
27.930
22.270
14.938
f1 (ppm)


CO2Et
N

(3k)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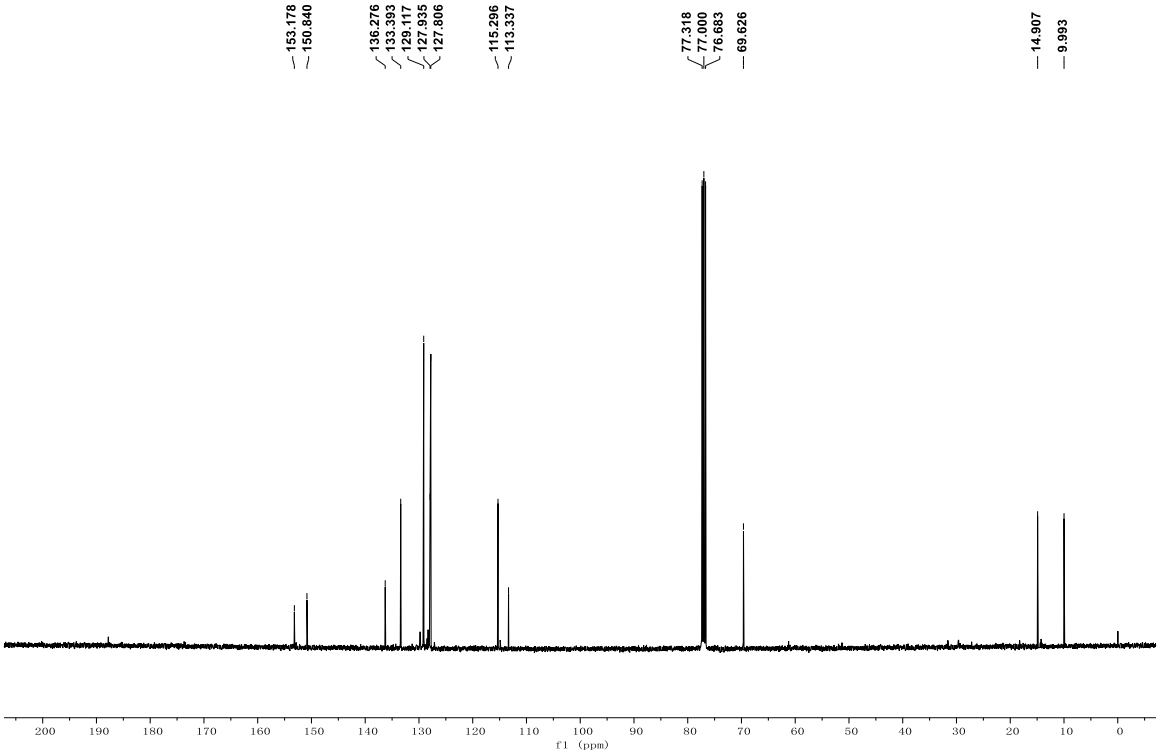
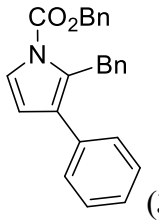
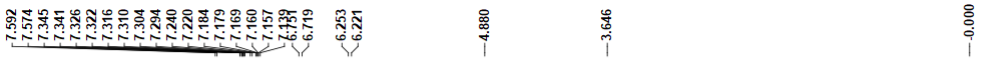
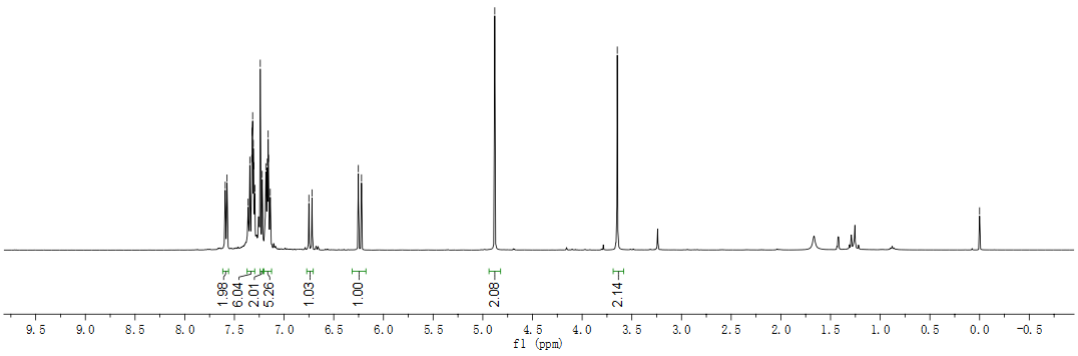
7.340
7.321
7.302
7.284
6.732
6.700
6.246
6.214
4.012
3.994
3.976
3.959
2.046
1.257
1.239
0.000
2.04
3.07
1.00
0.96
2.03
3.07
3.37
f1 (ppm)

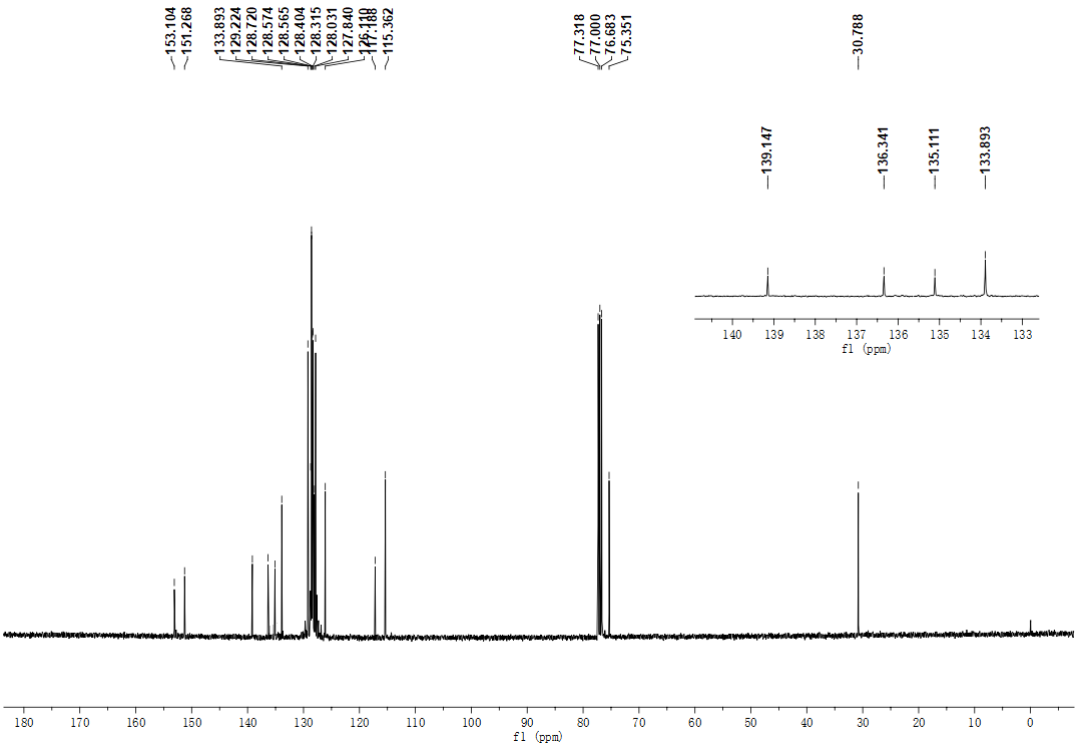

153.178
150.840
136.276
133.393
129.117
127.935
127.806
115.296
113.337
77.318
77.000
76.683
69.626
14.907
9.993
f1 (ppm)

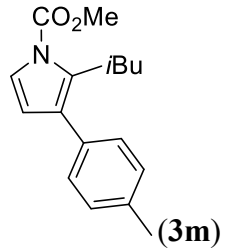

CO2Bn
N
Bn

(3l)

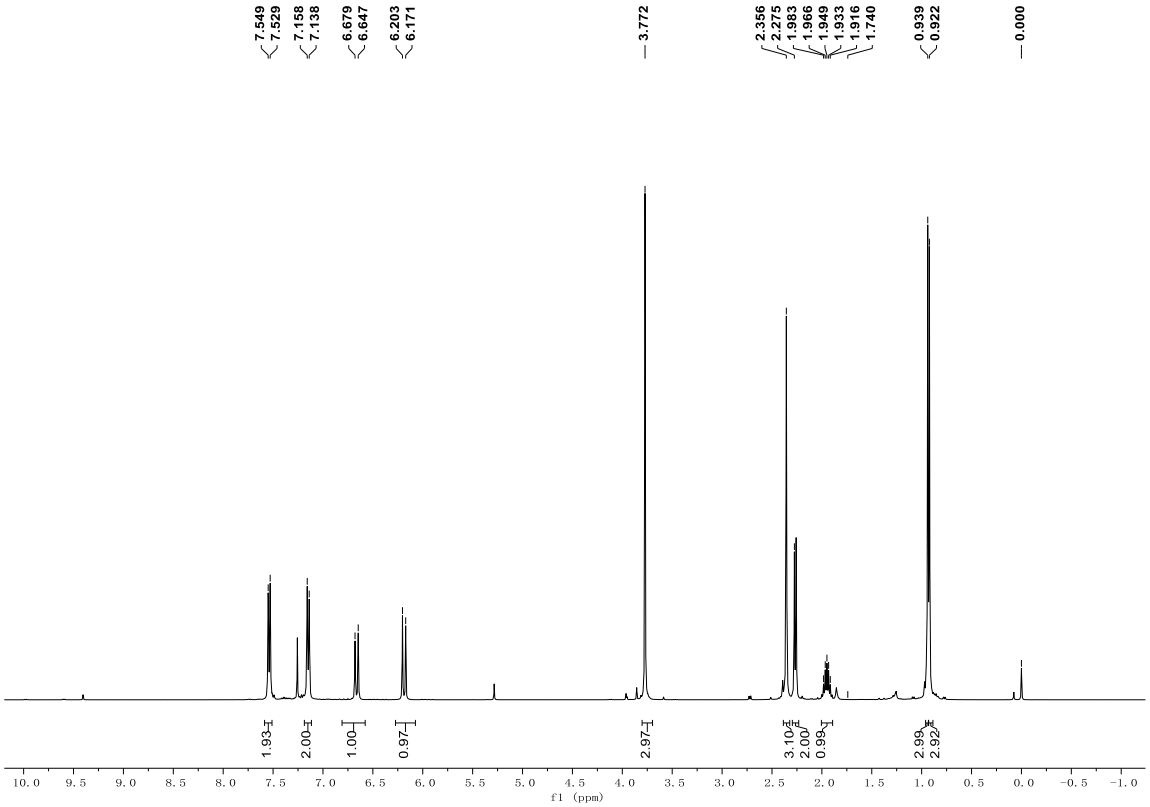

7.592
7.574
7.345
7.341
7.326
7.322
7.316
7.310
7.304
7.294
7.240
7.220
7.184
7.179
7.169
7.160
7.157
6.719
6.253
6.221
4.880
3.646
0.000

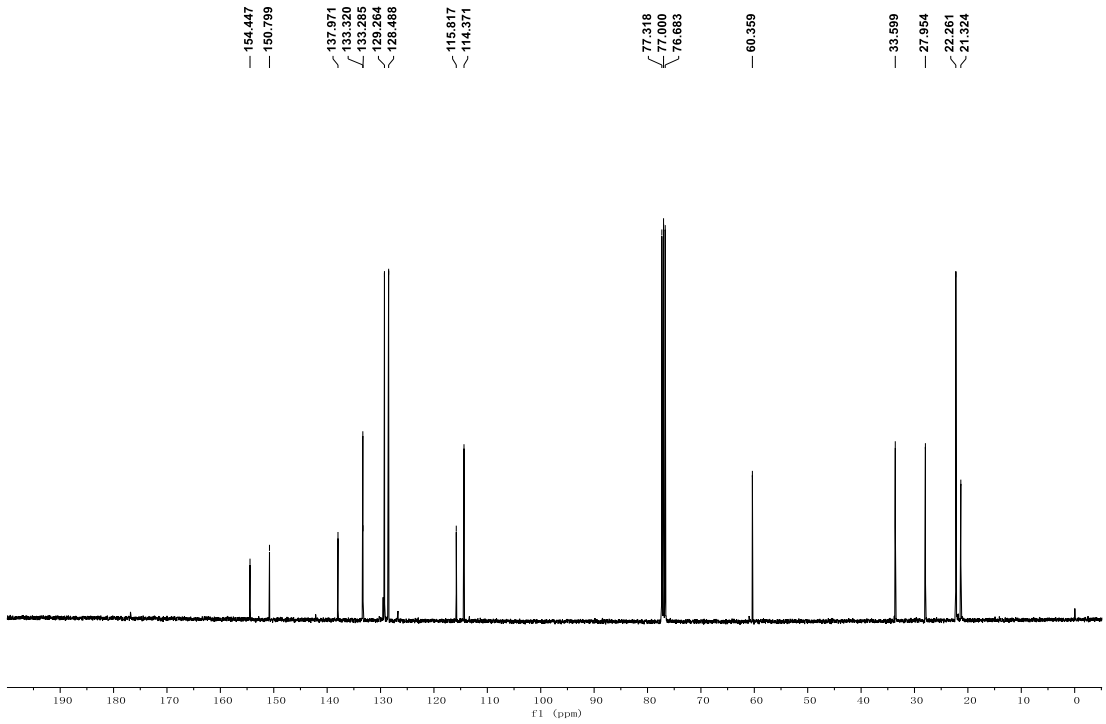

1.98
6.04
2.01
5.26
1.03
1.00
2.08
2.14
f1 (ppm)

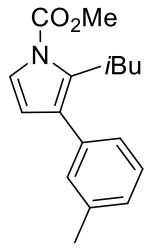

153.104
151.268
133.893
129.224
128.720
128.574
128.565
128.404
128.315
128.031
127.840
115.362
77.318
77.000
76.683
75.351
30.788
139.147
136.341
135.111
133.893
f1 (ppm)


CO2Me
N
iBu

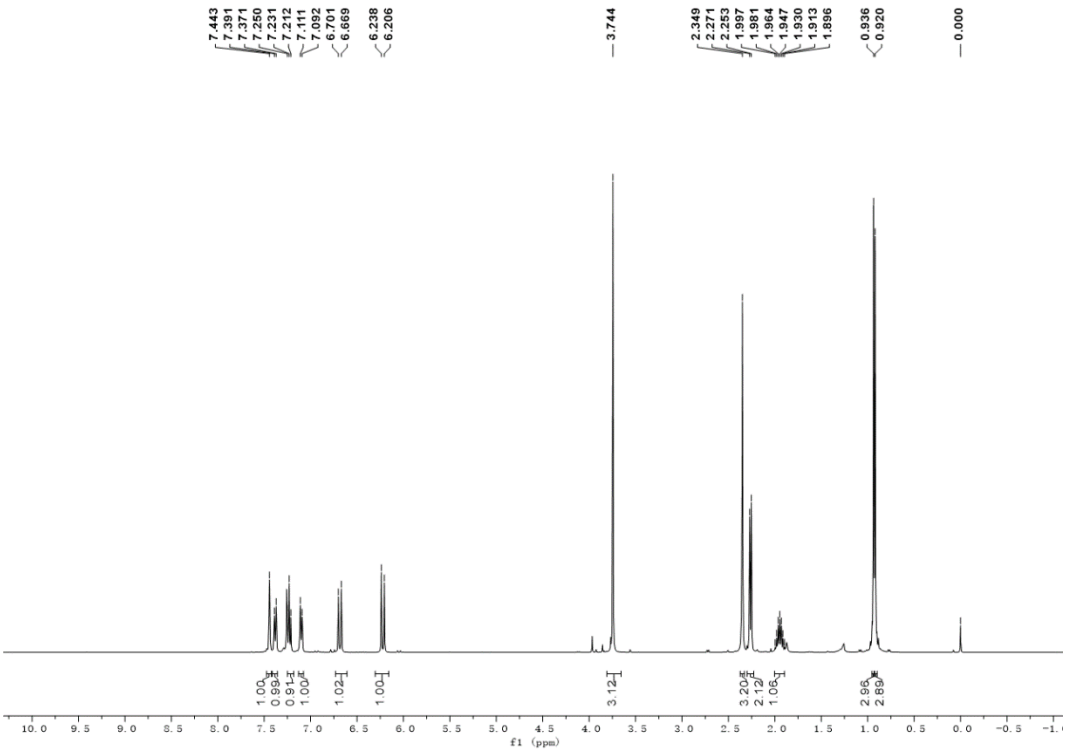
(3m)

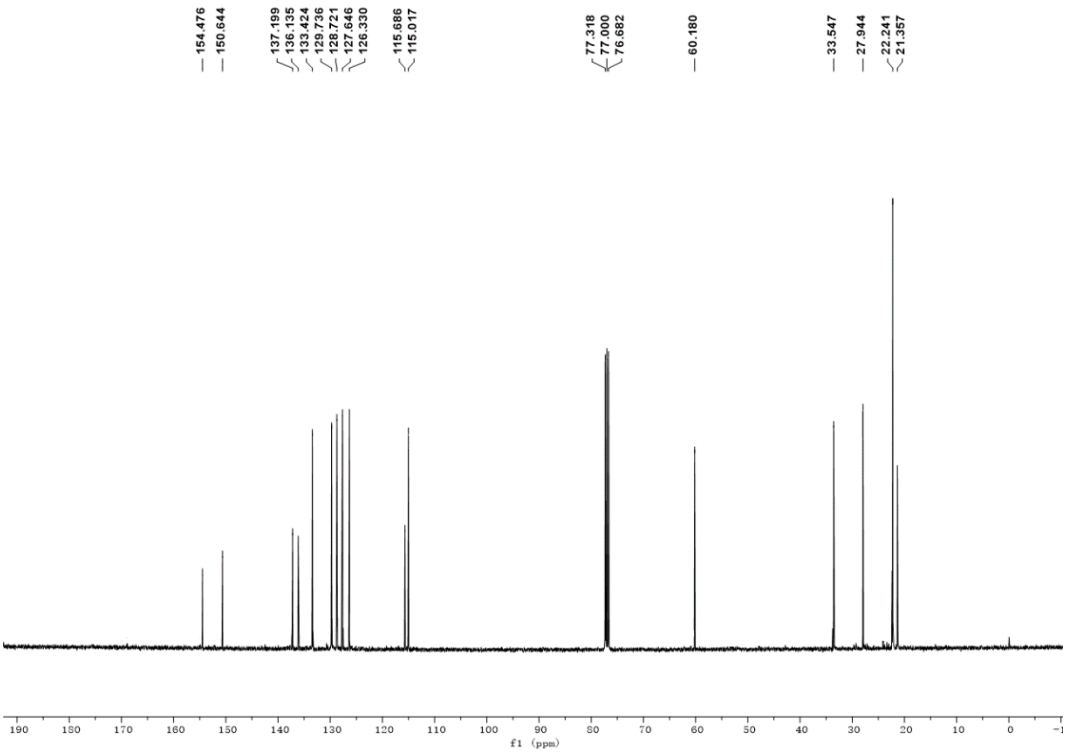

7.549
7.529
7.158
7.138
6.679
6.647
6.203
6.171
3.772
2.356
2.275
1.983
1.966
1.949
1.933
1.916
1.740
0.939
0.922
0.000
1.93
2.00
1.00
0.97
2.97
3.10
2.00
0.99
2.99
2.92
f1 (ppm)

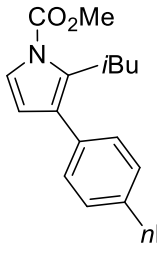

154.447
150.799
137.971
133.320
133.285
129.264
128.488
115.817
114.371
77.318
77.000
76.683
60.359
33.599
27.954
22.261
21.324
f1 (ppm)


CO2Me
N
iBu

(3n)

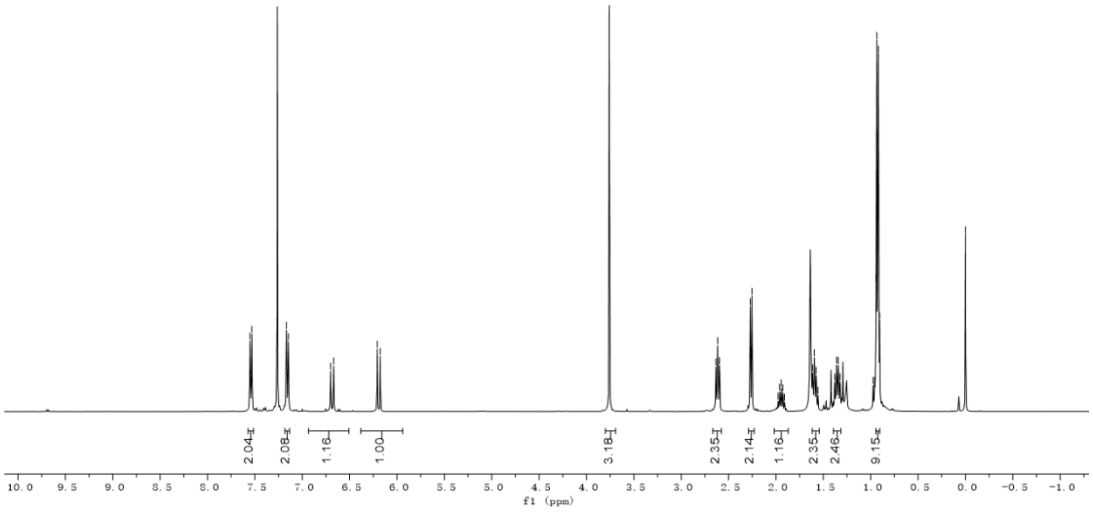

7.443
7.391
7.371
7.250
7.231
7.212
7.111
7.092
6.701
6.669
6.238
6.206
3.744
2.349
2.271
2.253
1.997
1.981
1.964
1.947
1.930
1.913
1.896
0.936
0.920
0.000
1.00
0.99
0.91
1.00
1.02
1.00
3.12
3.20
2.12
1.06
2.95
2.89
f1 (ppm)

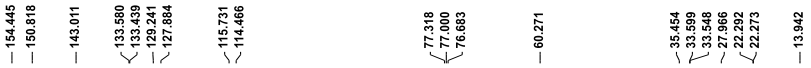

154.476
150.644
137.199
136.135
133.424
129.736
128.721
127.646
126.330
115.686
115.017
77.318
77.000
76.682
60.180
33.547
27.944
22.241
21.357
f1 (ppm)

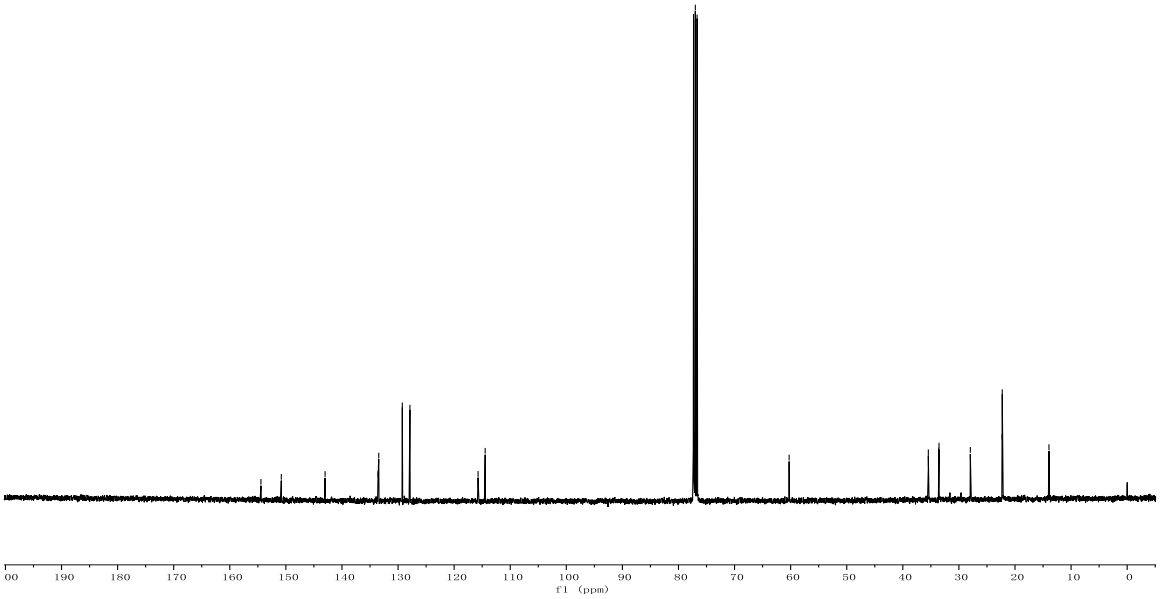

CO2Me
N
iBu
nBu

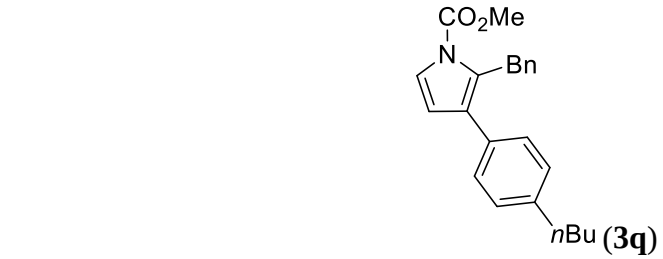
(3p)


7.551
7.531
7.167
7.147
6.701
6.669
6.209
6.177
3.759
2.634
2.615
2.596
2.271
2.253
1.978
1.961
1.944
1.927
1.910
1.614
1.595
1.576
1.557
1.380
1.361
1.342
1.324
0.975
0.943
0.935
0.925
0.919
0.906
0.000


2.04
2.08
1.16
1.00
3.18
2.35
2.14
1.16
2.35
2.46
9.15
f1 (ppm)

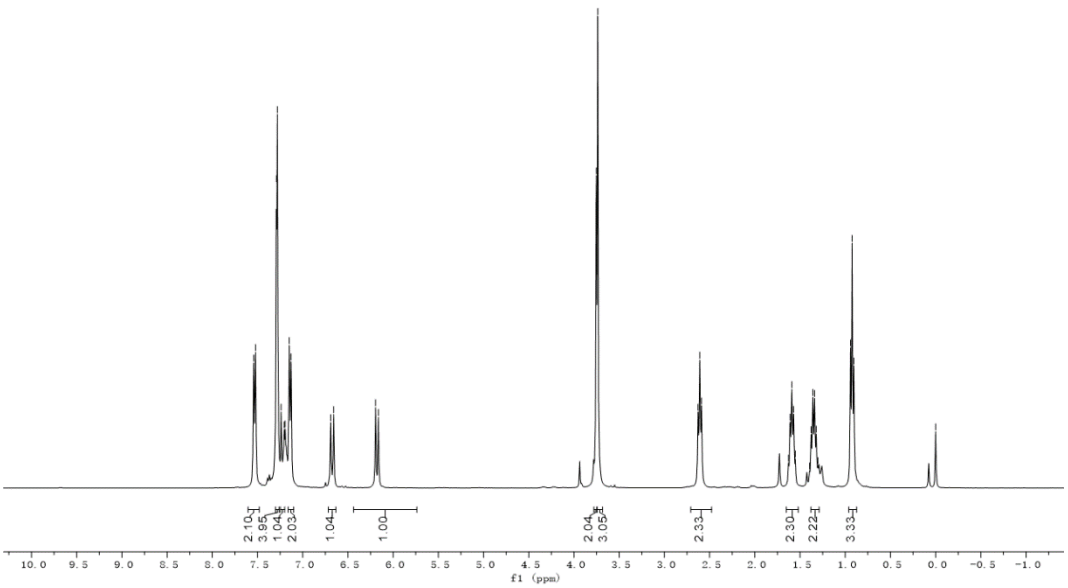

154.445
150.818
143.011
133.580
133.439
129.241
127.884
115.731
114.466
77.318
77.000
76.683
60.271
35.454
33.599
33.548
27.966
22.292
22.273
13.942


f1 (ppm)

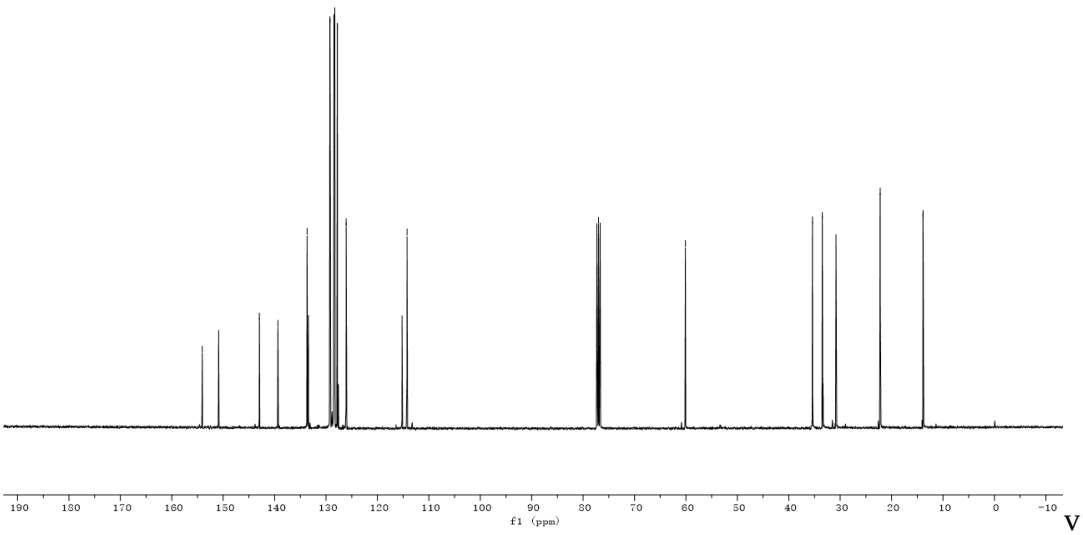

CO2Me
N
Bn
nBu

(3q)

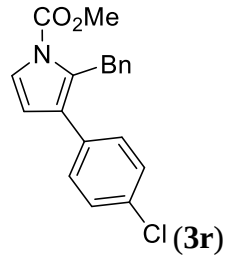

7.542
7.523
7.291
7.281
7.240
7.205
7.194
7.149
7.129
6.690
6.658
6.195
6.163
3.753
3.737
2.628
2.609
2.590
1.627
1.609
1.590
1.572
1.552
1.394
1.376
1.358
1.339
1.321
1.303
0.942
0.923
0.905
0.000


2.10
3.95
1.04
2.03
1.04
1.00
2.04
3.05
2.33
2.30
2.22
3.33
f1 (ppm)

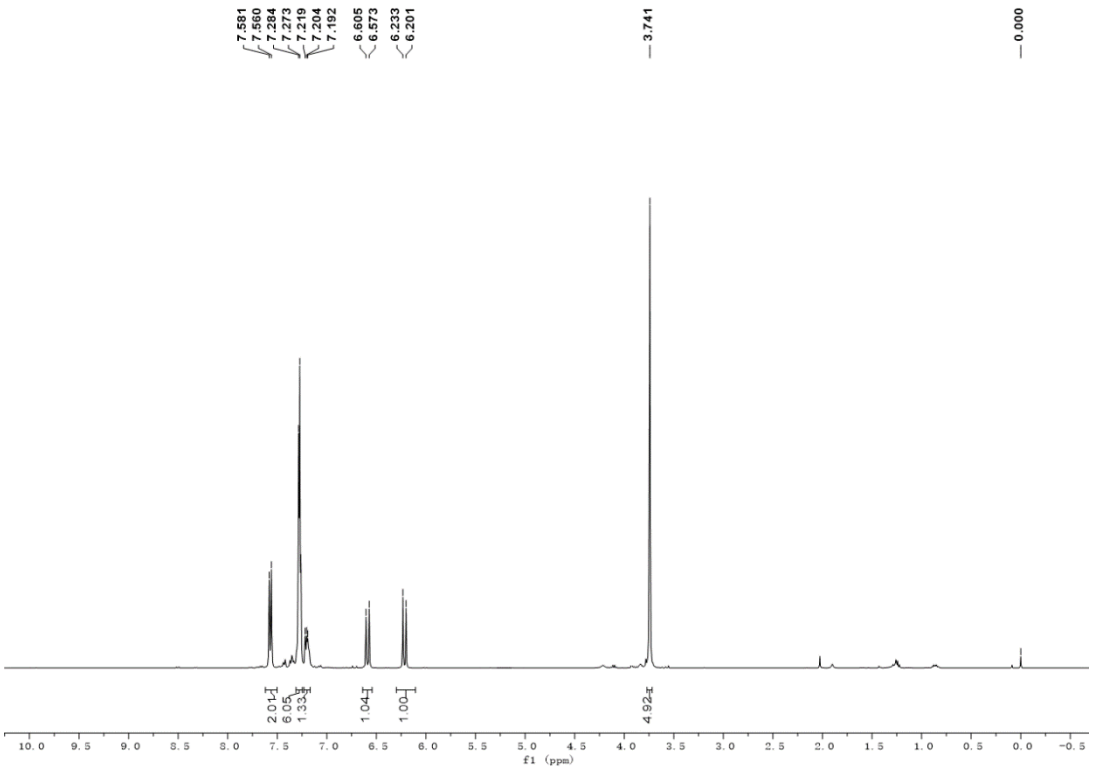

154.068
150.884
142.967
139.357
133.676
133.430
129.240
128.458
128.307
127.799
126.083
115.207
114.243
77.317
77.000
76.682
60.104
35.385
33.471
30.818
22.222
13.884

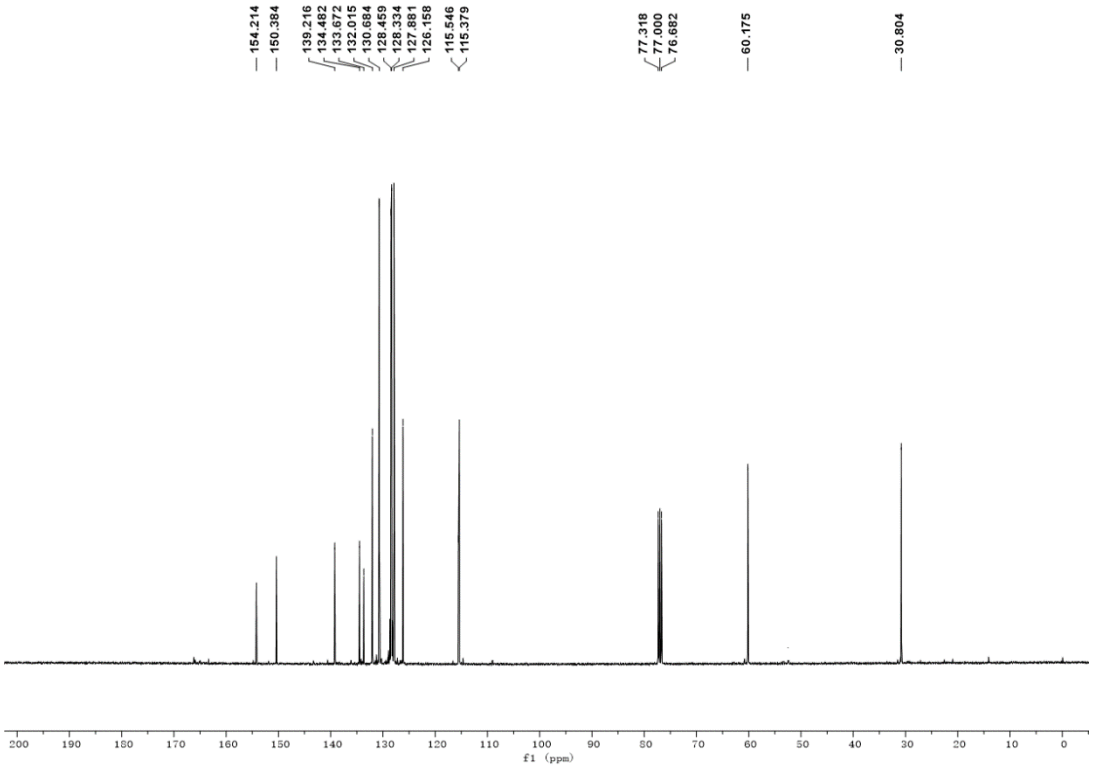

f1 (ppm)

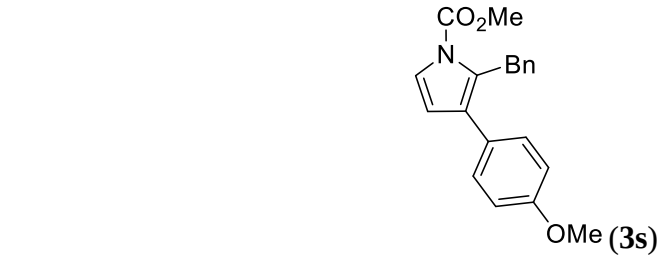
V


CO2Me
N
Bn
Cl

(3r)

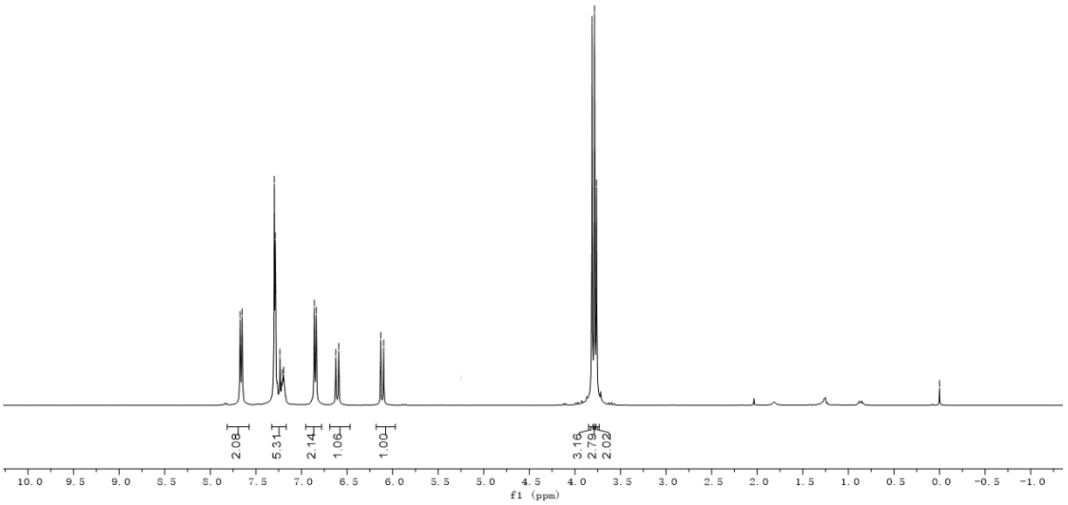

7.581
7.560
7.284
7.273
7.219
7.204
7.192
6.605
6.573
6.233
6.201
3.741
0.000
2.01
6.05
1.33
1.04
1.00
4.92
f1 (ppm)


154.214
150.384
139.216
134.482
133.672
132.015
130.684
128.459
128.334
127.881
126.158
115.546
115.379
77.318
77.000
76.682
60.175
30.804
f1 (ppm)

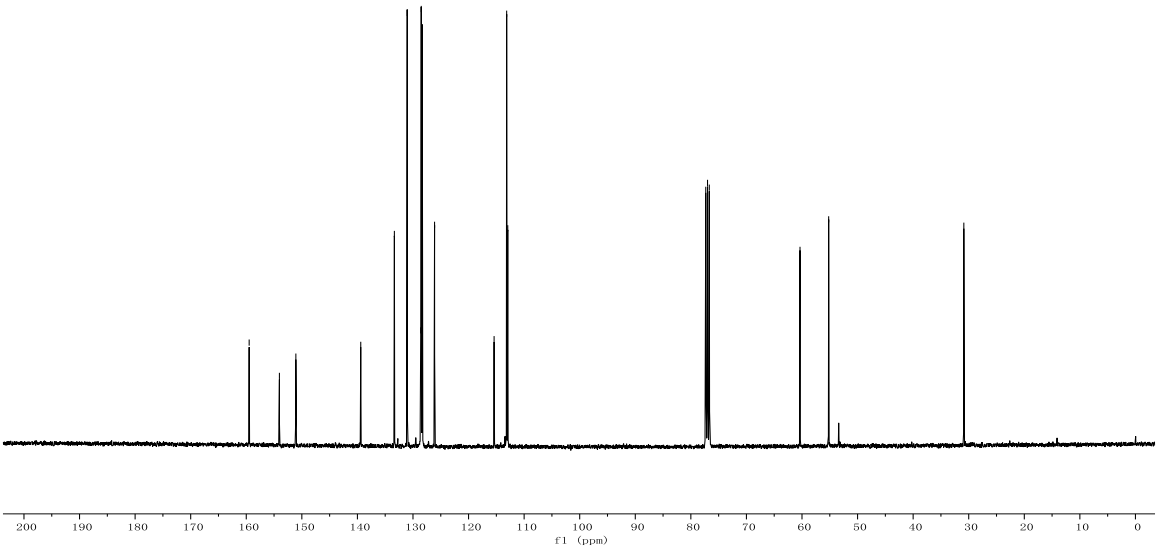

CO2Me
N
Bn
OMe

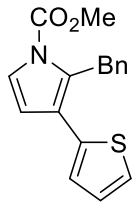
(3s)


7.673
7.651
7.298
7.288
7.236
7.208
7.195
6.859
6.837
6.623
6.591
6.130
6.098
3.811
3.785
3.763
0.000

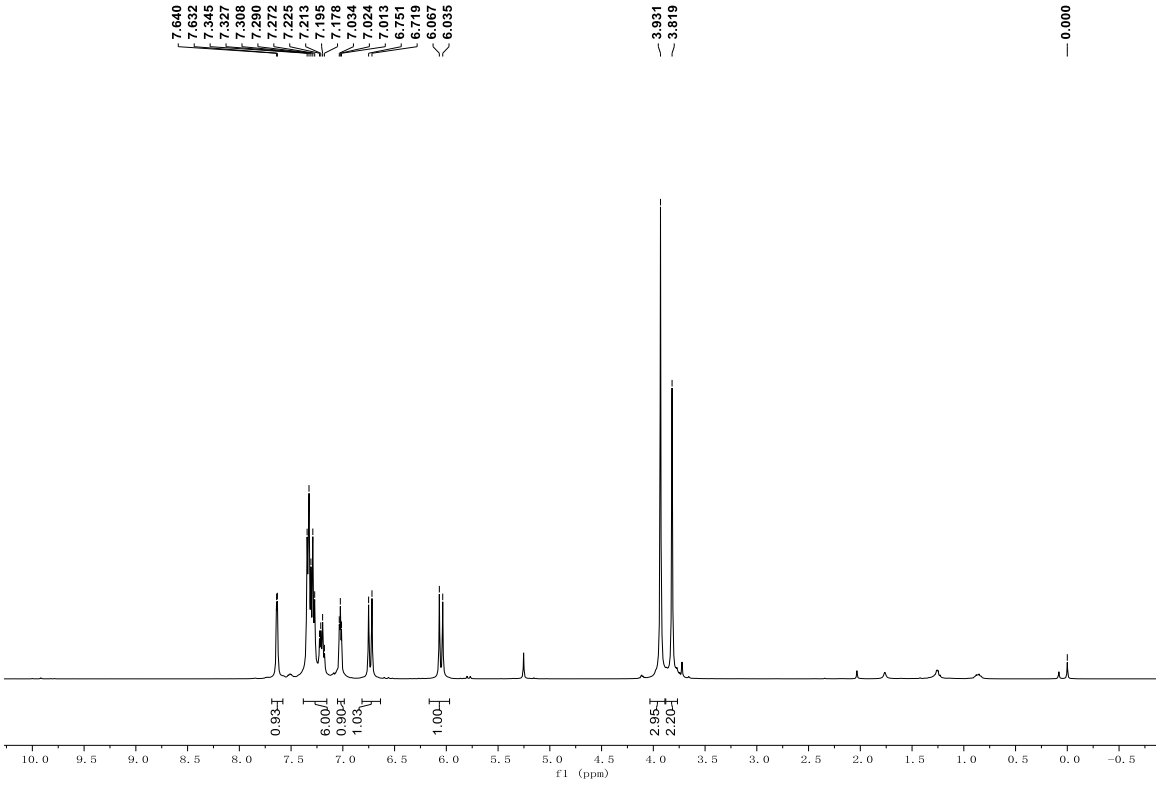

2.08
5.31
2.14
1.06
1.00
3.16
2.79
2.02
f1 (ppm)


159.478
154.036
151.074
139.399
133.349
131.039
128.605
128.515
128.335
126.116
115.403
113.144
112.946
77.318
77.000
76.682
60.359
55.200
30.880


f1 (ppm)


CO2Me
N
Bn
S

(3t)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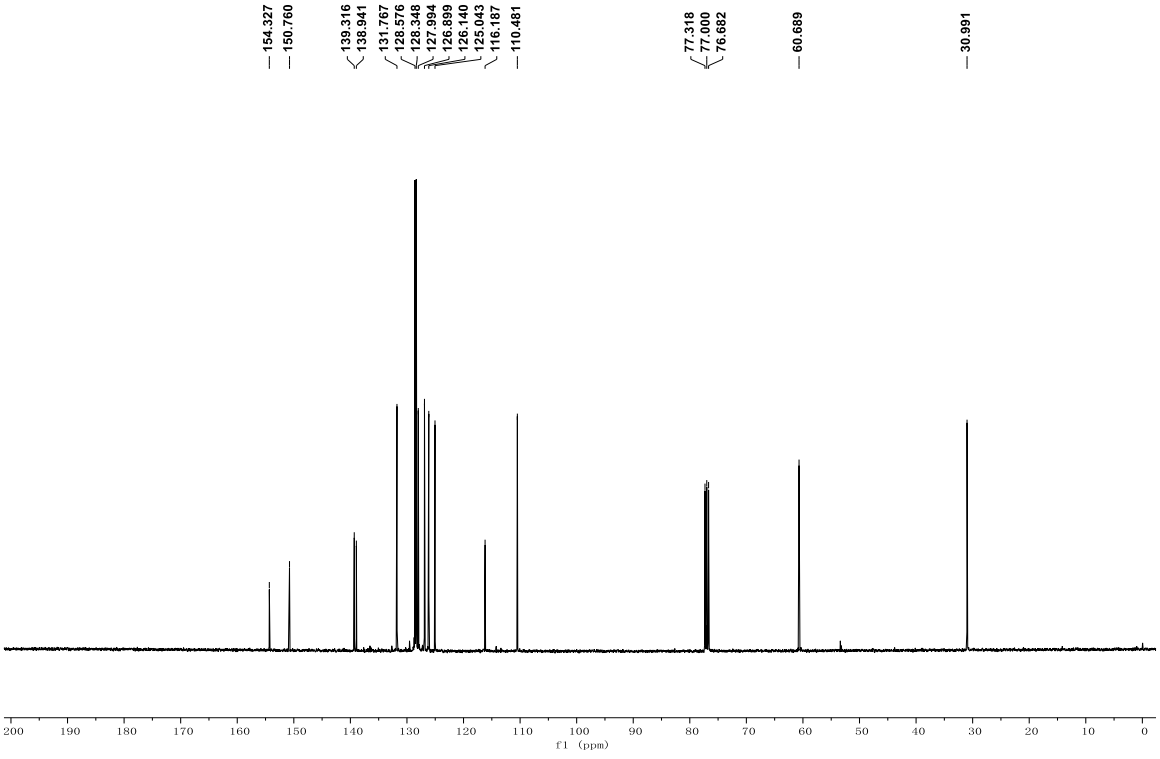
7.632
7.345
7.327
7.308
7.290
7.272
7.225
7.213
7.195
7.178
7.034
7.024
7.013
6.751
6.719
6.067
6.035
3.931
3.819
0.000
0.93
6.00
0.90
1.03
1.00
2.95
2.20
f1 (ppm)


154.327
150.760
139.316
138.941
131.767
128.576
128.348
127.994
126.899
126.140
125.043
116.187
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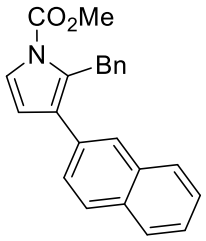
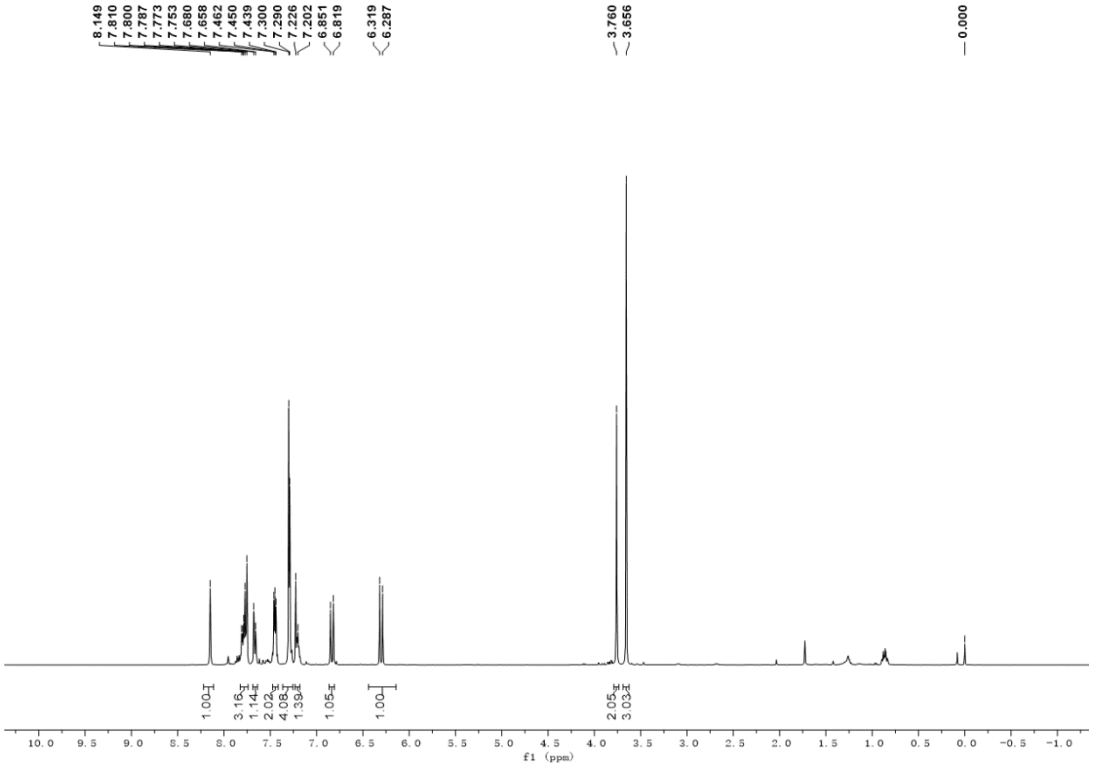
77.318
77.000
76.682
60.689
30.991
f1 (ppm)


CO2Me
N
Bn

(3u)


8.149
7.810
7.800
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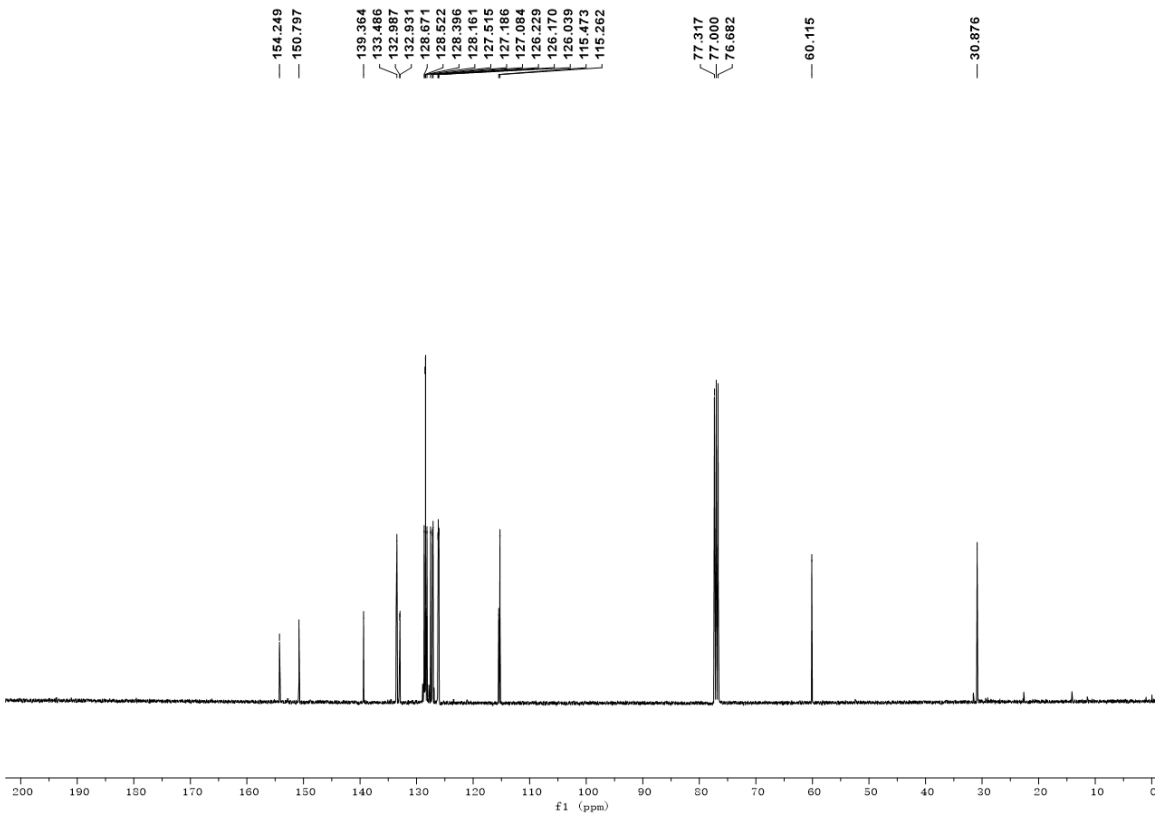
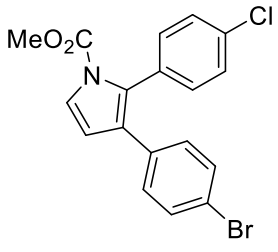
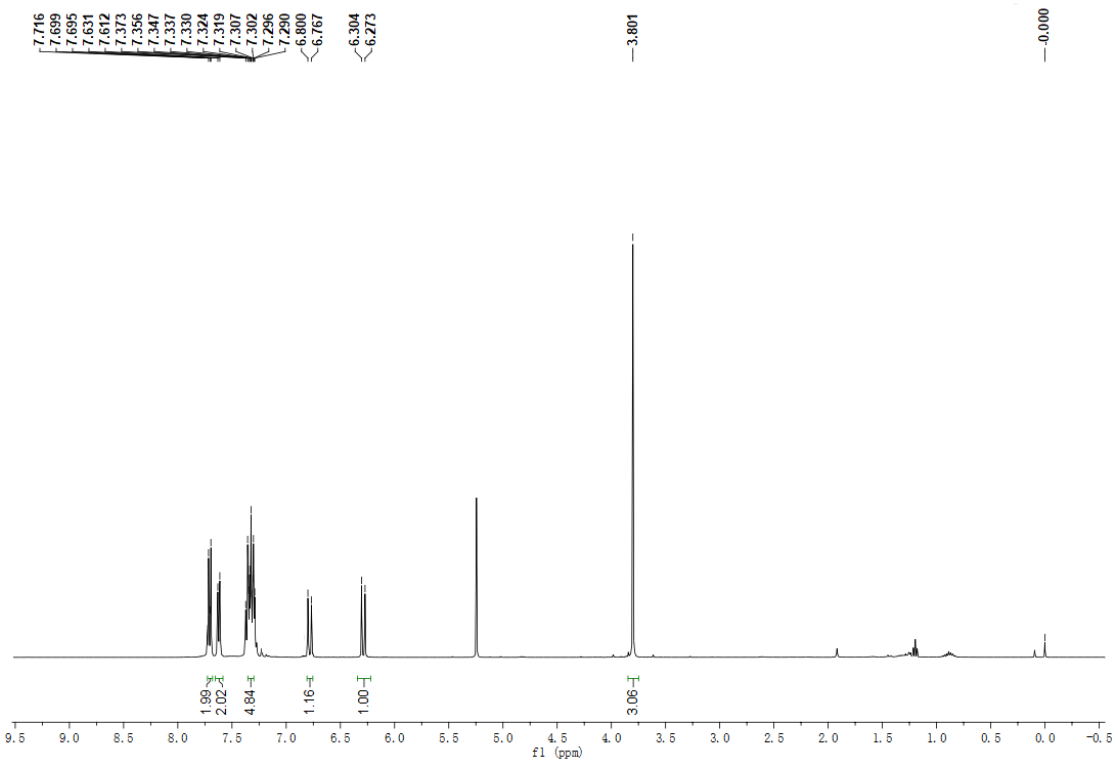
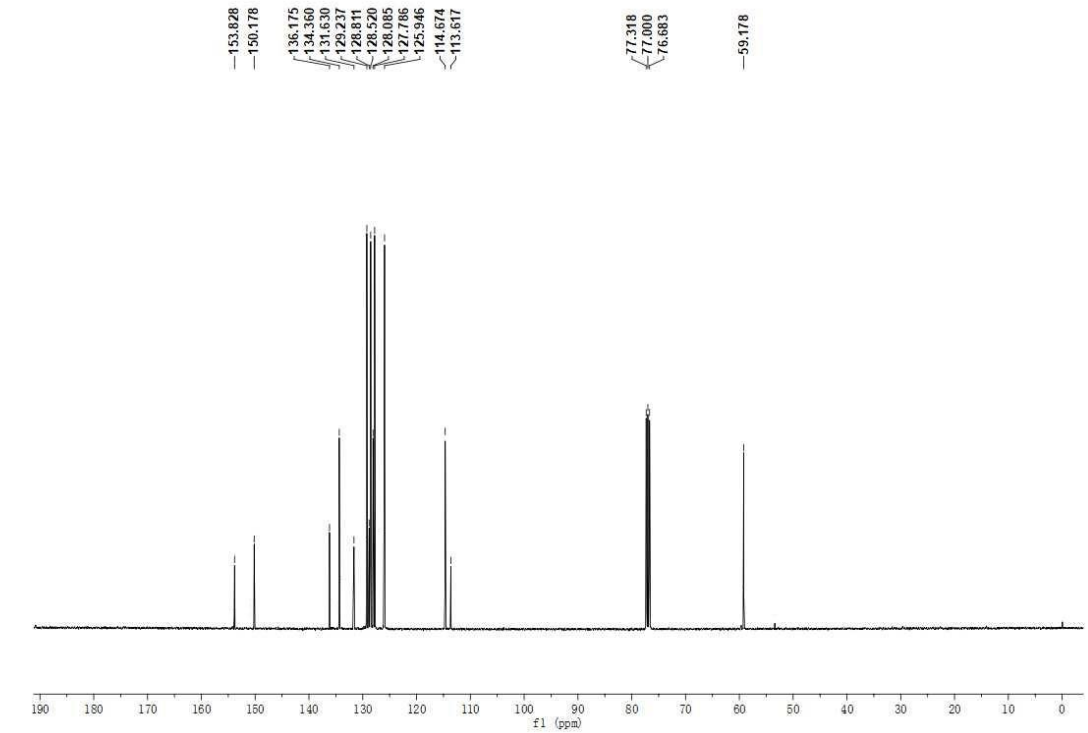
7.773
7.753
7.680
7.658
7.462
7.450
7.439
7.300
7.290
7.226
7.202
6.851
6.819
6.319
6.287
3.760
3.656
0.000
1.00
3.16
1.14
2.02
4.08
1.39
1.05
1.00
2.05
3.03
f1 (ppm)

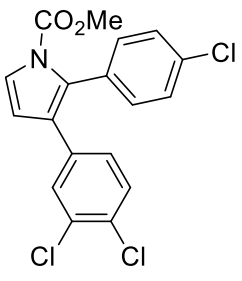

154.249
150.797
139.364
133.486
132.987
132.931
128.671
128.522
128.396
128.161
127.515
127.186
127.084
126.229
126.170
126.039
115.473
115.262
77.317
77.000
76.682
60.115
30.876
f1 (ppm)


MeO2C
N
Cl
Br

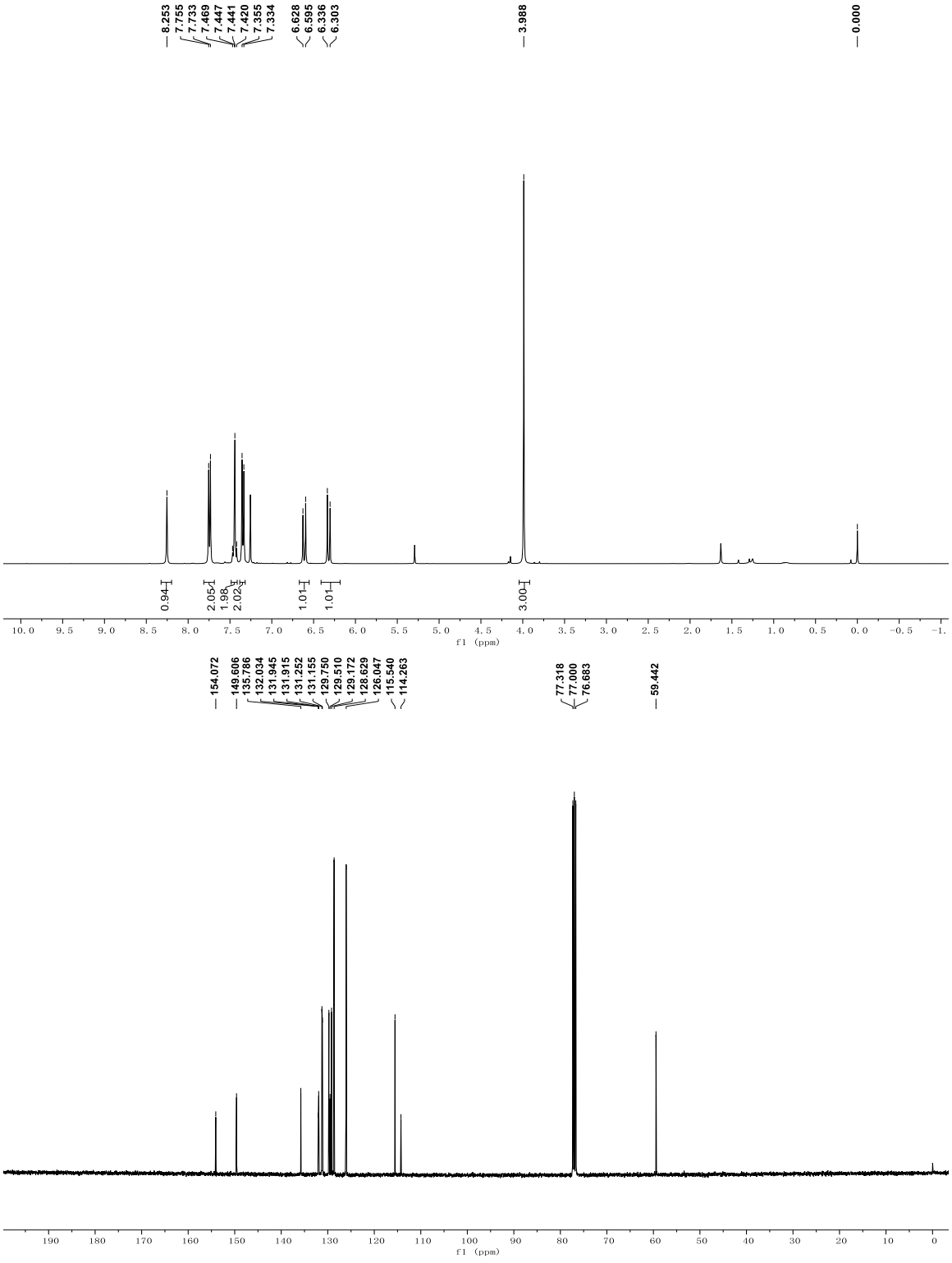
(3v)


7.716
7.699
7.695
7.631
7.612
7.373
7.356
7.347
7.337
7.330
7.324
7.319
7.307
7.302
7.296
7.290
6.800
6.767
6.304
6.273
3.801
0.000
1.99
2.02
4.84
1.16
1.00
3.06
f1 (ppm)


153.828
150.178
136.175
134.360
131.630
129.237
128.811
128.520
128.085
127.786
125.946
114.674
113.617
77.318
77.000
76.683
59.178
f1 (ppm)


CO2Me
N
Cl
Cl
Cl

(3w)



5 References

1. Wang, C.-J.; Liang, G.; Xue, Z.-Y.; Gao, F. *J. Am. Chem. Soc.* **2008**, *130*, 17250.

2. (a) Belot, S.; Vogt, K. A.; Besnard, C.; Krause. N.; Alexakis, A. *Angew. Chem. Ed. Int.* **2009**, *48*, 8923; (b) Hack, D.; Chauhan, P.; Deckers, K.; Hermann, G. N.; Mertens, L.; Raabe, G.; Enders, D. *Org. Lett.* **2014**, *16*, 5188.