Supporting Information

Copper-Mediated Cross-coupling/Cyclization/Oxidation: One-pot Reaction to Construct Polysubstituted Pyrroles

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1 General Information

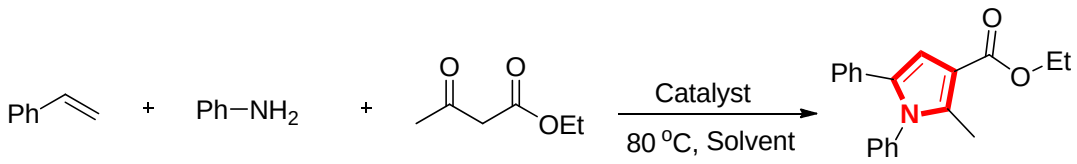
All manipulations were performed under an air atmosphere unless otherwise statement. Column chromatography was performed on silica gel (300−400 mesh). NMR spectra were obtained using a Bruker Avance 500 spectrometer (^{1}H at 500 MHz and ^{13}C at 125 MHz). Chemical shifts for ^{1}H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: δ 77.0 ppm). High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with APCI or ECI ionization source.

Materials. Unless stated otherwise, commercial reagents were used without further purification. All reagents were weighed and handled in air at room temperature.

2 General Experimental Procedure

The reaction mixture of terminal alkenes **1** (0.75 mmol), aromatic amines **2** (0.5 mmol), *β*-keto esters **3** (0.5mmol), CuCl (10 mol %), and DMSO (4 mL) in a 10 mL round bottom flask was stirred at 80 ^{o}C for 24 h. Upon completion, the reaction mixture was diluted with water (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under vacuum. The residue was purified by flash column chromatography to afford the product.

3 Optimization of Reaction Conditions[a]



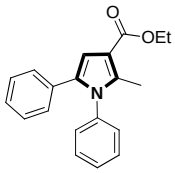
1a **2a** **3a** **4aaa**

Entry	Catalyst	Solvent	Yield (%)[b]
1	$CuCl_2$	DMSO	63
2	CuI	DMSO	40
3	$Cu(OAc)_2$	DMSO	0
4	$Cu(OTf)_2$	DMSO	0
5	$CuSO_4$	DMSO	0
6	$Bi(OTf)_3$	DMSO	0
7	$InCl_2$	DMSO	0
8	$AgCO_3$	DMSO	0
9	AgOAc	DMSO	0
10	$Pd(OAc)_2$	DMSO	0

[a]Reaction conditions: styrene **1a** (0.75 mmol), aniline **2a** (0.5 mmol), ethyl acetoacetate **3a** (0.5 mmol), catalyst (10 mol % to **2a**), solvent (4.0 mL), 80 °C, 24 h. [b]Isolated yield of pure product based on **2a**.

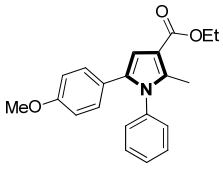
4 Characterization of the Compounds

Ethyl 2-methyl-1,5-diphenyl-1*H*-pyrrole-3-carboxylate (4aaa)



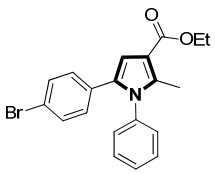
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.39 (m, 3H), 7.19-7.15 (m, 5H), 7.11-7.07 (m, 2H), 6.85 (s, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.6, 138.1, 138.0, 133.9, 132.4, 129.2, 128.5, 128.2, 128.1, 128.0, 126.5, 112.8, 110.0, 59.5, 14.5, 12.5. **ESI HRMS** exact mass calcd for $(C_{20}H_{19}NO_2Na)^+$ requires m/z 328.13135, found m/z 328.13166.

Ethyl 5-(4-methoxyphenyl)-2-methyl-1-phenyl-1*H*-pyrrole-3-carboxylate (4baa)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.36 (m, 3H), 7.13 (dd, *J* = 7.6, 1.7 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.71 (s, 1H), 6.68 (d, *J* = 8.7 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 2.39 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.7, 158.3, 138.2, 137.5, 133.8, 129.5, 129.2, 128.6, 128.2, 125.1, 113.5, 112.7 109.1, 59.5, 55.1, 14.6, 12.5. **ESI HRMS** exact mass calcd for $(C_{21}H_{21}NO_3Na)^+$ requires m/z 358.14191, found m/z 358.13989.

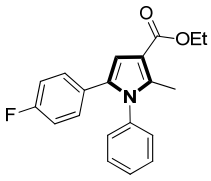
Ethyl 5-(4-bromophenyl)-2-methyl-1-phenyl-1*H*-pyrrole-3-carboxylate (4caa)



^{1}H NMR (500 MHz, $CDCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.42 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.16 (dt, *J* = 5.3, 1.9 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.84 (s, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.4, 138.4, 137.8, 132.6, 131.3, 131.2, 129.4, 129.3,

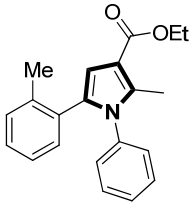
128.5, 128.4, 120.5, 113.0, 110.3, 59.55, 14.5, 12.5. **ESI HRMS** exact mass calcd for $(C_{20}H_{18}NO_2BrNa)^+$ requires m/z 406.04186, 408.03981, found m/z 406.03936, 408.03726.

Ethyl 5-(4-fluorophenyl)-2-methyl-1-phenyl-1*H*-pyrrole-3-carboxylate (4daa)



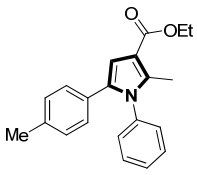
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.37 (m, 3H), 7.13-7.10 (m, 2H), 7.02-6.99 (m, 2H), 6.85-6.81 (m, 2H), 6.75 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.5, 162.6, 160.6, 138.0, 137.9, 132.9, 129.9, 129.8, 129.3, 128.5, 128.4, 127.6, 127.5, 115.1, 114.9, 112.9, 109.9, 59.6, 14.6. 12.5. **ESI HRMS** exact mass calcd for $(C_{20}H_{18}NO_2FNa)^+$ requires m/z 346.12193, found m/z 346.11985.

Ethyl 2-methyl-1-phenyl-5-(o-tolyl)-1*H*-pyrrole-3-carboxylate (4eaa)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.20 (m, 5H), 7.11-7.08 (m, 1H), 7.02 (dd, *J* = 7.9, 1.6 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.62 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 2.12 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.8, 137.7, 136.6, 132.7, 132.3, 131.7, 129.7, 129.0, 128.7, 128.1, 127.8, 127.8, 125.0, 110.6, 59.5, 20.4, 14.6, 12.7. **ESI HRMS** exact mass calcd for $(C_{21}H_{21}NO_2Na)^+$ requires m/z 342.14700, found m/z 342.14532.

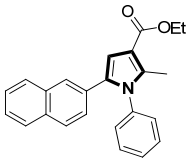
Ethyl 2-methyl-1-phenyl-5-(p-tolyl)-1*H*-pyrrole-3-carboxylate (4faa)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.37 (m, 3H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.14 (dd, *J* = 7.0, 4.8 Hz, 3H), 7.08 (t, *J* = 6.8 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 1H),

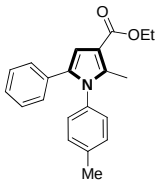
6.76 (s, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.40 (s, 3H), 2.25 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.6, 138.2, 137.8, 136.2, 134.0, 129.5, 129.1, 128.7, 128.5, 128.2, 128.0, 112.7, 109.5, 59.5, 21.0, 14.6, 12.5. **ESI HRMS** exact mass calcd for $(C_{21}H_{21}NO_2Na)^+$ requires m/z 342.14700, found m/z 342.14529.

Ethyl 2-methyl-5-(naphthalen-2-yl)-1-phenyl-1*H*-pyrrole-3-carboxylate (4gaa)



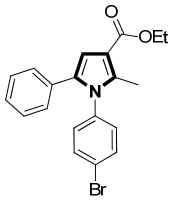
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74-7.68 (m, 1H), 7.59 (d, J = 8.1 Hz, 2H), 7.51 (s, 1H), 7.41-7.36 (m, 5H), 7.21-7.15 (m, 3H), 6.94 (s, 1H), 4.35 (q, J = 7.1 Hz, 2H), 2.45 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.6, 138.4, 138.2, 133.8, 133.2, 131.9, 129.8, 129.3, 128.6, 128.3, 127.9, 127.5, 126.6, 126.3, 126.1, 125.7, 113.1, 110.5, 59.5, 14.6, 12.5. **ESI HRMS** exact mass calcd for $(C_{24}H_{21}NO_2Na)^+$ requires m/z 378.14700, found m/z 378.14514.

Ethyl 2-methyl-5-phenyl-1-(p-tolyl)-1*H*-pyrrole-3-carboxylate (4aba)



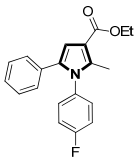
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19-7.11 (m, 5H), 7.08-7.05 (m, 2H), 7.01 (d, J = 8.2 Hz, 2H), 6.79 (s, 1H), 4.32 (q, J = 7.1 Hz, 2H), 2.39 (s, 3H), 2.38 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.6, 138.2, 138.1, 135.5, 133.9, 132.5, 129.8, 128.2, 128.1, 128.0, 126.4, 112.7, 110.0, 59.5, 21.1, 14.56, 12.5. **ESI HRMS** exact mass calcd for $(C_{21}H_{21}NO_2Na)^+$ requires m/z 342.14700, found m/z 342.14514.

Ethyl 1-(4-bromophenyl)-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (4aca)



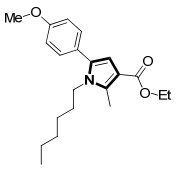
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.5 Hz, 2H), 7.20-7.14 (m, 3H), 7.05-7.00 (m, 4H), 6.79 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.4, 137.8, 137.1, 133.8, 132.4, 132.0, 130.0, 128.2, 126.7, 125.6, 122.2, 113.2, 110.3, 59.6, 14.5, 12.5. **ESI HRMS** exact mass calcd for $(C_{20}H_{18}NO_2BrNa)^+$ requires m/z 406.04186, 408.03981, found m/z 406.03955, 408.03743.

Ethyl 1-(4-fluorophenyl)-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (4ada)



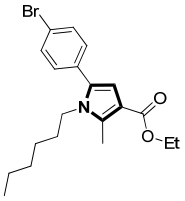
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19-7.13 (m, 3H), 7.13-7.08 (m, 3H), 7.08 -7.06 (m, 1H), 7.04 (dd, *J* = 7.8, 1.5 Hz, 2H), 6.79 (s, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.5, 163.0, 161.0, 138.0, 134.1, 134.0, 132.2, 130.2, 130.1, 128.2, 128.1, 126.6, 116.3, 116.1, 113.0, 110.1, 59.5, 14.5, 12.4. **ESI HRMS** exact mass calcd for $(C_{20}H_{18}NO_2FNa)^+$ requires m/z 346.12193, found m/z 346.11985.

Ethyl 1-hexyl-5-(4-methoxyphenyl)-2-methyl-*1H*-pyrrole-3-carboxylate (4bea)



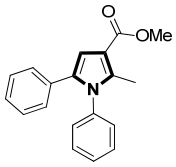
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 6.7, 2.0 Hz, 2H), 6.94-6.92 (m, 2H), 6.47 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.82-3.78 (m, 2H), 2.59 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.26-1.06 (m, 8H), 0.81 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.7, 165.5, 136.7, 131.9, 131.6, 129.8, 121.6, 112.1, 110.1, 59.3, 55.1, 44.1, 31.1, 30.6, 26.1, 22.4, 14.5, 13.9, 11.6. **ESI HRMS** exact mass calcd for $(C_{21}H_{30}NO_3)^+$ requires m/z 344.22257, found m/z 344.22287.

Ethyl 5-(4-bromophenyl)-1-hexyl-2-methyl-*1H*-pyrrole-3-carboxylate (4cea)



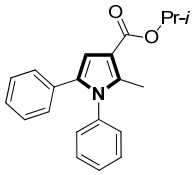
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.51 (m, 2H), 7.23-7.19 (m, 2H), 6.53 (s, 1H), 4.29-4.25 (m, 2H), 3.85-3.81 (m, 2H), 2.59 (s, 3H), 1.34 (d, *J* = 7.1 Hz, 3H), 1.2-1.07 (m, 8H), 0.82 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.5, 136.7, 131.9, 131.6, 130.8, 129.8, 121.6, 112.1, 110.1, 59.3, 44.1, 31.1, 30.6, 26.1, 22.4, 14.5, 13.9, 11.6. **ESI HRMS** exact mass calcd for $(C_{20}H_{27}NO_2Br)^+$ requires m/z 392.12252, 394.12047, found m/z 392.12285, 394.12066.

Methyl 2-methyl-1,5-diphenyl-1*H*-pyrrole-3-carboxylate (4aab)



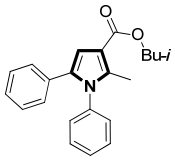
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.37 (m, 3H), 7.15-7.12 (m, 5H), 7.05-7.03 (m, 2H), 6.79 (s, 1H), 3.85 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.0, 138.2, 138.1, 134.0, 132.4, 129.2, 128.5, 128.3, 128.1, 128.0, 126.5, 112.5, 110.0, 50.9, 12.5. **ESI HRMS** exact mass calcd for $(C_{19}H_{17}NO_2Na)^+$ requires m/z 314.11570, found m/z 314.11377.

Isopropyl 2-methyl-1,5-diphenyl-1*H*-pyrrole-3-carboxylate (4aac)



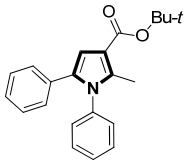
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.36 (m, 3H), 7.15-7.11 (m, 5H), 7.05 (dd, *J* = 7.9, 1.6 Hz, 2H), 6.81 (s, 1H), 5.23 (dt, *J* = 12.5, 6.3 Hz, 1H), 2.41 (s, 3H), 1.36 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.1, 138.1, 137.9, 133.8, 132.4, 129.1, 128.5, 128.2, 128.1, 128.0, 126.4, 113.3, 110.1, 66.6, 22.2, 12.5. **ESI HRMS** exact mass calcd for $(C_{21}H_{21}NO_2Na)^+$ requires m/z 342.14700, found m/z 342.14500.

Isobutyl 2-methyl-1,5-diphenyl-1*H*-pyrrole-3-carboxylate (4aad)



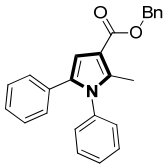
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.37 (m, 3H), 7.17-7.12 (m, 5H), 7.06 (d, *J* = 7.3 Hz, 2H), 6.82 (d, *J* = 1.6 Hz, 1H), 4.07 (dd, *J* = 6.5, 0.9 Hz, 2H), 2.42 (s, 3H), 2.07 (td, *J* = 13.3, 6.7 Hz, 1H), 1.03 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.6, 138.1, 137.9, 133.9, 132.4, 129.1, 128.5, 128.2, 128.1, 128.0, 126.5, 112.9, 110.0, 69.8, 28.0, 19.3, 12.5. **ESI HRMS** exact mass calcd for $(C_{22}H_{23}NO_2Na)^+$ requires m/z 356.16265, found m/z 356.16055.

Tert-butyl 2-methyl-1,5-diphenyl-1*H*-pyrrole-3-carboxylate (4aae)



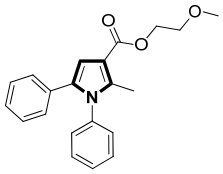
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.36 (m, 3H), 7.15-7.11 (m, 5H), 7.05-7.03 (m, 2H), 6.75 (s, 1H), 2.38 (s, 3H), 1.59 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.1, 138.2, 137.4, 133.7, 132.5, 129.1, 128.6, 128.2, 128.1, 128.0, 126.4, 114.4, 110.3, 76.8, 28.5, 12.5. **ESI HRMS** exact mass calcd for $(C_{22}H_{23}NO_2Na)^+$ requires m/z 356.16265, found m/z 356.16104.

Benzyl 2-methyl-1,5-diphenyl-1*H*-pyrrole-3-carboxylate (4aaf)



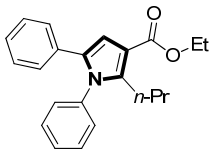
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.3 Hz, 2H), 7.39-7.35 (m, 6H), 7.15-7.11 (m, 5H), 7.03 (dd, *J* = 7.7, 1.8 Hz, 2H), 6.83 (s, 1H), 5.33 (s, 2H), 2.42 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.3, 138.4, 138.1, 137.0, 134.0, 132.3, 129.2, 128.5, 128.5, 128.1, 128.0, 127.9, 127.8, 126.9, 126.5, 112.5, 110.1, 65.3, 12.6. **ESI HRMS** exact mass calcd for $(C_{25}H_{21}NO_2Na)^+$ requires m/z 390.14700, found m/z 390.14484.

2-Methoxyethyl 2-methyl-1,5-diphenyl-1*H*-pyrrole-3-carboxylate (4aag)



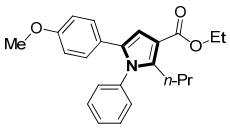
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.37 (m, 3H), 7.15-7.12 (m, 5H), 7.05-7.02 (m, 2H), 6.83 (s, 1H), 4.44-4.42 (m, 2H), 3.73-3.71 (m, 2H), 3.43 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.4, 138.4, 138.1, 134.0, 132.3, 129.2, 128.5, 128.2, 128.0, 127.9, 126.5, 112.5, 110.1, 70.9, 62.6, 59.0, 12.5. **ESI HRMS** exact mass calcd for $(C_{21}H_{21}NO_3Na)^+$ requires m/z 358.14191, found m/z 358.13999.

Ethyl 1,5-diphenyl-2-propyl-*1H*-pyrrole-3-carboxylate (4aah)



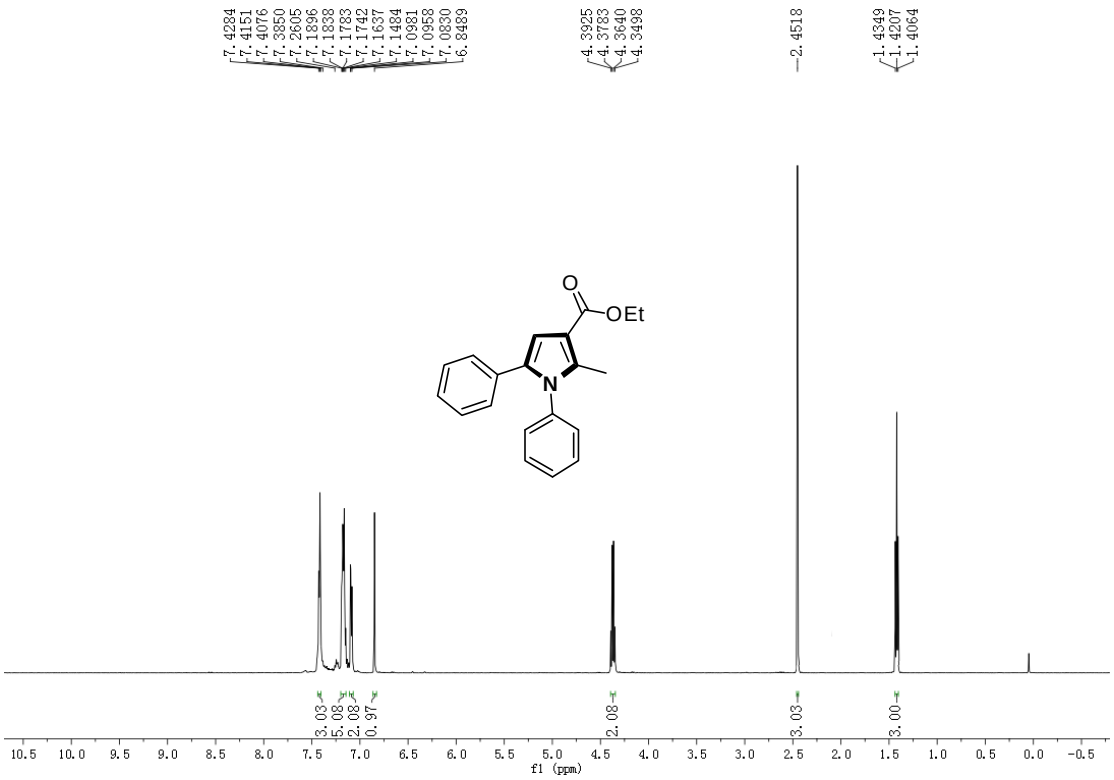
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.36 (m, 3H), 7.19-7.10 (m, 5H), 7.06-7.01 (m, 2H), 6.81 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.82-2.75 (m, 2H), 1.49-1.42 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.3, 142.8, 138.1, 133.9, 132.4, 129.1, 128.8, 128.3, 128.2, 128.0, 126.4, 112.5, 110.2, 59.5, 27.8, 23.3, 14.5, 14.1. **ESI HRMS** exact mass calcd for $(C_{22}H_{24}NO_2)^+$ requires m/z 334.18070, found m/z 334.18114.

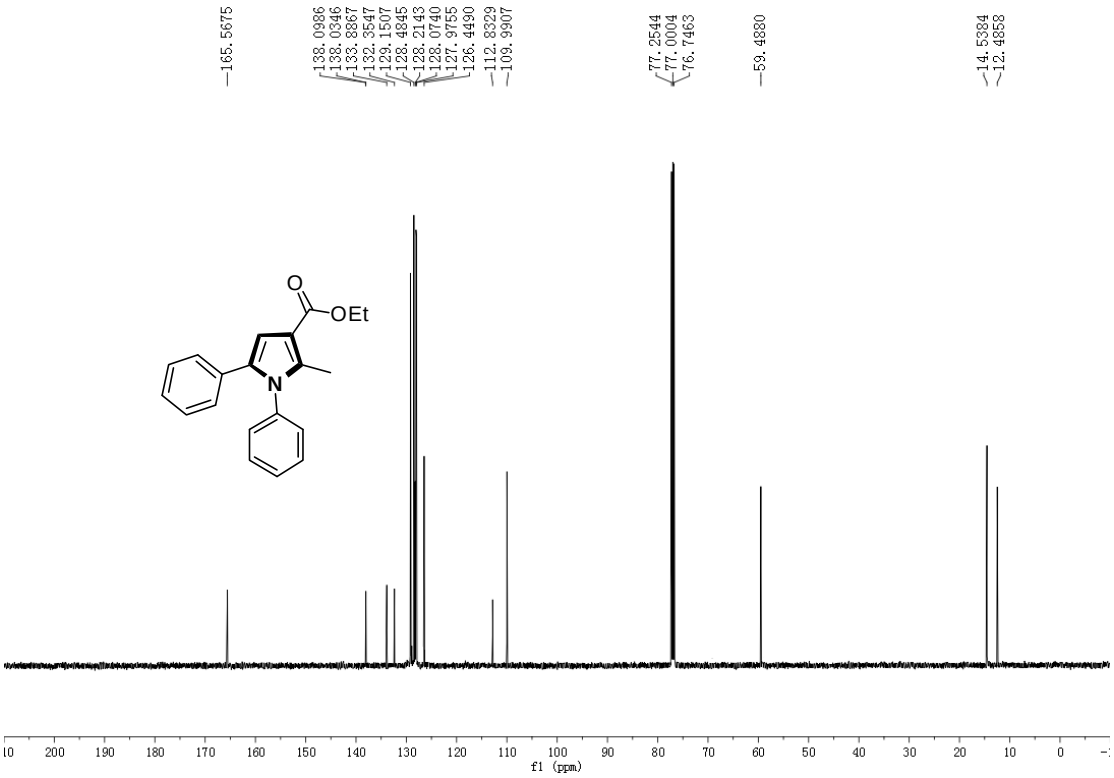
Ethyl 5-(4-methoxyphenyl)-1-phenyl-2-propyl-1H-pyrrole-3-carboxylate (4bah)

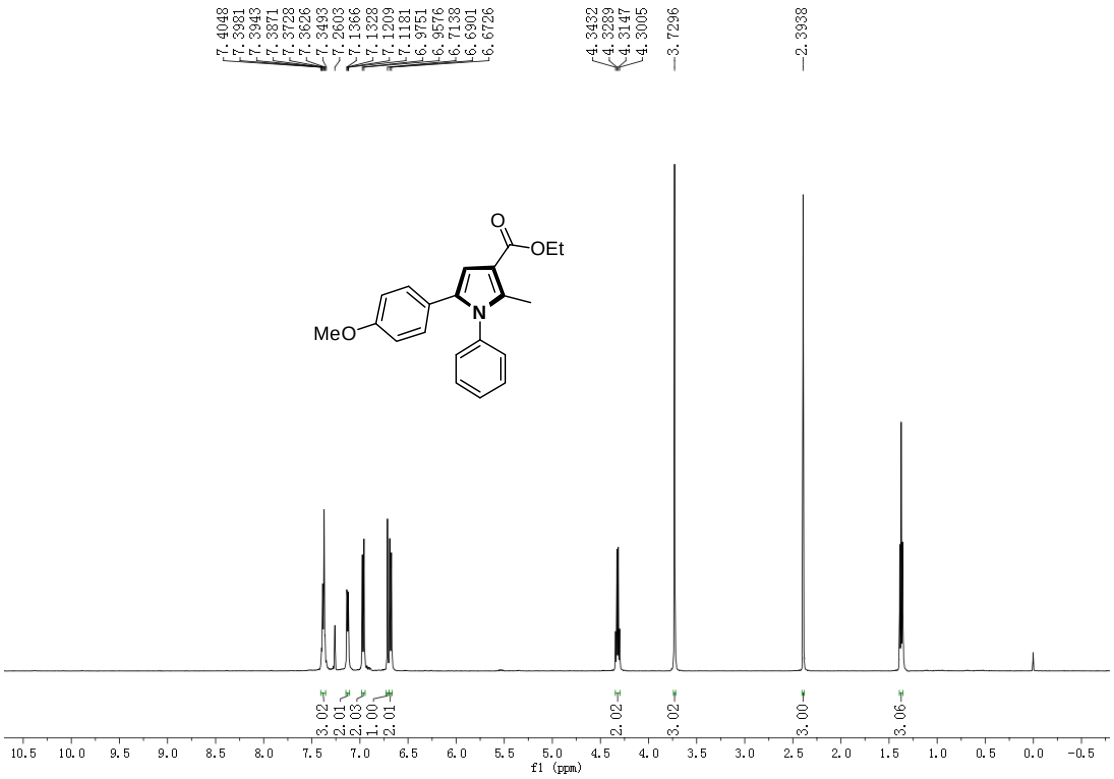


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41- 7.35 (m, 3H), 7.17-7.12 (m, 2H), 6.97-6.94 (m, 2H), 6.72 (s, 1H), 6.69-6.65 (m, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 2.80-2.74 (m, 2H), 1.48-1.41 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125MHz, $CDCl_3$) δ 165.4, 158.3, 142.3, 138.1, 133.8, 129.5, 129.0, 128.8, 128.3, 125.1, 113.4, 112.3, 109.3, 59.4, 55.1, 27.8, 23.3, 14.5, 14.1. **ESI HRMS** exact mass calcd for $(C_{23}H_{25}NO_3Na)^+$ requires m/z 386.17321, found m/z 386.17362.

5 Copies of ^{1}H NMR and ^{13}C NMR Spectra of Products



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6.6726
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4.3147
4.3005
3.7296
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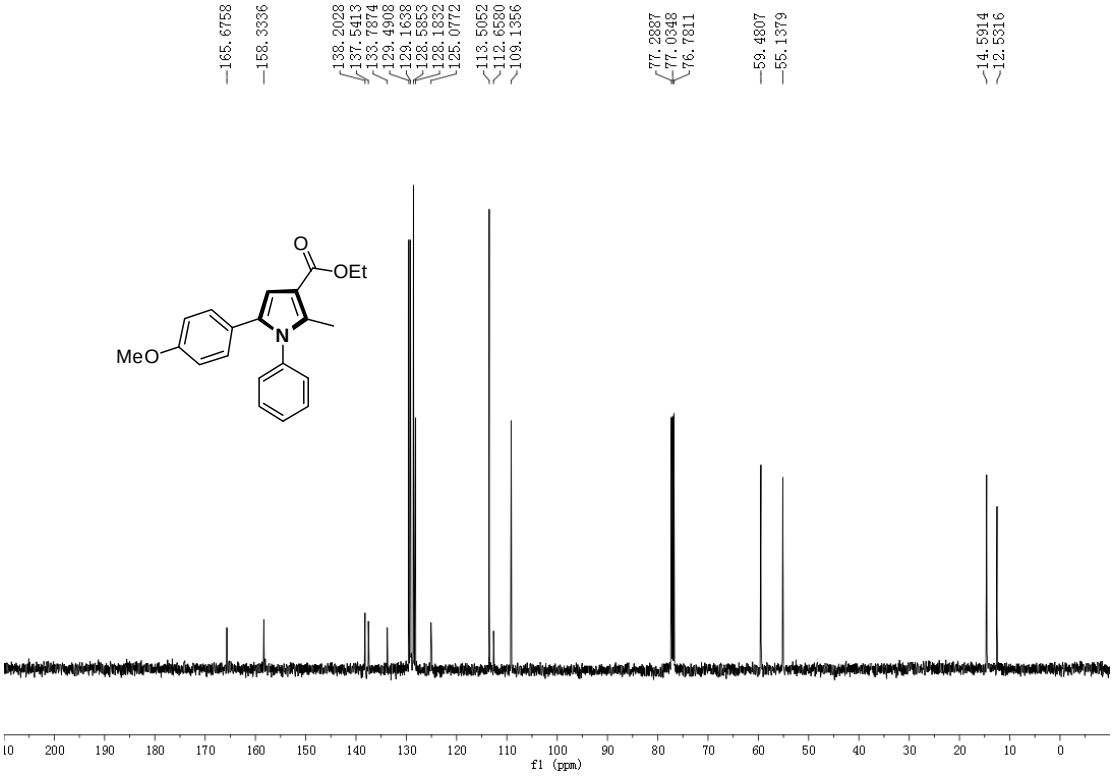
f1 (ppm)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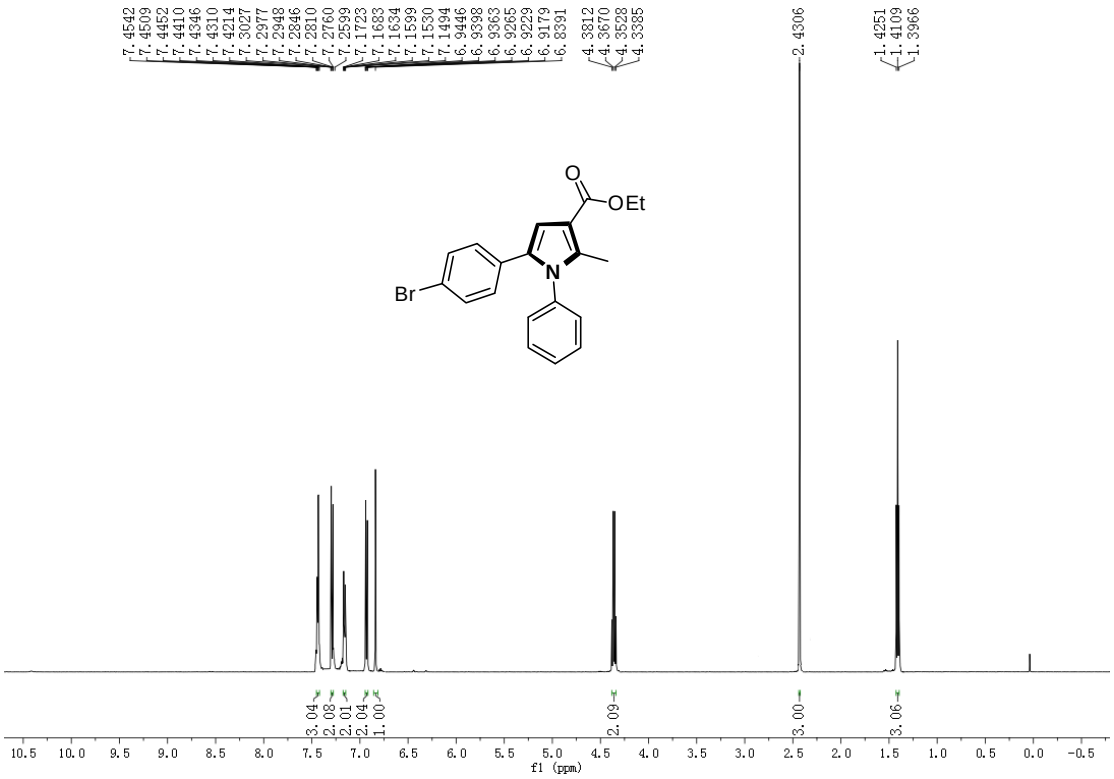
MeO
N
f1 (ppm)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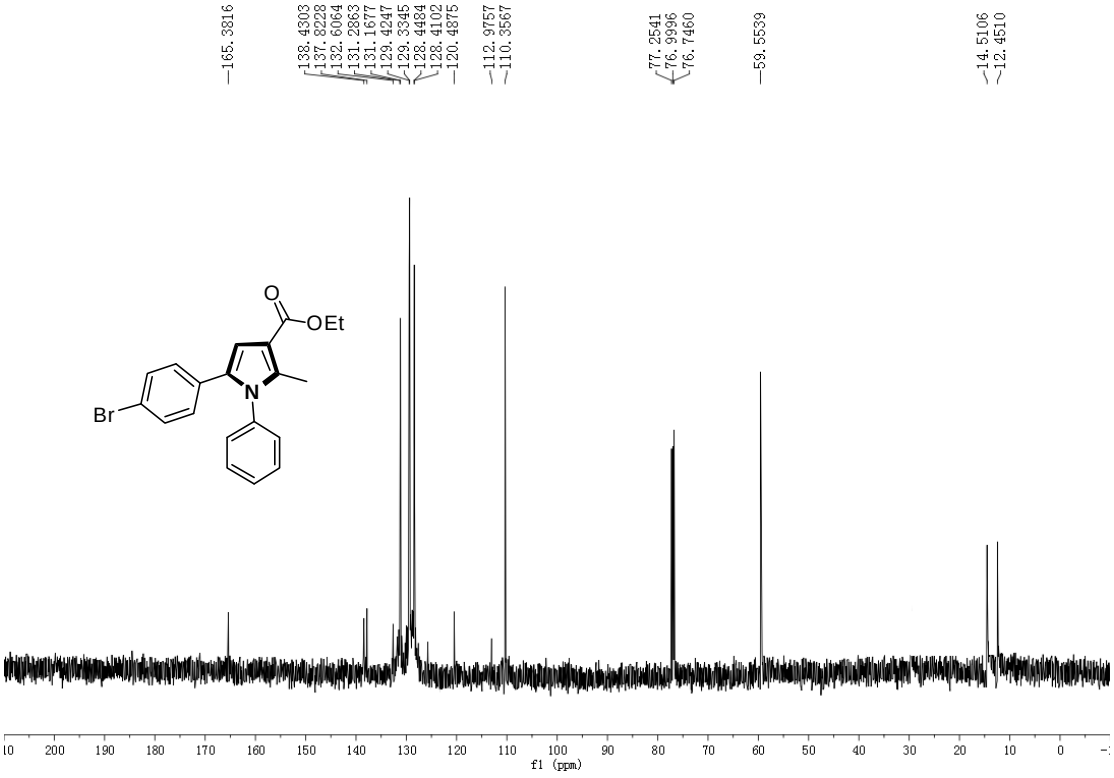
3.06
f1 (ppm)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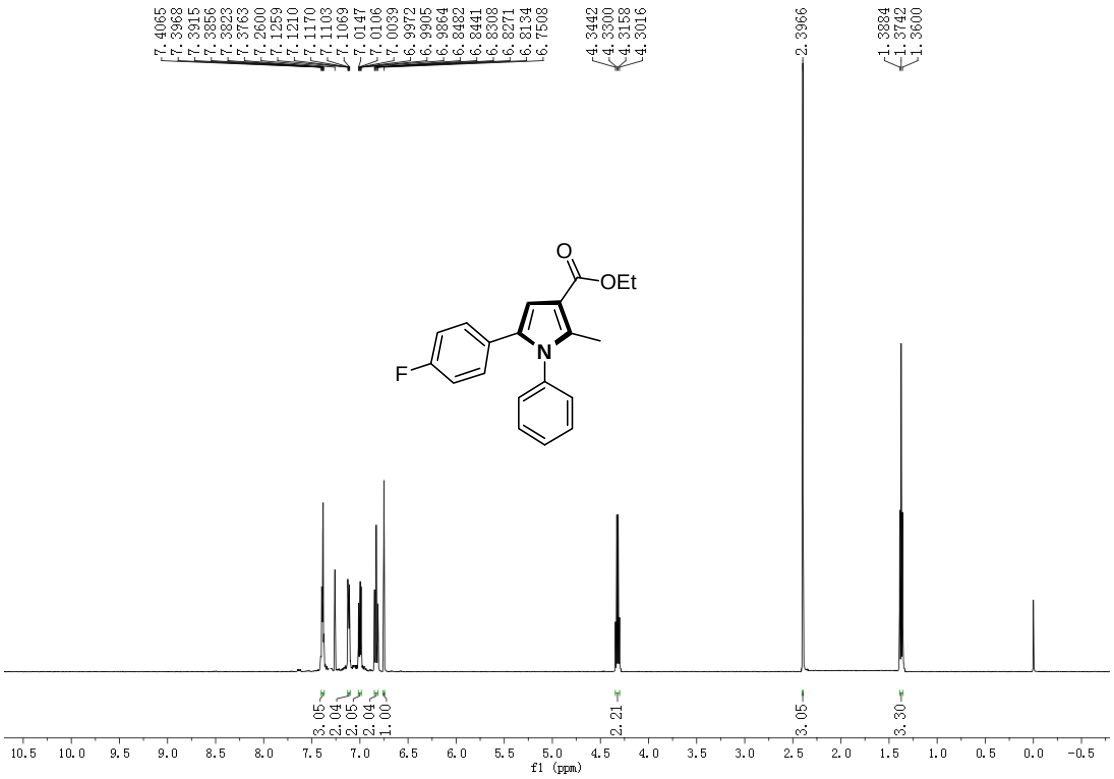
OEt
Br
N
f1 (ppm)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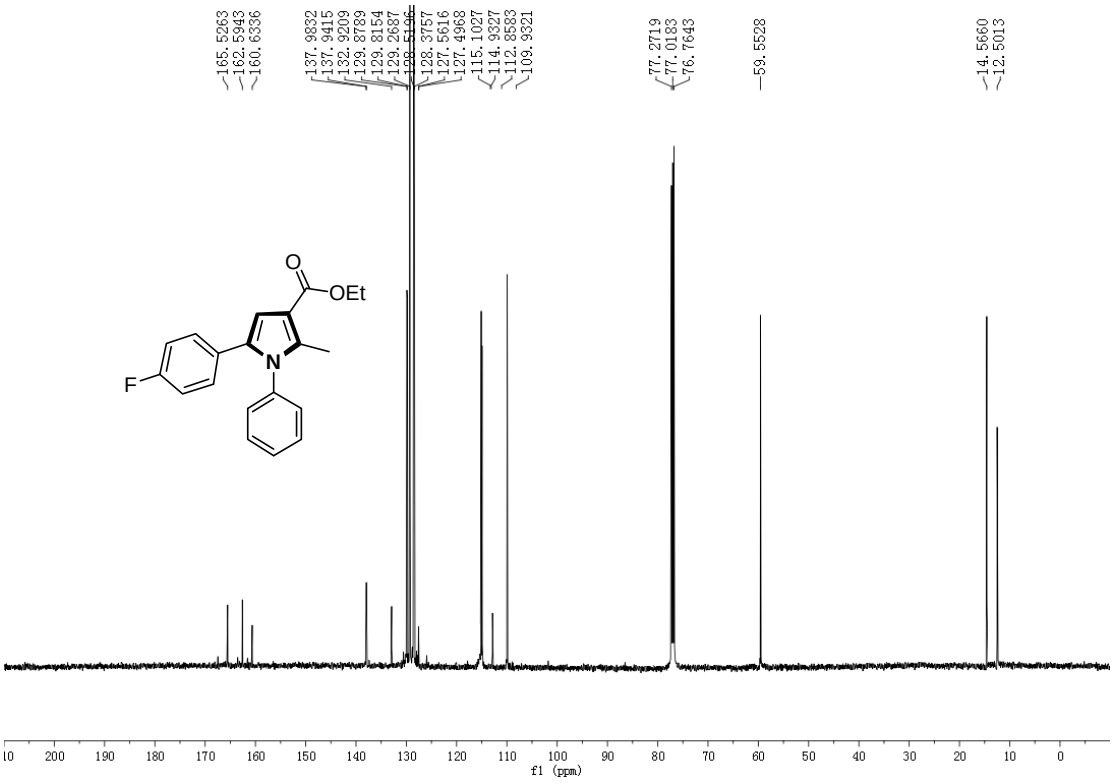
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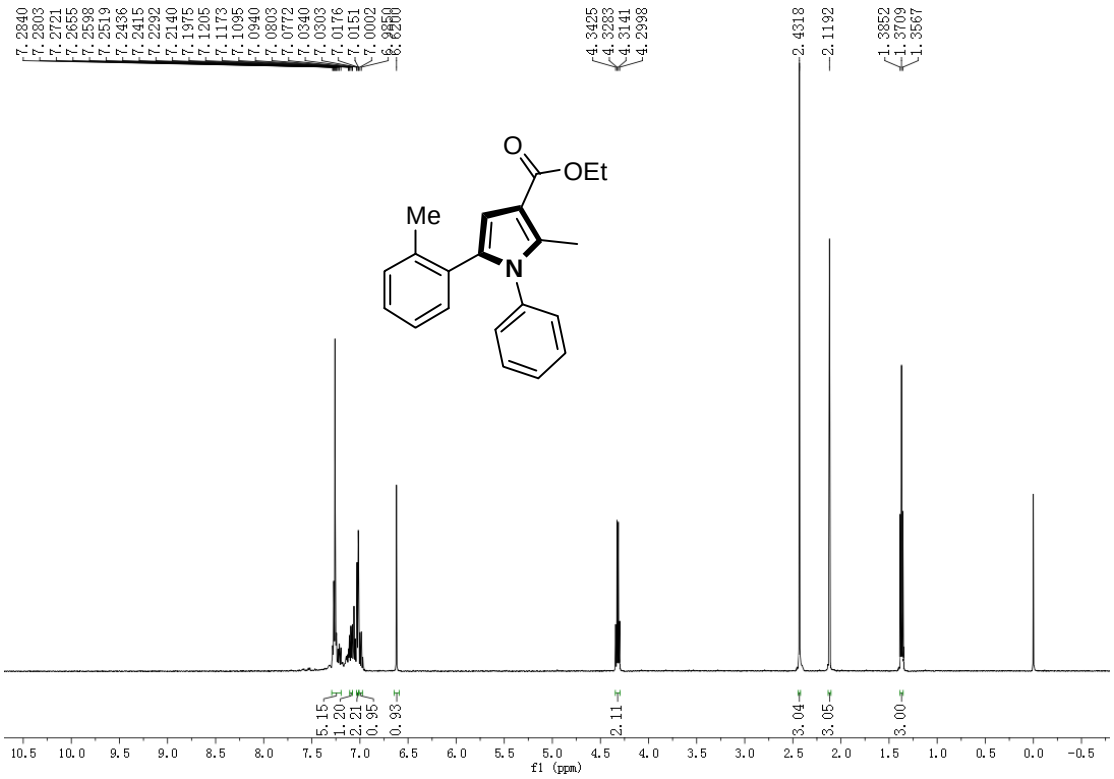
F
N
f1 (ppm)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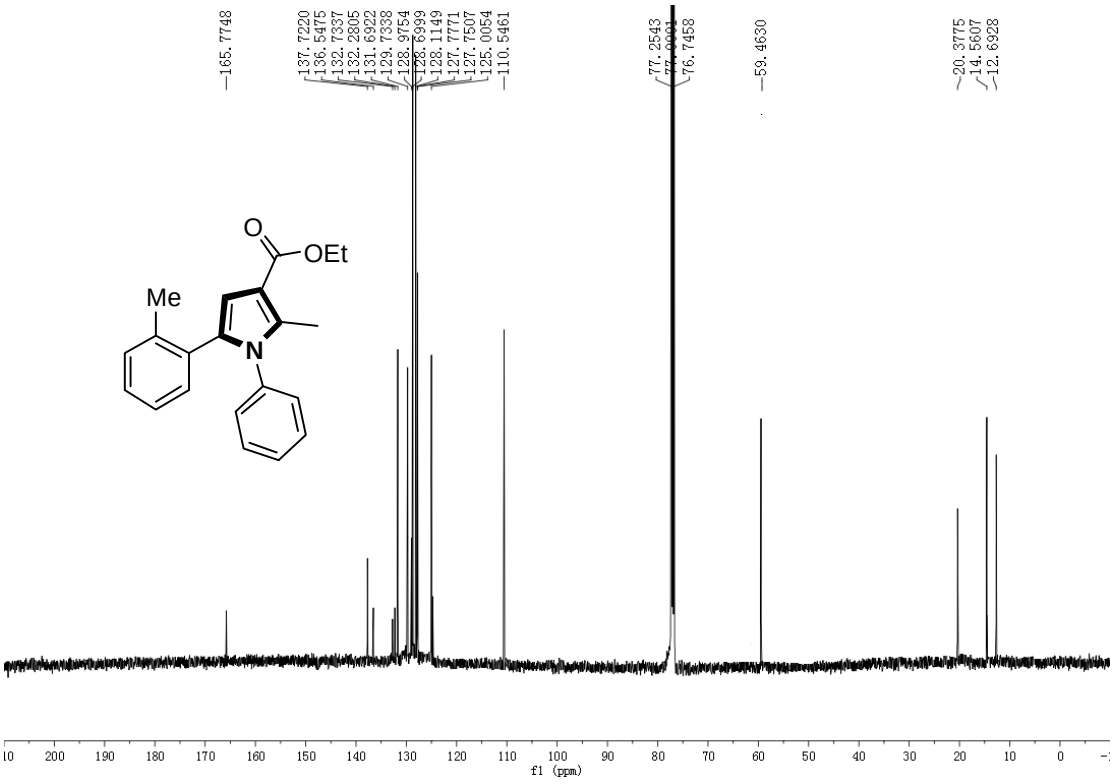
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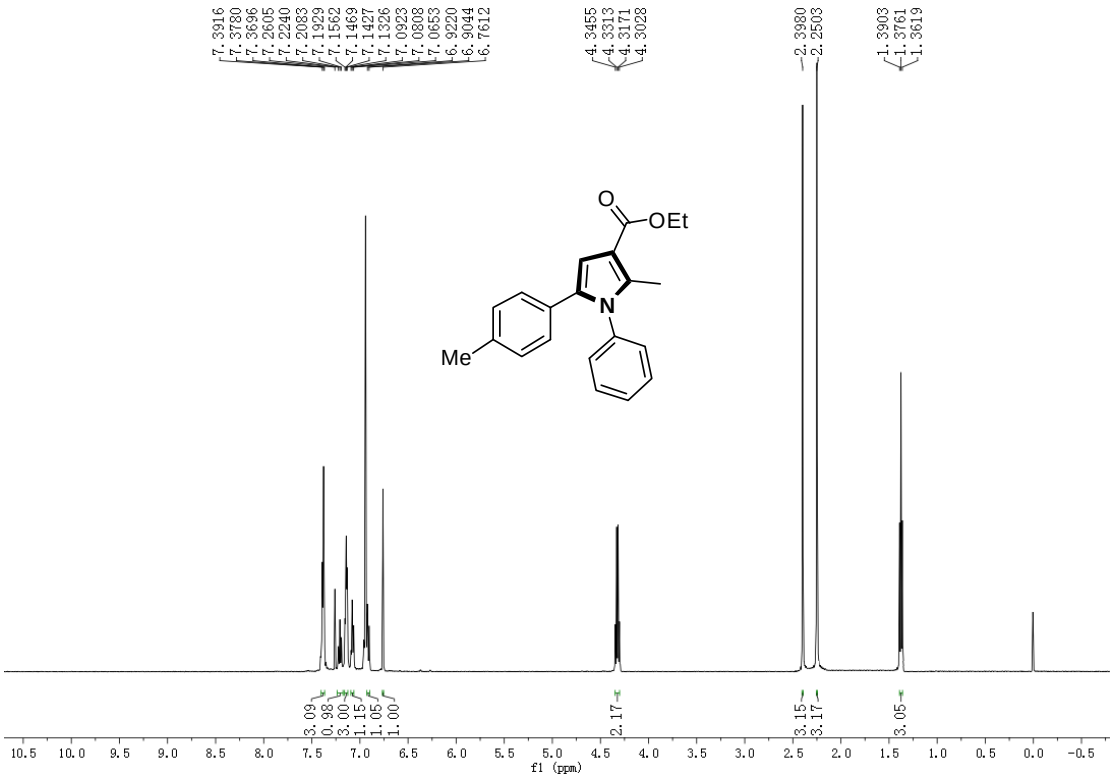
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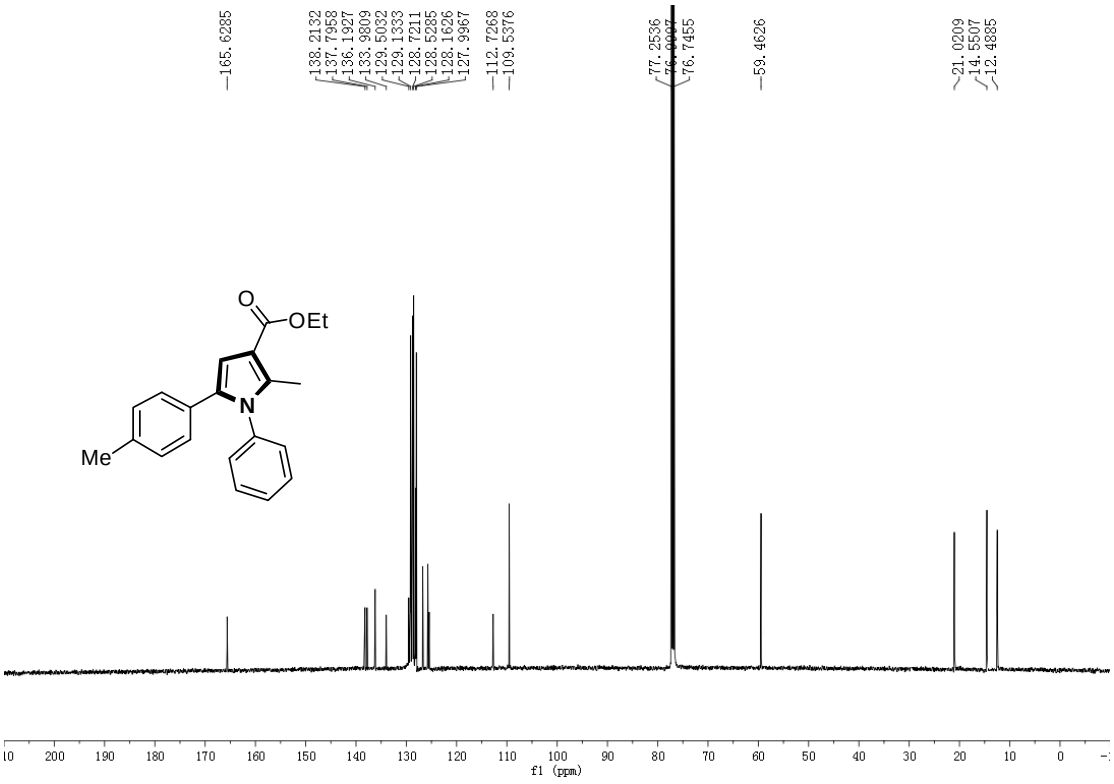
f1 (ppm)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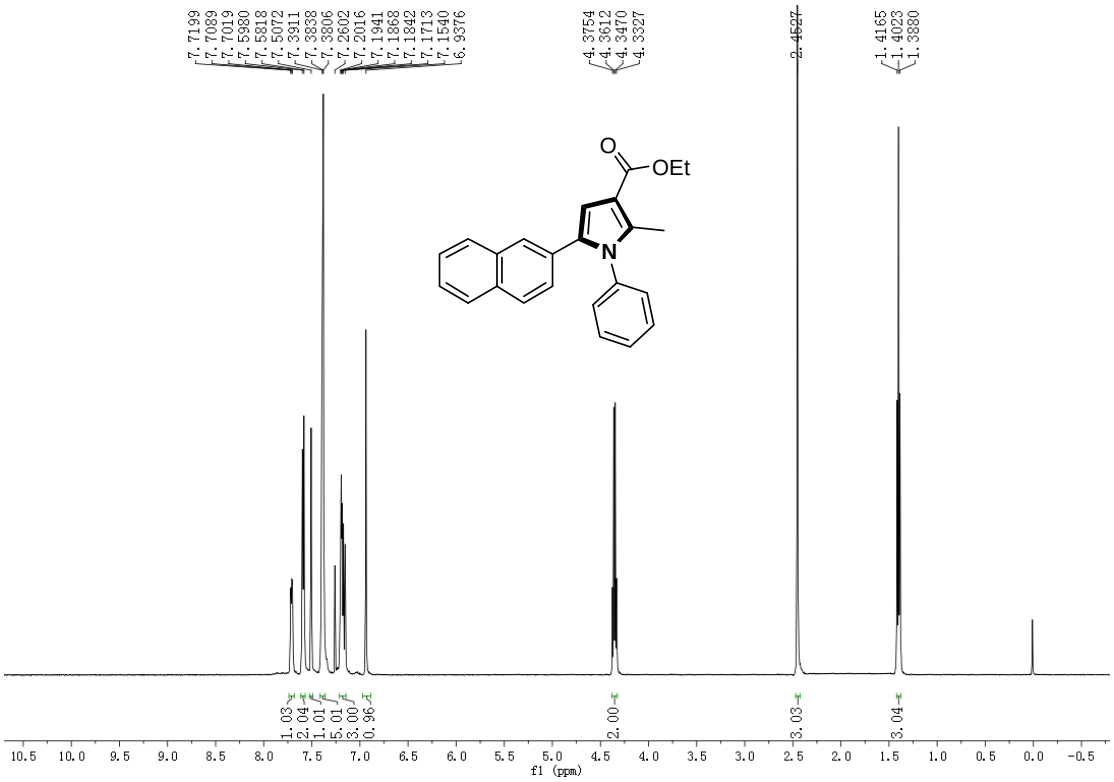
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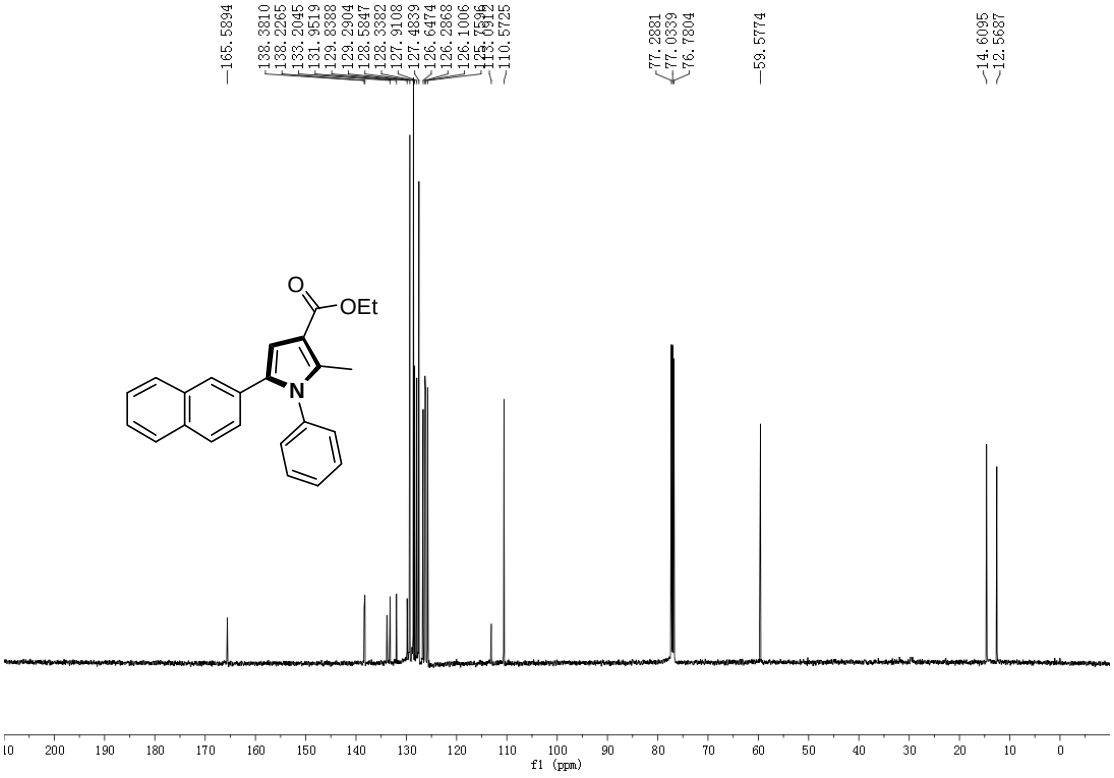
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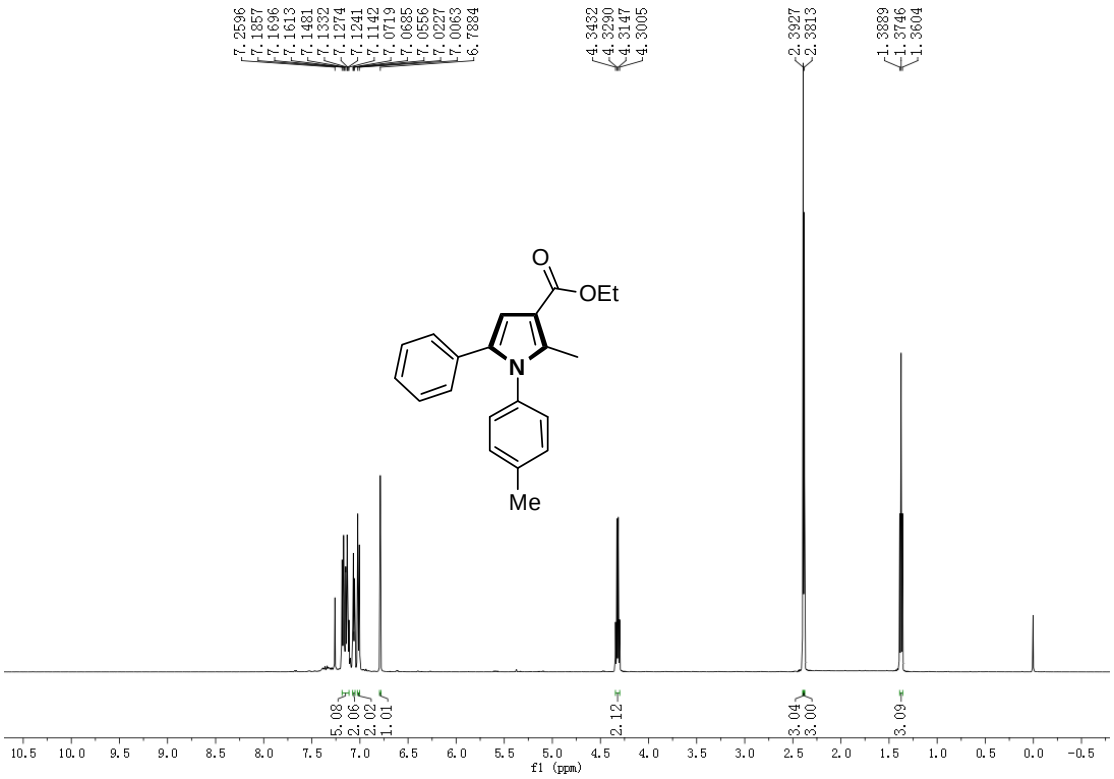
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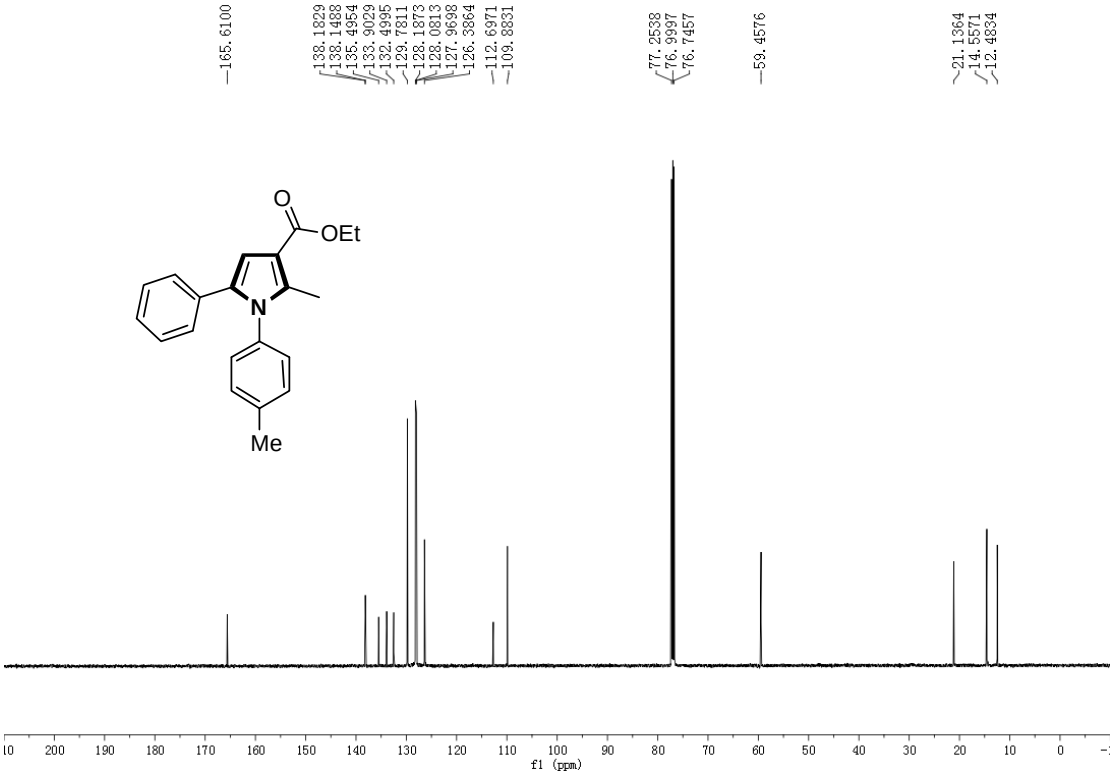
3.09
f1 (ppm)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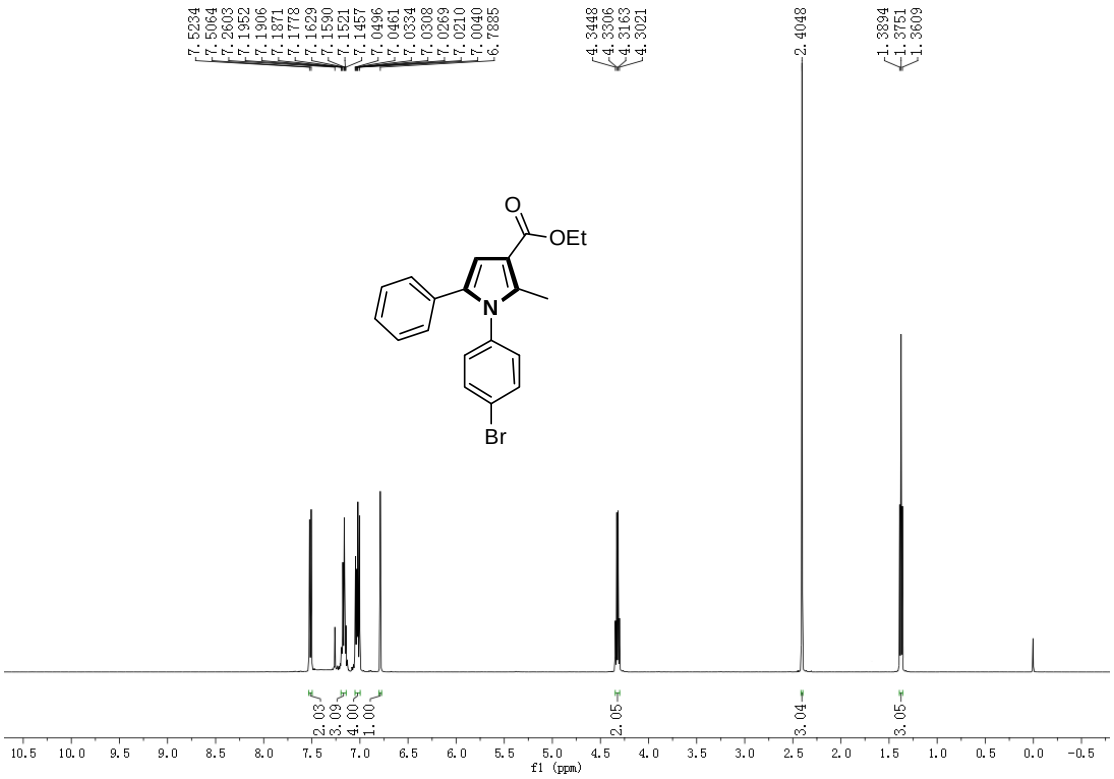
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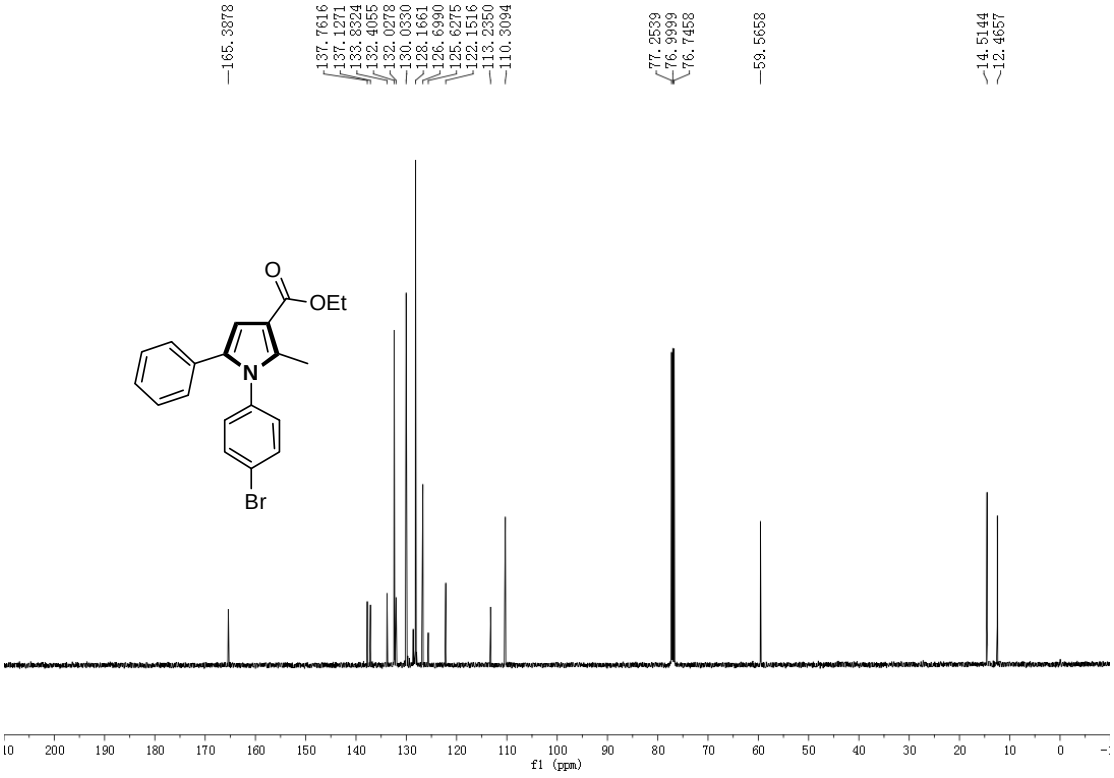
3.05
f1 (ppm)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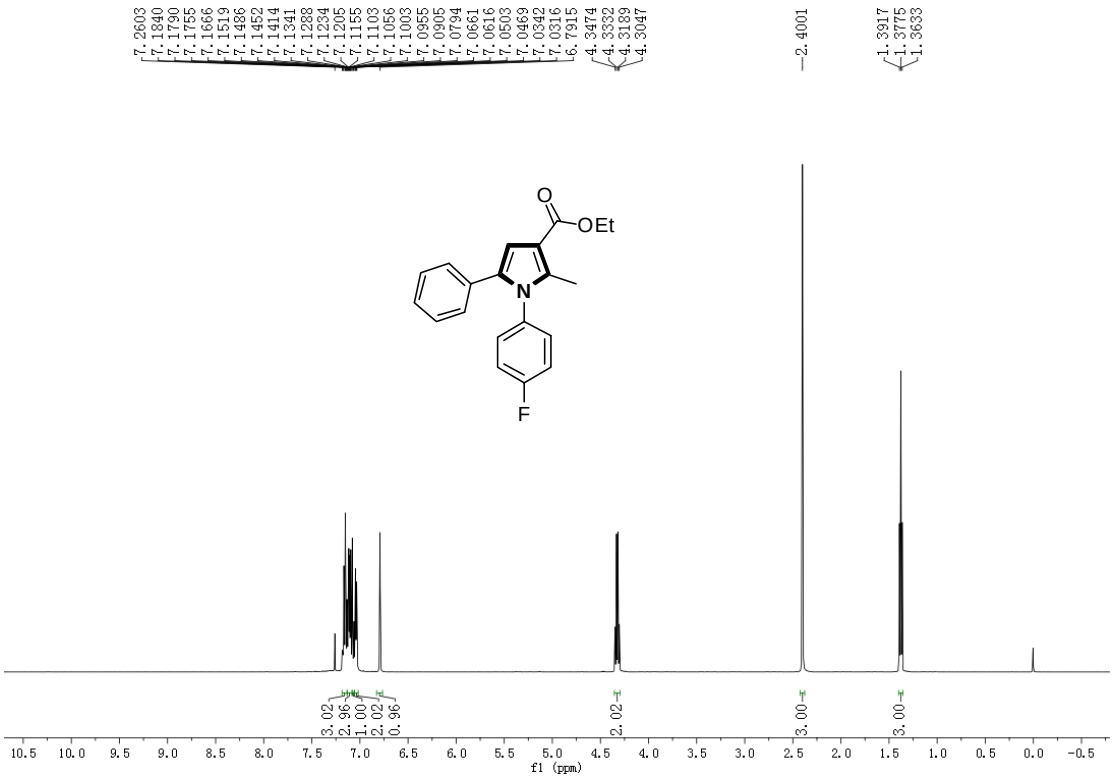
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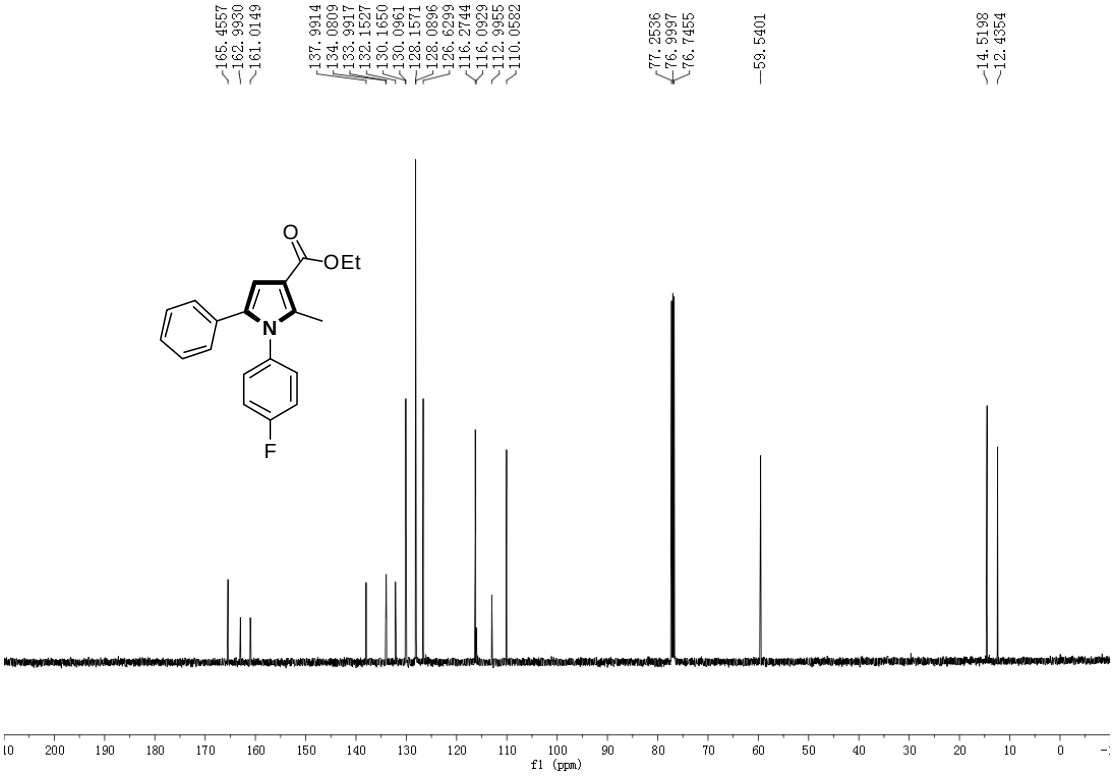
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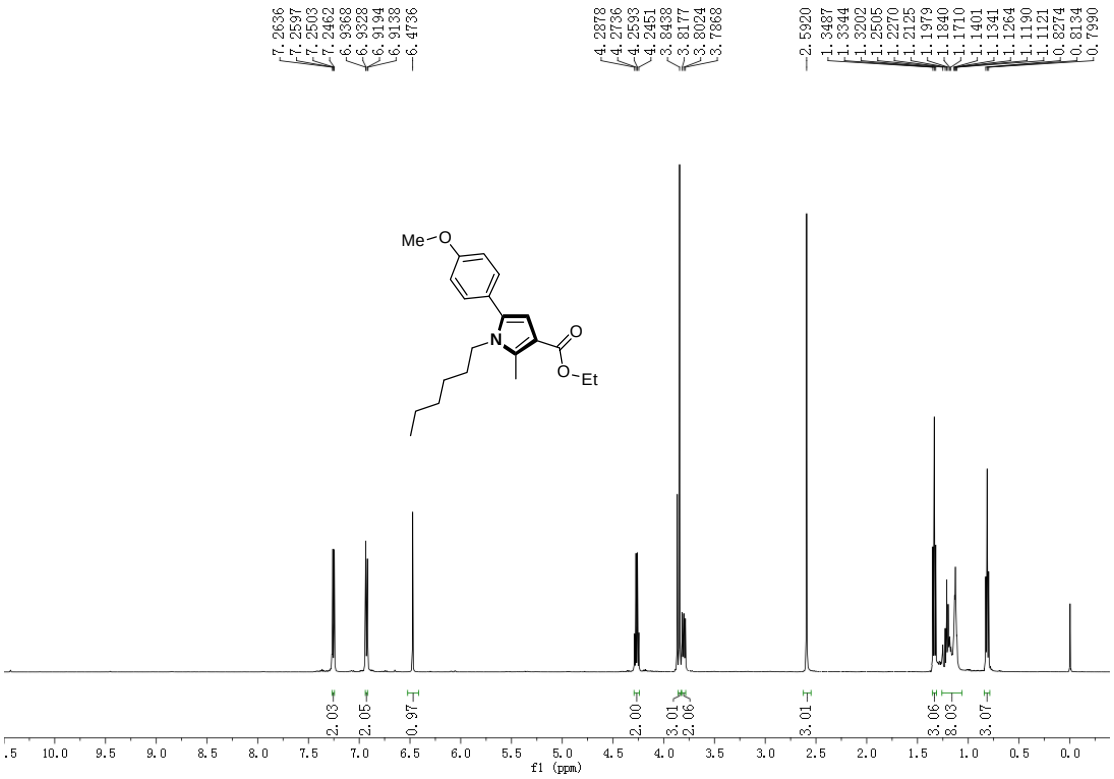
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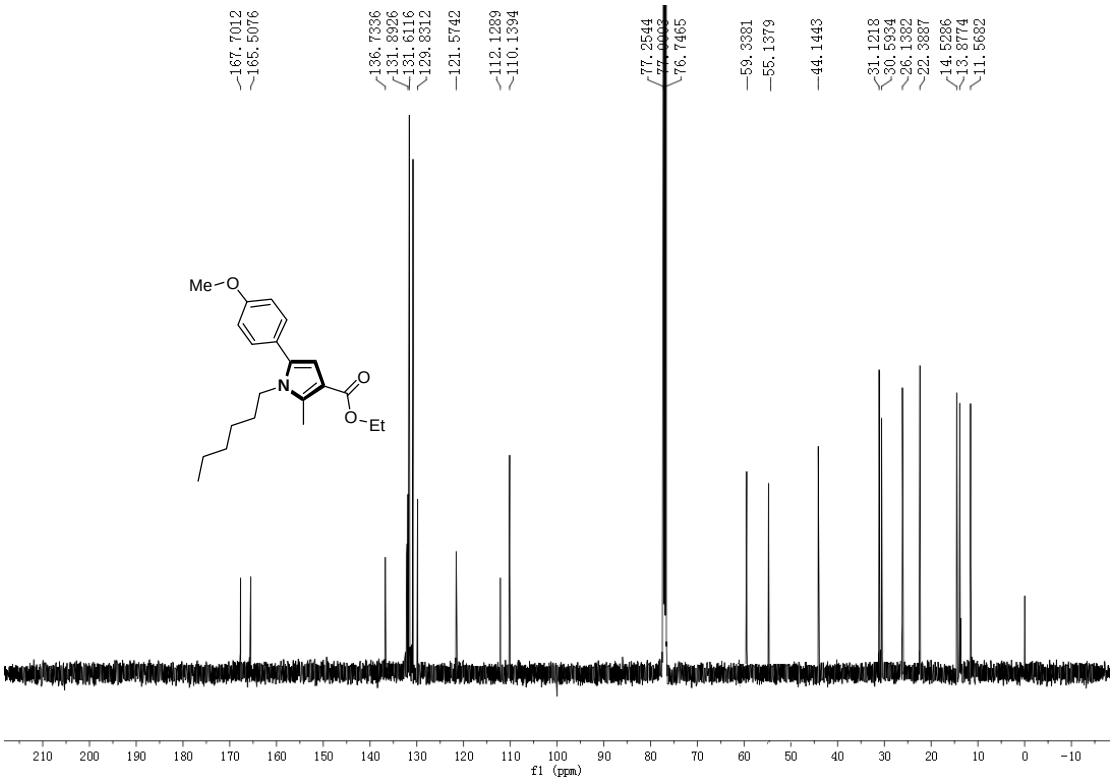
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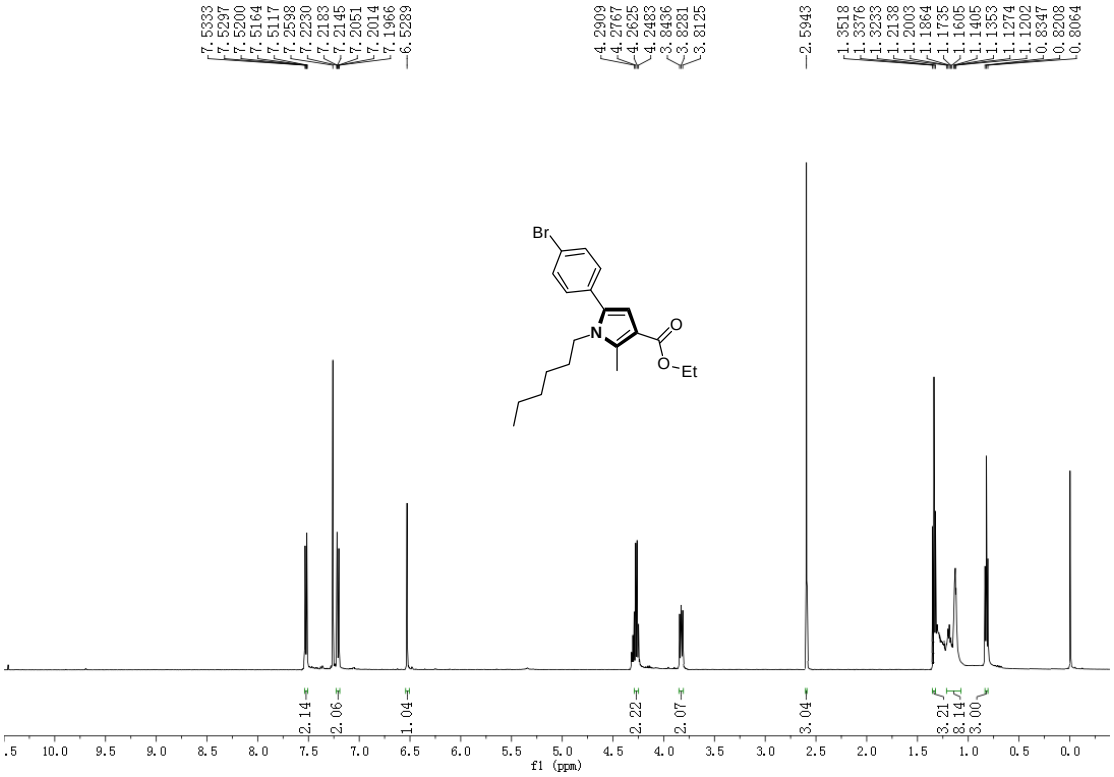
59.3381
55.1379
44.1443
31.1218
30.5934
26.1382
22.3887
14.5286
13.8774
11.5682
Me
O
N
O
O
Et
f1 (ppm)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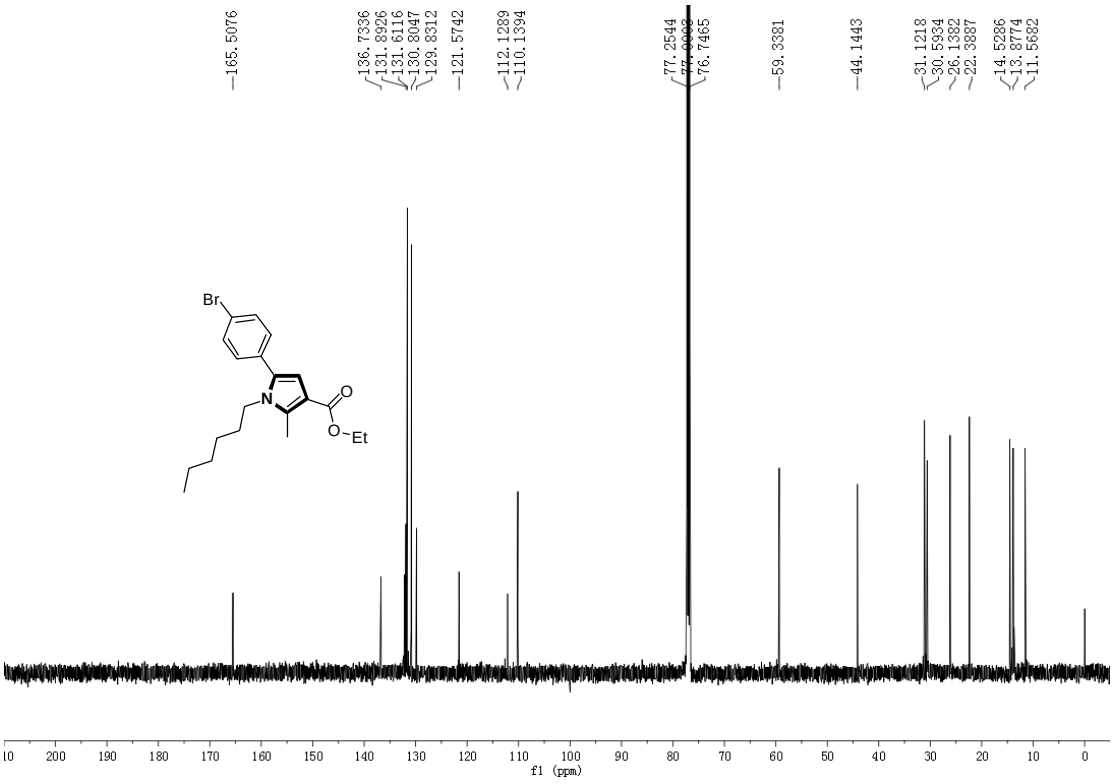
7.5117
7.2598
7.2230
7.2183
7.2145
7.2051
7.2014
7.1966
6.5289
4.2909
4.2767
4.2625
4.2483
3.8436
3.8281
3.8125
2.5943
1.3518
1.3376
1.3233
1.2138
1.2003
1.1864
1.1735
1.1605
1.1405
1.1353
1.1274
1.1202
0.8347
0.8208
0.8064
Br
N
O
O
Et
2.14
2.06
1.04
2.22
2.07
3.04
3.21
8.14
3.00
f1 (ppm)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130.8047
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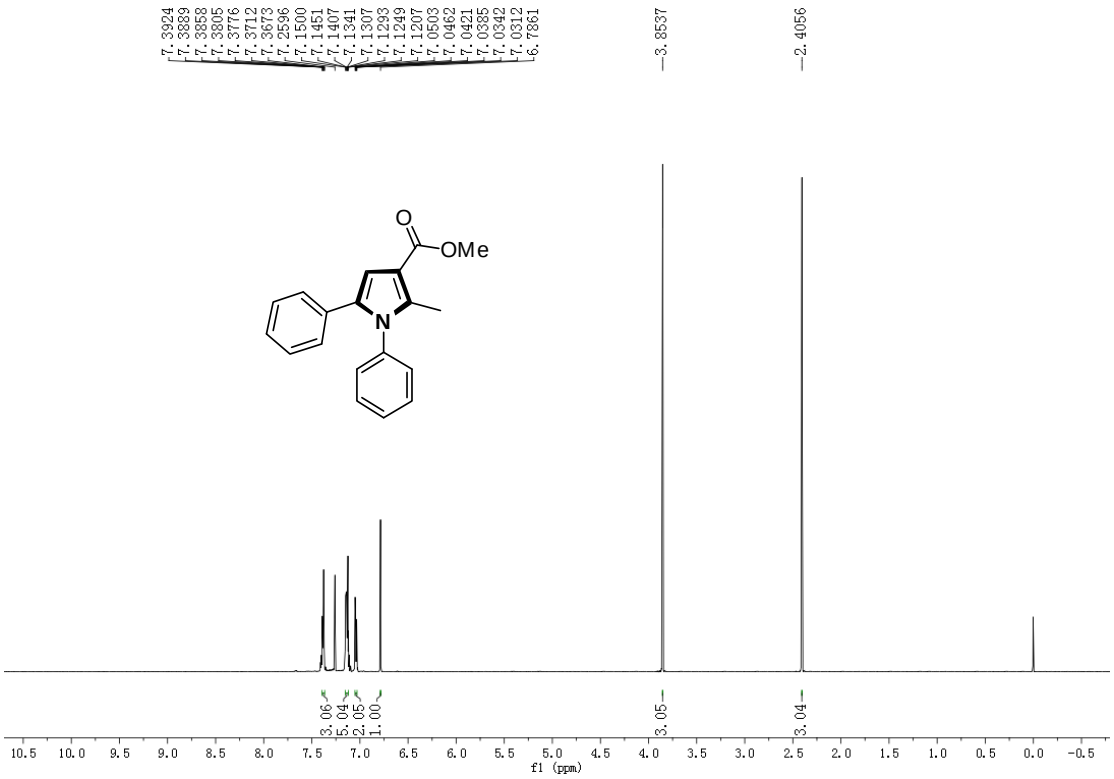
112.1289
110.1394
77.2544
77.0003
76.7465
59.3381
44.1443
31.1218
30.5934
26.1382
22.3887
14.5286
13.8774
11.5682
Br
N
O
O
Et
f1 (ppm)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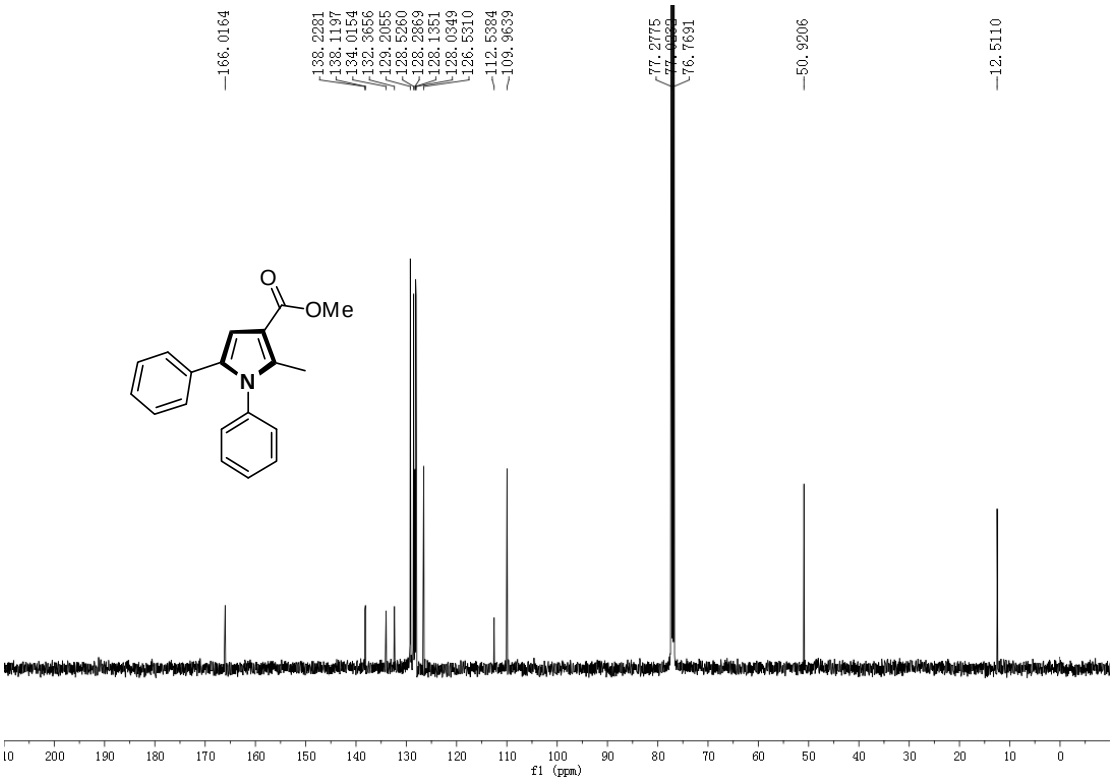
7.1407
7.1341
7.1307
7.1293
7.1249
7.1207
7.0503
7.0462
7.0421
7.0385
7.0342
7.0312
6.7861
3.8537
2.4056
O
OMe
N
3.06
5.04
2.05
1.00
3.05
3.04
f1 (ppm)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129.2055
128.5260
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128.1351
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126.5310
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77.0989
76.7691
50.9206
12.5110
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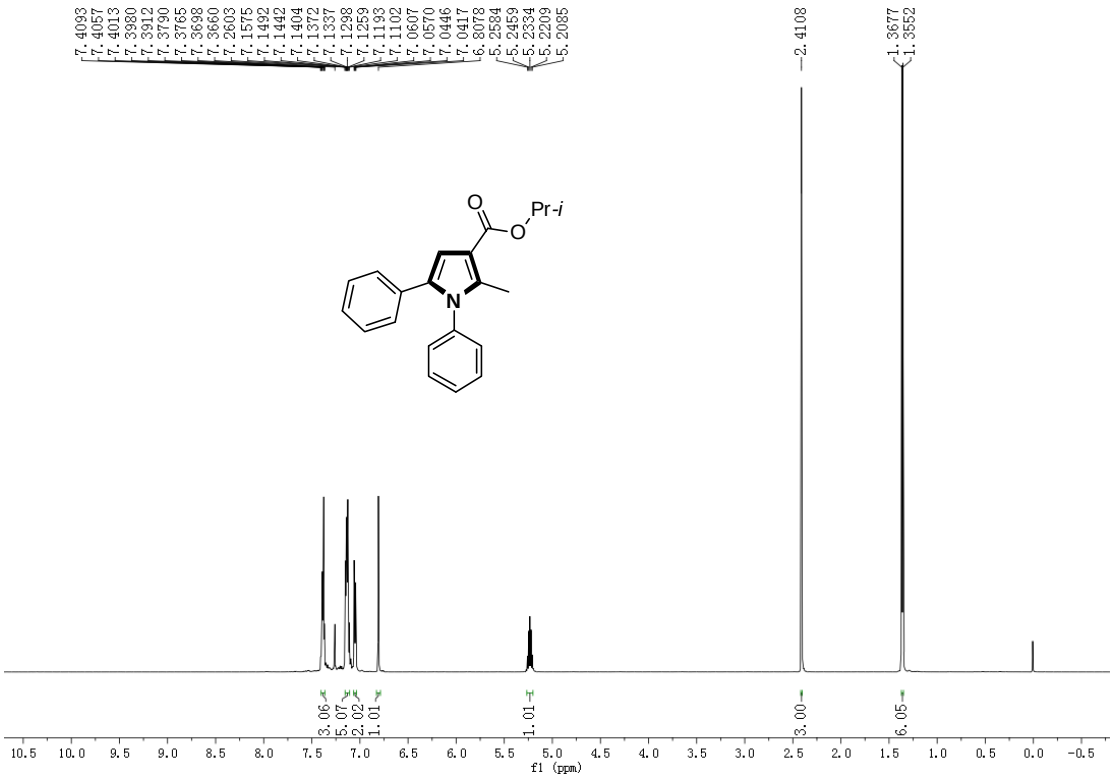
OMe
N
f1 (ppm)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7.3660
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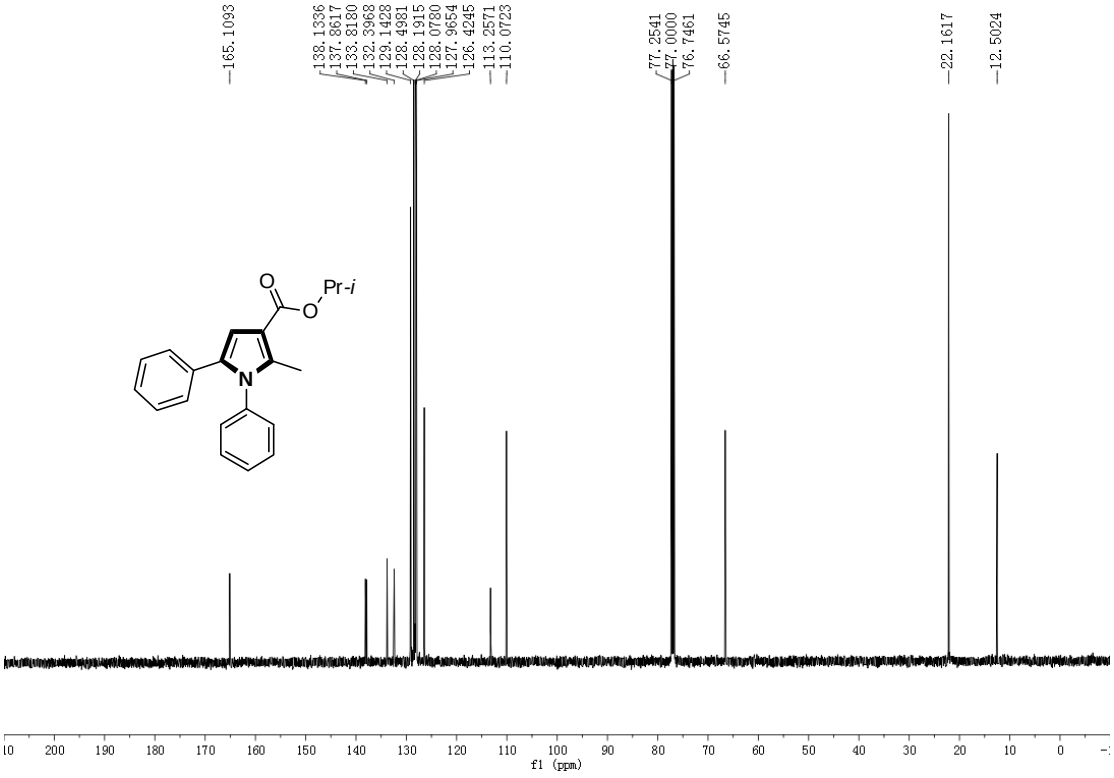
7.1575
7.1492
7.1442
7.1404
7.1372
7.1337
7.1298
7.1259
7.1193
7.1102
7.0607
7.0570
7.0446
7.0417
6.8078
5.2584
5.2459
5.2334
5.2209
5.2085
2.4108
1.3677
1.3552
O
O
Pr-i
N
3.06
5.07
2.02
1.01
1.01
3.00
6.05
f1 (ppm)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126.4245
113.2571
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77.0000
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22.1617
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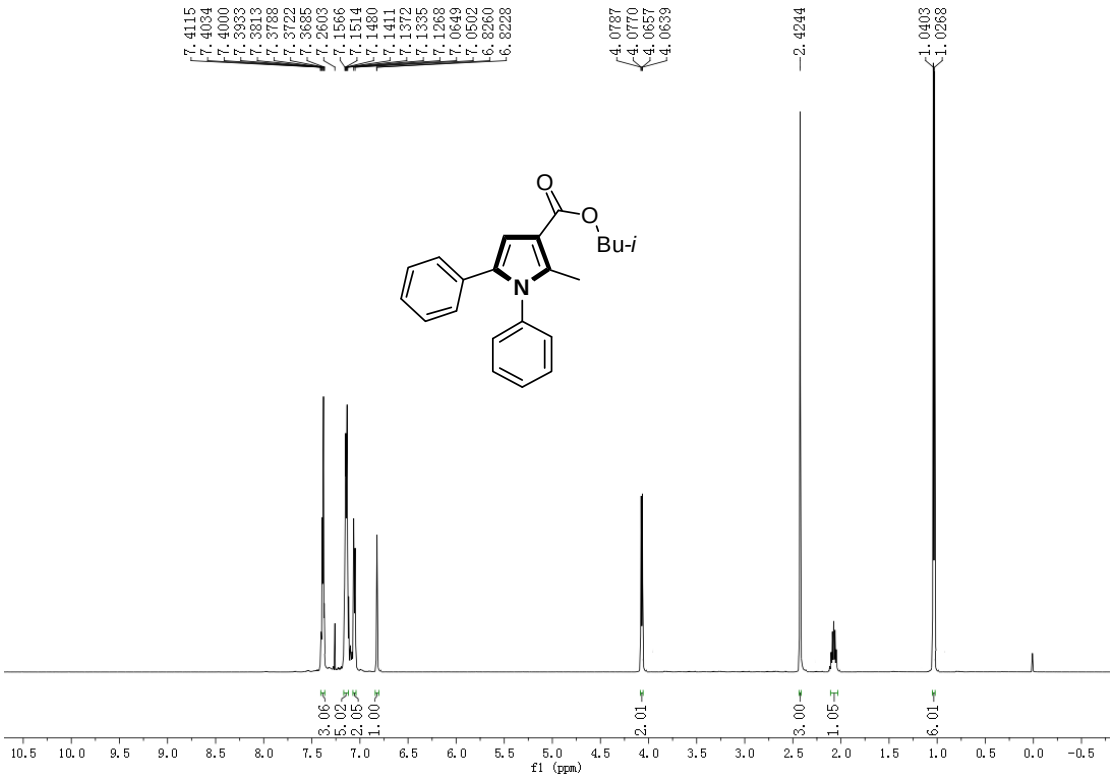
O
O
Pr-i
N
f1 (ppm)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7.3933
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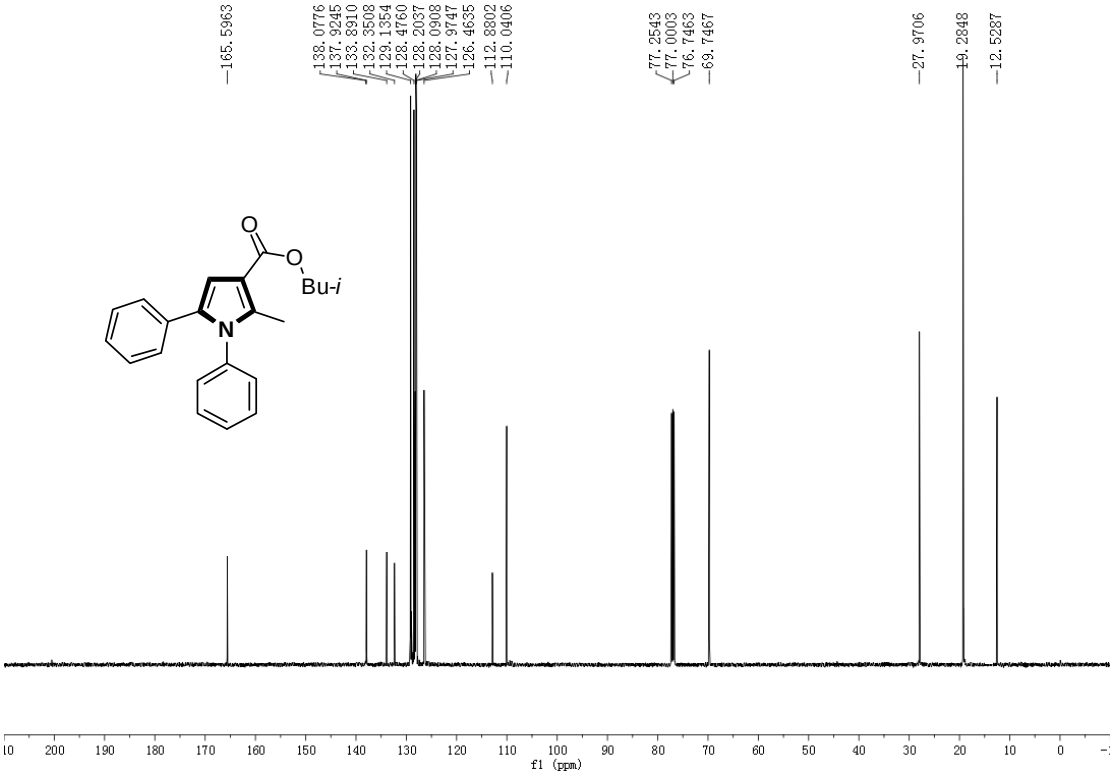
7.3722
7.3685
7.2603
7.1566
7.1514
7.1480
7.1411
7.1372
7.1335
7.1268
7.0649
7.0502
6.8260
6.8228
4.0787
4.0770
4.0657
4.0639
2.4244
1.0403
1.0268
O
O
Bu-i
N
3.06
5.02
2.05
1.00
2.01
3.00
1.05
6.01
f1 (ppm)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132.3508
129.1354
128.4760
128.2037
128.0908
127.9747
126.4635
112.8802
110.0406
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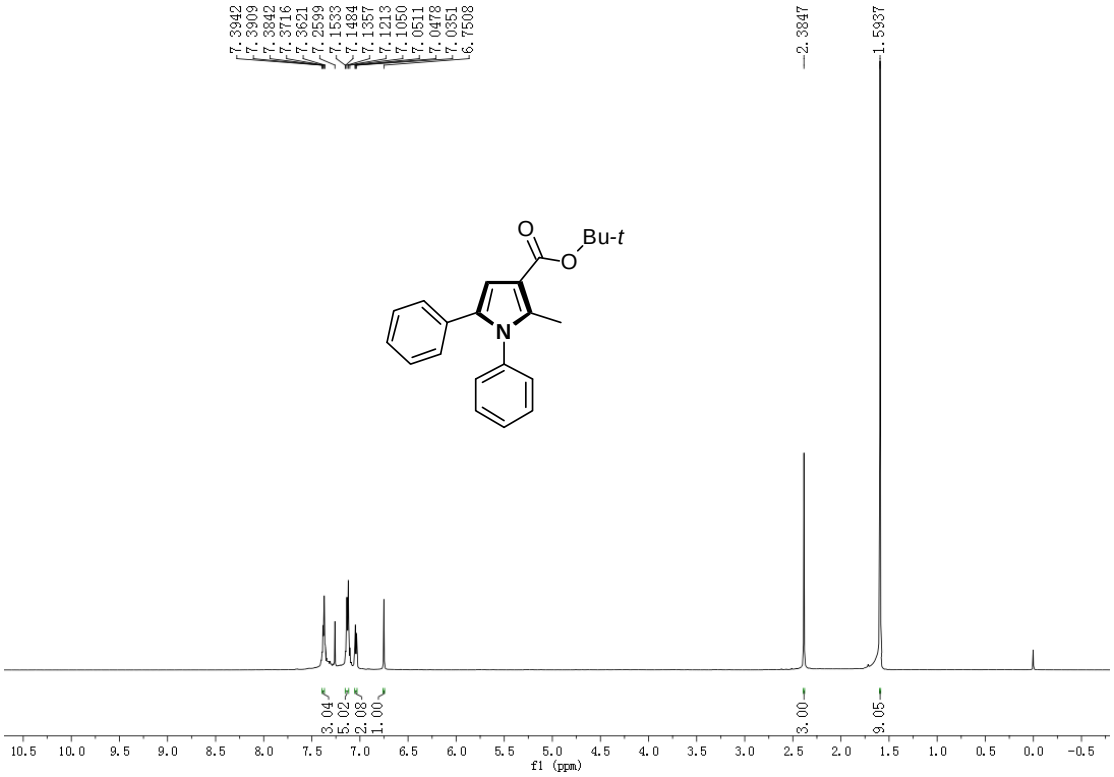
77.0003
76.7463
69.7467
27.9706
19.2848
12.5287
O
O
Bu-i
N
f1 (ppm)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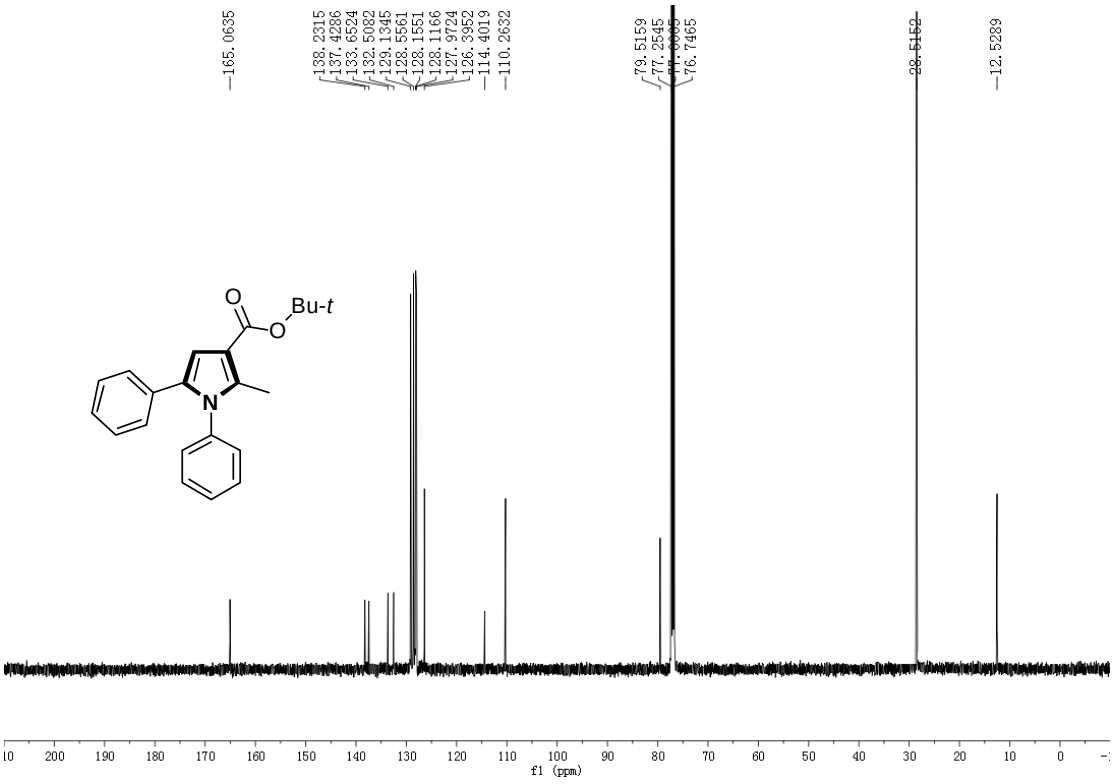
7.3842
7.3716
7.3621
7.2599
7.1533
7.1484
7.1357
7.1213
7.1050
7.0511
7.0478
7.0351
6.7508
2.3847
1.5937
O
O
Bu-t
N
3.04
5.02
2.08
1.00
3.00
9.05
f1 (ppm)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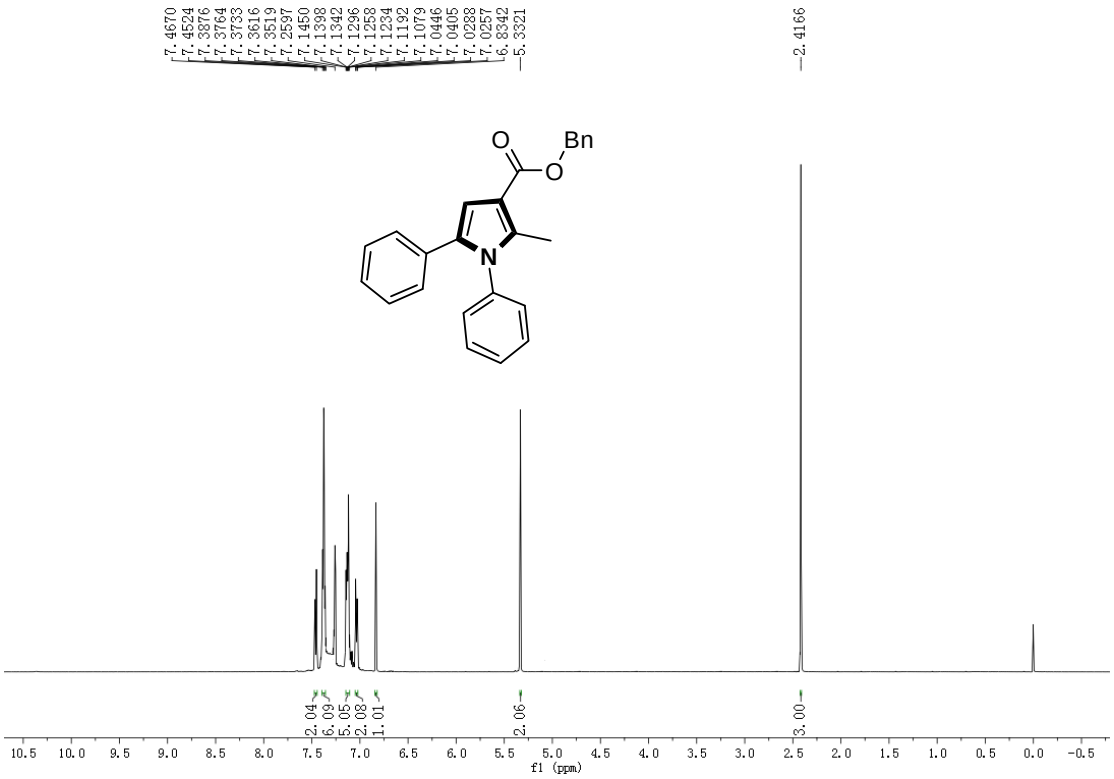
137.4286
133.6524
132.5082
129.1345
128.5561
128.1551
128.1166
127.9724
126.3952
114.4019
110.2632
79.5159
77.2545
76.7465
28.5152
12.5289
O
O
Bu-t
N
f1 (ppm)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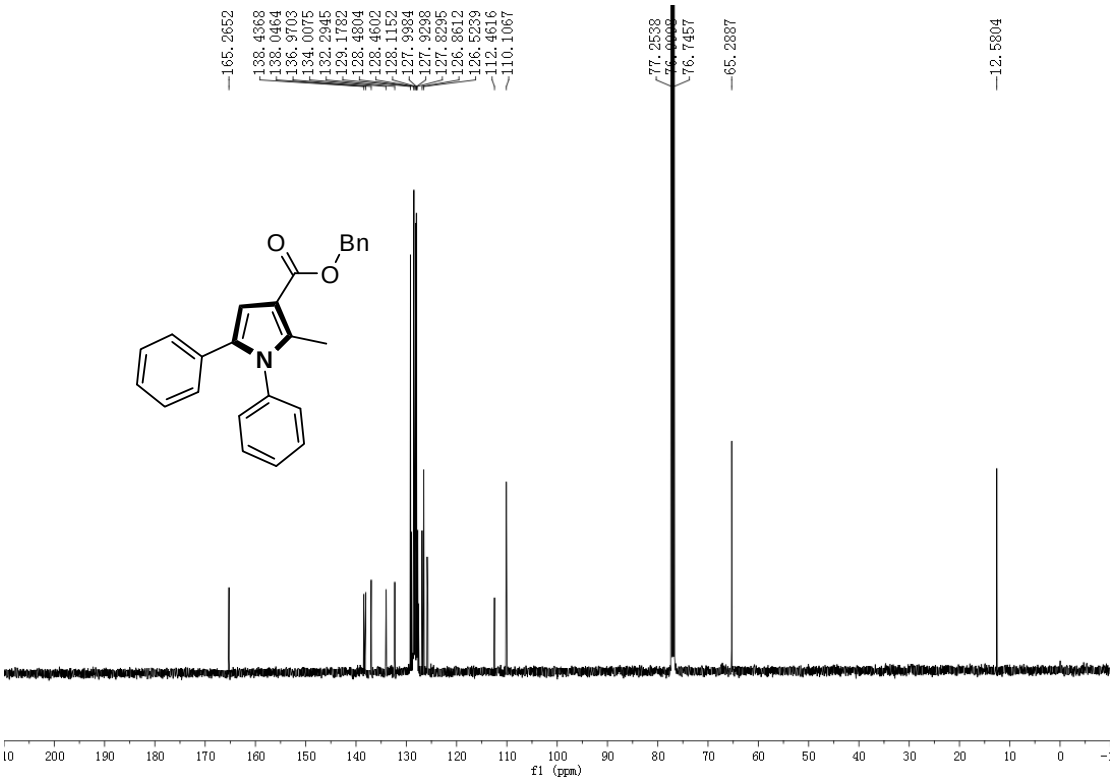
7.4524
7.3876
7.3764
7.3733
7.3616
7.3519
7.2597
7.1450
7.1398
7.1342
7.1296
7.1258
7.1234
7.1192
7.1079
7.0446
7.0405
7.0288
7.0257
6.8342
5.3321
2.4166
O
Bn
O
N
2.04
6.09
5.05
2.08
1.01
2.06
3.00
f1 (ppm)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134.0075
132.2945
129.1782
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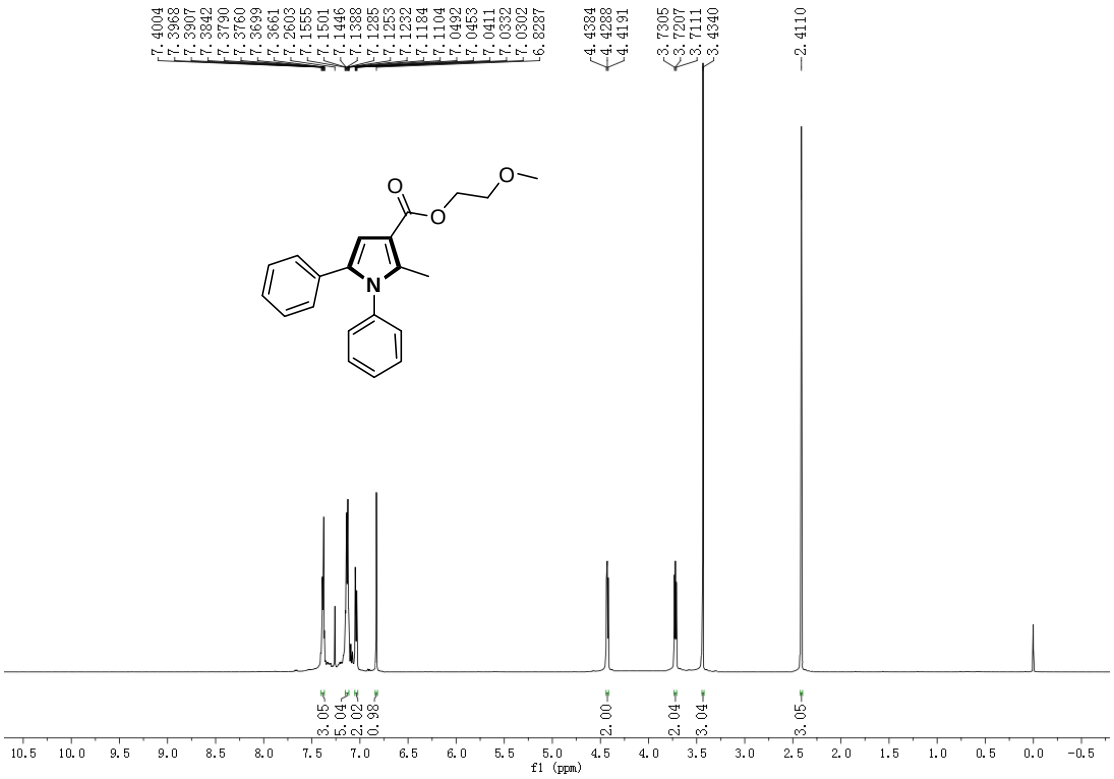
128.4602
128.1152
127.9984
127.9298
127.8295
126.8612
126.5239
112.4616
110.1067
77.2538
76.0000
76.7457
65.2887
12.5804
O
Bn
O
N
f1 (ppm)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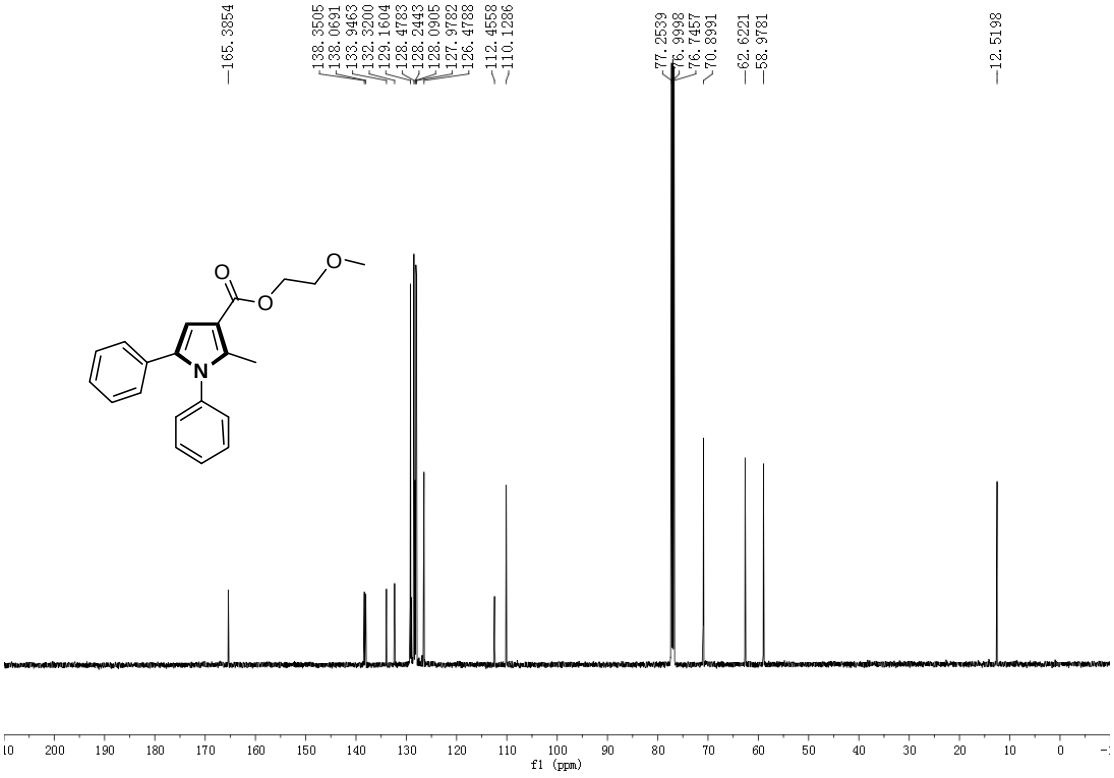
7.3842
7.3790
7.3760
7.3699
7.3661
7.2603
7.1555
7.1501
7.1446
7.1388
7.1285
7.1253
7.1232
7.1184
7.1104
7.0492
7.0453
7.0411
7.0332
7.0302
6.8287
4.4384
4.4288
4.4191
3.7305
3.7207
3.7111
3.4340
2.4110
O
O
O
N
3.05
5.04
2.02
0.98
2.00
2.04
3.04
3.05
f1 (ppm)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132.3200
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128.4783
128.2443
128.0905
127.9782
126.4788
112.4558
110.1286
77.2539
76.9998
76.7457
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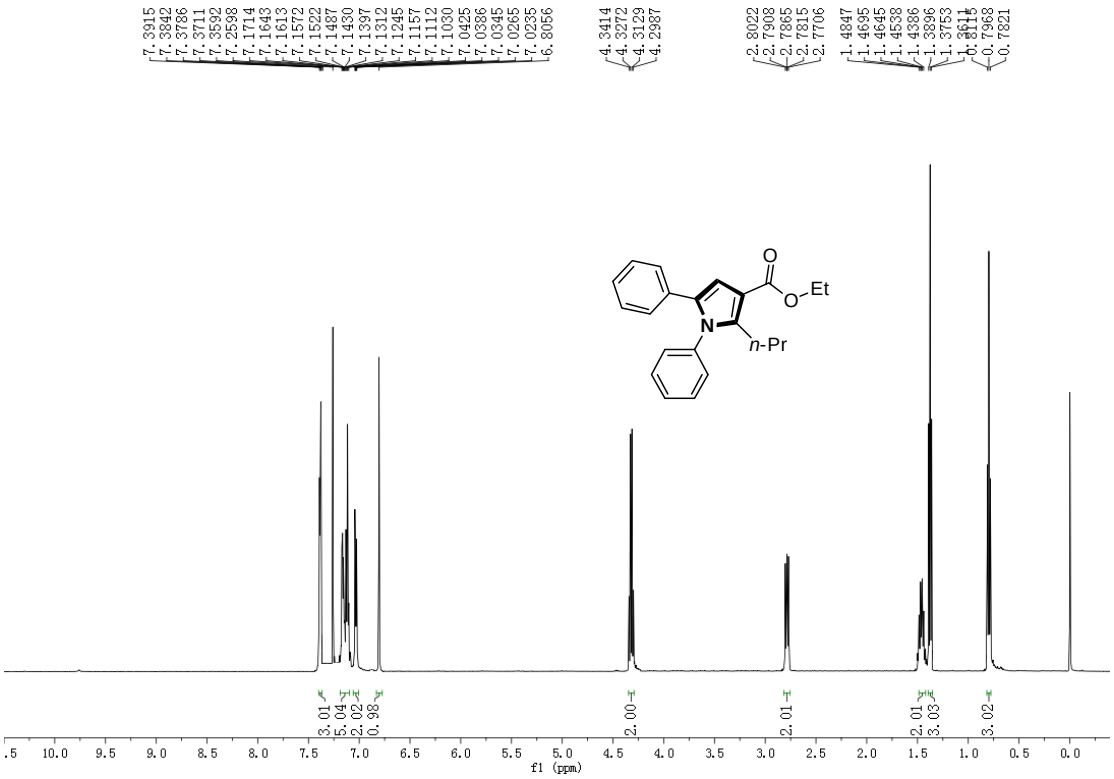
62.6221
58.9781
12.5198
O
O
O
N
f1 (ppm)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7.3842
7.3786
7.3711
7.3592
7.2598
7.1714
7.1643
7.1613
7.1572
7.1522
7.1487
7.1430
7.1397
7.1312
7.1245
7.1157
7.1112
7.1030
7.0425
7.0386
7.0345
7.0265
7.0235
6.8056
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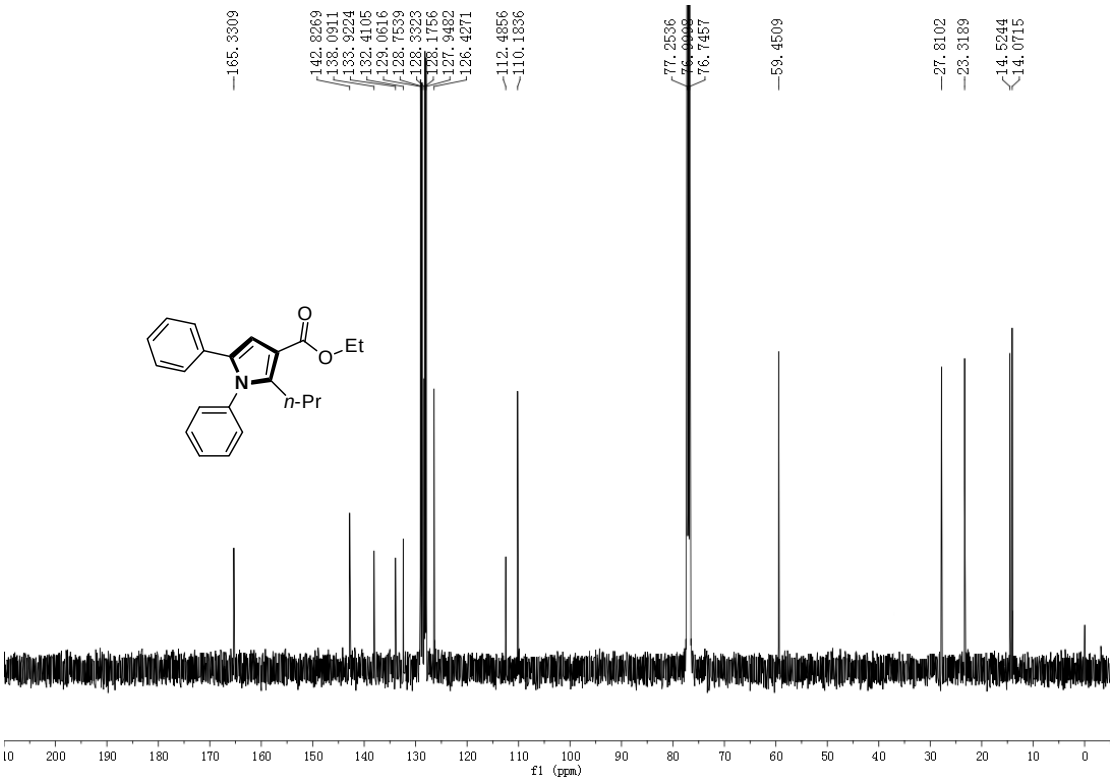
4.3272
4.3129
4.2987
2.8022
2.7908
2.7865
2.7815
2.7706
1.4847
1.4695
1.4645
1.4538
1.4386
1.3896
1.3753
1.3611
0.8115
0.7968
0.7821
O
O
Et
N
n-Pr
3.01
5.04
2.02
0.98
2.00
2.01
2.01
3.03
3.02
f1 (ppm)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128.3323
128.1756
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112.4856
110.1836
77.2536
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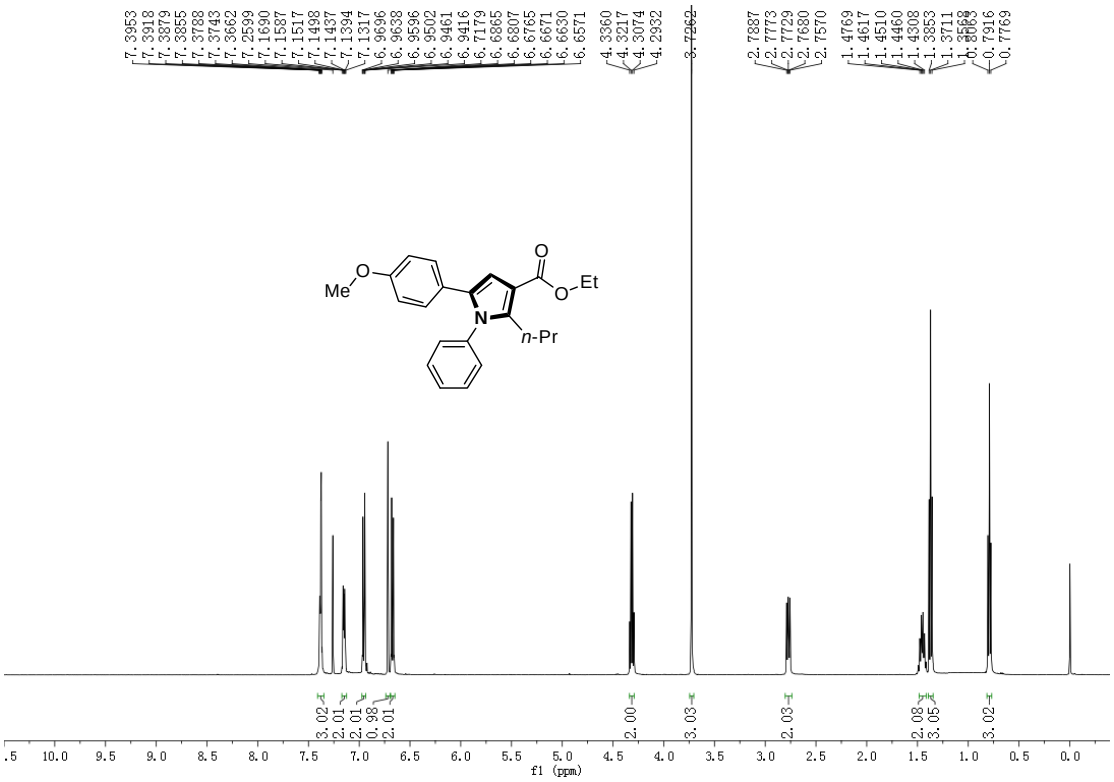
27.8102
23.3189
14.5244
14.0715
O
O
Et
N
n-Pr
f1 (ppm)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7.3879
7.3855
7.3788
7.3743
7.3662
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7.1690
7.1587
7.1517
7.1498
7.1437
7.1394
7.1317
6.9696
6.9638
6.9596
6.9502
6.9461
6.9416
6.7179
6.6865
6.6807
6.6765
6.6671
6.6630
6.6571
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4.3074
4.2932
3.7262
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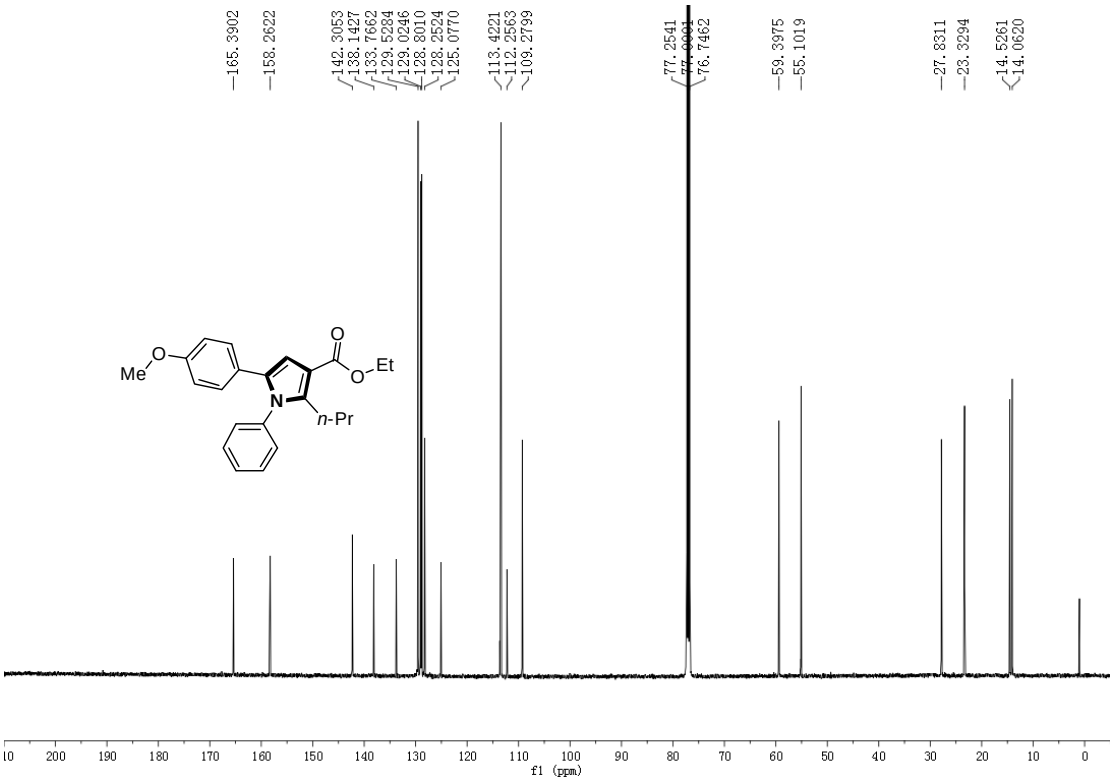
2.7773
2.7729
2.7680
2.7570
1.4769
1.4617
1.4510
1.4460
1.4308
1.3853
1.3711
0.7916
0.7769
Me
O
O
Et
N
n-Pr
3.02
2.01
2.01
0.98
2.01
2.00
3.03
2.03
2.08
3.05
3.02
f1 (ppm)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113.4221
112.2563
109.2799
77.2541
77.0001
76.7462
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23.3294
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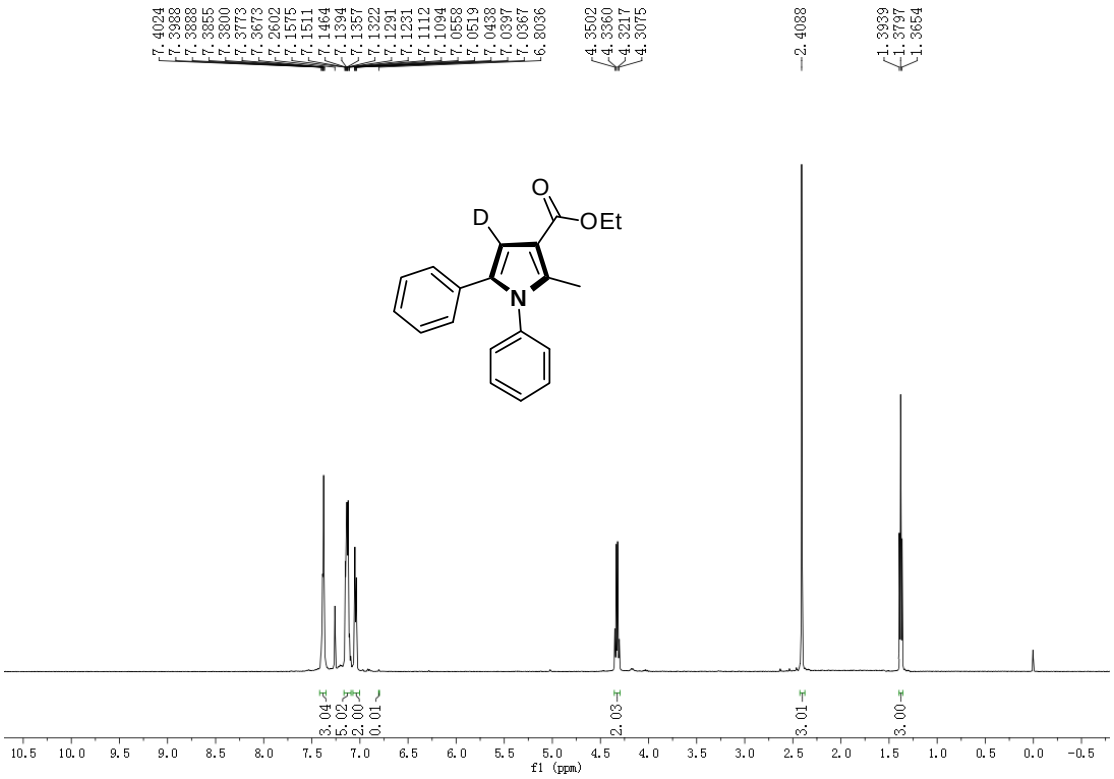
Me
O
O
Et
N
n-Pr
f1 (ppm)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7.3800
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7.3673
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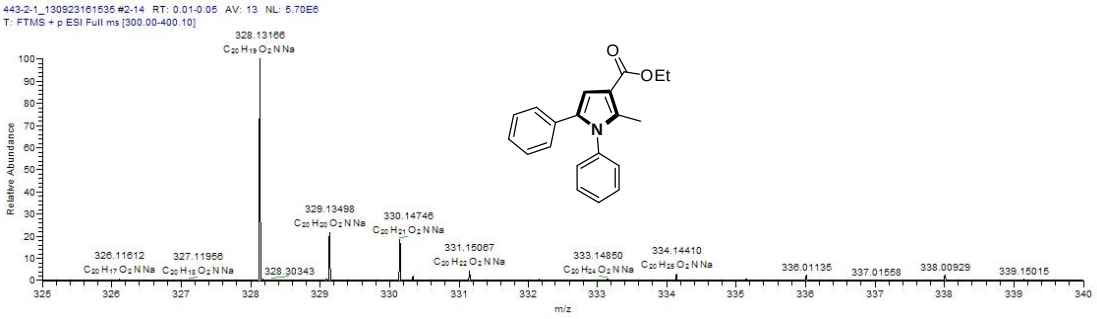
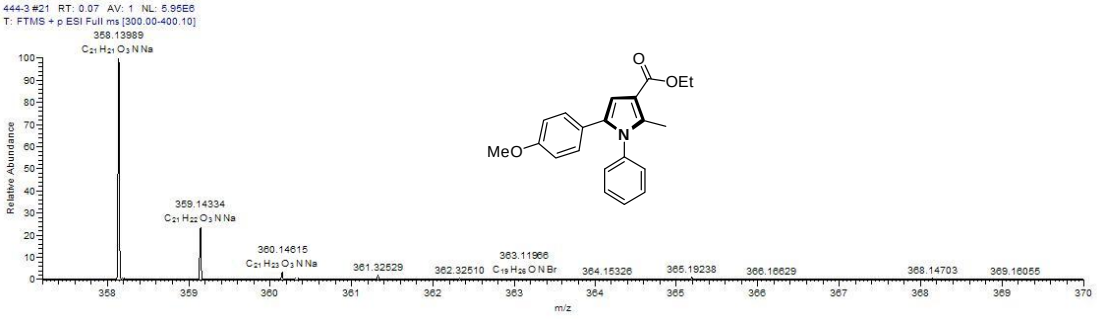
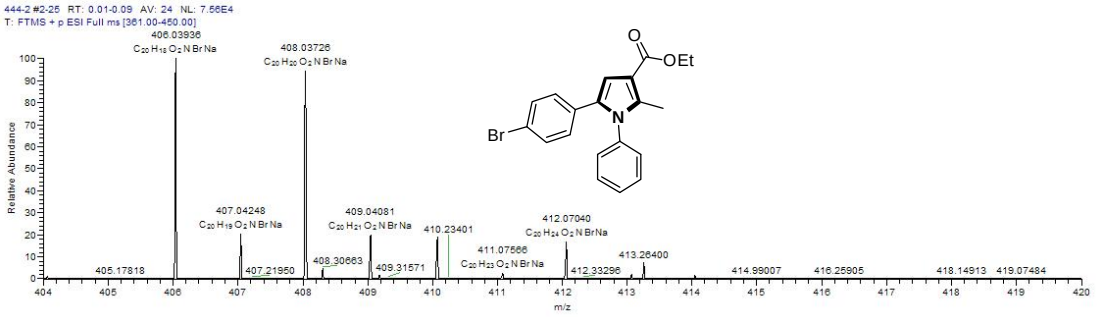
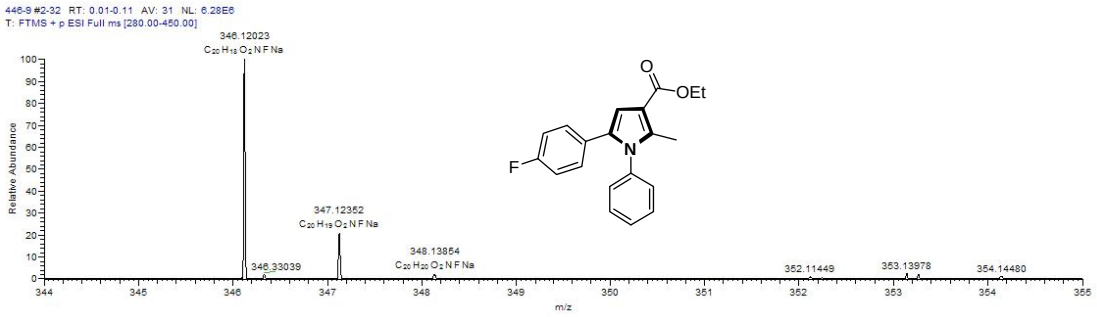
7.1575
7.1511
7.1464
7.1394
7.1357
7.1322
7.1291
7.1231
7.1112
7.1094
7.0558
7.0519
7.0438
7.0397
7.0367
6.8036
4.3502
4.3360
4.3217
4.3075
2.4088
1.3939
1.3797
1.3654
O
OEt
D
N
3.04
5.02
2.00
0.01
2.03
3.01
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

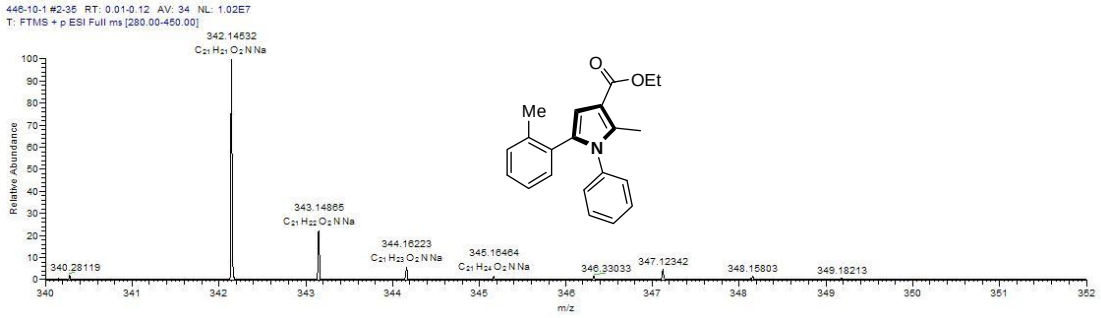
6 **Copies of HRMS Spectra of Products**

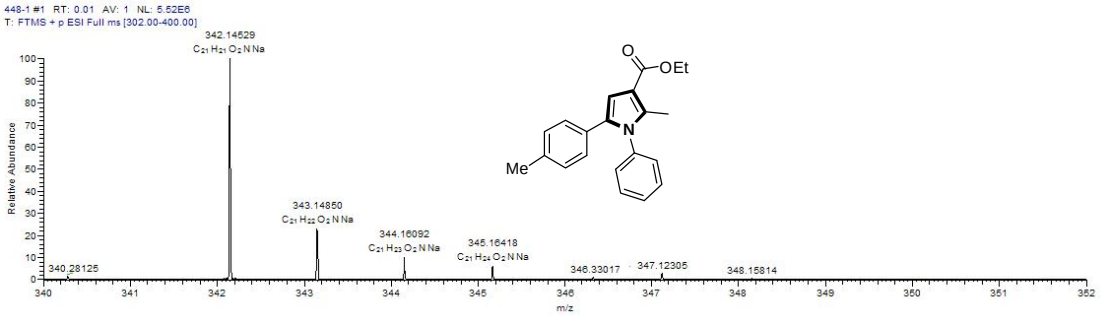


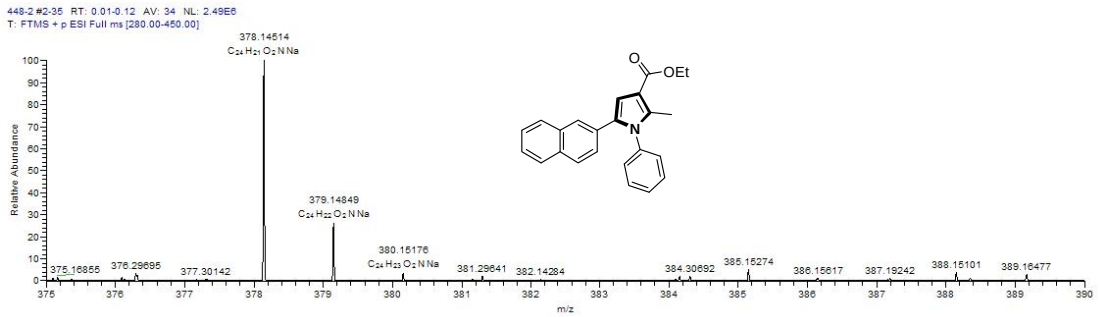


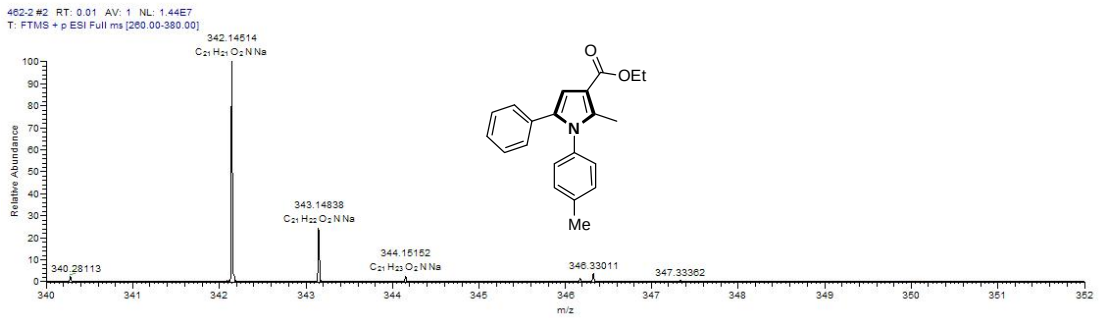


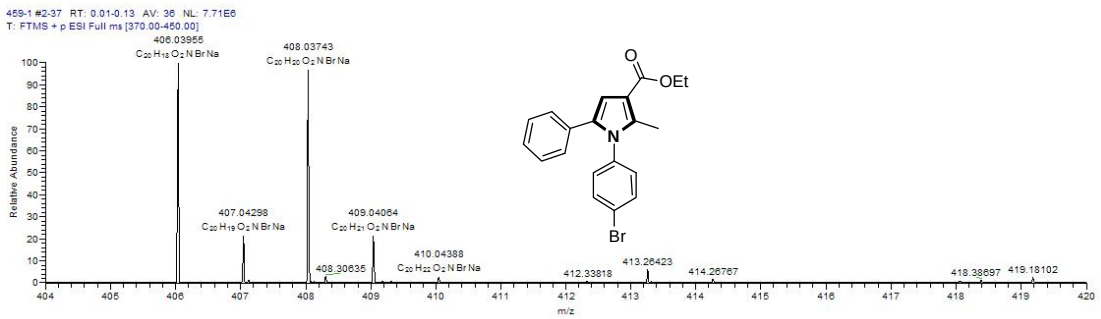


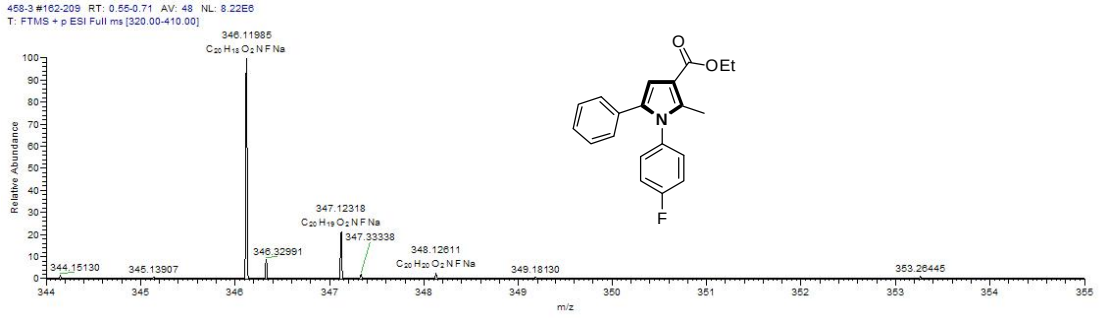

446-10-1 #2-35 RT: 0.01-0.12 AV: 34 NL: 1.02E7
T: FTMS + p ESI Full ms [280.00-450.00]
342.14532
C21 H21 O2 N Na
343.14865
C21 H22 O2 N Na
344.16223
C21 H23 O2 N Na
345.16464
C21 H24 O2 N Na
340.28119
346.33033
347.12342
348.15803
349.18213
Relative Abundance
m/z
O
OEt
Me
N

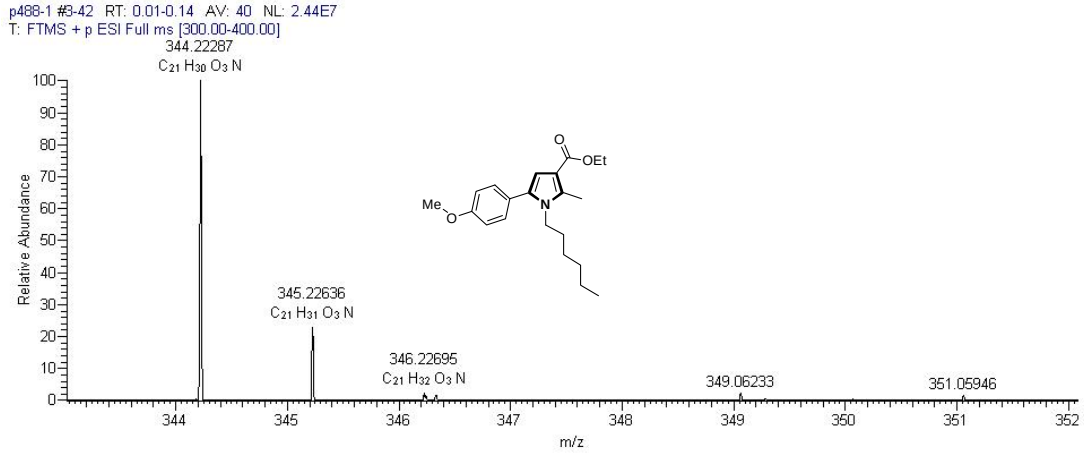

448-1 #1 RT: 0.01 AV: 1 NL: 5.52E6
T: FTMS + p ESI Full ms [302.00-400.00]
342.14529
C21 H21 O2 N Na
343.14850
C21 H22 O2 N Na
344.16092
C21 H23 O2 N Na
345.16418
C21 H24 O2 N Na
340.28125
346.33017
347.12305
348.15814
Relative Abundance
m/z
O
OEt
Me
N

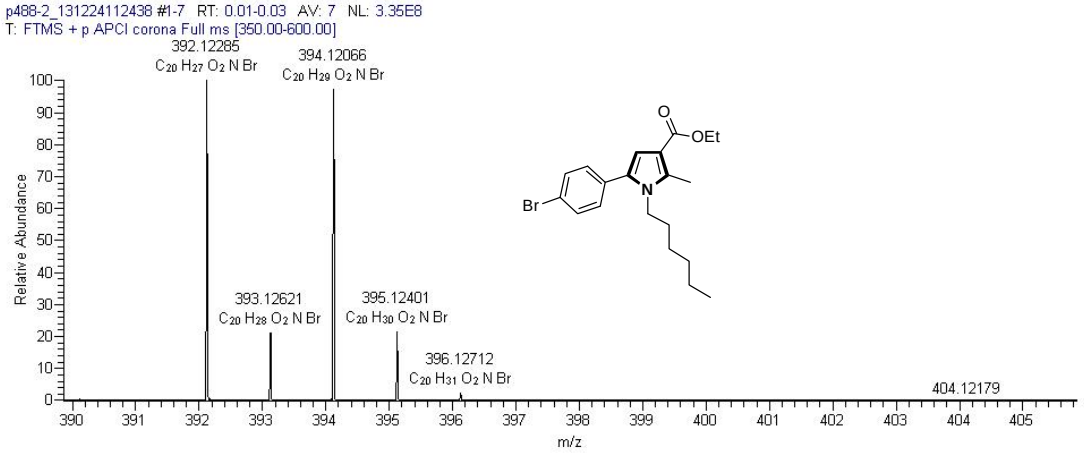

448-2 #2-35 RT: 0.01-0.12 AV: 34 NL: 2.49E6
T: FTMS + p ESI Full ms [280.00-450.00]
378.14514
C24 H21 O2 N Na
379.14849
C24 H22 O2 N Na
380.15176
C24 H23 O2 N Na
375.16855
376.29695
377.30142
381.29641
382.14284
384.30692
385.15274
386.15617
387.19242
388.15101
389.16477
Relative Abundance
m/z
O
OEt
N

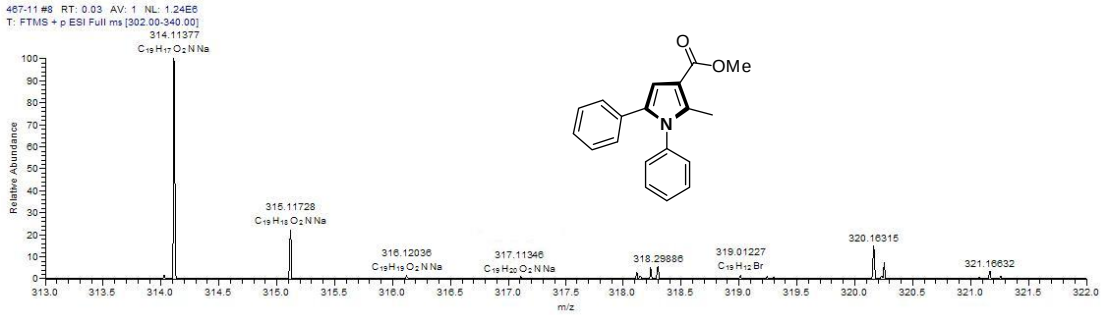

462-2 #2 RT: 0.01 AV: 1 NL: 1.44E7
T: FTMS + p ESI Full ms [260.00-380.00]
342.14514
C21 H21 O2 N Na
343.14838
C21 H22 O2 N Na
344.15152
C21 H23 O2 N Na
340.28113
346.33011
347.33362
Relative Abundance
m/z
O
OEt
N
Me

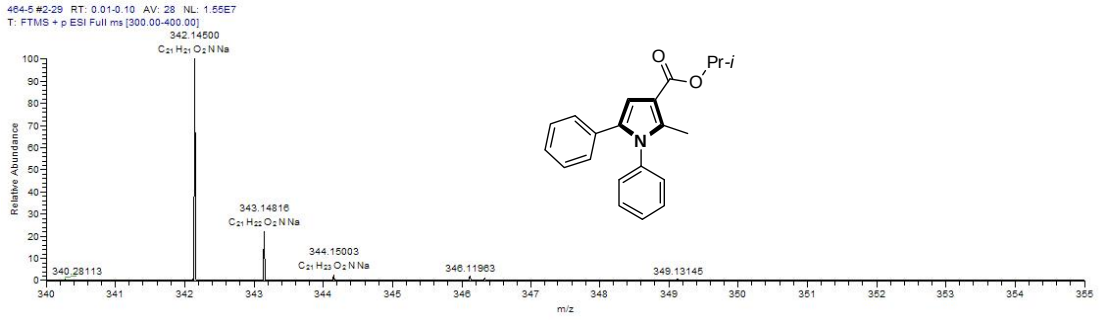

459-1 #2-37 RT: 0.01-0.13 AV: 36 NL: 7.71E6
T: FTMS + p ESI Full ms [370.00-450.00]
406.03955
C20 H19 O2 N Br Na
408.03743
C20 H20 O2 N Br Na
407.04298
C20 H19 O2 N Br Na
409.04064
C20 H21 O2 N Br Na
410.04388
C20 H22 O2 N Br Na
408.30635
412.33818
413.26423
414.26767
418.38697
419.18102
Relative Abundance
m/z
O
OEt
N
Br

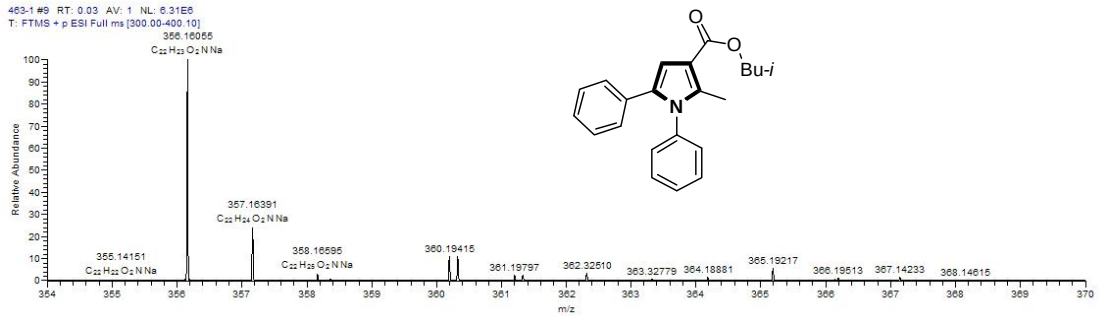

458-3 #162-209 RT: 0.55-0.71 AV: 48 NL: 8.22E6
T: FTMS + p ESI Full ms [320.00-410.00]
346.11985
C20 H19 O2 N F Na
347.12318
C20 H19 O2 N F Na
347.33338
346.32991
348.12611
C20 H20 O2 N F Na
344.15130
345.13907
349.18130
353.26445
Relative Abundance
m/z
OEt
N
F

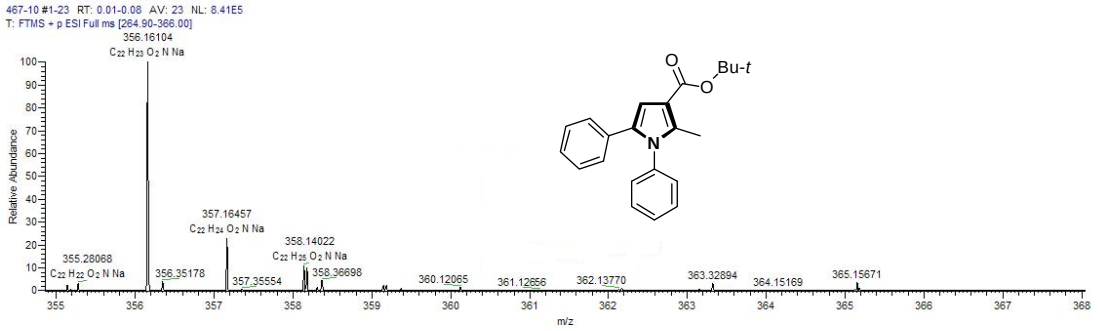

p488-1 #3-42 RT: 0.01-0.14 AV: 40 NL: 2.44E7
T: FTMS + p ESI Full ms [300.00-400.00]
344.22287
C21 H30 O3 N
345.22636
C21 H31 O3 N
346.22695
C21 H32 O3 N
349.06233
351.05946
Relative Abundance
m/z
OEt
Me
O
N

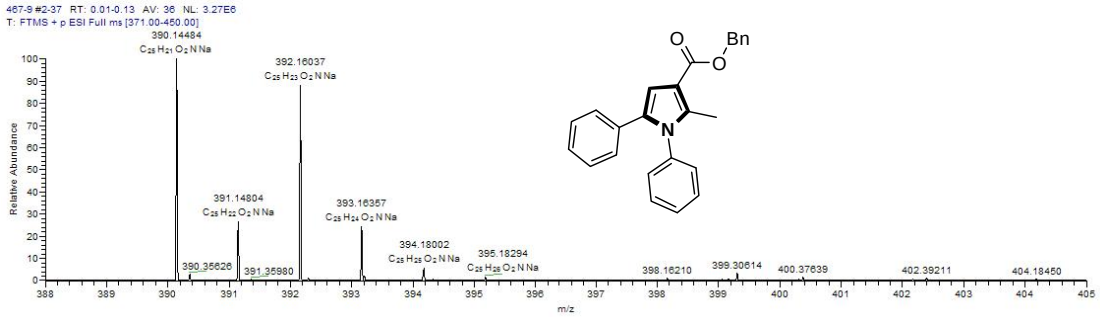

p488-2_131224112438 #1-7 RT: 0.01-0.03 AV: 7 NL: 3.35E8
T: FTMS + p APCI corona Full ms [350.00-600.00]
392.12285
C20 H27 O2 N Br
394.12066
C20 H29 O2 N Br
393.12621
C20 H28 O2 N Br
395.12401
C20 H30 O2 N Br
396.12712
C20 H31 O2 N Br
404.12179
Relative Abundance
m/z
OEt
Br
N

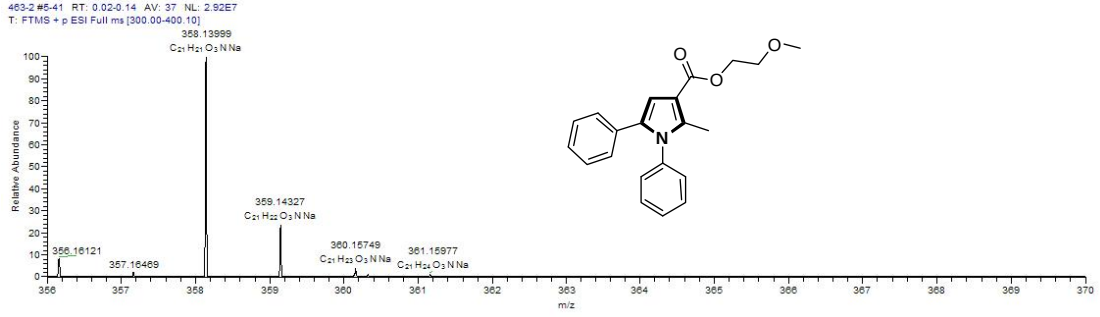

467-11 #8 RT: 0.03 AV: 1 NL: 1.24E6
T: FTMS + p ESI Full ms [302.00-340.00]
314.11377
C19 H17 O2 N Na
315.11728
C19 H18 O2 N Na
316.12036
C19 H19 O2 N Na
317.11346
C19 H20 O2 N Na
318.29886
319.01227
C19 H12 Br
320.16315
321.16632
Relative Abundance
m/z
OMe
N

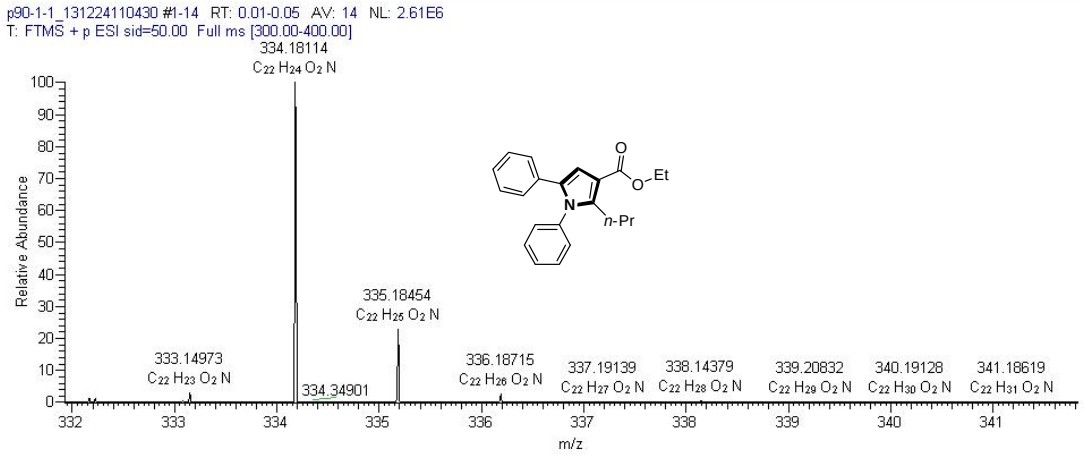

464-5 #2-29 RT: 0.01-0.10 AV: 28 NL: 1.55E7
T: FTMS + p ESI Full ms [300.00-400.00]
342.14500
C21 H21 O2 N Na
343.14816
C21 H22 O2 N Na
344.15003
C21 H23 O2 N Na
340.28113
346.11963
349.13145
Relative Abundance
m/z
O
O
Pr-i
N

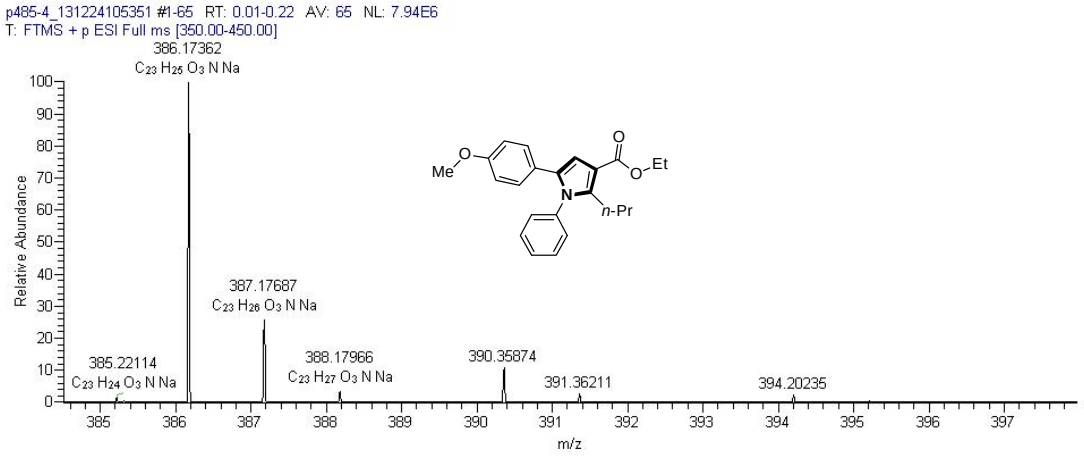

463-1 #9 RT: 0.03 AV: 1 NL: 6.31E6
T: FTMS + p ESI Full ms [300.00-400.10]
356.16055
C22 H23 O2 N Na
357.16391
C22 H24 O2 N Na
355.14151
C22 H22 O2 N Na
358.16695
C22 H25 O2 N Na
360.19415
361.19797
362.32510
363.32779
364.18881
365.19217
366.19513
367.14233
368.14615
Relative Abundance
m/z
O
O
Bu-i
N


467-10 #1-23 RT: 0.01-0.08 AV: 23 NL: 8.41E5
T: FTMS + p ESI Full ms [264.90-366.00]
356.16104
C22 H23 O2 N Na
357.16457
C22 H24 O2 N Na
358.14022
C22 H25 O2 N Na
355.28068
C22 H22 O2 N Na
356.35178
357.35554
358.36698
360.12065
361.12656
362.13770
363.32894
364.15169
365.15671
Relative Abundance
m/z
O
O
Bu-t
N


467-9 #2-37 RT: 0.01-0.13 AV: 36 NL: 3.27E6
T: FTMS + p ESI Full ms [371.00-450.00]
390.14484
C25 H21 O2 N Na
392.16037
C25 H23 O2 N Na
391.14804
C25 H22 O2 N Na
393.16357
C25 H24 O2 N Na
394.18002
C25 H25 O2 N Na
395.18294
C25 H26 O2 N Na
390.35626
391.35980
398.16210
399.30614
400.37639
402.39211
404.18450
Relative Abundance
m/z
O
O
Bn
N


463-2 #5-41 RT: 0.02-0.14 AV: 37 NL: 2.92E7
T: FTMS + p ESI Full ms [300.00-400.10]
358.13999
C21 H21 O3 N Na
359.14327
C21 H22 O3 N Na
356.16121
357.16469
360.15749
C21 H23 O3 N Na
361.15977
C21 H24 O3 N Na
Relative Abundance
m/z
O
O
O
N


p90-1-1_131224110430 #1-14 RT: 0.01-0.05 AV: 14 NL: 2.61E6
T: FTMS + p ESI sid=50.00 Full ms [300.00-400.00]
334.18114
C22 H24 O2 N
335.18454
C22 H25 O2 N
333.14973
C22 H23 O2 N
334.34901
336.18715
C22 H26 O2 N
337.19139
C22 H27 O2 N
338.14379
C22 H28 O2 N
339.20832
C22 H29 O2 N
340.19128
C22 H30 O2 N
341.18619
C22 H31 O2 N
Relative Abundance
m/z
O
O
Et
N
n-Pr


p485-4_131224105351 #1-65 RT: 0.01-0.22 AV: 65 NL: 7.94E6
T: FTMS + p ESI Full ms [350.00-450.00]
386.17362
C23 H25 O3 N Na
387.17687
C23 H26 O3 N Na
385.22114
C23 H24 O3 N Na
388.17966
C23 H27 O3 N Na
390.35874
391.36211
394.20235
Relative Abundance
m/z
Me
O
O
O
Et
N
n-Pr