Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

Cu/Pd-catalyzed chemoselective synthesis of C-3 dicarbonyl indoles and bis(indolyl)alkanes from aldehydes and indoles

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General experimental

All general reagents and solvents were commercially available and used as received. ^{1}H and ^{13}C NMR spectra were measured on magnet system 400'54 ascend instrument purchased from Bruker Biospin AG. Chemical data for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent ($CDCl_3$, 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = penta, dd = doublet of doublets, dt = doublet of triplets, ddt = doublet of doublet of triplets, dtd = doublet of triplet of doublets, m = multiplet, br = broad), coupling constant (J) in Hertz (Hz), and integration. ^{13}C NMR were recorded at 75 MHz, 100 MHz or 125 MHz and chemical data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent. Column chromatography was generally performed on Silicycle silica gel (200-300 mesh). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm coated silica gel plates (HSGF 254) and visualized the course of the reactions using a UV light (254 nm or 365 nm).

Experimental procedures

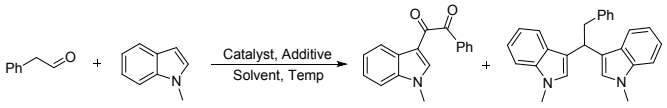
(1) Cu-catalyzed synthesis of C-3 dicarbonyl indoles

Aldehydes **1** (1.0 mmol), indoles **2** (1.5 mmol), CuBr (0.05 mmol, 5%), pyridine (0.2 mmol, 20%) were dissolved in 3 mL 1,4-dioxane and stirred at 90℃ for 10 h in the sealed tube with O_2 balloon protected. To determine the status of the reaction, it was monitored by TLC. After its completion, reaction mixture was cooled to room temperature then quenched with saturated NH_4Cl solution and extracted with ethyl acetate. Organic layer was washed with brine solution and dried over anhydrous Na_2SO_4. Removal of the organic solvent in a vacuum rotavaper followed by flash silica gel column chromatographic purification (hexane/ethyl acetate 50:1) afforded the desired products **3** in good yields (68-94%).

(2) Pd-catalyzed synthesis of bis(indolyl)alkanes

Aldehydes **1** (1.0 mmol), indoles **2** (2.5 mmol), $PdCl_2$ (0.02 mmol, 2%) were dissolved in 3 mL toluene and stirred at 100℃ for 5 h in the sealed tube under Ar conditions. To determine the status of the reaction, it was monitored by TLC. After its completion, reaction mixture was cooled to room temperature then quenched with saturated NH_4Cl solution and extracted with ethyl acetate. Organic layer was washed with brine solution and dried over anhydrous Na_2SO_4. Removal of the organic solvent in a vacuum rotavaper followed by flash silica gel column chromatographic purification (hexane/ethyl acetate 80:1) afforded the desired products **4** in good yields (73-96%).

Optimization of reaction conditions[a]



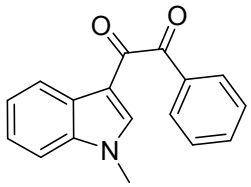
1a 2a 3aa 4aa

Entry	Catalyst	Additive	Solvent	Indole (Eq)	Temp (°C)	Yield[b] **3aa**	Yield[b] **4aa**
1	$Cu(OAc)_2$	-	toluene	2.0	90	22%	6%
2	$Cu(TFA)_2$	-	toluene	2.0	90	17%	10%
3	CuBr	-	toluene	2.0	90	74%	-[c]
4	CuCl	-	toluene	2.0	90	67%	-
5	CuI	-	toluene	2.0	90	59%	-
6	$Pd(OAc)_2$	-	toluene	2.0	90	39%	12%
7	$Pd(TFA)_2$	-	toluene	2.0	90	49%	28%
8	$Pd(dba)_2$	-	toluene	2.0	90	23%	26%
9	$PdCl_2$	-	toluene	2.0	90	-	76%
10	$Pd(PPh_3)_4$	-	toluene	2.0	90	14%	34%
11	CuBr	TFA	toluene	2.0	90	57%	-
12	CuBr	AcOH	toluene	2.0	90	65%	-
13	CuBr	K_2CO_3	toluene	2.0	90	Trace	-
14	CuBr	Cs_2CO_3	toluene	2.0	90	Trace	-
15	CuBr	DBU	toluene	2.0	90	21%	-
16	CuBr	Et_3N	toluene	2.0	90	47%	-
17	CuBr	pyridine	toluene	2.0	90	88%	-
18	CuBr	2,2'-bipyridine	toluene	2.0	90	78%	-
19	CuBr	3-Mepyridine	toluene	2.0	90	82%	-
20	CuBr	DMAP	toluene	2.0	90	68%	-
21	CuBr	pyridine	toluene	2.0	80	81%	-
22	CuBr	pyridine	toluene	2.0	100	87%	-
23	CuBr	pyridine	toluene	2.0	110	85%	-
24	CuBr	pyridine	ACN	2.0	90	88%	-
25	CuBr	pyridine	Dioxane	2.0	90	90%	-
26	CuBr	pyridine	DMF	2.0	90	75%	-
27	CuBr	pyridine	DCE	2.0	90	77%	-
28	CuBr	pyridine	-	2.0	90	65%	-
29	CuBr (2%)	pyridine	Dioxan	2.0	90	78%	-

			e				
30	CuBr (5%)	pyridine	Dioxan e	2.0	90	91%	-
31	CuBr (5%)	pyridine	Dioxan e	1.0	90	84%	-
32	CuBr (5%)	pyridine	Dioxan e	1.5	90	92%	-
33	CuBr (5%)	pyridine	Dioxan e	2.5	90	90%	-
34	$PdCl_2$	K_2CO_3	toluene	2.0	90	-	46%
35	$PdCl_2$	pyridine	toluene	2.0	90	-	15%
36	$PdCl_2$	TFA	toluene	2.0	90	-	57%
37	$PdCl_2$	AcOH	toluene	2.0	90	-	68%
38	$PdCl_2$	-	toluene	2.0	30	-	Trace
39	$PdCl_2$	-	toluene	2.0	80	-	71%
40	$PdCl_2$	-	toluene	2.0	100	-	83%
41	$PdCl_2$	-	toluene	2.0	110	-	81%
42	$PdCl_2$	-	ACN	2.0	100	-	80%
43	$PdCl_2$	-	Dioxan e	2.0	100	-	76%
44	$PdCl_2$	-	DMF	2.0	100	-	69%
46	$PdCl_2$	-	DCE	2.0	100	-	63%
47	$PdCl_2$ (2%)	-	toluene	2.0	100	-	83%
48	$PdCl_2$ (5%)	-	toluene	2.0	100	-	84%
49	$PdCl_2$ (2%)	-	toluene	2.5	100	-	89%
50	$PdCl_2$ (2%)	-	toluene	3.0	100	-	88%
51	$PdCl_2$ (2%)	-	toluene	2.5	100	-	93%[d]
52	$PdCl_2$ (2%)	-	toluene	2.5	100	-	87%[d,e]
52	$PdCl_2$ (2%)	-	toluene	2.5	100	-	93%[d,f]
52	$PdCl_2$ (2%)	-	toluene	2.5	100	-	92%[d,g]

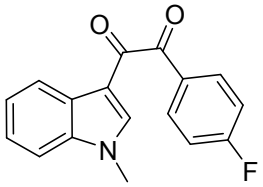
[a] Reaction conditions: 1.0 mmol **1a**, 2.0 mmol **2a**, 10% catalyst, 20% additives solved in 3 mL solvent and stirred at 90°C for 10 h in the sealed tube with O_2 balloon protected, unless otherwise noted. [b] Isolated yield. [c] No target product was detected. [d] Under Ar condition. [e] Reaction time was 2 h. [f] Reaction time was 5 h. [g] Reaction time was 15 h.

Analytical data of products 3 and 4



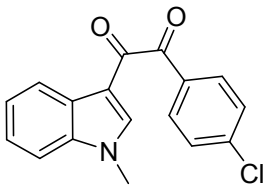
Product 3aa: Light yellow solid, Yield 92%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 – 8.33 (m, 1H), 8.03 (d, J = 7.4 Hz, 2H), 7.74 (s, 1H), 7.55 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 7.32 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.88, 187.69, 139.64, 137.86, 134.41, 133.62, 130.46, 128.87, 126.52, 124.35, 123.64, 122.85, 113.04, 110.11, 33.91; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{17}H_{13}NO_2$ 286.0838 found 286.0832.



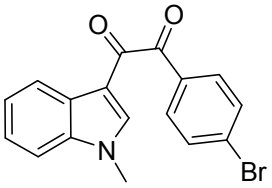
Product 3ba: Light yellow solid, Yield 94%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 – 8.40 (m, 1H), 8.18 – 8.11 (m, 2H), 7.83 (d, J = 5.1 Hz, 1H), 7.39 (dd, J = 5.4, 2.6 Hz, 3H), 7.16 (t, J = 8.7 Hz, 2H), 3.84 (d, J = 10.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.11, 187.16, 167.90, 165.34, 139.78, 137.88, 133.34, 133.25, 130.12, 130.09, 126.55, 124.44, 123.73, 122.80, 116.25, 116.04, 112.92, 110.19, 33.95; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{17}H_{12}FNO_2$ 304.0744 found 304.0747.



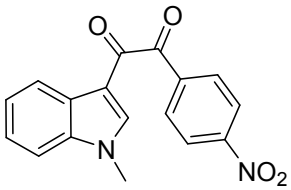
Product 3ca: Light yellow solid, Yield 93%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 – 8.39 (m, 1H), 8.05 (d, J = 8.6 Hz, 2H), 7.82 (s, 1H), 7.46 (d, J = 8.6 Hz, 2H), 7.39 (dd, J = 6.2, 3.4 Hz, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.36, 186.81, 140.95, 139.78, 137.84, 131.99, 131.82, 129.20, 126.50, 124.43, 123.72, 122.77, 112.84, 110.16, 33.92; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{17}H_{12}ClNO_2$ 320.0449 found 320.0443.



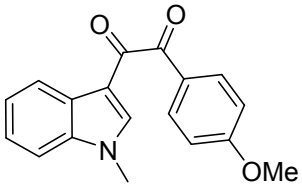
Product 3da: Light brown solid, Yield 88%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 – 8.37 (m, 1H), 7.97 (d, J = 8.6 Hz, 2H), 7.82 (s, 1H), 7.63 (d, J = 8.6 Hz, 2H), 7.39 (dd, J = 6.4, 3.7 Hz, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.55, 186.73, 139.79, 137.84, 132.39, 132.19, 131.86, 129.83, 126.49, 124.43, 123.72, 122.76, 112.83, 110.16, 33.92; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{17}H_{12}BrNO_2$ 363.9944 found 363.9939.



Product 3ea: Light brown solid, Yield 90%;

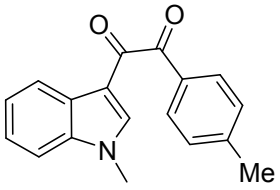
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 – 8.43 (m, 1H), 8.30 (td, J = 9.0, 2.1 Hz, 4H), 7.91 (s, 1H), 7.42 (d, J = 2.8 Hz, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.36, 185.23, 150.92, 140.07, 138.41, 137.92, 131.54, 126.59, 124.70, 124.01, 123.89, 122.85, 112.68, 110.29, 34.06; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{17}H_{12}N_2O_4$ 331.0689 found 331.0684.



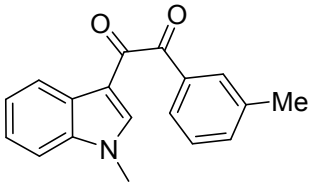
Product 3fa: Light yellow solid, Yield 87%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 – 8.42 (m, 1H), 8.12 – 8.06 (m, 2H), 7.80 (s, 1H), 7.40 – 7.35 (m, 3H), 6.98 – 6.93 (m, 2H), 3.88 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.62, 188.26, 164.69,

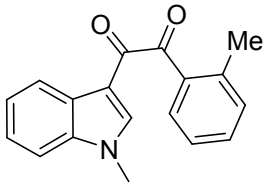
139.61, 137.82, 132.89, 126.59, 126.54, 124.23, 123.52, 122.80, 114.19, 113.12, 110.07, 55.71, 33.86; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{18}H_{15}NO_3$ 316.0944 found 316.0947.



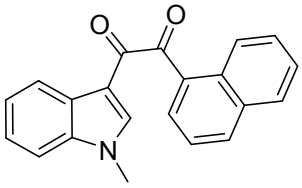
Product 3ga: Light yellow solid, Yield 85%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 – 8.30 (m, 1H), 7.89 (d, J = 8.2 Hz, 2H), 7.67 (s, 1H), 7.31 – 7.24 (m, 3H), 7.17 (t, J = 6.5 Hz, 2H), 3.69 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.64, 188.05, 145.54, 139.57, 137.78, 131.07, 130.50, 129.56, 126.44, 124.23, 123.49, 122.71, 112.98, 110.08, 33.81, 21.96; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{18}H_{15}NO_2$ 300.0995 found 300.0996.



Product 3ha: Light yellow solid, Yield 86%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, J = 5.5, 2.8 Hz, 1H), 7.97 – 7.83 (m, 2H), 7.83 – 7.71 (m, 1H), 7.45 – 7.35 (m, 5H), 3.85 – 3.79 (m, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.24, 188.03, 139.64, 138.78, 137.88, 135.30, 133.62, 130.84, 128.82, 127.68, 126.49, 124.34, 123.61, 122.81, 113.05, 110.16, 33.91, 21.45; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{18}H_{15}NO_2$ 300.0995 found 300.0995.

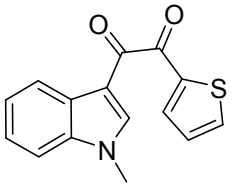


Product 3ia: Light yellow solid, Yield 84%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.28 (m, 1H), 7.76 (s, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.39 – 7.14 (m, 6H), 3.76 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.56, 188.31, 140.95, 139.40, 137.80, 133.19, 133.09, 132.80, 132.26, 126.62, 125.88, 124.28, 123.55, 122.81, 33.89, 21.74; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{18}H_{15}NO_2$ 300.0995 found 300.0993.

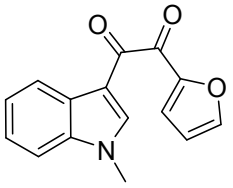


Product 3ja: Light yellow solid, Yield 82%;

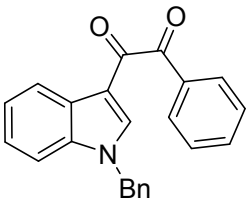
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, J = 8.6 Hz, 1H), 8.54 – 8.45 (m, 1H), 8.08 (d, J = 7.3 Hz, 2H), 7.93 (d, J = 8.1 Hz, 1H), 7.88 (s, 1H), 7.73 – 7.67 (m, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.43 – 7.38 (m, 3H), 3.84 (d, *J* = 8.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.72, 188.44, 139.48, 137.83, 135.13, 134.40, 134.20, 131.48, 130.01, 128.97, 128.87, 126.90, 126.64, 126.07, 124.59, 124.34, 123.63, 122.89, 113.35, 110.11, 33.94; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{21}H_{15}NO_2$ 336.0995 found 336.0993.



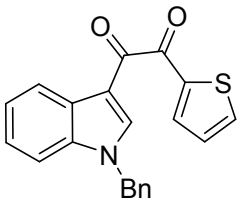
Product 3ka: Light yellow solid, Yield 76%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 – 8.47 (m, 1H), 8.16 (s, 1H), 8.11 (dd, J = 3.8, 1.1 Hz, 1H), 7.79 (dd, J = 4.9, 1.1 Hz, 1H), 7.40 – 7.36 (m, 3H), 7.18 (dd, J = 4.8, 3.9 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.70, 184.66, 140.44, 139.51, 137.63, 136.83, 136.79, 128.49, 127.09, 124.27, 123.64, 122.87, 112.22, 110.10, 33.92; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{15}H_{11}NO_2S$ 292.0403 found 292.0402.



Product 3la: Light yellow solid, Yield 81%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 – 8.44 (m, 1H), 8.14 (s, 1H), 7.75 (d, J = 0.8 Hz, 1H), 7.66 (d, J = 3.6 Hz, 1H), 7.39 – 7.36 (m, 3H), 6.61 (dd, J = 3.6, 1.6 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.19, 179.95, 150.35, 148.78, 140.36, 137.60, 127.01, 124.26, 124.15, 123.63, 122.79, 112.93, 112.25, 110.10, 33.92; HRMS (TOF) m/z [M + H]$^+$ Calcd for $C_{15}H_{11}NO_3$ 254.0812 found 254.0813.

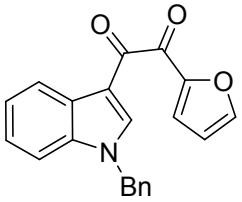


Product 3ab: Light yellow solid, Yield 86%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 7.8 Hz, 1H), 8.02 – 7.97 (m, 2H), 7.80 (s, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.7 Hz, 2H), 7.28 – 7.17 (m, 6H), 7.06 – 7.00 (m, 2H), 5.20 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.61, 187.73, 138.99, 137.32, 135.23, 134.38, 133.52, 130.44, 129.16, 128.82, 128.43, 127.09, 126.74, 124.41, 123.65, 122.84, 113.41, 110.77, 51.23; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{23}H_{17}NO_2$ 362.1151 found 362.1134.



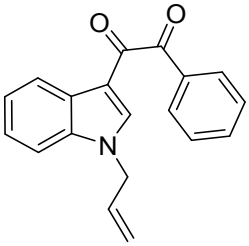
Product 3ac: Light yellow solid, Yield 73%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 7.9 Hz, 1H), 8.19 (s, 1H), 8.04 (dd, J = 3.9, 1.1 Hz, 1H), 7.71 (dd, J = 4.9, 1.1 Hz, 1H), 7.31 – 7.21 (m, 6H), 7.10 (dd, J = 8.4, 3.7 Hz, 3H), 5.28 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.75, 184.45, 139.85, 139.45, 137.12, 136.88, 136.84, 135.36, 129.22, 128.49, 128.48, 127.36, 127.14, 124.38, 123.71, 122.98, 112.69, 110.76, 51.33; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{21}H_{15}NO_2S$ 368.0716 found 368.0712.



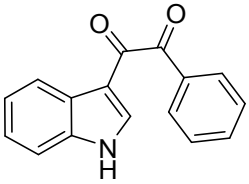
Product 3ad: Light yellow solid, Yield 77%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 7.8 Hz, 1H), 8.16 (s, 1H), 7.65 (d, J = 1.1 Hz, 1H), 7.59 (dd, J = 3.6, 0.6 Hz, 1H), 7.30 – 7.20 (m, 6H), 7.08 (dd, J = 7.5, 1.8 Hz, 2H), 6.52 (dd, J = 3.6, 1.7 Hz, 1H), 5.26 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.32, 179.73, 150.32, 148.79, 139.74, 137.09, 135.28, 129.20, 128.47, 127.27, 127.20, 124.36, 124.21, 123.69, 122.89, 112.93, 112.70, 110.75, 51.29; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{21}H_{15}NO_3$ 352.0944 found 352.0957.



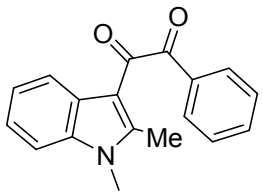
Product 3ae: Light yellow solid, Yield 68%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.34 (m, 1H), 8.04 – 7.97 (m, 2H), 7.74 (s, 1H), 7.54 – 7.49 (m, 1H), 7.41 – 7.36 (m, 2H), 7.31 – 7.23 (m, 3H), 5.87 (ddt, J = 16.9, 10.4, 5.6 Hz, 1H), 5.19 (dd, J = 10.3, 0.8 Hz, 1H), 5.09 (dd, J = 17.1, 0.8 Hz, 1H), 4.63 (dt, J = 5.6, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.73, 187.76, 138.63, 137.20, 134.38, 133.54, 131.52, 130.42, 128.83, 126.63, 124.29, 123.61, 122.83, 119.37, 113.25, 110.59, 49.81; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{19}H_{15}NO_2$ 312.0995 found 312.0980.



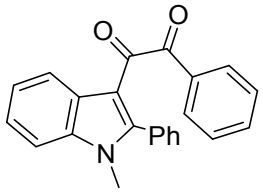
Product 3af: White solid, Yield 89%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.48 (d, J = 6.8 Hz, 1H), 8.10 (d, J = 7.3 Hz, 2H), 7.94 (d, J = 3.1 Hz, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.41 – 7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.49, 135.62, 134.51, 130.49, 128.93, 124.75, 123.70, 122.73, 111.75; HRMS (TOF) m/z [M + H]$^+$ Calcd for $C_{16}H_{11}NO_2$ 250.0863 found 250.0866.



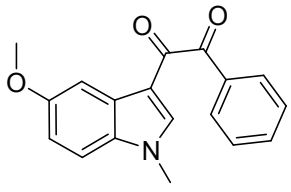
Product 3ag: Light yellow solid, Yield 84%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.2 Hz, 2H), 7.80 (d, J = 7.7 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.7 Hz, 2H), 7.22 – 7.09 (m, 3H), 3.59 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.53, 190.14, 147.68, 137.15, 134.50, 133.47, 130.15, 129.07, 126.23, 123.16, 123.14, 120.93, 110.70, 109.72, 29.92, 12.86; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{18}H_{15}NO_2$ 300.0993 found 300.0995.



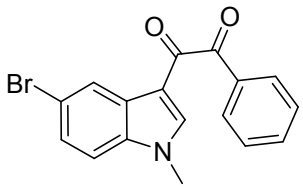
Product 3ah: Light yellow solid, Yield 75%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 – 8.41 (m, 1H), 7.49 (dd, J = 8.2, 1.1 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 7.31 (dd, J = 6.8, 3.1 Hz, 3H), 7.21 – 7.15 (m, 3H), 7.05 – 6.95 (m, 4H), 3.40 (d, J = 0.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.88, 191.16, 149.90, 137.25, 133.69, 133.60, 131.10, 129.80, 129.37, 129.06, 128.30, 128.02, 126.55, 124.22, 123.73, 122.68, 112.59, 110.07, 31.05; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{23}H_{17}NO_2$ 362.1151 found 362.1132.



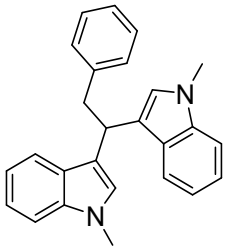
Product 3ai: Light yellow solid, Yield 87%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 2H), 7.88 (d, J = 2.4 Hz, 1H), 7.64 (s, 1H), 7.56 – 7.51 (m, 1H), 7.40 (t, J = 7.7 Hz, 2H), 7.19 – 7.15 (m, 1H), 6.91 (dd, J = 8.9, 2.5 Hz, 1H), 3.85 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.90, 187.59, 157.24, 139.49, 134.36, 133.62, 132.69, 130.40, 128.83, 127.41, 114.66, 112.67, 110.99, 104.05, 55.95, 34.06; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{18}H_{15}NO_3$ 316.0944 found 316.0947.



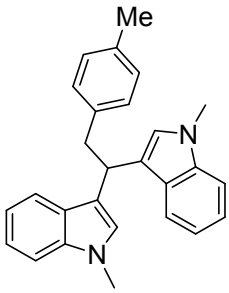
Product 3aj: Light yellow solid, Yield 73%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 1.8 Hz, 1H), 8.04 – 8.00 (m, 2H), 7.74 (s, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 – 7.39 (m, 3H), 7.19 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.45, 140.16, 136.53, 134.57, 133.43, 130.50, 128.92, 128.11, 127.39, 125.50, 117.45, 112.50, 111.55, 34.10; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{17}H_{12}BrNO_2$ 363.9944 found 363.9951.



Product 4aa: Light yellow solid, Yield 93%;

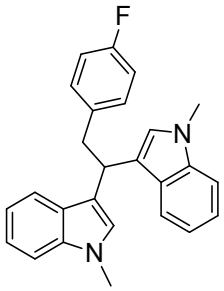
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.18 (m, 7H), 7.12 (t, *J* = 7.3 Hz, 2H), 6.88 (s, 2H), 4.89 (t, *J* = 7.4 Hz, 1H), 3.73 (s, 6H), 3.62 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.46, 137.36, 129.01, 127.98, 127.46, 126.74, 125.68, 121.30, 119.79, 118.51, 118.27, 109.13, 42.30, 36.08, 32.61; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{26}H_{24}N_2$ 387.1832 found 387.1844.



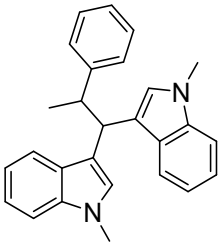
Product 4ba: Light yellow solid, Yield 89%;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.29 (dt, *J* = 15.0, 7.9 Hz, 4H), 7.15 – 7.01 (m, 6H), 6.87 (s, 2H), 4.86 (t, *J* = 7.3 Hz, 1H), 3.74 (s, 6H), 3.57 (d, *J* = 7.3 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.38, 137.38, 135.02, 128.85, 128.69, 127.49, 126.76, 121.28, 119.83, 118.49,

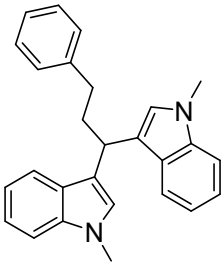
118.38, 109.12, 77.48, 77.06, 76.63, 41.81, 36.06, 32.63, 21.02; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{27}H_{26}N_2$ 401.1988 found 401.1996.



Product 4ca: Yellow solid, Yield 95%;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.22 (m, 4H), 7.08 (dd, *J* = 13.0, 6.2 Hz, 4H), 6.95 – 6.77 (m, 4H), 4.78 (t, *J* = 7.4 Hz, 1H), 3.73 (s, 6H), 3.55 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.90, 137.38, 137.09, 137.05, 130.38, 130.28, 127.41, 126.73, 121.39, 119.74, 118.60, 118.01, 114.80, 114.52, 109.19, 41.46, 36.44, 32.63; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{26}H_{23}FN_2$ 405.1737 found 405.1741.

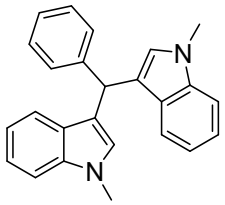


Product 4da: White solid, Yield 90%;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.33 – 7.10 (m, 10H), 7.06 – 6.91 (m, 2H), 6.81 (s, 1H), 4.86 (d, *J* = 9.0 Hz, 1H), 3.86 – 3.78 (m, 1H), 3.69 (d, *J* = 27.3 Hz, 6H), 1.37 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.97, 137.03, 136.81, 127.90, 127.70, 127.22, 126.89, 125.65, 121.20, 121.02, 119.71, 118.53, 118.27, 117.81, 117.76, 109.09, 108.80, 44.97, 40.34, 32.67, 32.57, 21.59; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{27}H_{26}N_2$ 401.1988 found 401.1983.

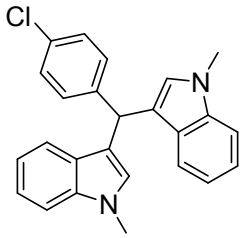


Product 4ea: White solid, Yield 94%;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 4H), 7.29 (dd, *J* = 12.3, 6.8 Hz, 5H), 7.14 (t, *J* = 7.4 Hz, 2H), 6.97 (s, 2H), 4.61 (t, *J* = 7.2 Hz, 1H), 3.80 (s, 6H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.65 (dd, *J* = 15.2, 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.93, 137.55, 128.75, 128.43,

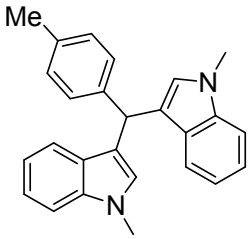
127.73, 126.48, 125.82, 121.53, 119.92, 119.03, 118.70, 109.30, 38.12, 34.74, 33.59, 32.81; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{27}H_{26}N_2$ 401.1988 found 401.1985.



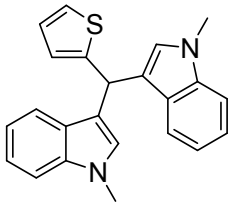
Product 4fa: White solid, Yield 87%;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 4H), 7.34 (t, *J* = 7.0 Hz, 4H), 7.27 (t, *J* = 7.5 Hz, 3H), 7.07 (t, *J* = 7.4 Hz, 2H), 6.61 (s, 2H), 5.96 (s, 1H), 3.73 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.51, 137.47, 128.73, 128.27, 128.21, 127.53, 126.04, 121.45, 120.07, 118.68, 118.33, 109.07, 40.16, 32.65; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{25}H_{22}N_2$ 373.1675 found 373.1682.



Product 4ga: Yellow solid, Yield 89%;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.9 Hz, 2H), 7.39 – 7.27 (m, 8H), 7.10 (t, *J* = 7.4 Hz, 2H), 6.61 (s, 2H), 5.95 (s, 1H), 3.76 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.27, 137.68, 131.89, 130.26, 128.53, 128.43, 127.53, 121.79, 120.13, 119.00, 117.99, 109.34, 39.76, 32.84; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{25}H_{21}ClN_2$ 407.1285 found 407.1287.

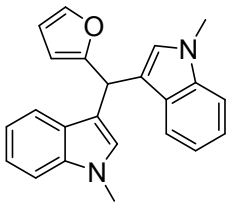


Product 4ha: Light yellow solid, Yield 83%;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.9 Hz, 2H), 7.39 – 7.27 (m, 6H), 7.18 (d, *J* = 7.7 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 2H), 6.64 (s, 2H), 5.95 (s, 1H), 3.75 (s, 6H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.68, 137.66, 135.54, 129.08, 128.75, 128.38, 127.75, 121.58, 120.28, 118.81, 118.72, 109.21, 39.91, 32.80, 21.27; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{26}H_{24}N_2$ 387.1832 found 387.1851.



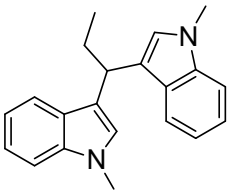
Product 4ia: Light brown solid, Yield 86%;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.23 (d, *J* = 3.6 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 2H), 7.00 (s, 2H), 6.81 (s, 2H), 6.25 (s, 1H), 3.77 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.43, 137.56, 127.98, 127.41, 126.57, 125.19, 123.65, 121.72, 120.07, 119.01, 118.50, 109.35, 35.44, 32.87; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{23}H_{20}N_2S$ 379.1239 found 379.1228.



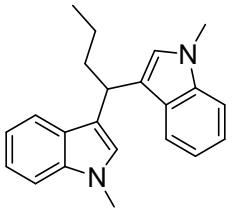
Product 4ja: Light brown solid, Yield 84%;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 2H), 7.45 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 2H), 6.84 (s, 2H), 6.39 (s, 1H), 6.16 (d, *J* = 2.5 Hz, 1H), 6.03 (s, 1H), 3.77 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.66, 141.34, 137.51, 127.85, 127.42, 121.68, 119.97, 119.01, 115.97, 110.30, 109.35, 106.63, 34.18, 32.84; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{23}H_{20}N_2O$ 363.1468 found 363.1475.



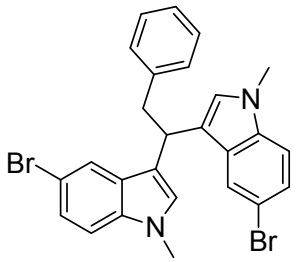
Product 4ka: Light yellow oil, Yield 89%;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.26 (m, 4H), 7.14 (t, *J* = 7.4 Hz, 2H), 6.94 (s, 2H), 4.48 (t, *J* = 7.3 Hz, 1H), 3.79 (s, 6H), 2.36 – 2.32 (m, 2H), 1.12 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.52, 127.89, 126.43, 121.45, 119.99, 119.30, 118.59, 109.26, 36.00, 32.78, 29.45, 13.36; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{21}H_{22}N_2$ 325.1675 found 325.1664.



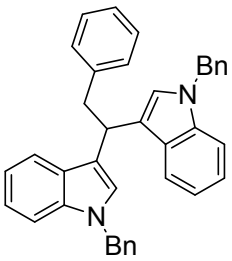
Product 4la: Light yellow oil, Yield 91%;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.38 – 7.22 (m, 4H), 7.12 (t, *J* = 7.3 Hz, 2H), 6.92 (s, 2H), 4.58 (t, *J* = 7.4 Hz, 1H), 3.77 (s, 6H), 2.27 (dd, *J* = 15.2, 7.5 Hz, 2H), 1.52 (dd, *J* = 15.2, 7.6 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.83, 127.18, 125.72, 120.79, 119.30, 118.86, 117.94, 108.62, 38.26, 33.08, 32.13, 21.04, 13.78; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{22}H_{24}N_2$ 339.1832 found 339.1856.



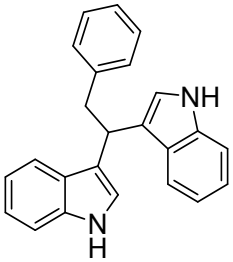
Product 4ab: Brown solid, Yield 90%;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (s, 2H), 7.30 (d, *J* = 9.0 Hz, 2H), 7.23 – 7.11 (m, 7H), 6.84 (s, 2H), 4.70 (t, *J* = 7.4 Hz, 1H), 3.72 (s, 6H), 3.50 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.71, 135.99, 128.95, 128.88, 128.05, 127.77, 125.97, 124.25, 122.10, 117.48, 112.10, 110.69, 42.09, 35.89, 32.81; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{26}H_{22}Br_2N_2$ 543.0042 found 543.0019.



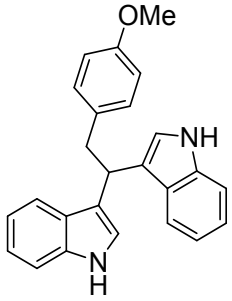
Product 4ad: Light yellow solid, Yield 84%;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8 Hz, 2H), 7.35 – 7.23 (m, 8H), 7.23 – 7.07 (m, 8H), 7.03 (dd, *J* = 11.1, 6.4 Hz, 7H), 5.29 (s, 4H), 4.86 (t, *J* = 7.5 Hz, 1H), 3.62 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.30, 137.97, 137.03, 129.14, 128.67, 127.92, 127.73, 127.38, 126.53, 126.32, 125.67, 121.52, 120.04, 118.78, 118.46, 109.67, 49.79, 41.75, 36.7; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{38}H_{32}N_2$ 539.2458 found 539.2466.

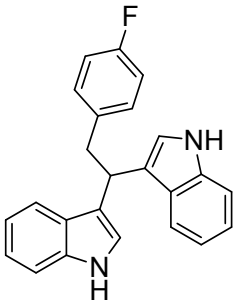


Product 4ae: Light brown solid, Yield 95%;

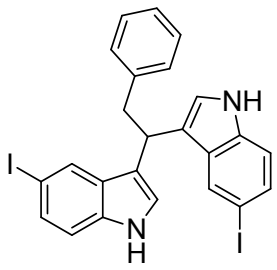
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 2H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.13 (m, 7H), 7.06 (t, *J* = 7.4 Hz, 2H), 6.90 (s, 2H), 4.83 (t, *J* = 7.4 Hz, 1H), 3.58 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.48, 136.78, 129.17, 128.14, 127.19, 125.89, 122.16, 121.93, 119.85, 119.62, 119.25, 111.27, 41.93, 36.43; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{24}H_{20}N_2$ 359.1519 found 359.1533.



Product 4af: Brown solid, Yield 91%;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (s, 2H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.07 (dd, *J* = 14.1, 7.7 Hz, 4H), 6.91 (s, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 4.79 (t, *J* = 7.3 Hz, 1H), 3.76 (s, 3H), 3.53 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.71, 136.62, 133.50, 129.90, 127.05, 123.55, 122.03, 121.74, 119.72, 119.48, 119.06, 113.45, 111.12, 55.20, 40.83, 36.52; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{25}H_{22}N_2O$ 389.1624 found 389.1645.

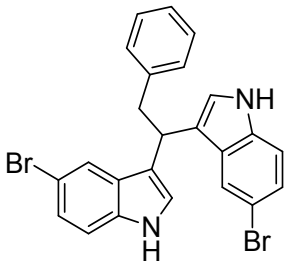


Product 4ag: Light yellow solid, Yield 96%;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (s, 2H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.11 – 6.98 (m, 4H), 6.86 (dd, *J* = 17.0, 8.2 Hz, 4H), 4.75 (t, *J* = 7.4 Hz, 1H), 3.53 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.90, 136.94, 136.90, 136.65, 130.39, 130.29, 126.98, 121.98, 121.87, 119.66, 119.25, 119.18, 114.81, 114.53, 111.17, 40.95, 36.63; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{24}H_{19}FN_2$ 377.1424 found 377.1418.



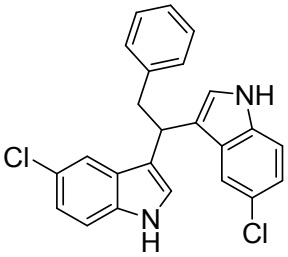
Product 4ah: Light yellow solid, Yield 94%;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.78 (s, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.21 – 7.02 (m, 7H), 6.88 (s, 2H), 4.65 (t, *J* = 7.4 Hz, 1H), 3.46 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.62, 135.67, 130.27, 129.44, 129.01, 128.44, 128.11, 126.10, 122.73, 118.48, 113.19, 82.83, 41.65, 36.13; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{24}H_{18}I_2N_2$ 610.9452 found 610.9450.



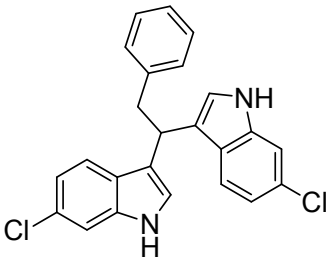
Product 4ai: White solid, Yield 92%;

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.59 (s, 2H), 7.24 – 7.14 (m, 7H), 7.06 (d, *J* = 6.9 Hz, 2H), 6.93 (s, 2H), 4.66 (t, *J* = 7.4 Hz, 1H), 3.48 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.81, 135.43, 129.17, 128.77, 128.28, 126.22, 124.98, 123.30, 122.31, 118.88, 112.82, 112.70, 41.69, 36.43; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{24}H_{18}Br_2N_2$ 514.9729 found 514.9742.



Product 4aj: White solid, Yield 83%;

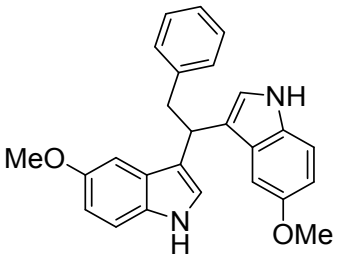
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.43 (s, 2H), 7.23 – 7.14 (m, 5H), 7.08 (dd, *J* = 18.2, 7.7 Hz, 4H), 6.96 (s, 2H), 4.66 (t, *J* = 7.4 Hz, 1H), 3.49 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.86, 135.18, 129.18, 128.27, 128.12, 126.19, 125.08, 123.46, 122.43, 119.25, 118.96, 112.36, 41.64, 36.50; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{24}H_{18}Cl_2N_2$ 427.0739 found 427.0745.



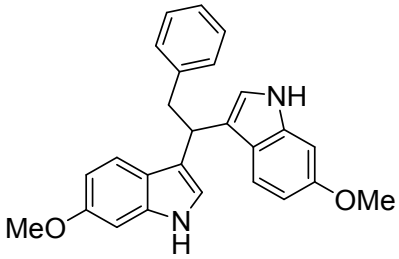
Product 4ak: Light yellow solid, Yield 88%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.32 (dd, *J* = 11.8, 5.0 Hz, 4H), 7.19 – 7.11 (m, 3H), 7.06 – 7.01 (m, 2H), 6.95 (dd, *J* = 8.5, 1.7 Hz, 4H), 4.68 (t, *J* = 7.5 Hz, 1H), 3.48 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR

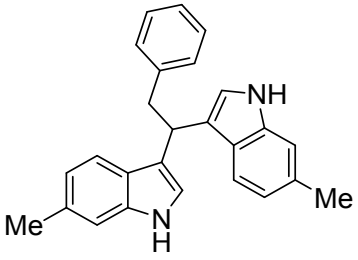
(100 MHz, $CDCl_3$) δ 140.84, 136.99, 129.10, 128.19, 127.94, 126.06, 125.61, 122.53, 120.56, 120.05, 119.49, 111.17, 41.74, 36.39; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{24}H_{18}Cl_2N_2$ 427.0739 found 427.0735.



Product 4an: Light brown solid, Yield 96%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 2H), 7.21 – 7.11 (m, 7H), 6.99 (d, *J* = 2.1 Hz, 2H), 6.89 (d, *J* = 2.0 Hz, 2H), 6.83 (dd, *J* = 8.8, 2.3 Hz, 2H), 4.70 (t, *J* = 7.4 Hz, 1H), 3.77 (s, 6H), 3.53 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.61, 141.44, 131.88, 129.18, 128.11, 127.50, 125.88, 122.95, 119.18, 111.83, 111.66, 101.98, 56.00, 41.74, 36.34; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{26}H_{24}N_2O_2$ 419.1730 found 419.1735.

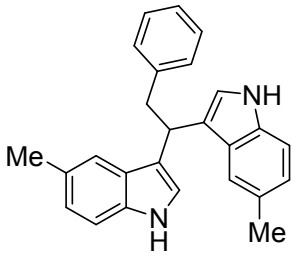


Product 4ao: Light brown solid, Yield 78%;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.19 – 7.08 (m, 5H), 6.74 (dd, *J* = 43.8, 7.1 Hz, 6H), 4.69 (t, *J* = 7.1 Hz, 1H), 3.80 (s, 6H), 3.50 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.44, 141.55, 137.53, 129.20, 128.12, 125.87, 121.72, 120.90, 120.44, 119.65, 109.17, 94.93, 55.82, 42.02, 36.65; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{26}H_{24}N_2O_2$ 419.1730 found 419.1738.



Product 4ap: Light yellow solid, Yield 73%;
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.09 (m, 7H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.82 (s, 2H), 4.77 (t, *J* = 7.3 Hz, 1H), 3.55 (d, *J* = 7.3 Hz, 2H), 2.46 (s, 6H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 141.65, 137.29, 131.65, 129.20, 128.13, 125.85, 125.12, 121.55, 121.02, 119.57, 119.56, 111.26, 41.93, 36.53, 21.84; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{26}H_{24}N_2$ 387.1832 found 387.1851.

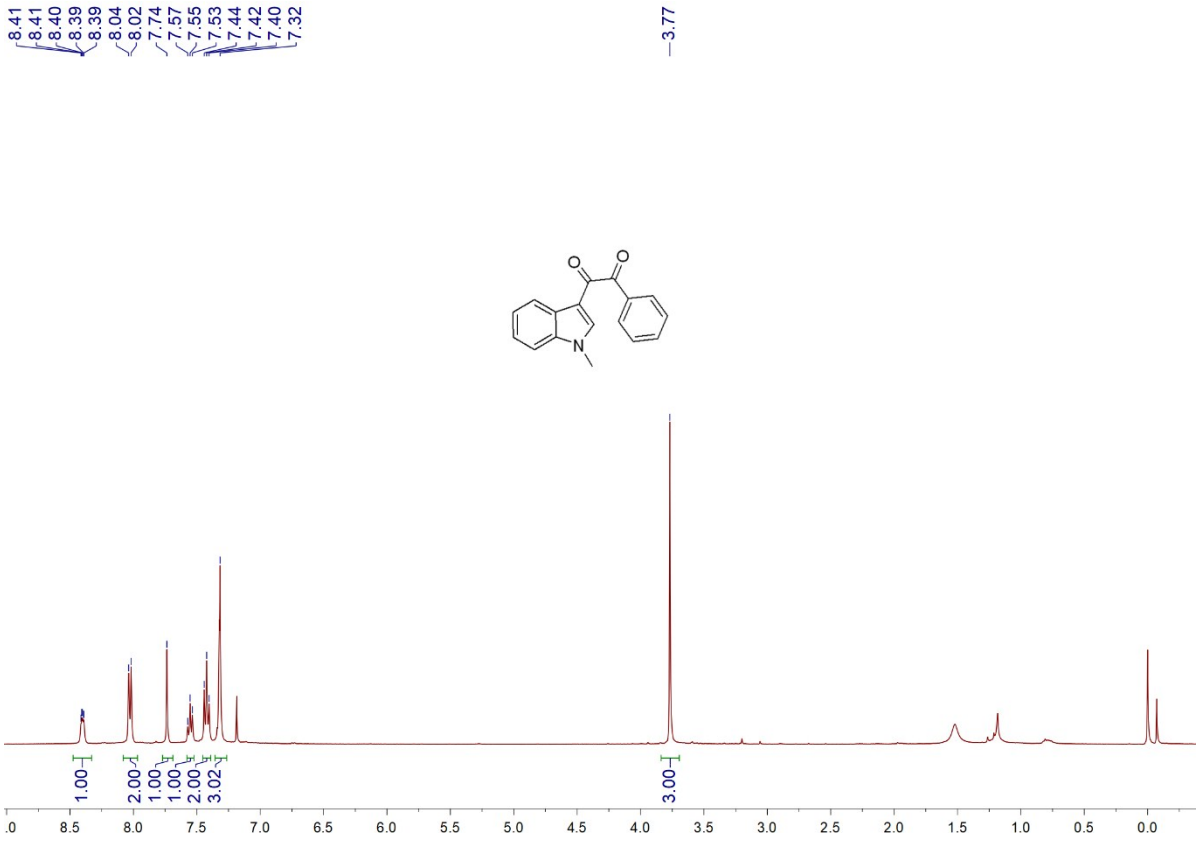


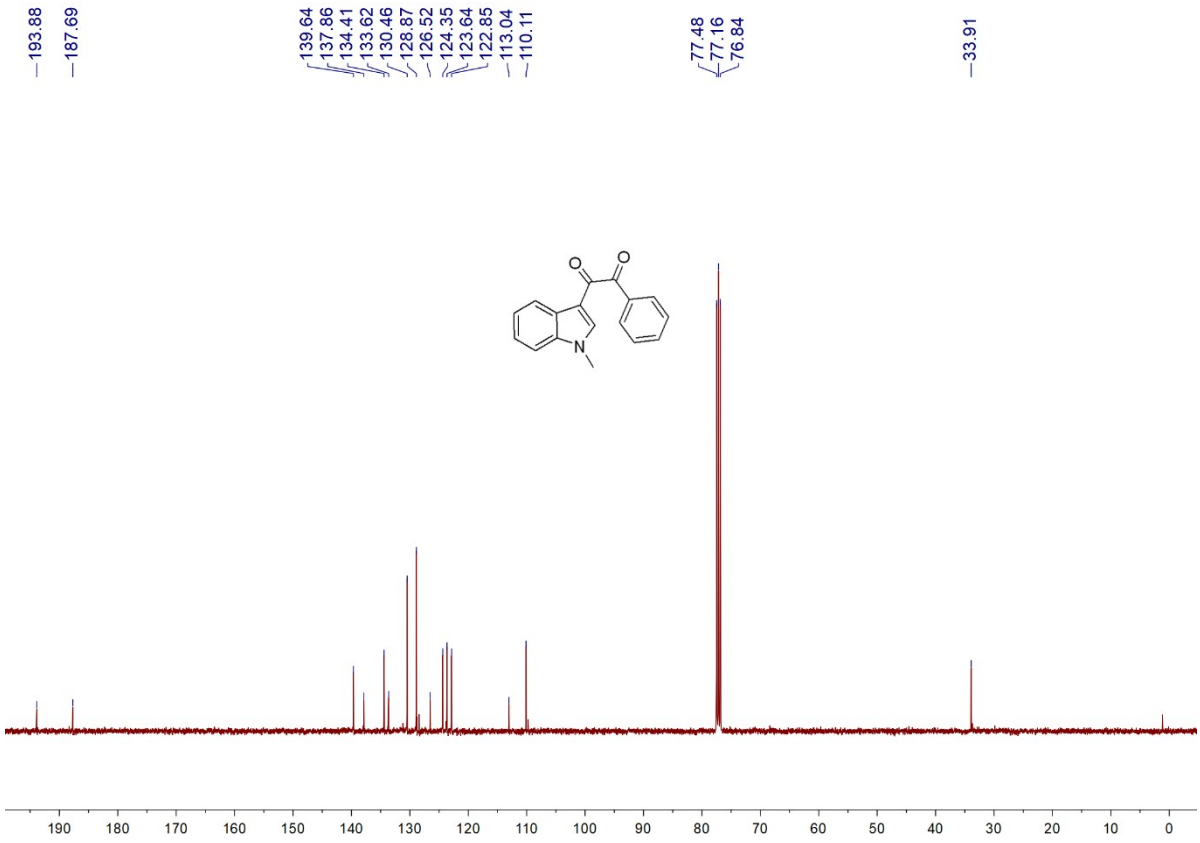
Product 4aq: Light yellow solid, Yield 92%;

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.43 (s, 2H), 7.22 (t, *J* = 5.3 Hz, 7H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 1.8 Hz, 2H), 4.84 (t, *J* = 7.3 Hz, 1H), 3.58 (d, *J* = 7.4 Hz, 2H), 2.45 (d, *J* = 14.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.49, 134.98, 129.05, 128.20, 127.97, 127.28, 125.69, 123.38, 122.29, 119.34, 119.02, 110.77, 41.80, 35.97, 21.56; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{26}H_{24}N_2$ 387.1832 found 387.1845.

^{1}H NMR and ^{13}C NMR spectra of the products 3 and 4

Product 3aa

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123.64
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33.91
O
O
N
190
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160
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120
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100
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50
40
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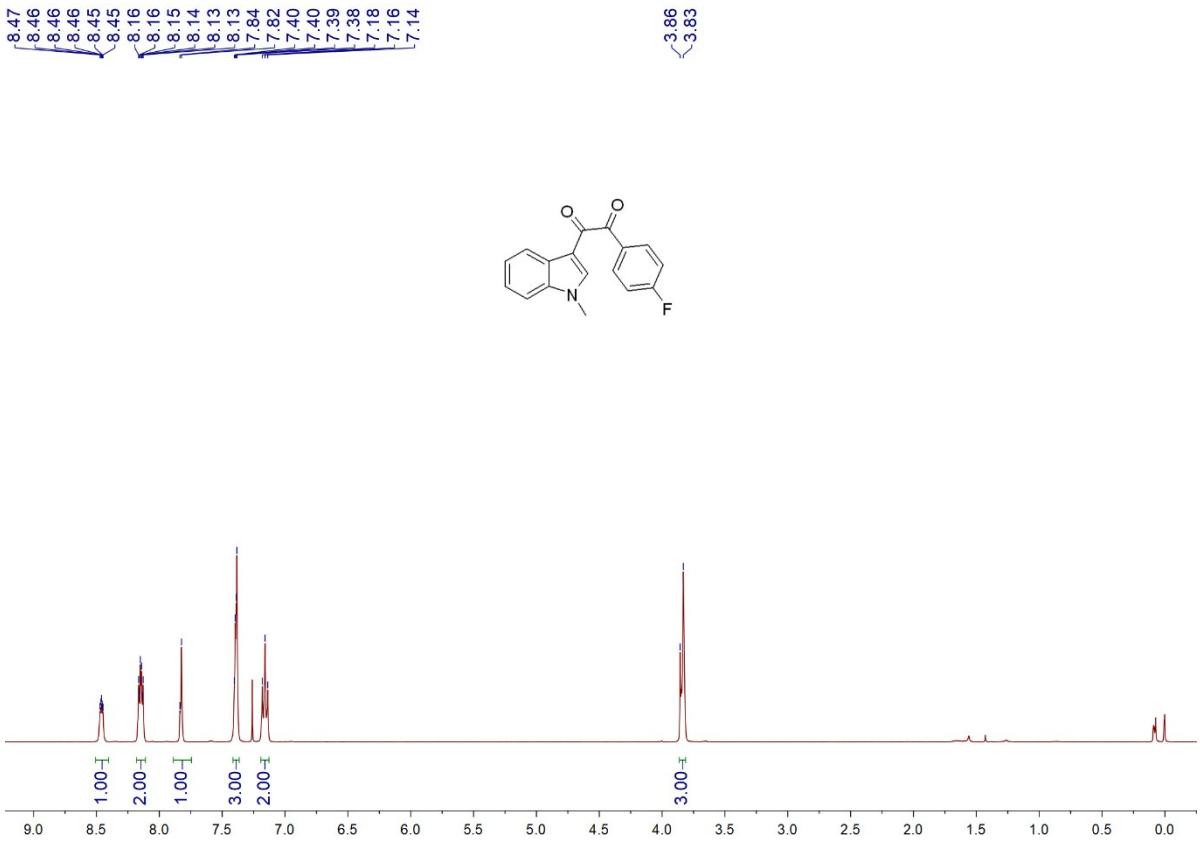
20
10
0

Product 3ba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7.14
3.86
3.83
O
O
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F
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3.00
2.00
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8.5
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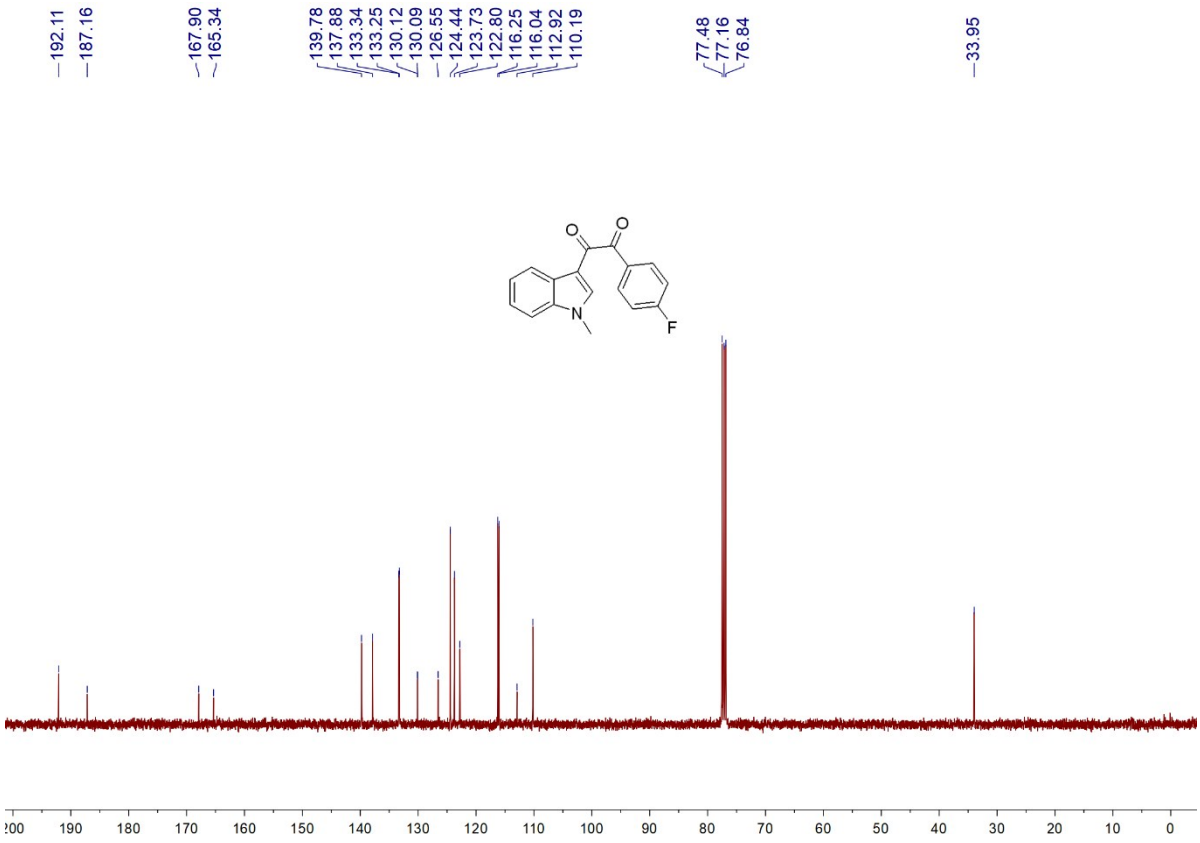
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133.25
130.12
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124.44
123.73
122.80
116.25
116.04
112.92
110.19
77.48
77.16
76.84
33.95
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F
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100
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60
50
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10
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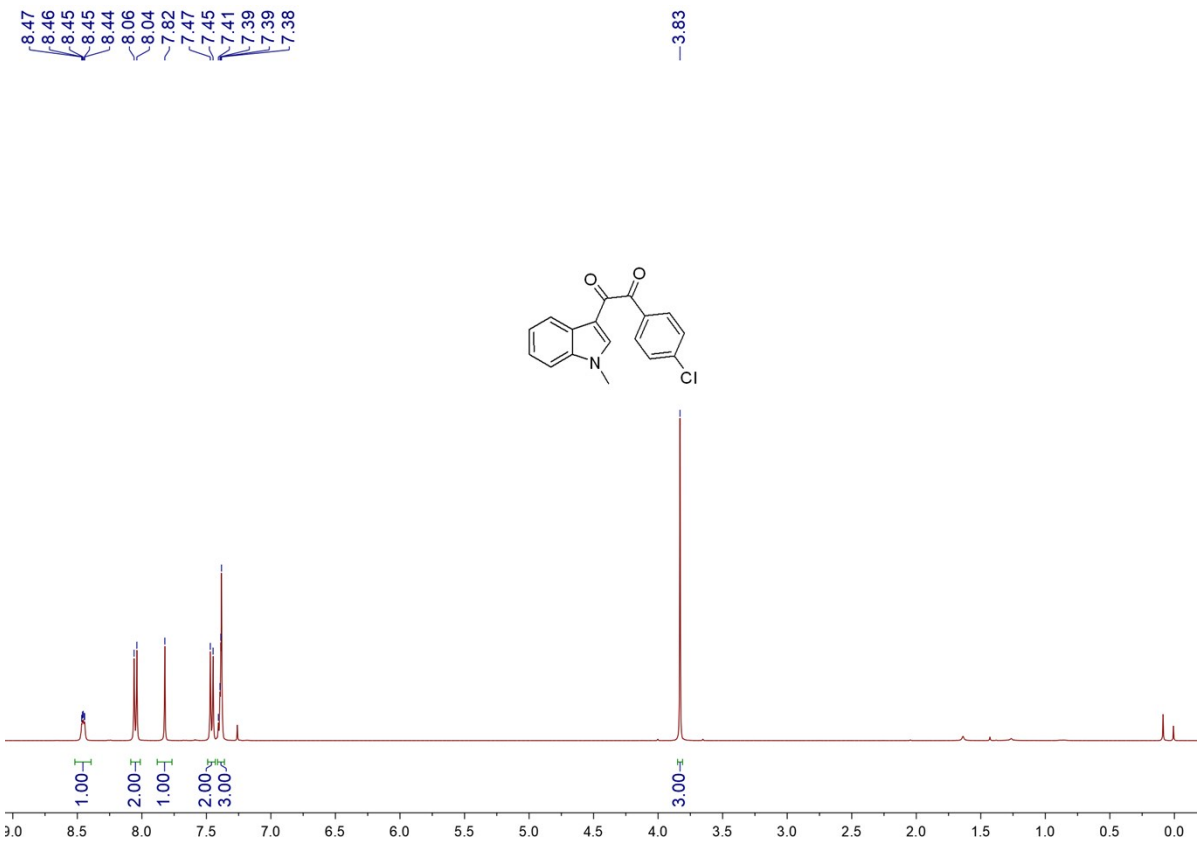
Product 3ca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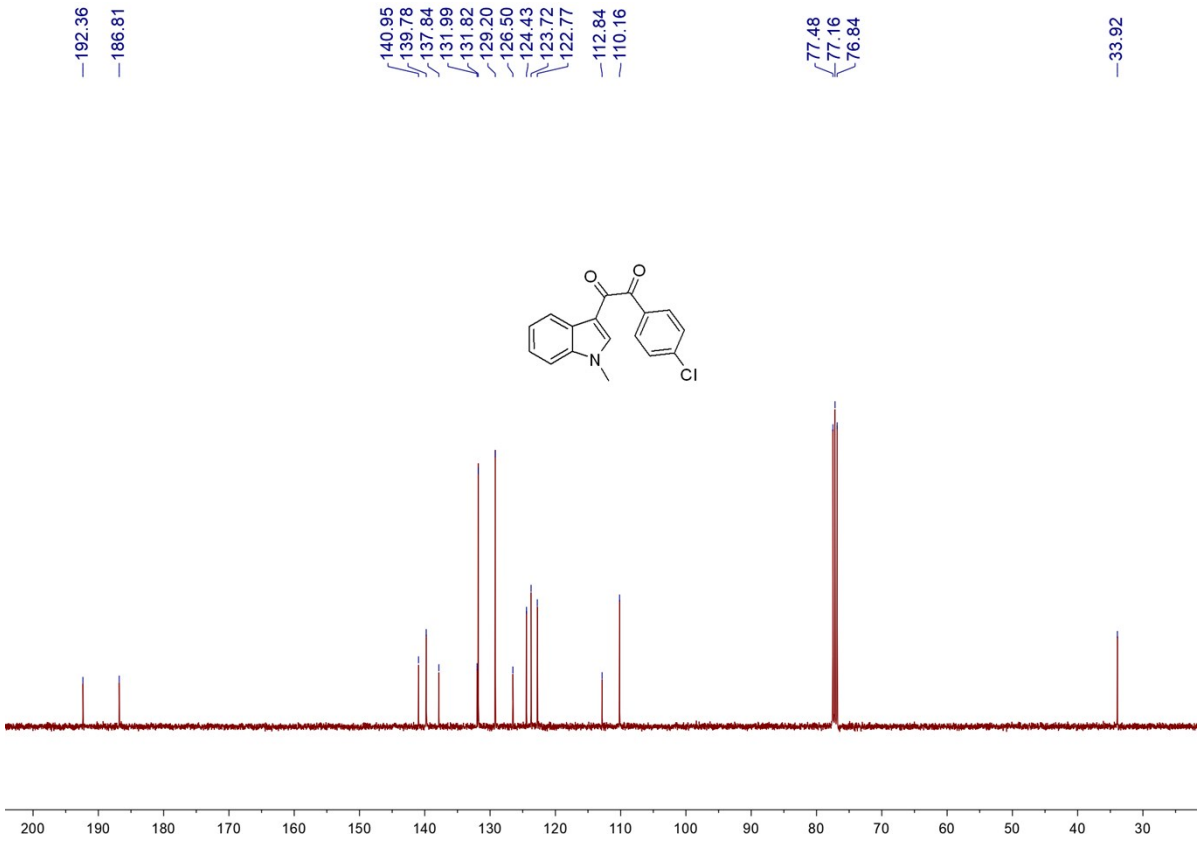
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90
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70
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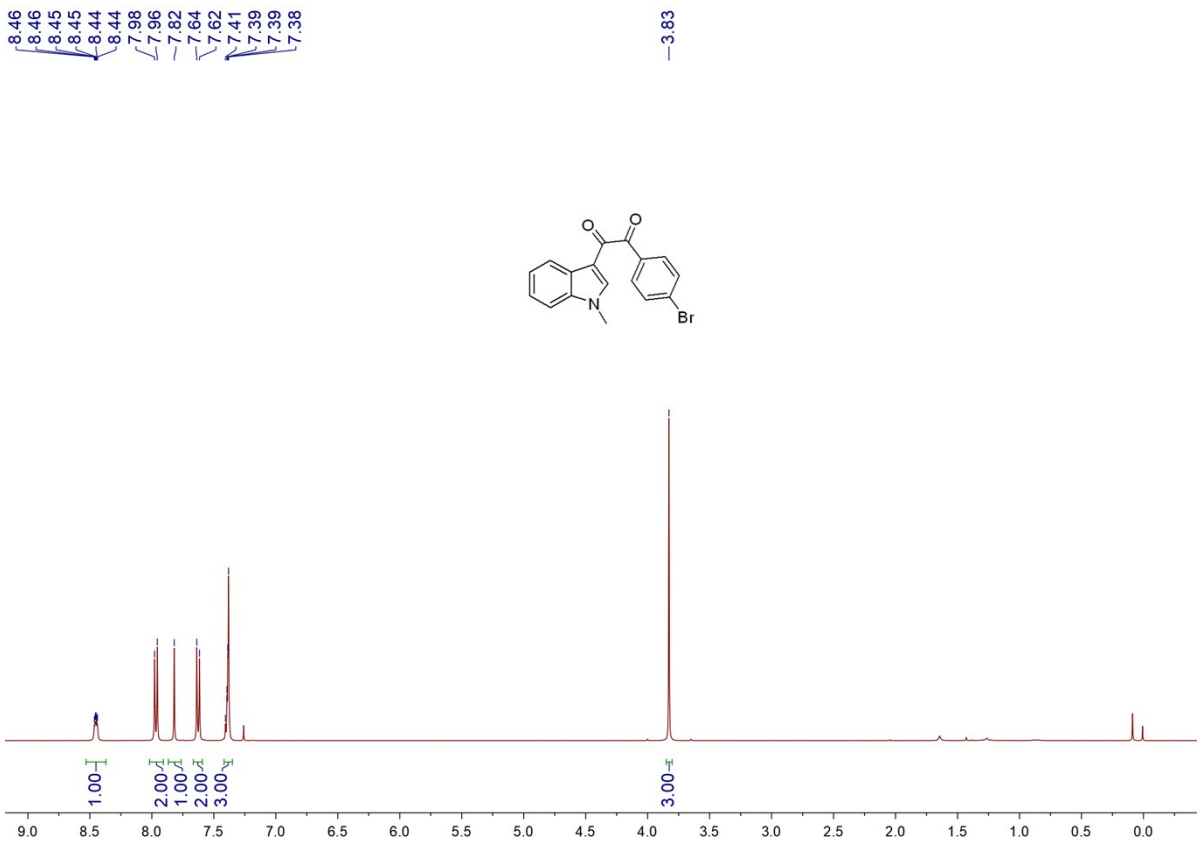
30

Product 3da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7.39
7.39
7.38
3.83
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O
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1.00
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3.00
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8.5
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7.5
7.0
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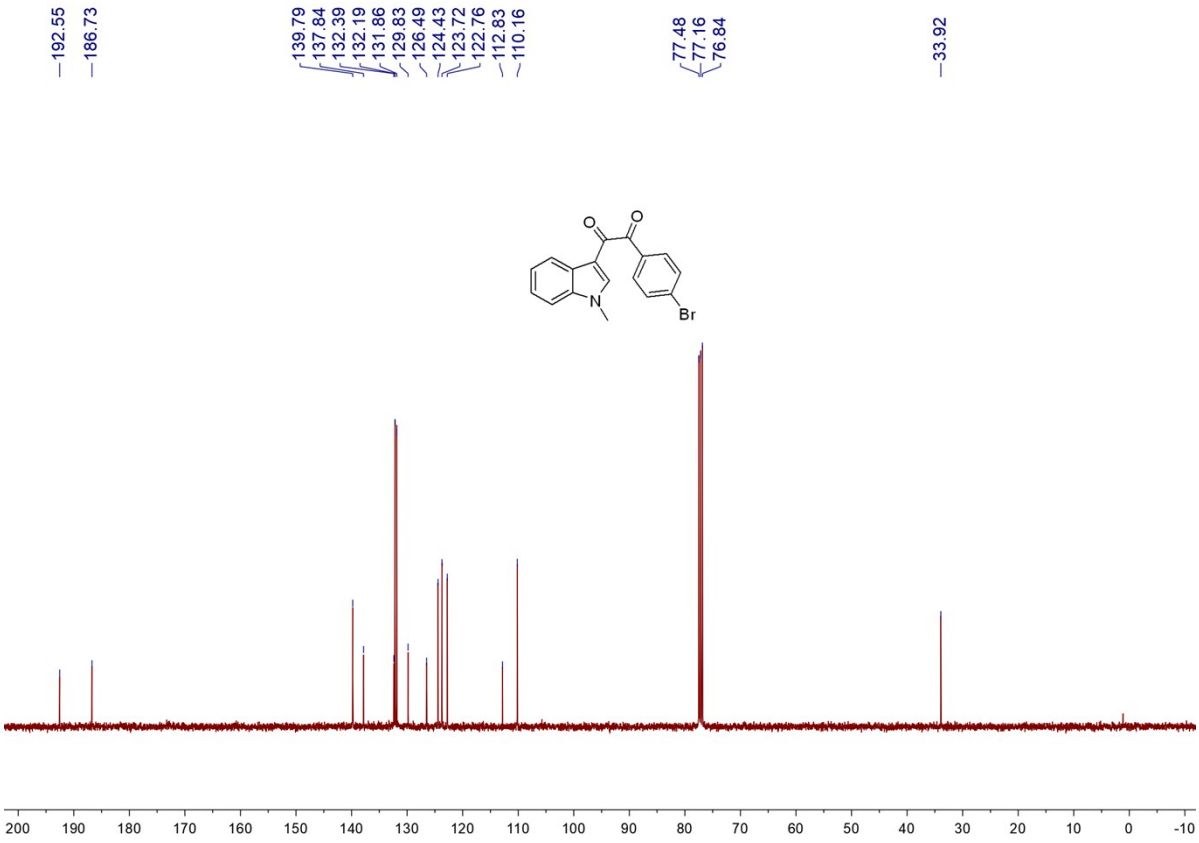
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33.92
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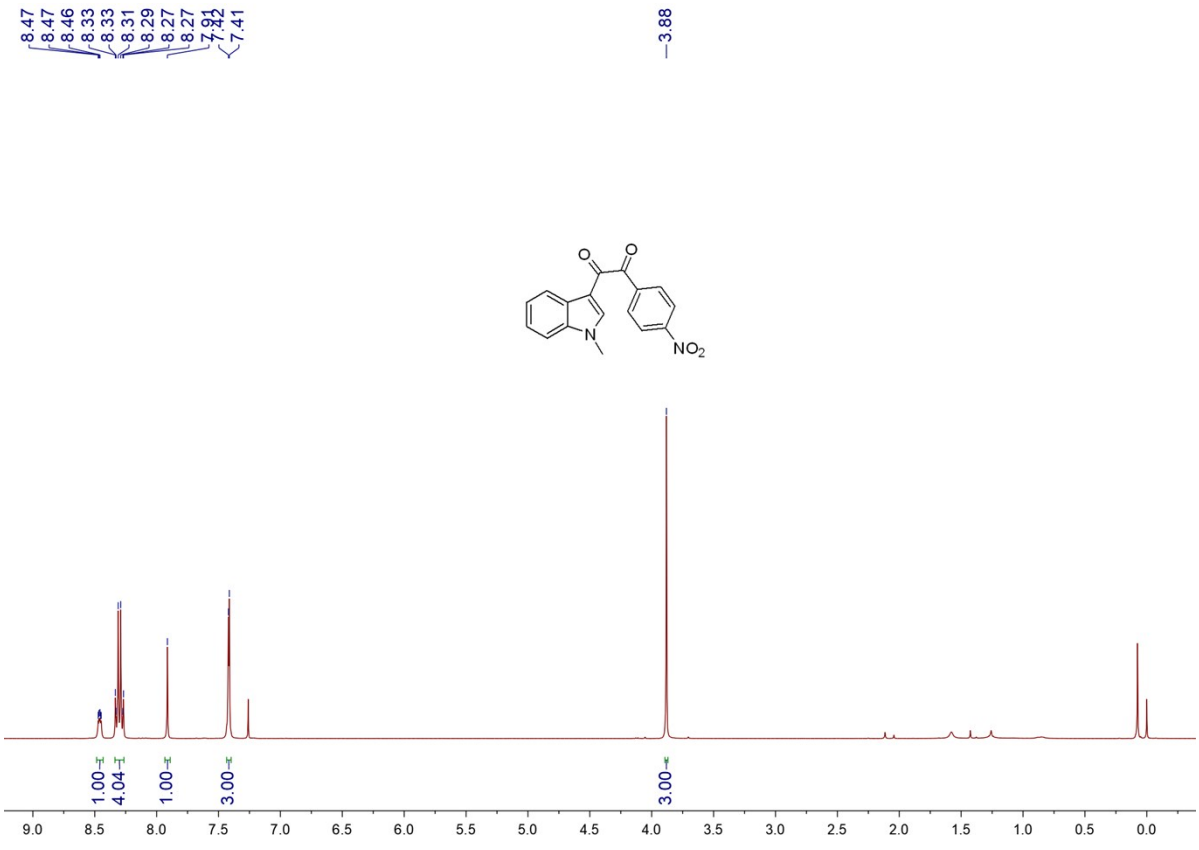
Product 3ea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O
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3.00
3.00
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8.0
7.5
7.0
6.5
6.0
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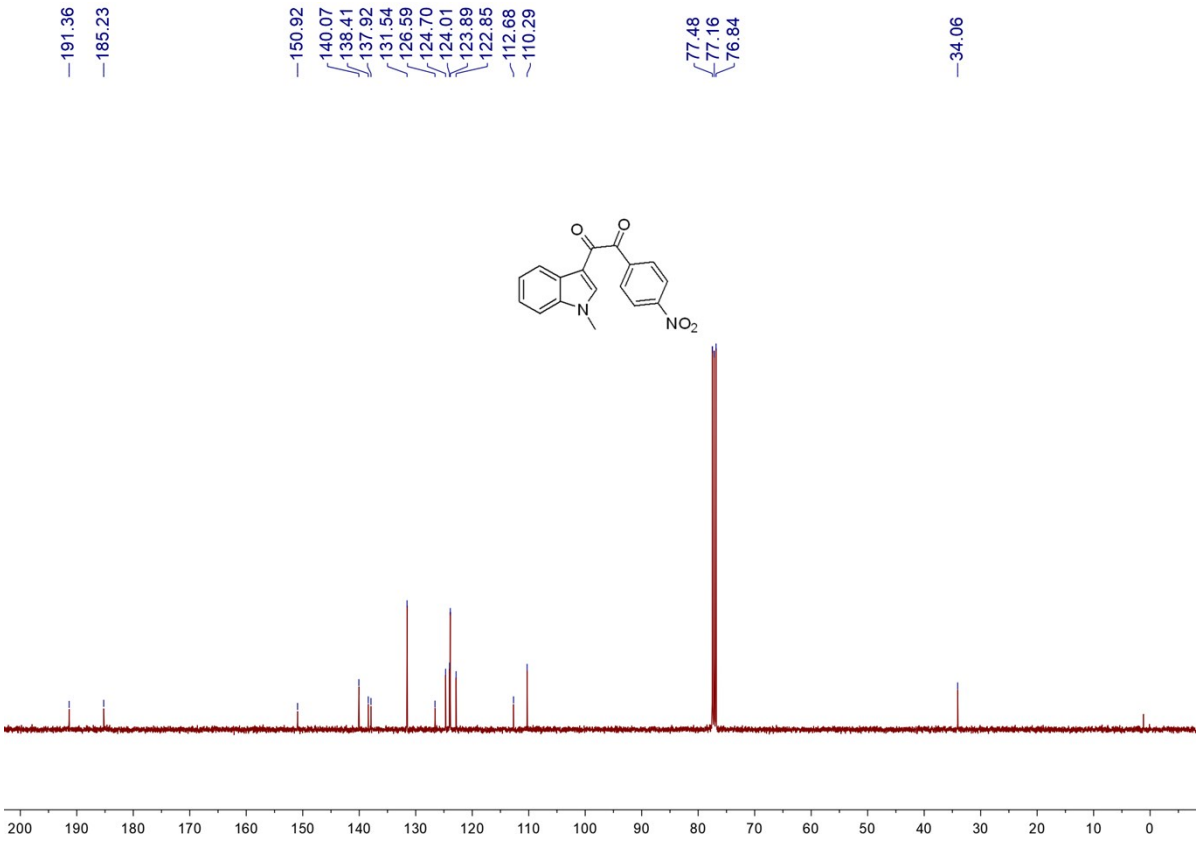
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34.06
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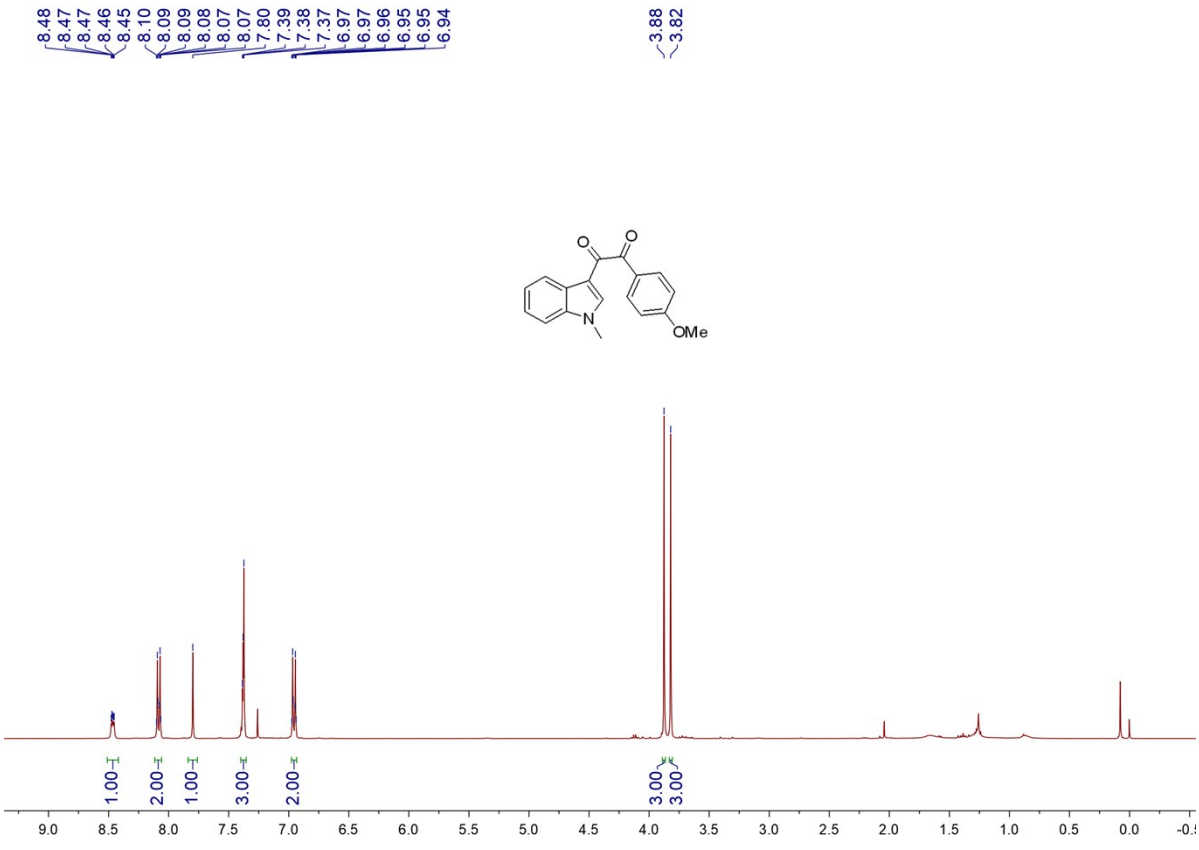
O
N
NO2

Product 3fa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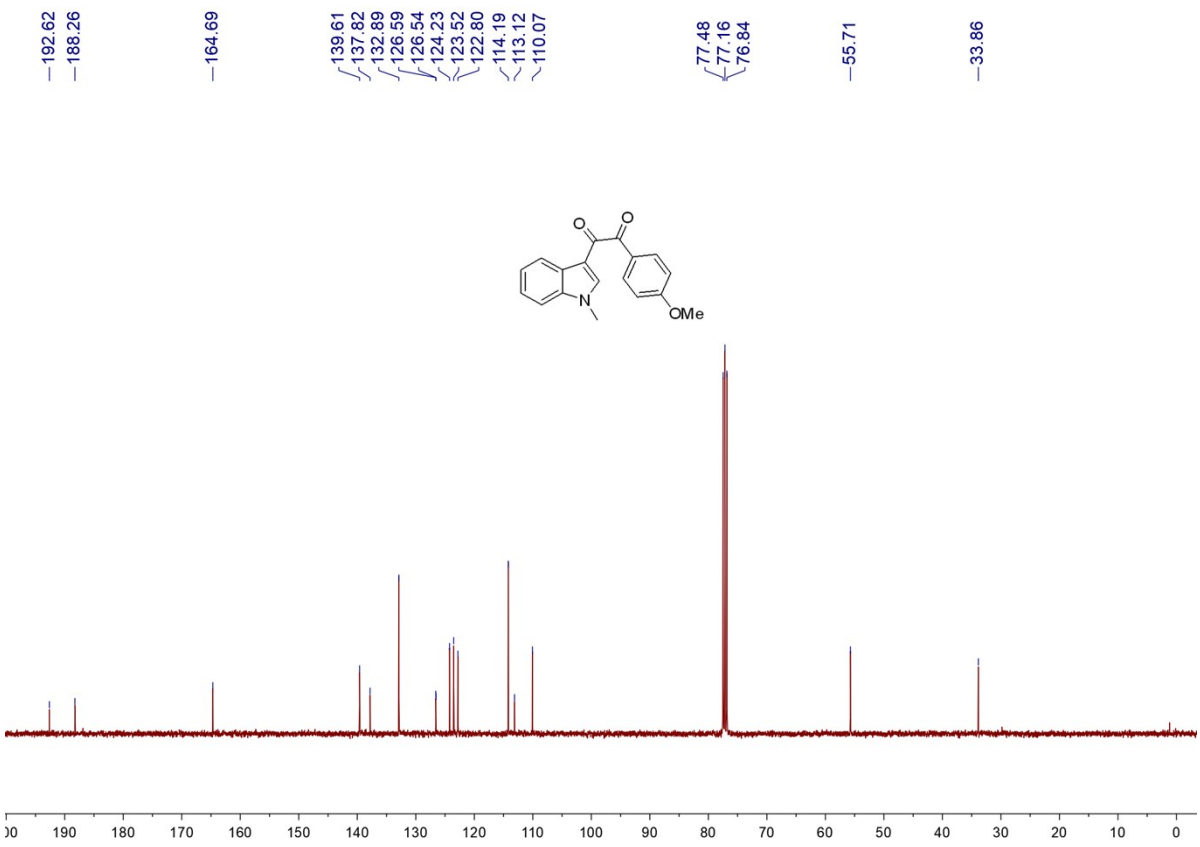
3.00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77.16
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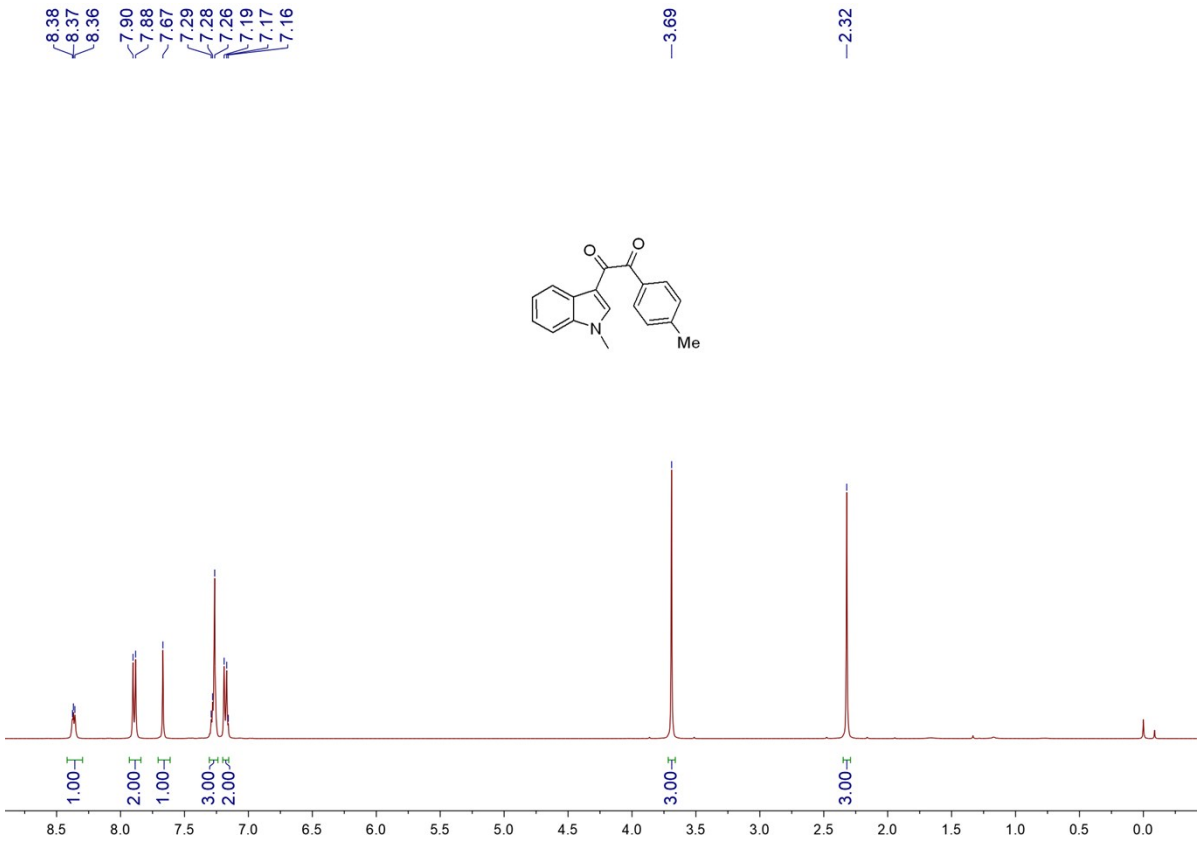
Product 3ga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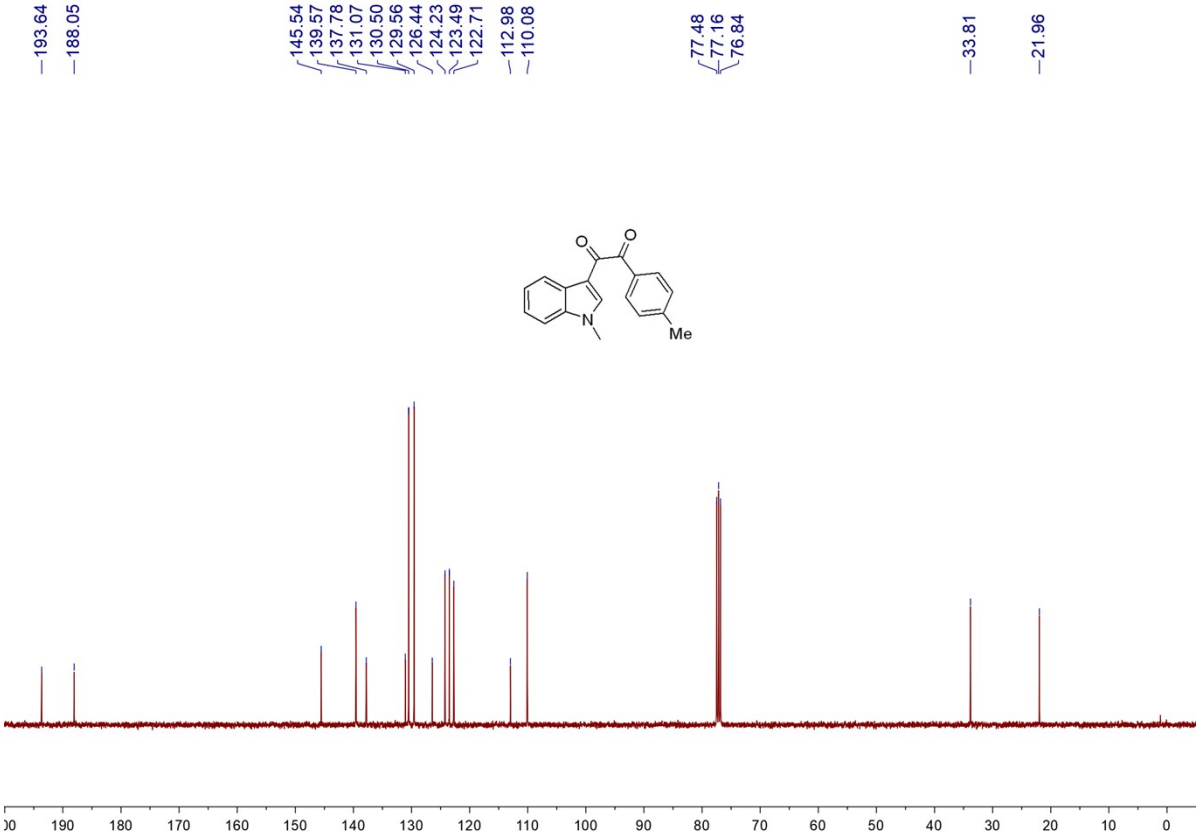
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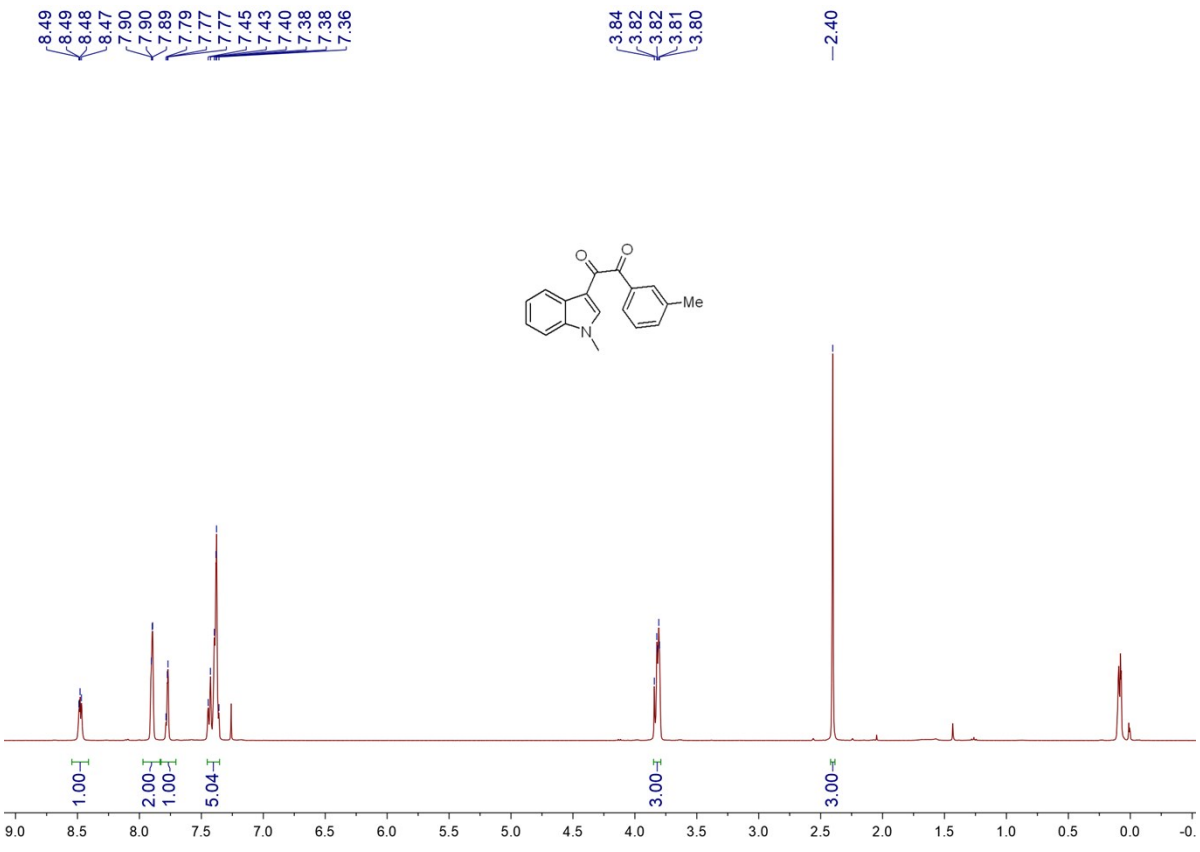
Me

Product 3ha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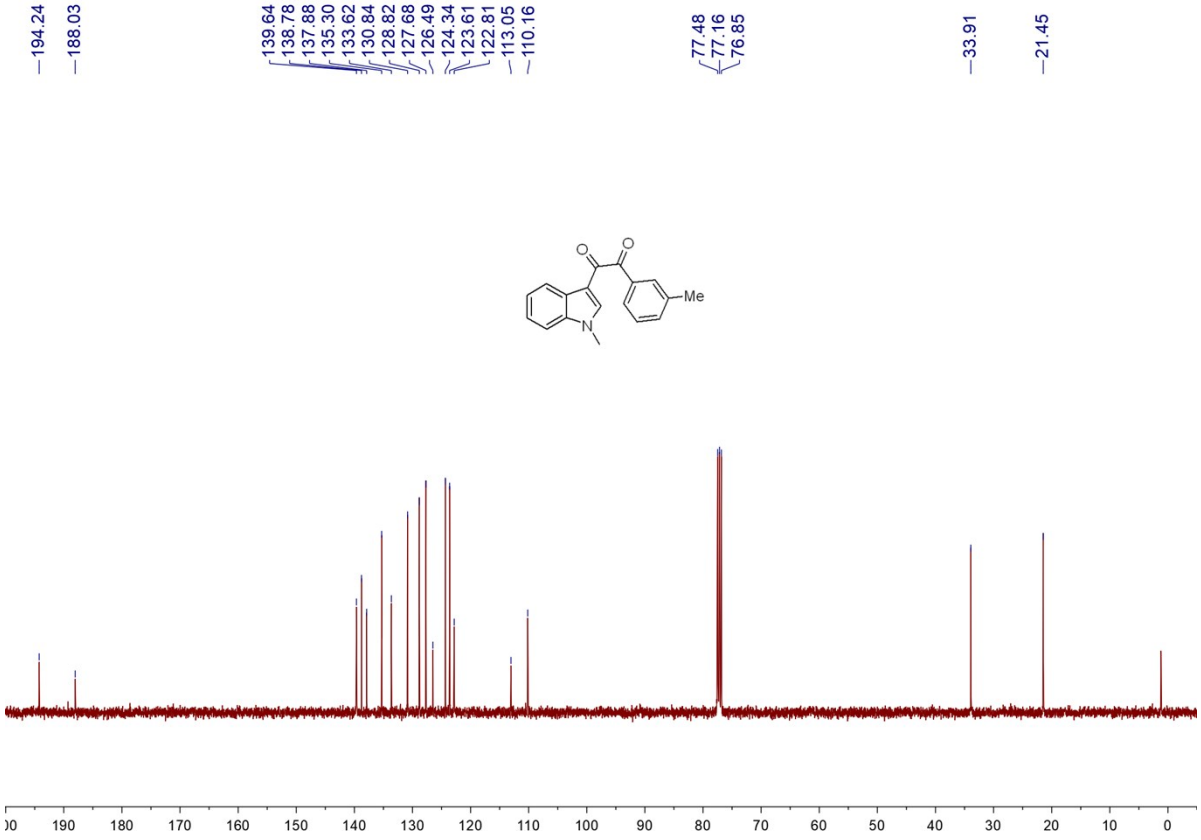
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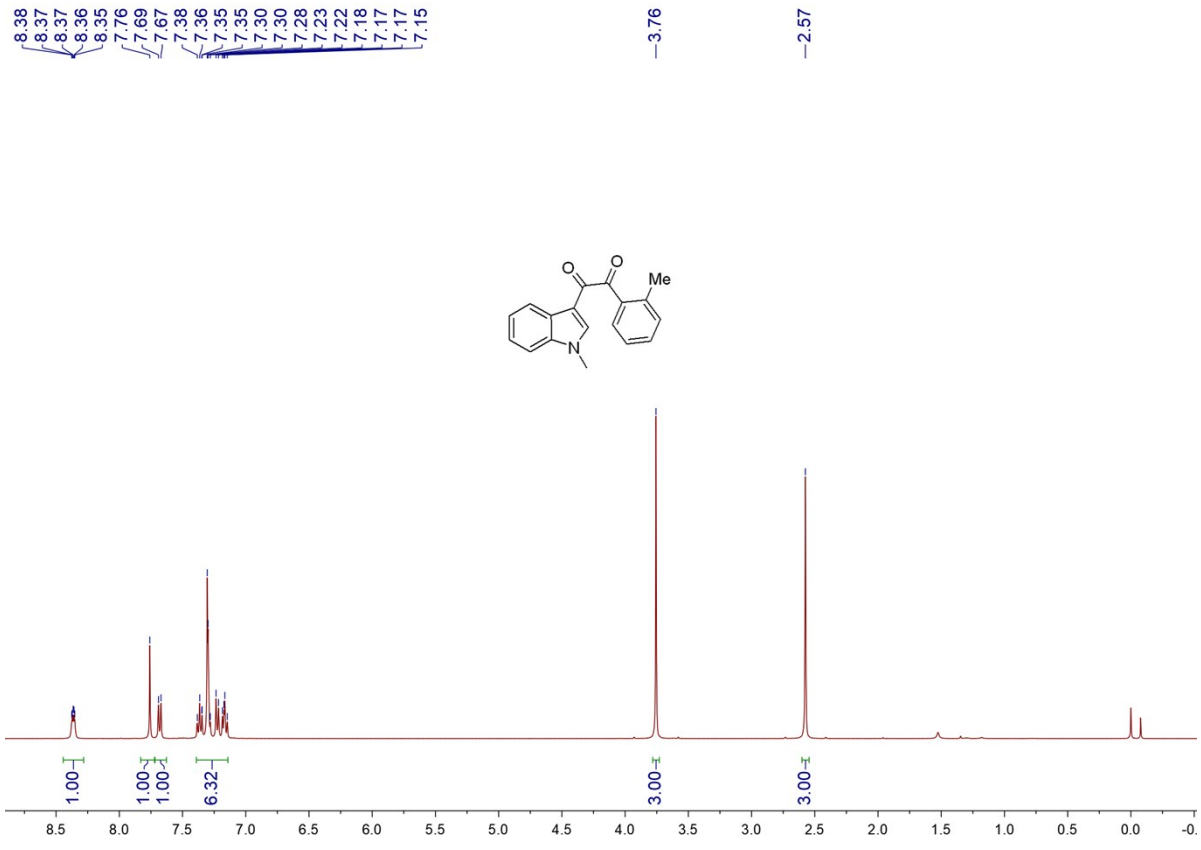
Product 3ia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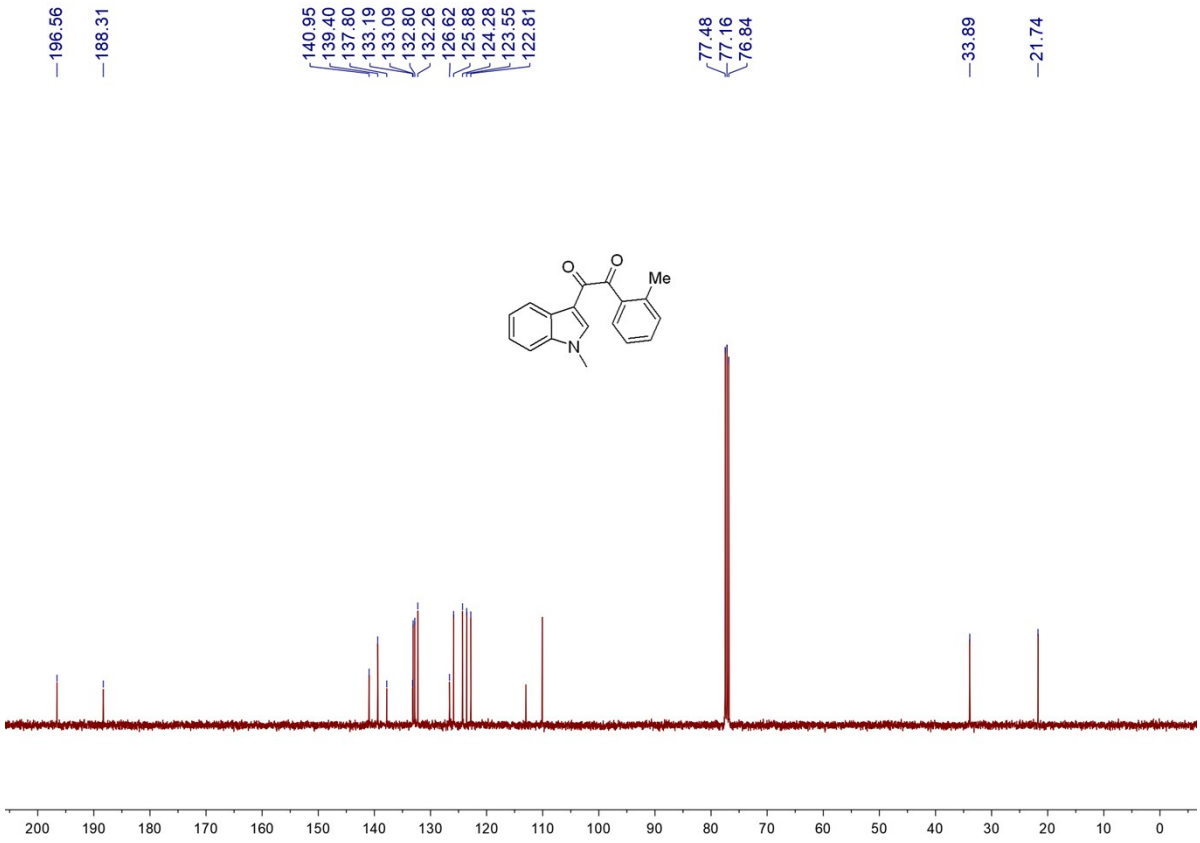
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O
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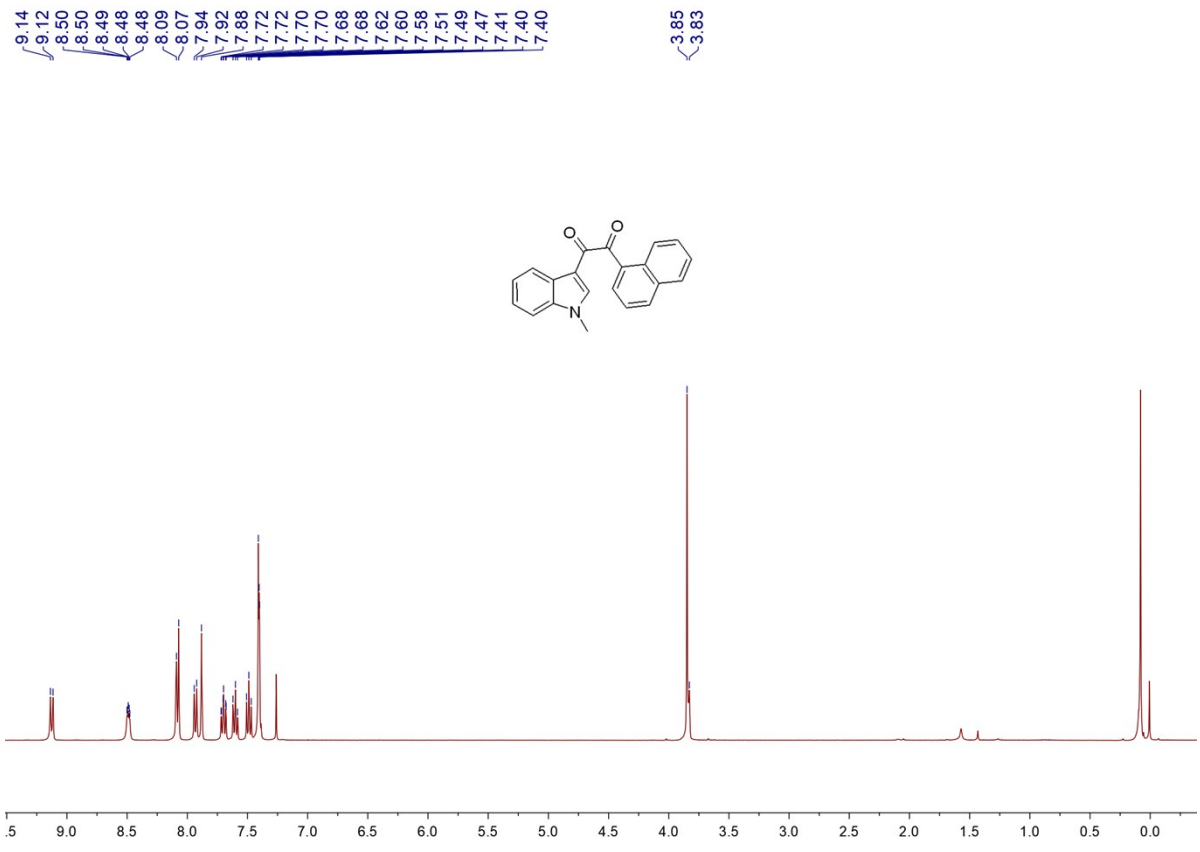
Product 3ja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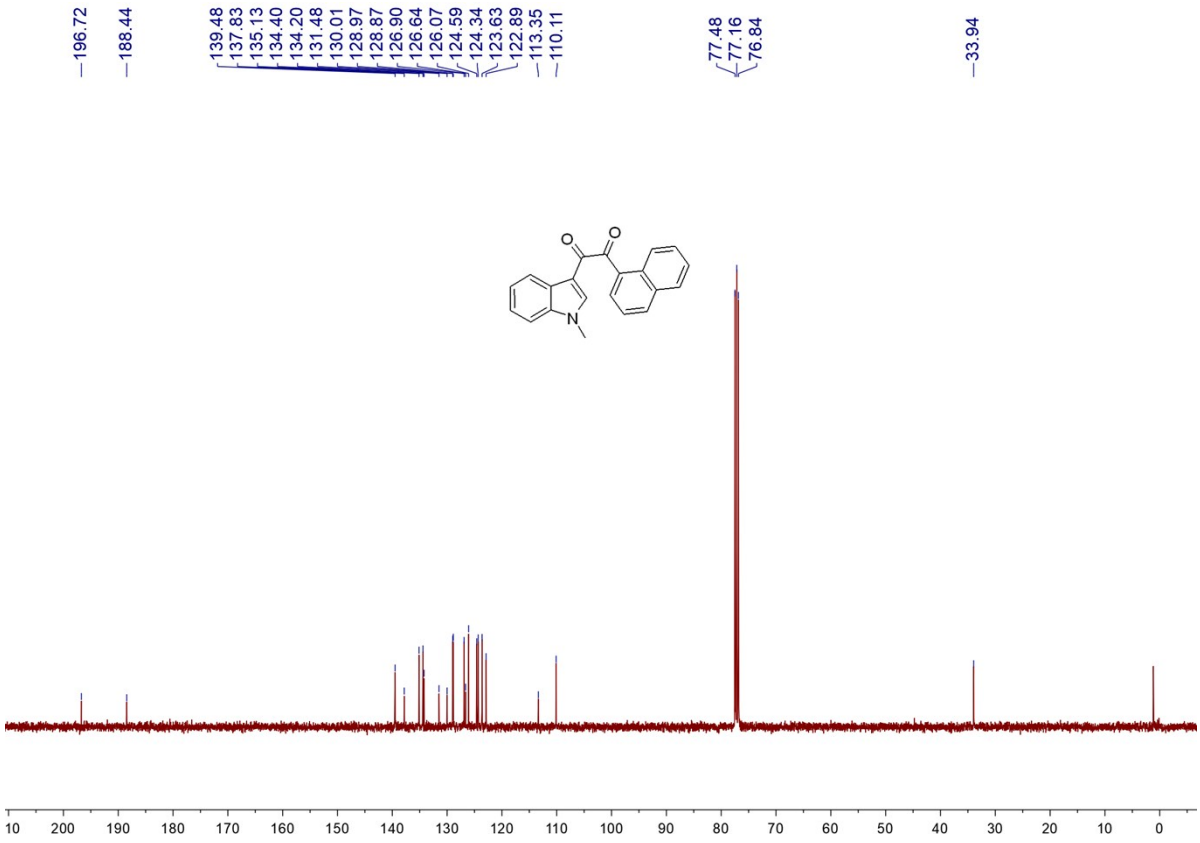
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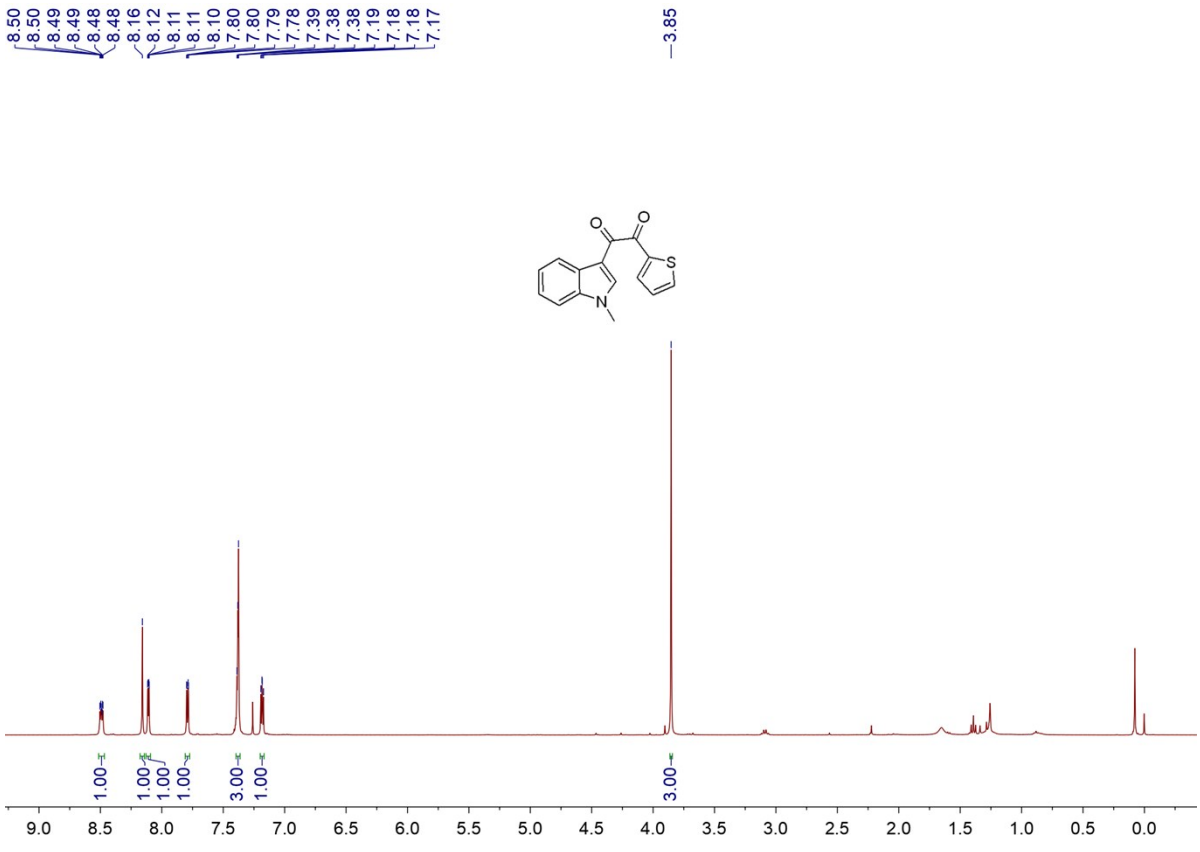
Product 3ka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7.18
7.17
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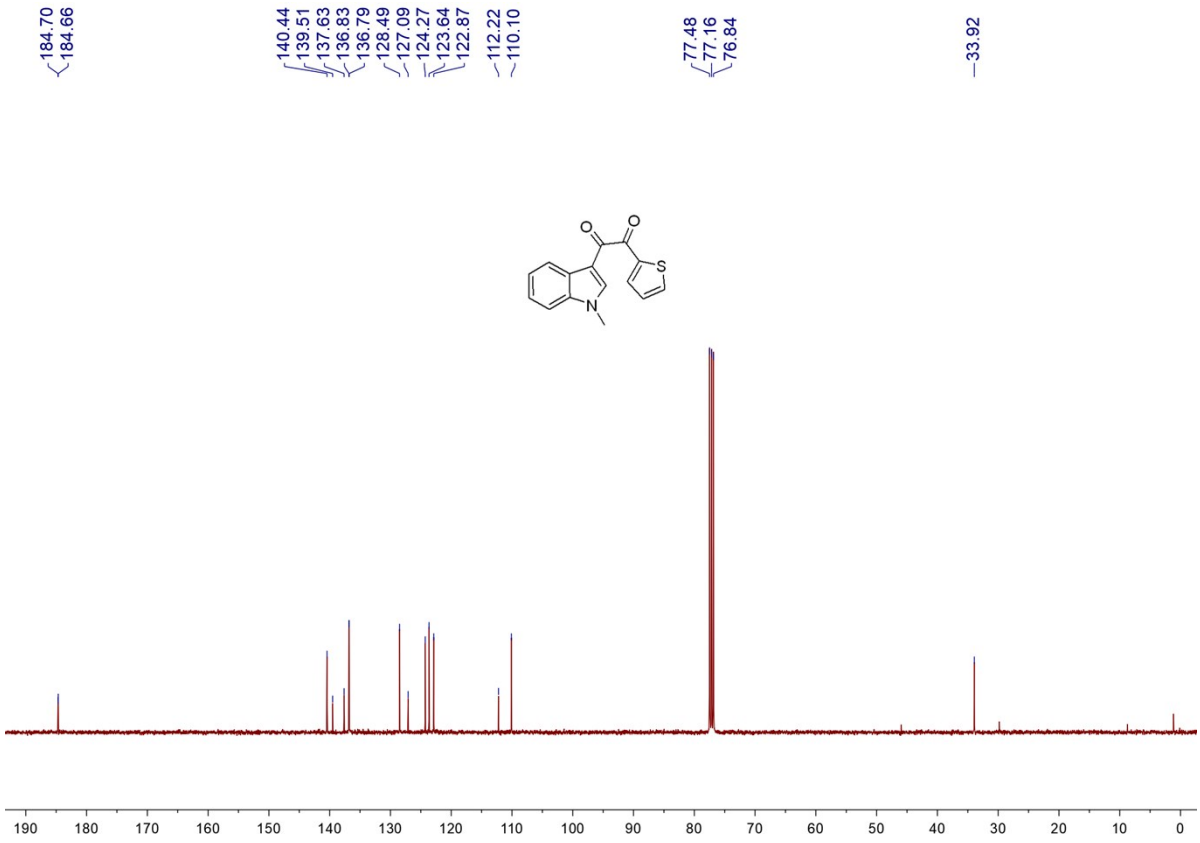
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O
S
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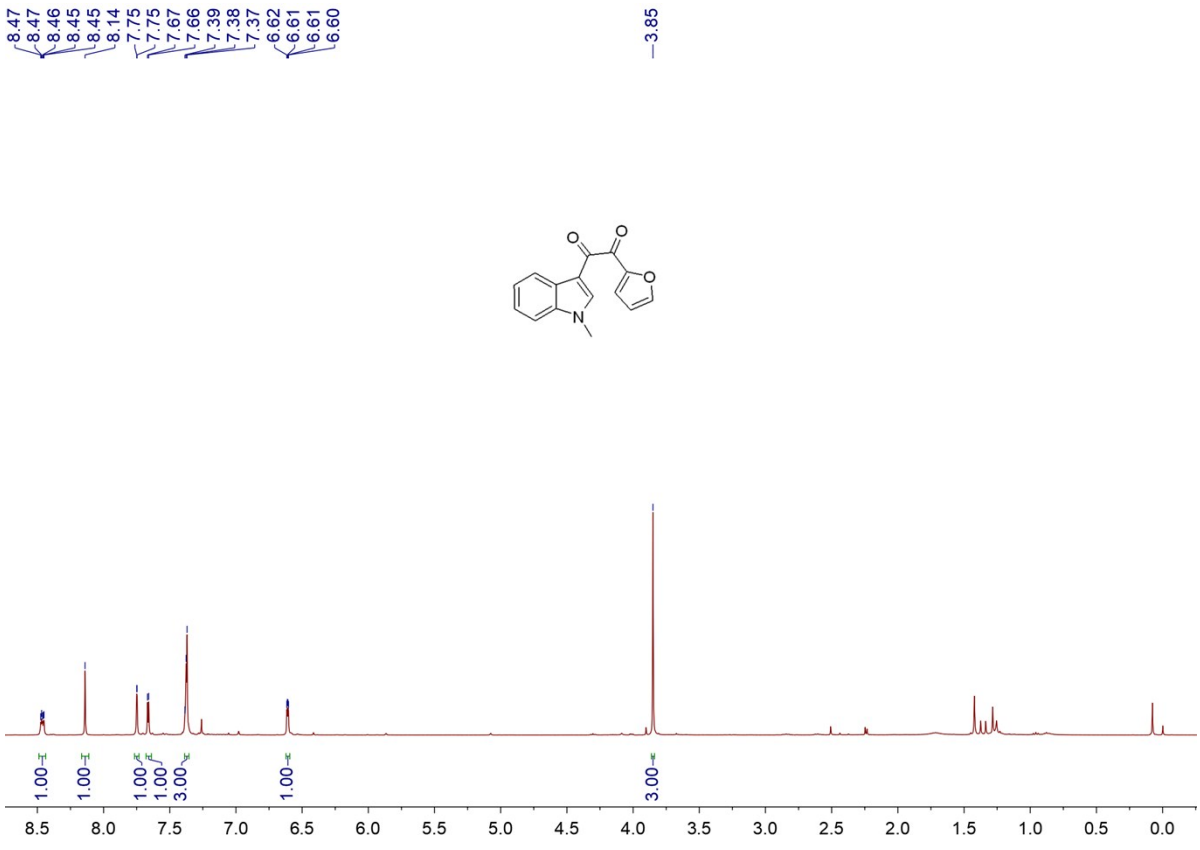
Product 3la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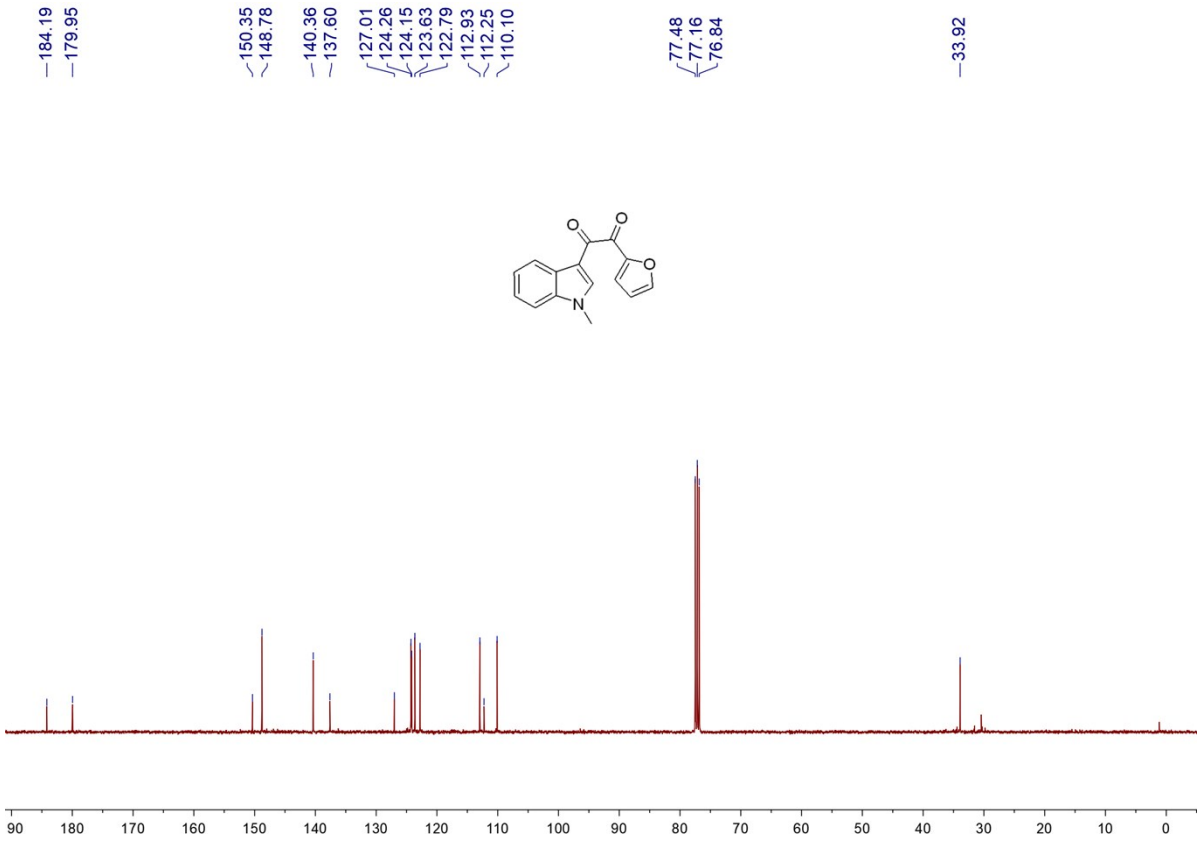
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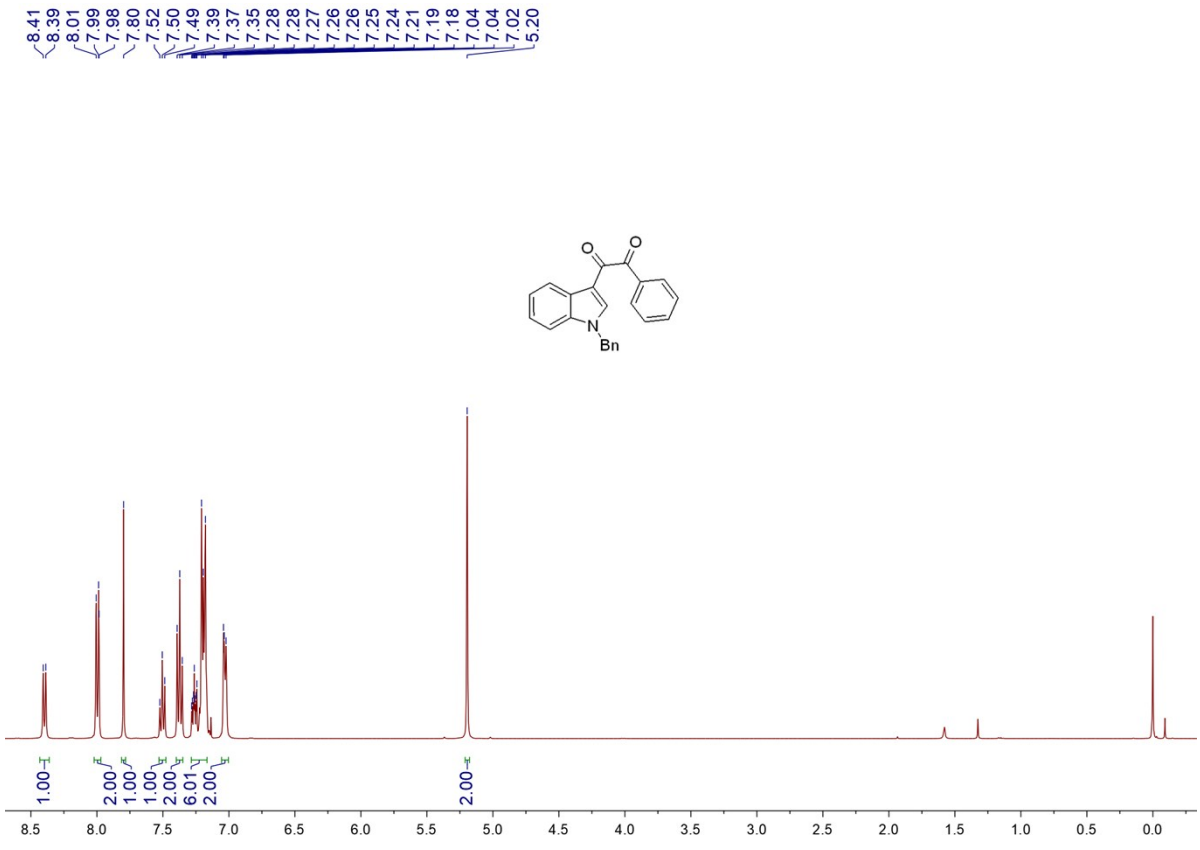
Product 3ab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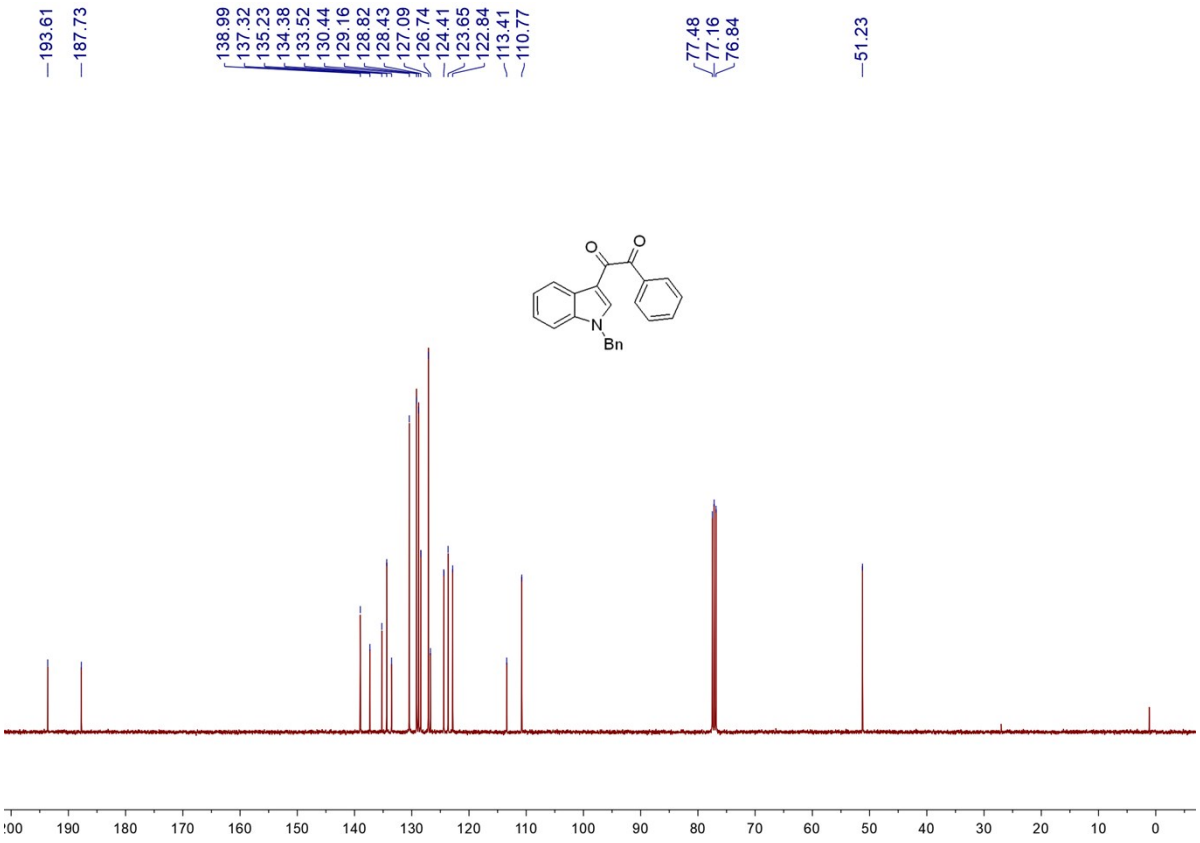
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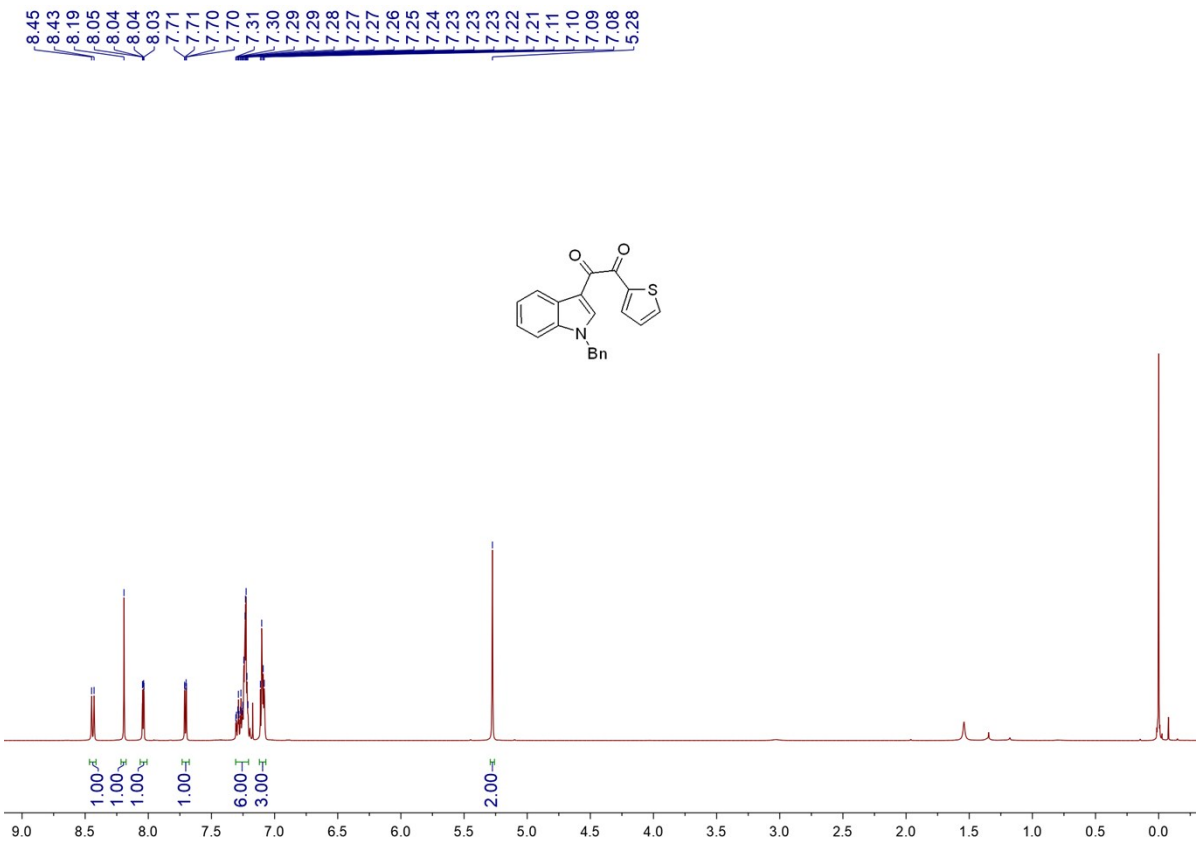
Product 3ac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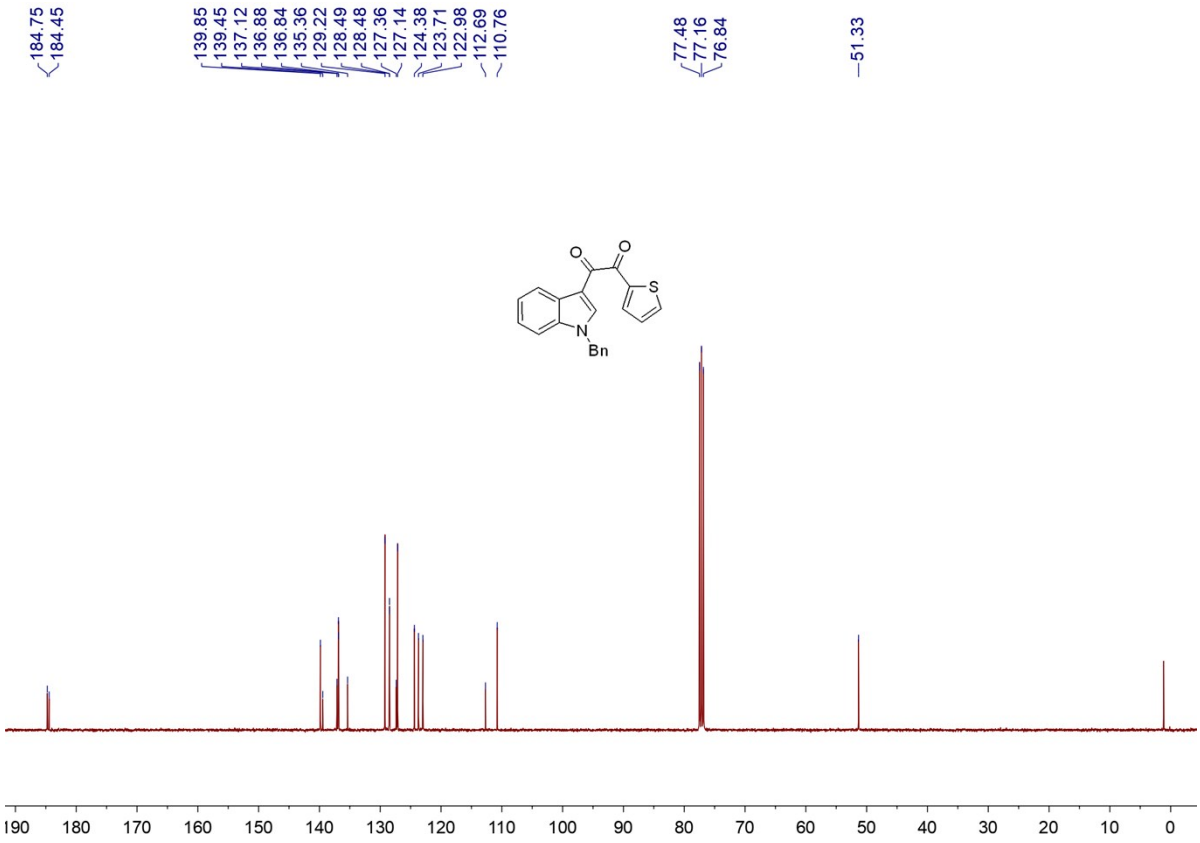
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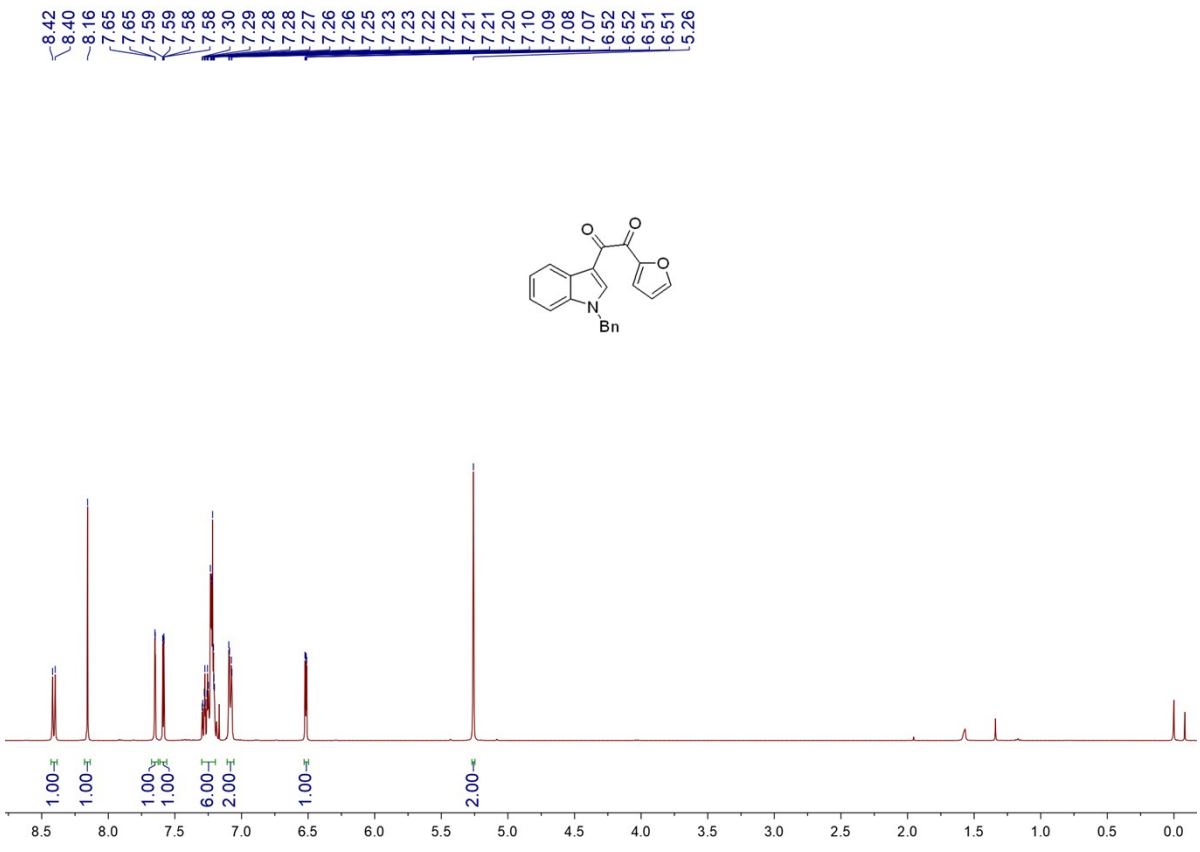
Product 3ad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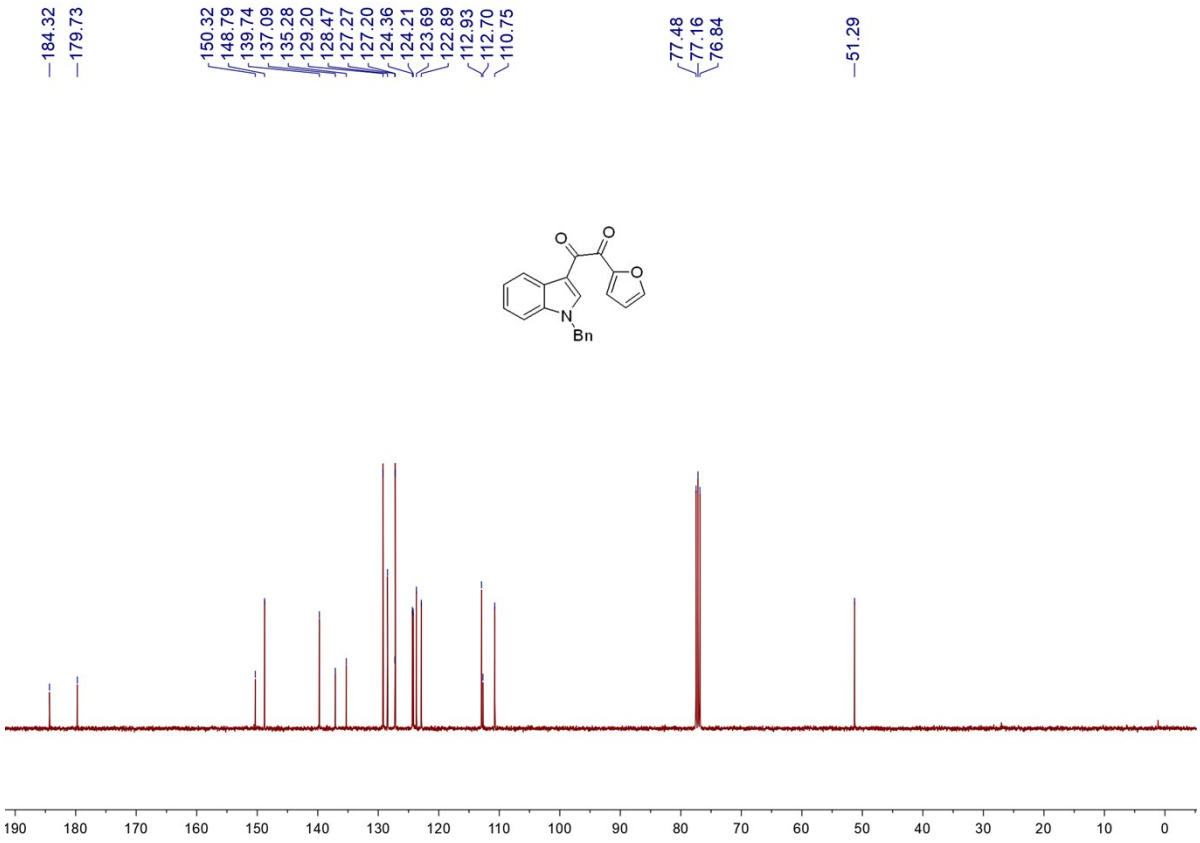
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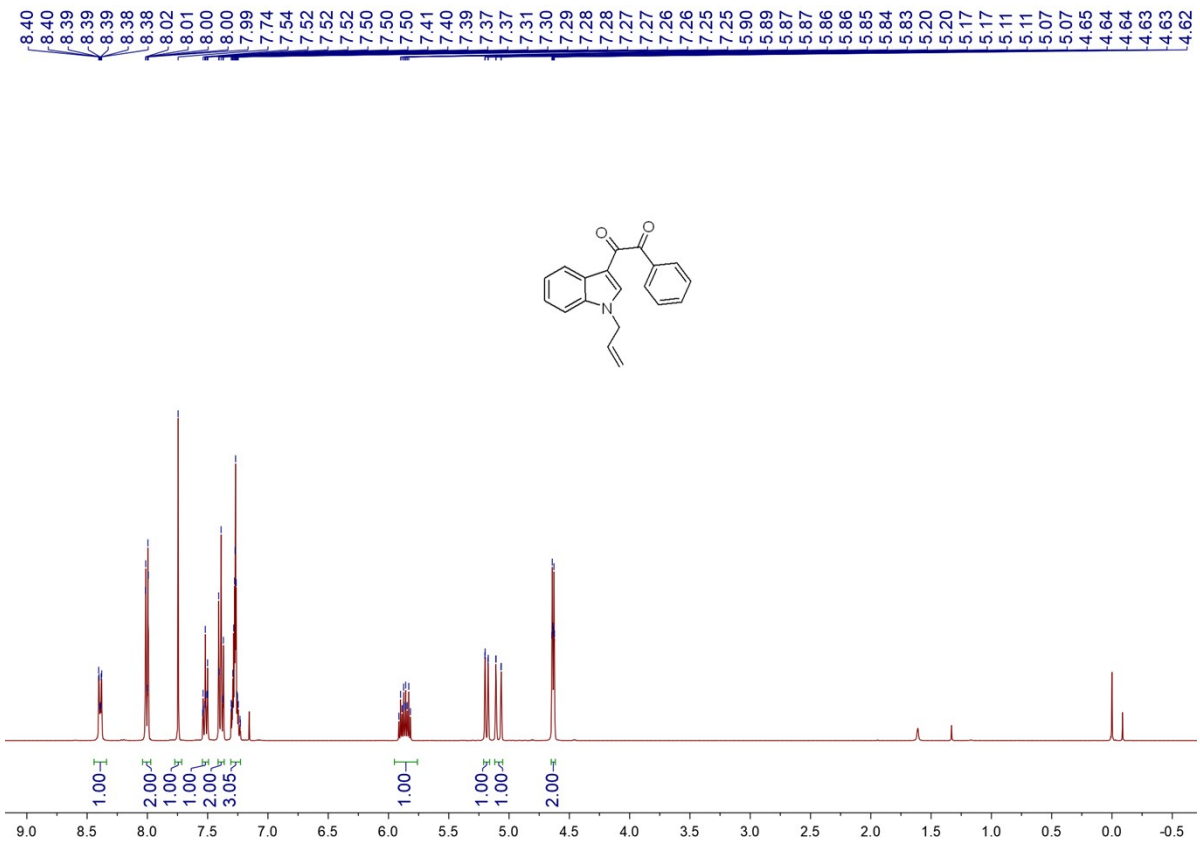
Product 3ae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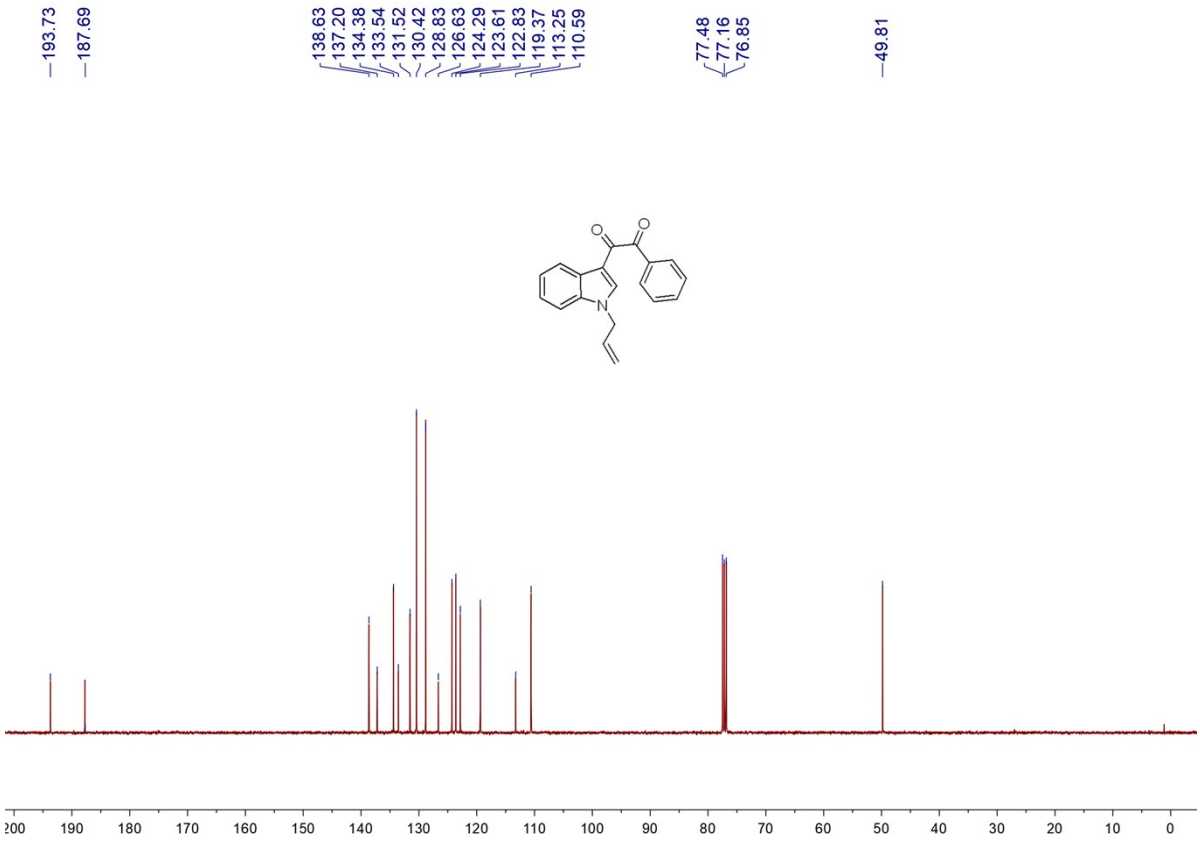
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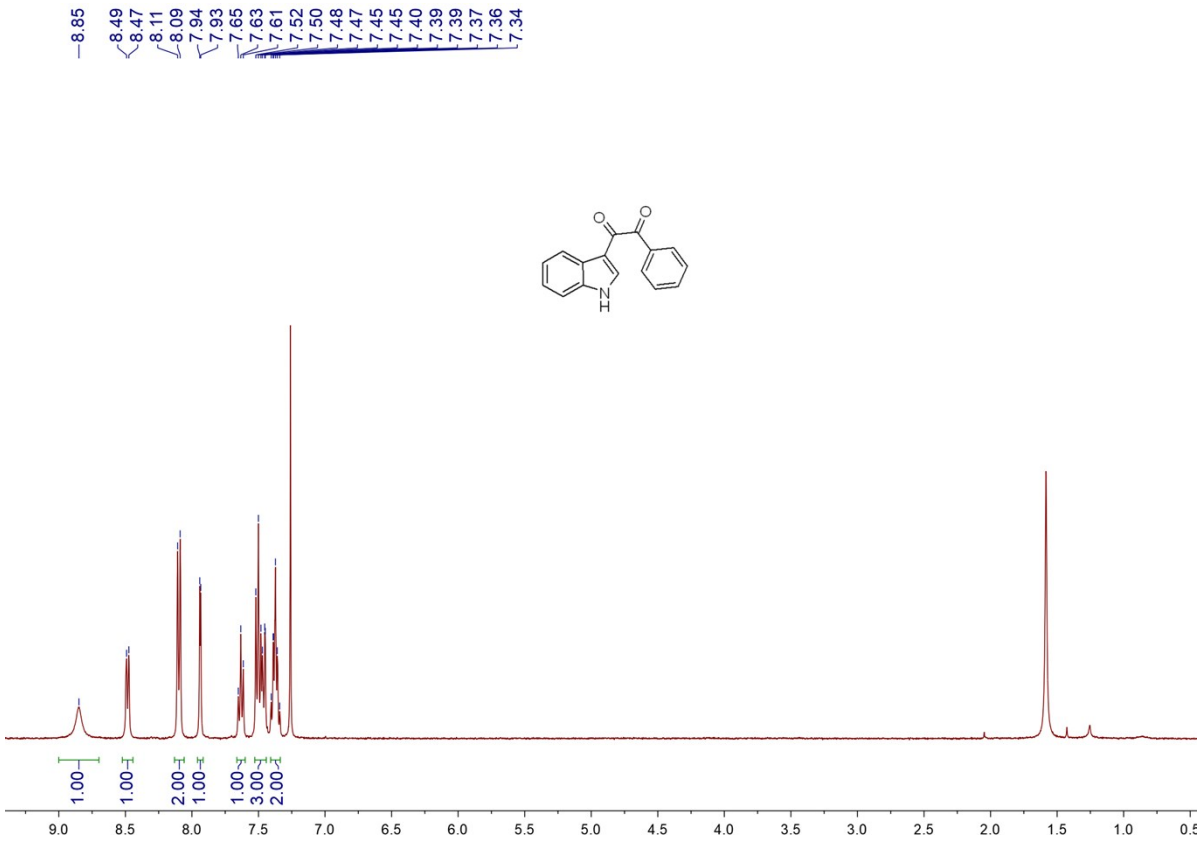
Product 3af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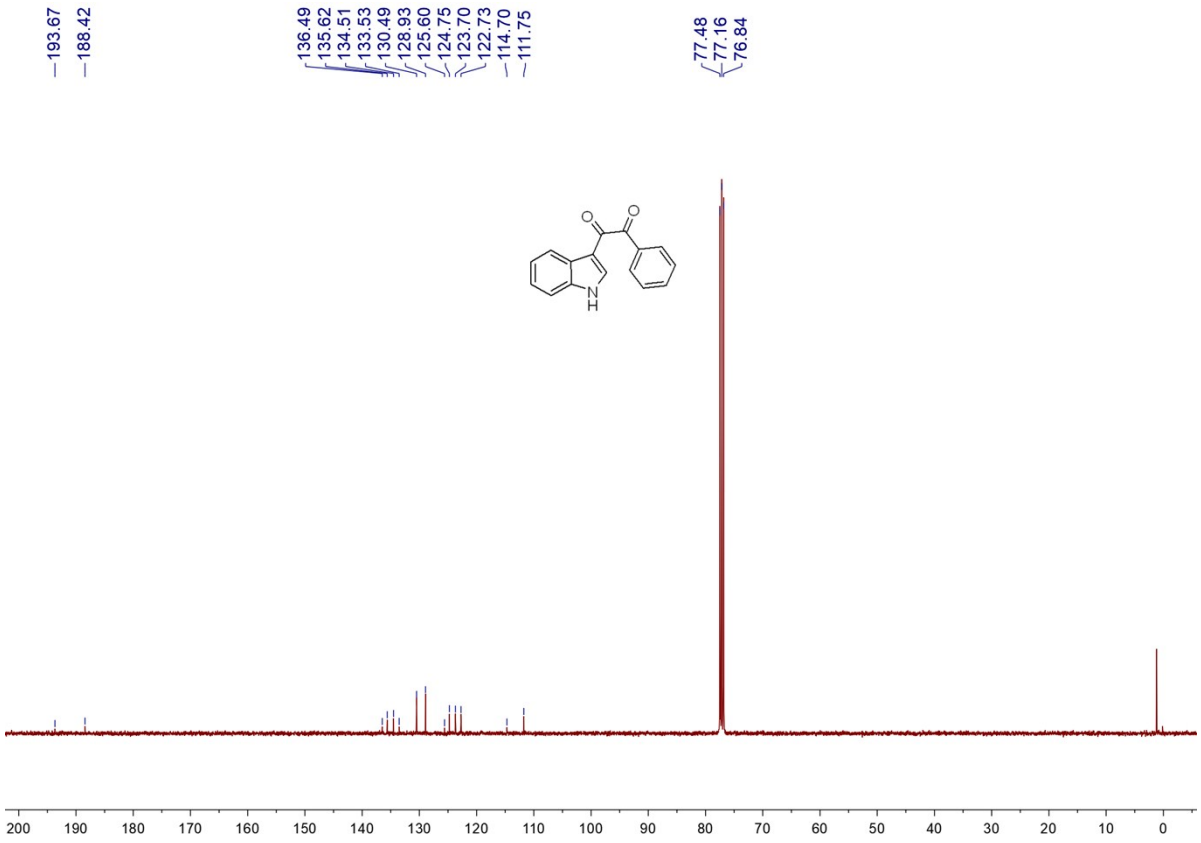
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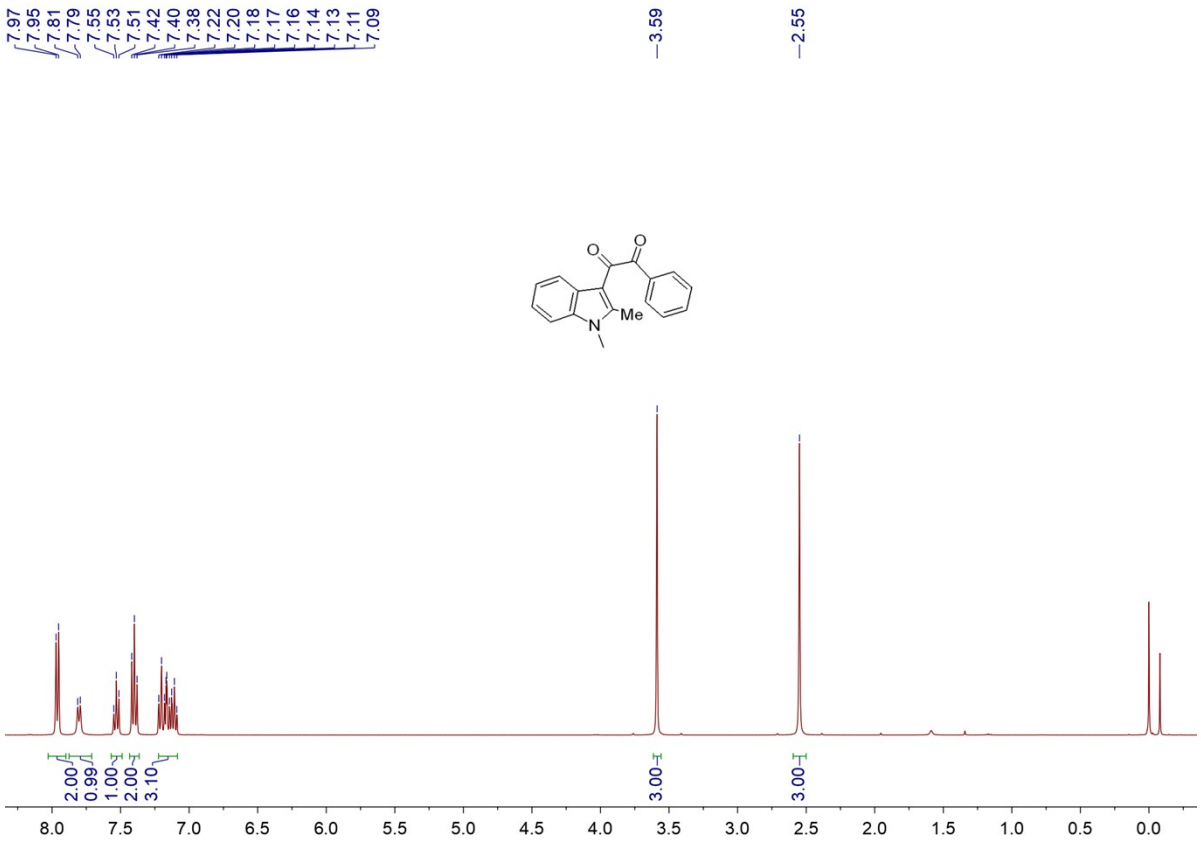
Product 3ag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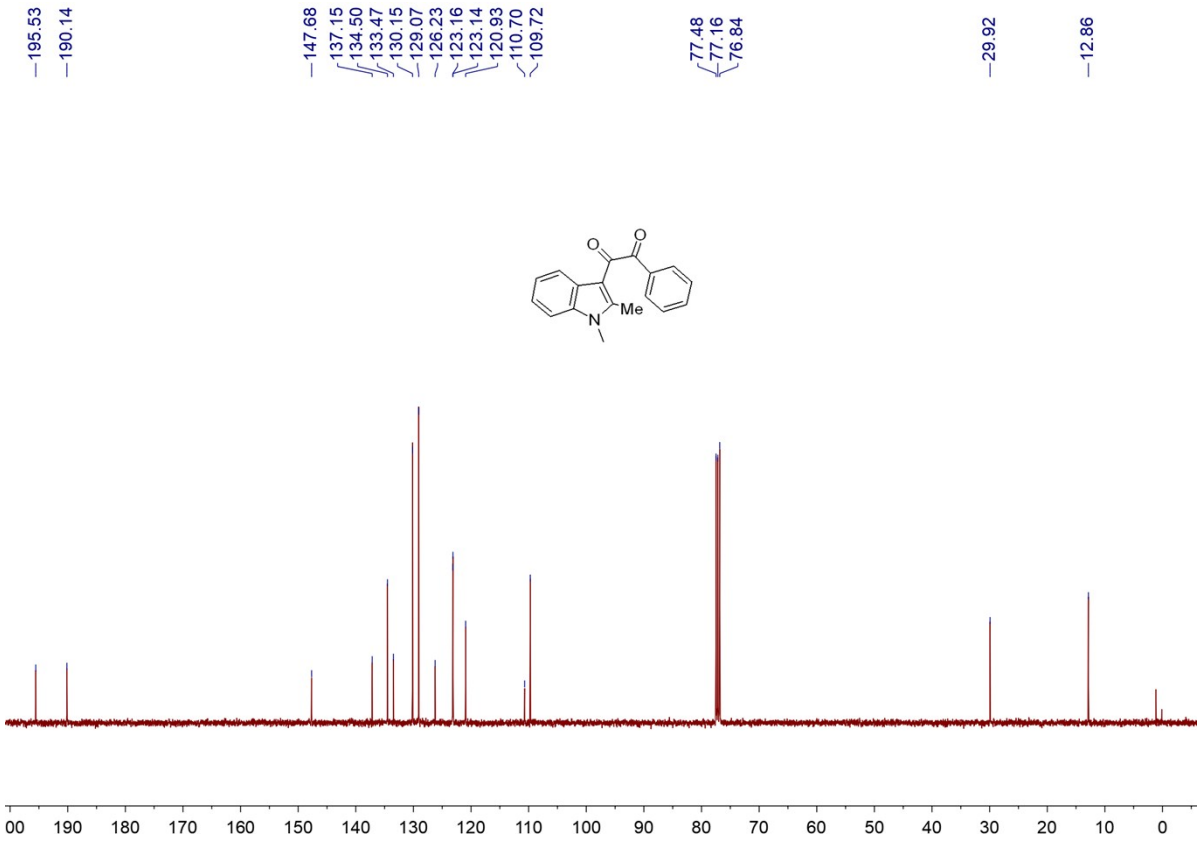
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Me
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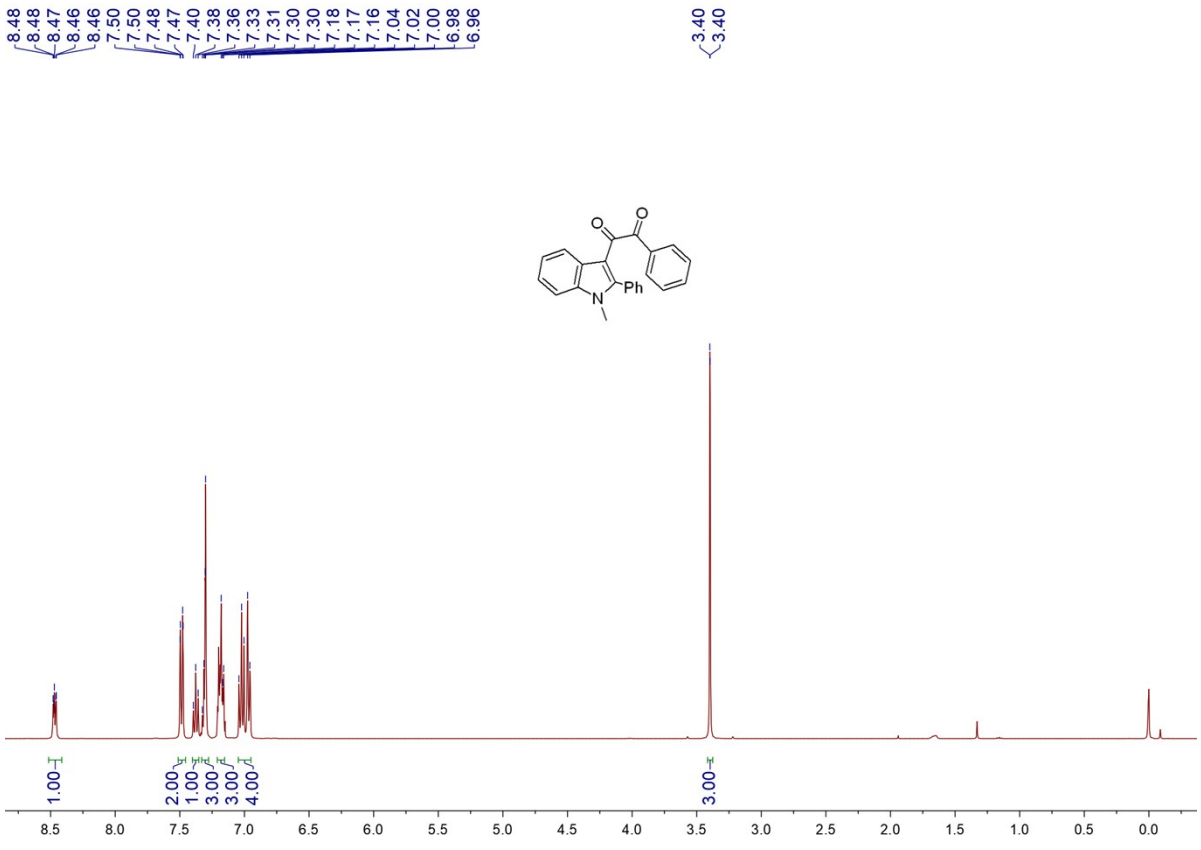
Product 3ah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7.16
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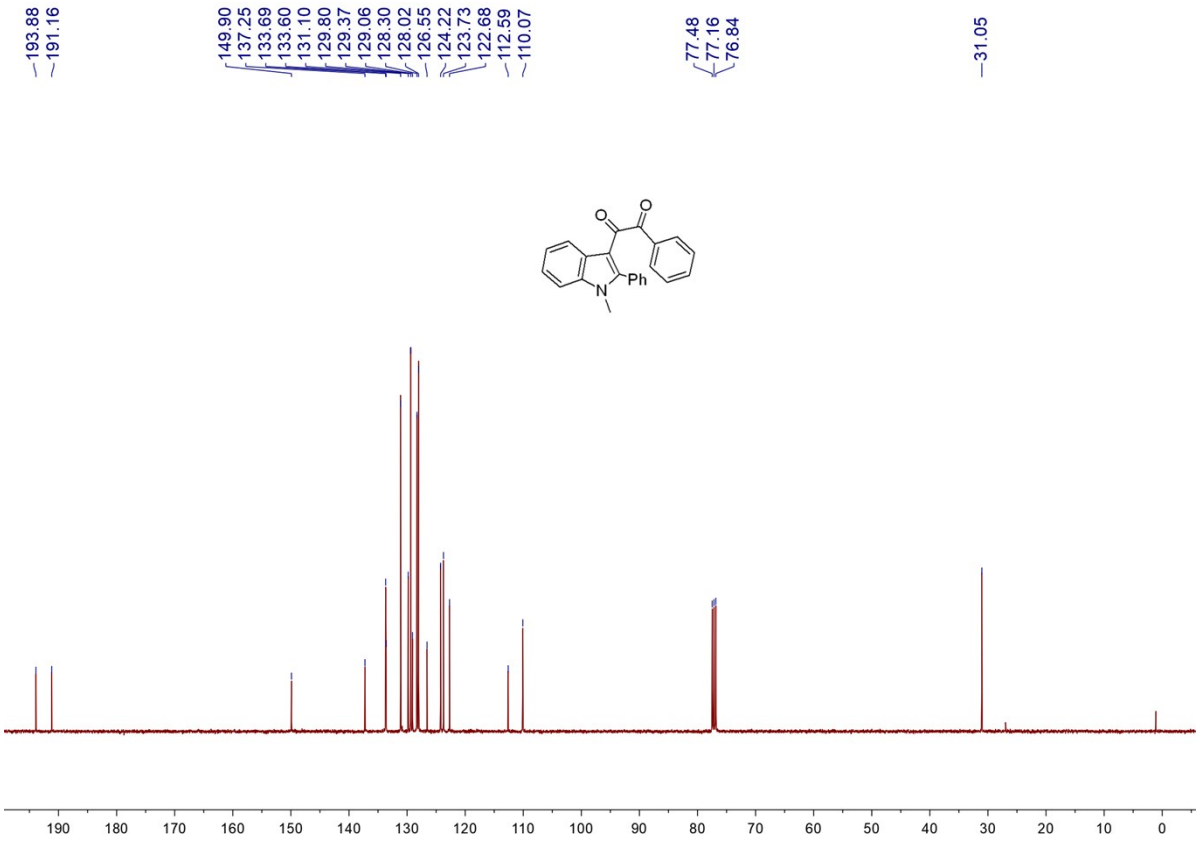
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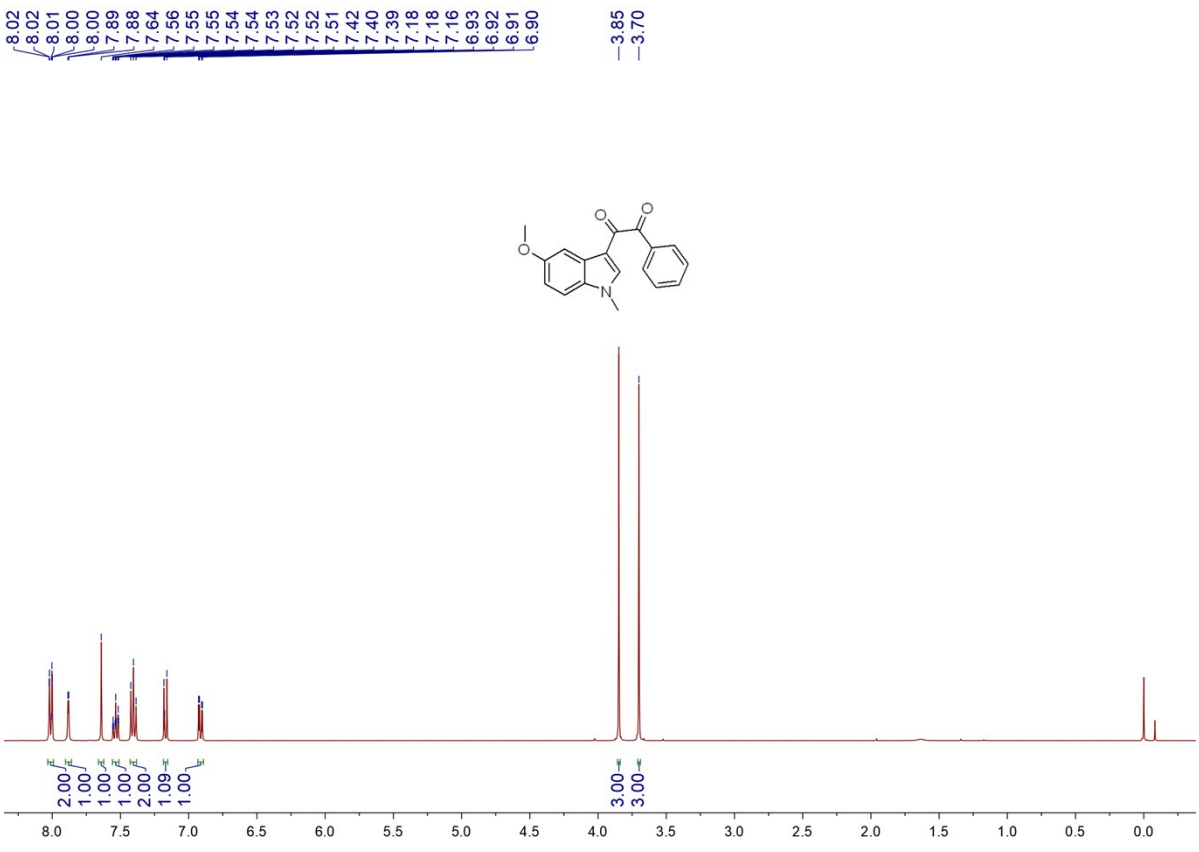
Product 3ai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6.91
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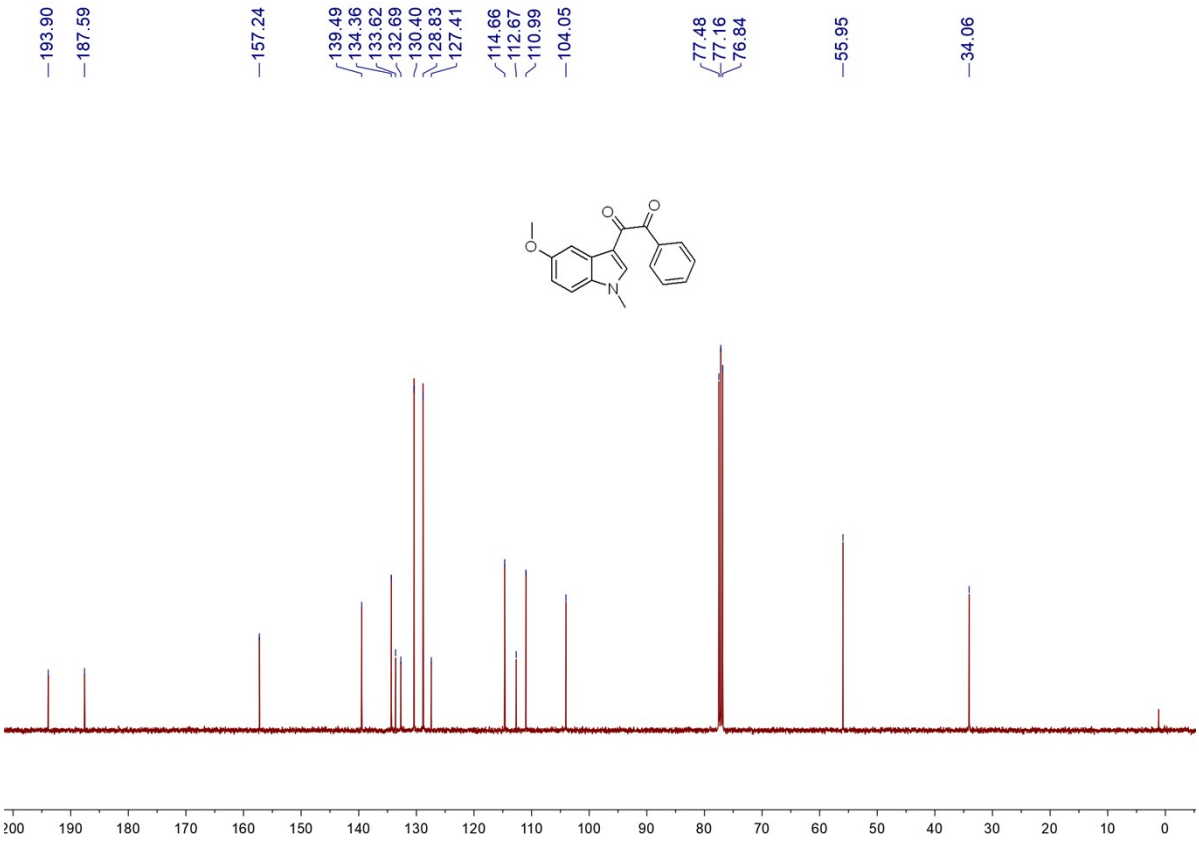
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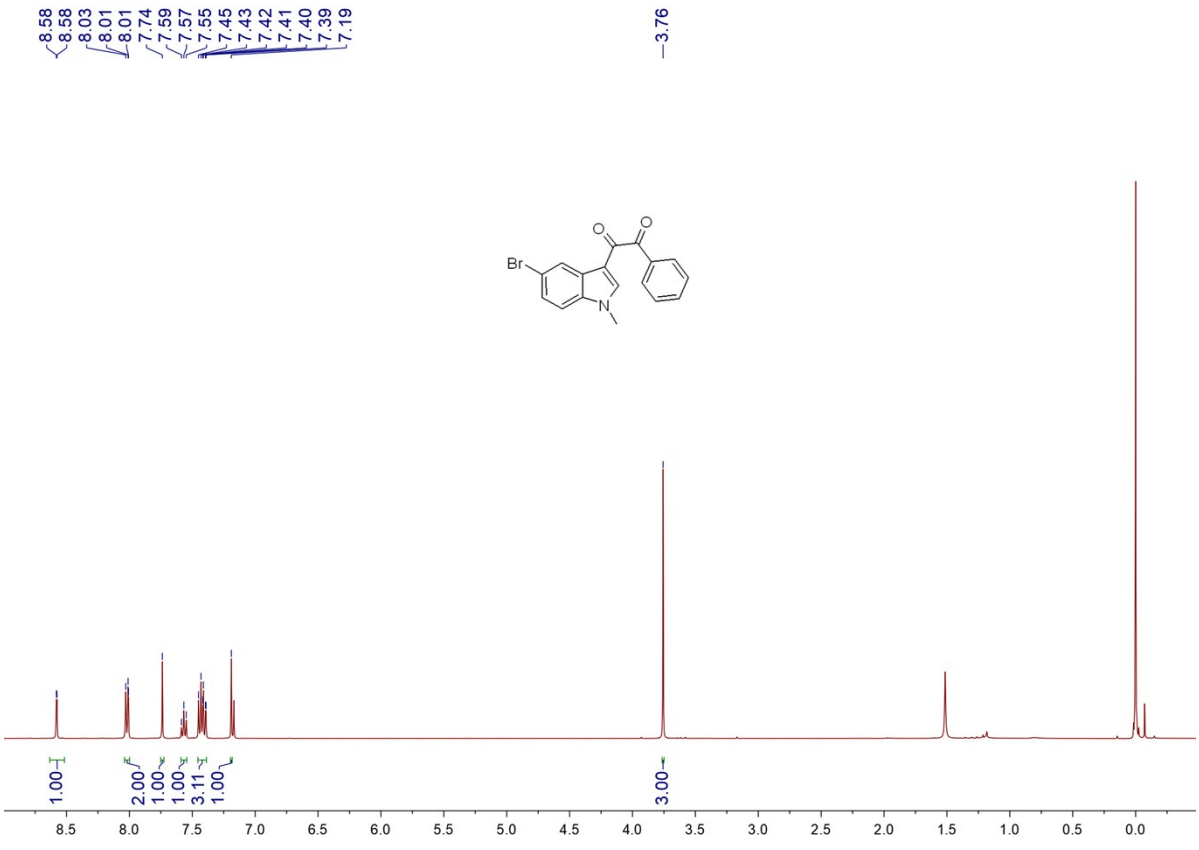
Product 3aj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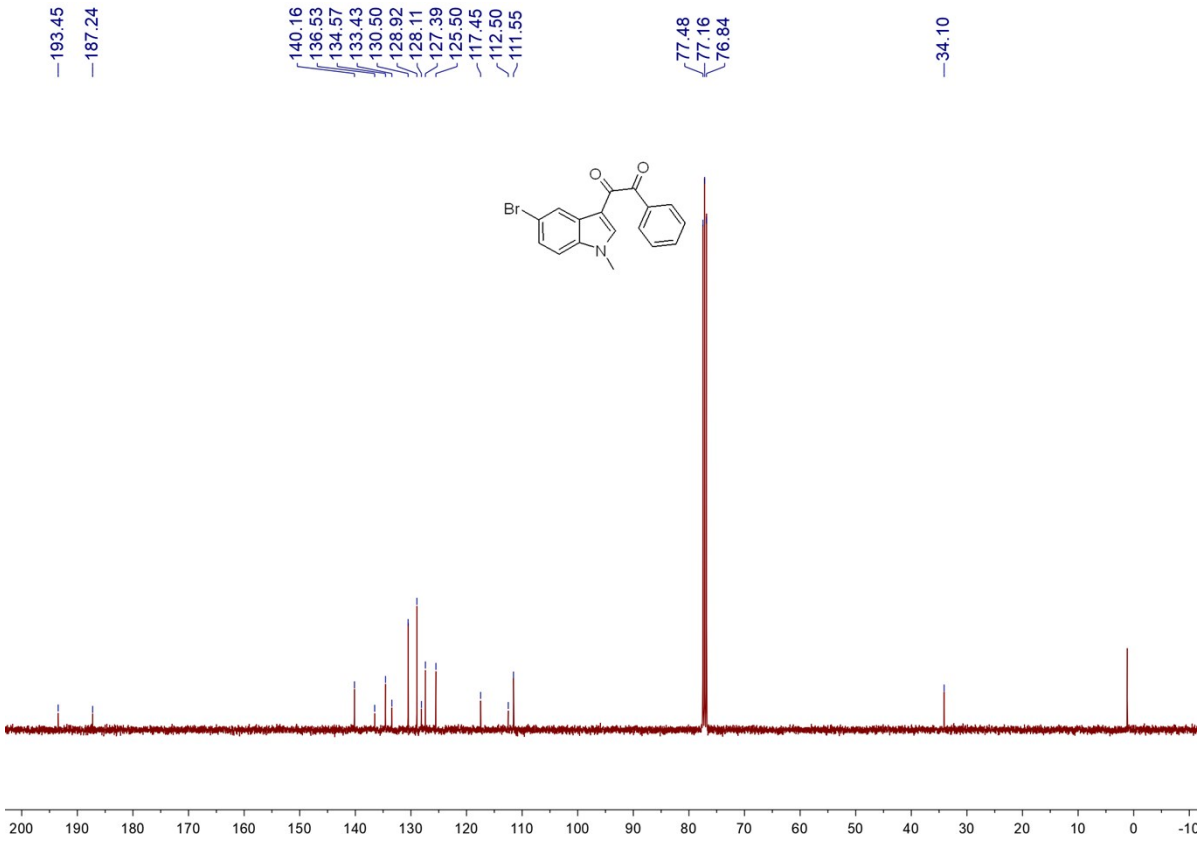
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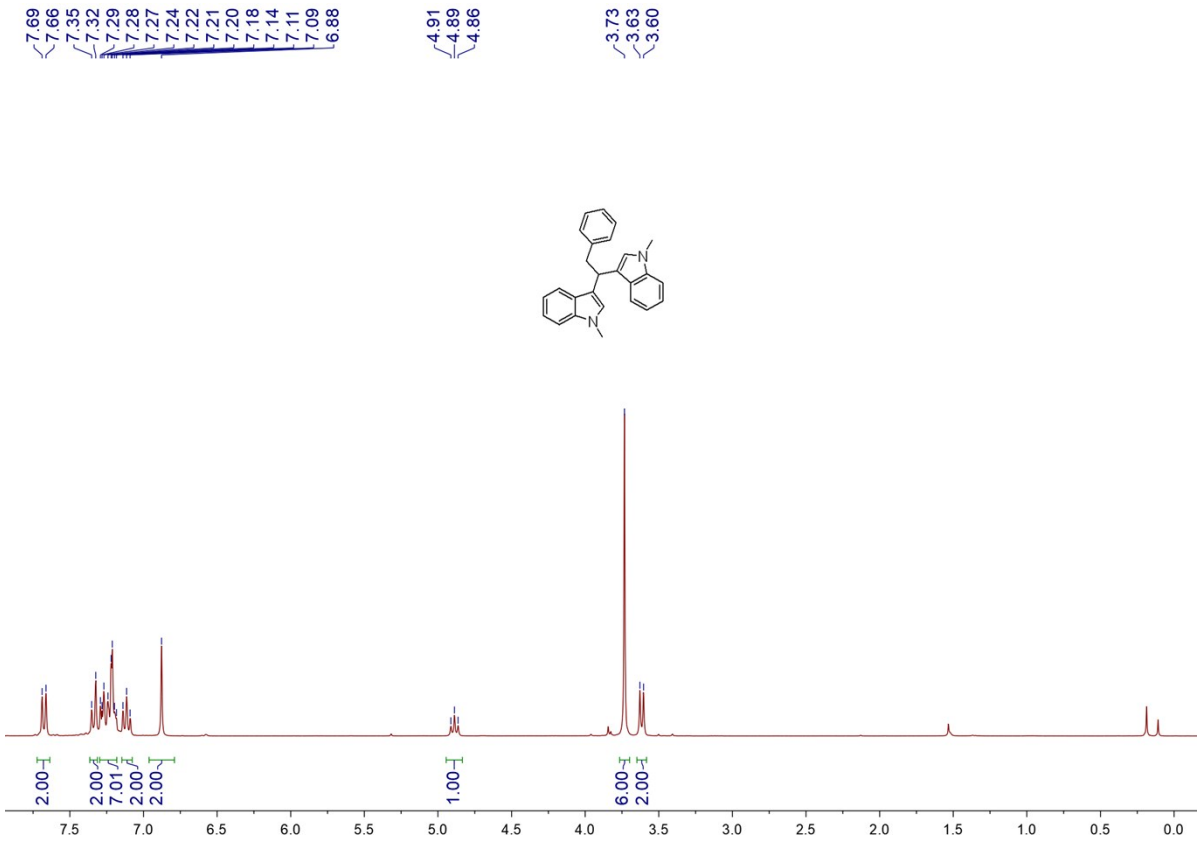
Product 4aa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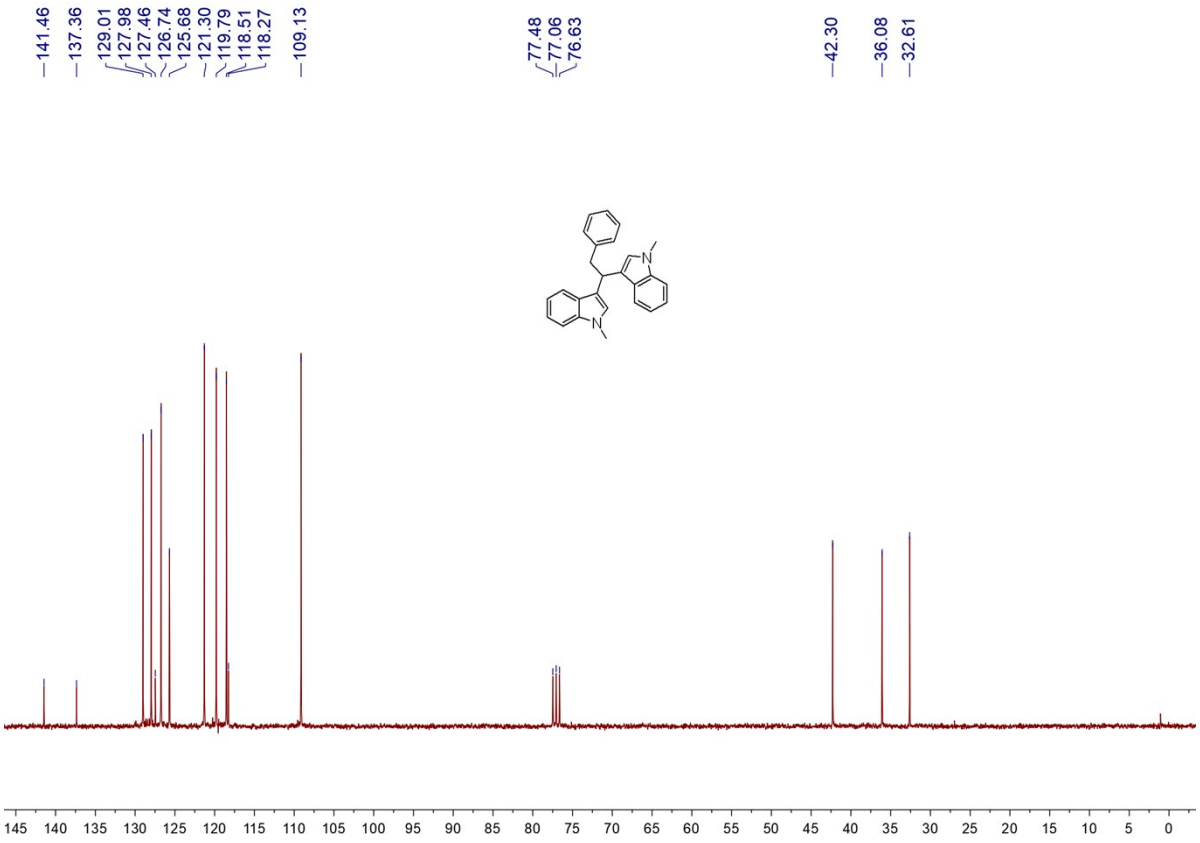
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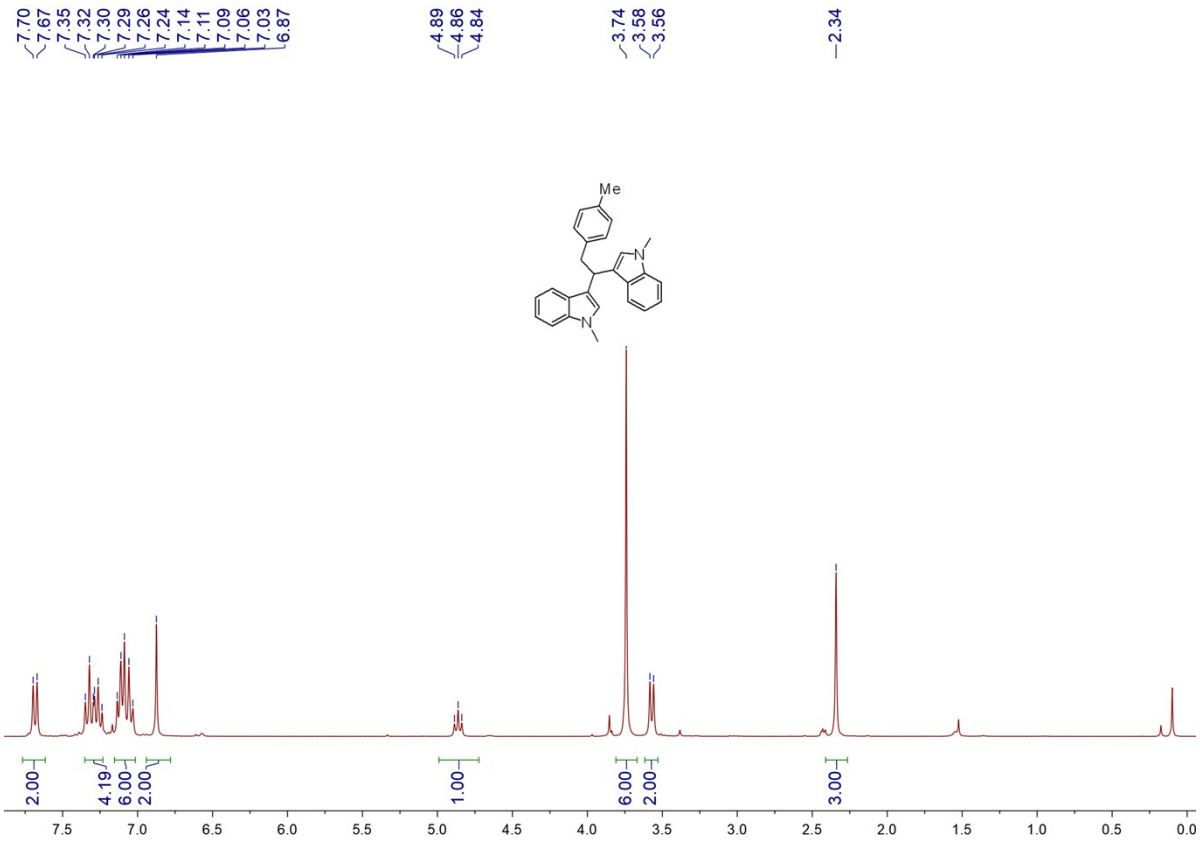
Product 4ba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4.86
4.84
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3.56
2.34
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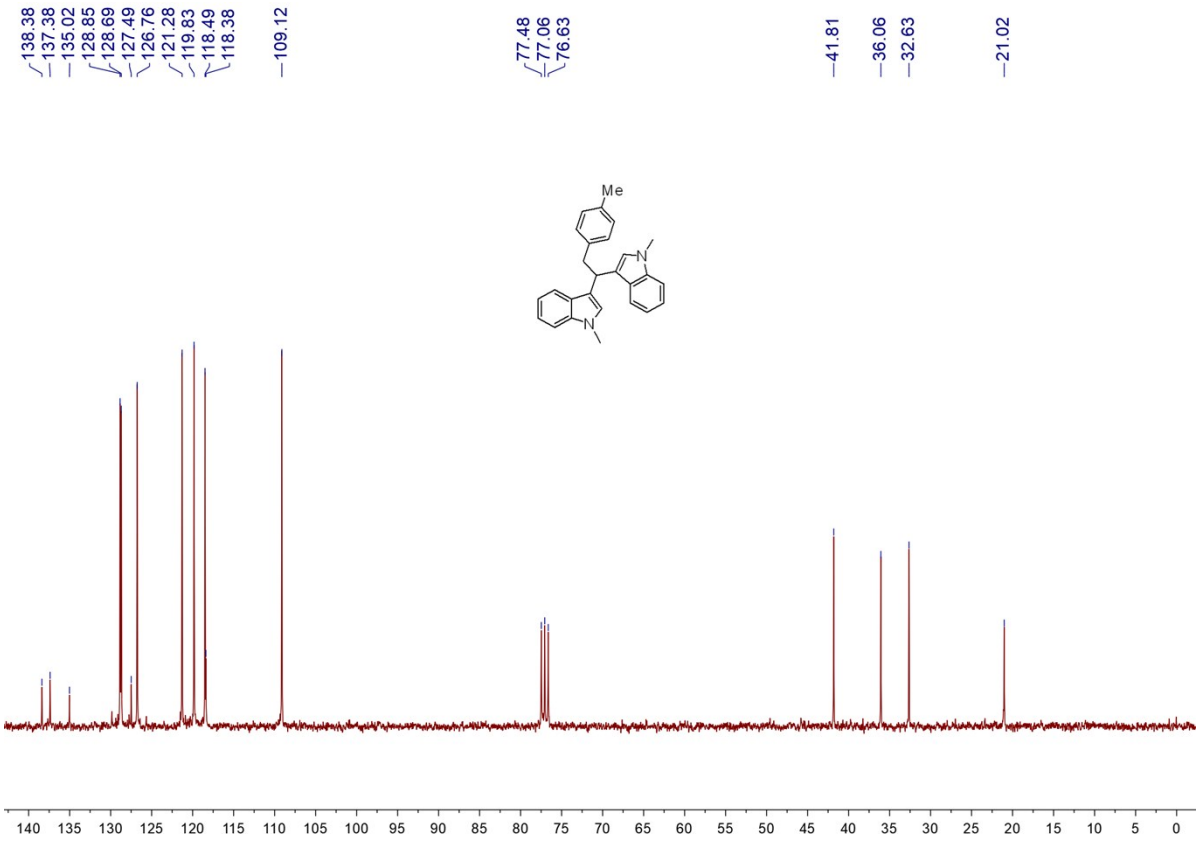
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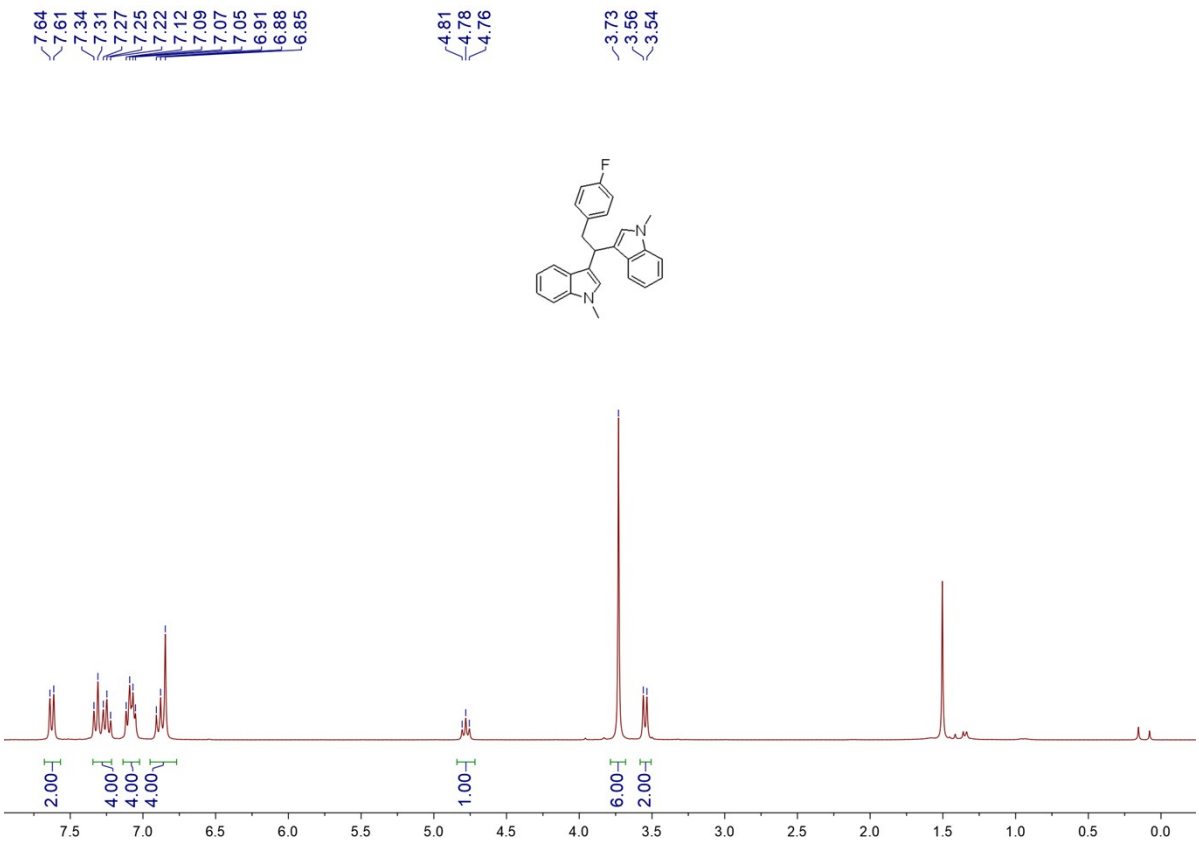
Product 4ca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4.00
1.00
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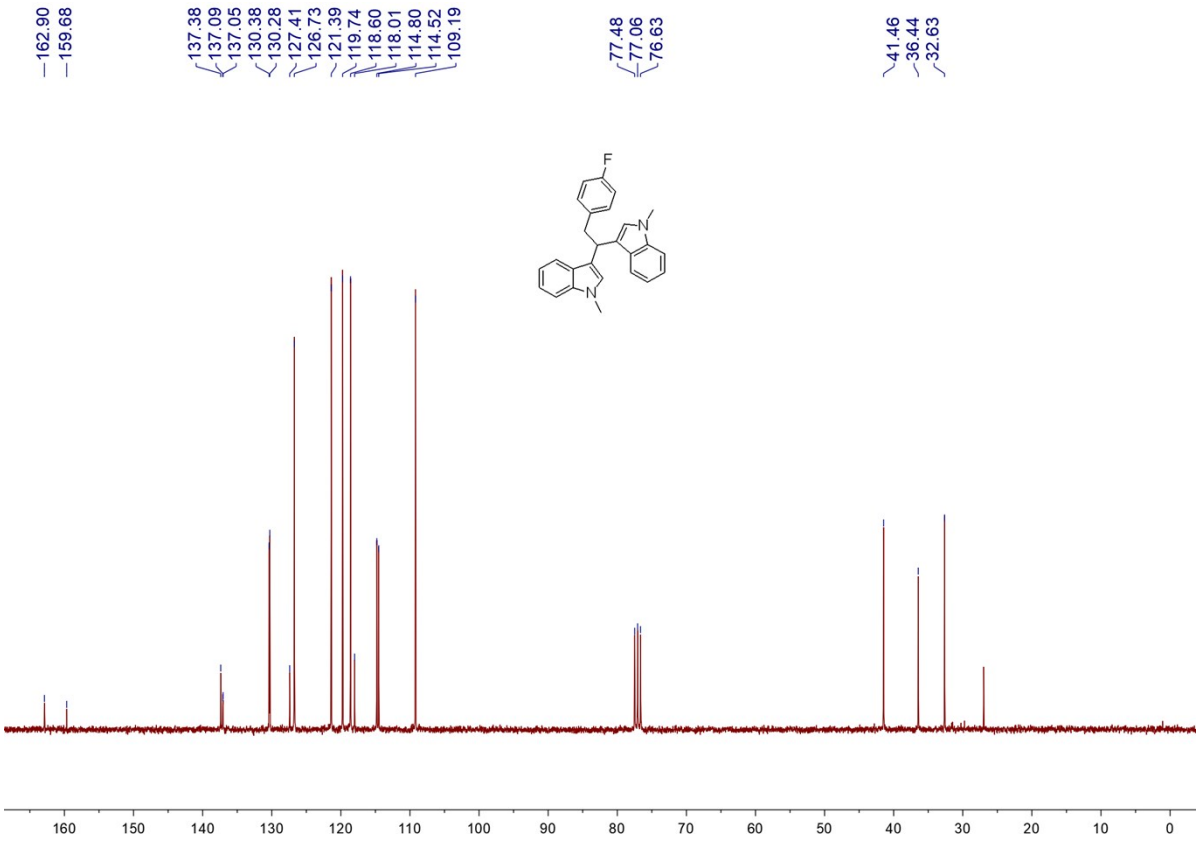
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109.19
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77.06
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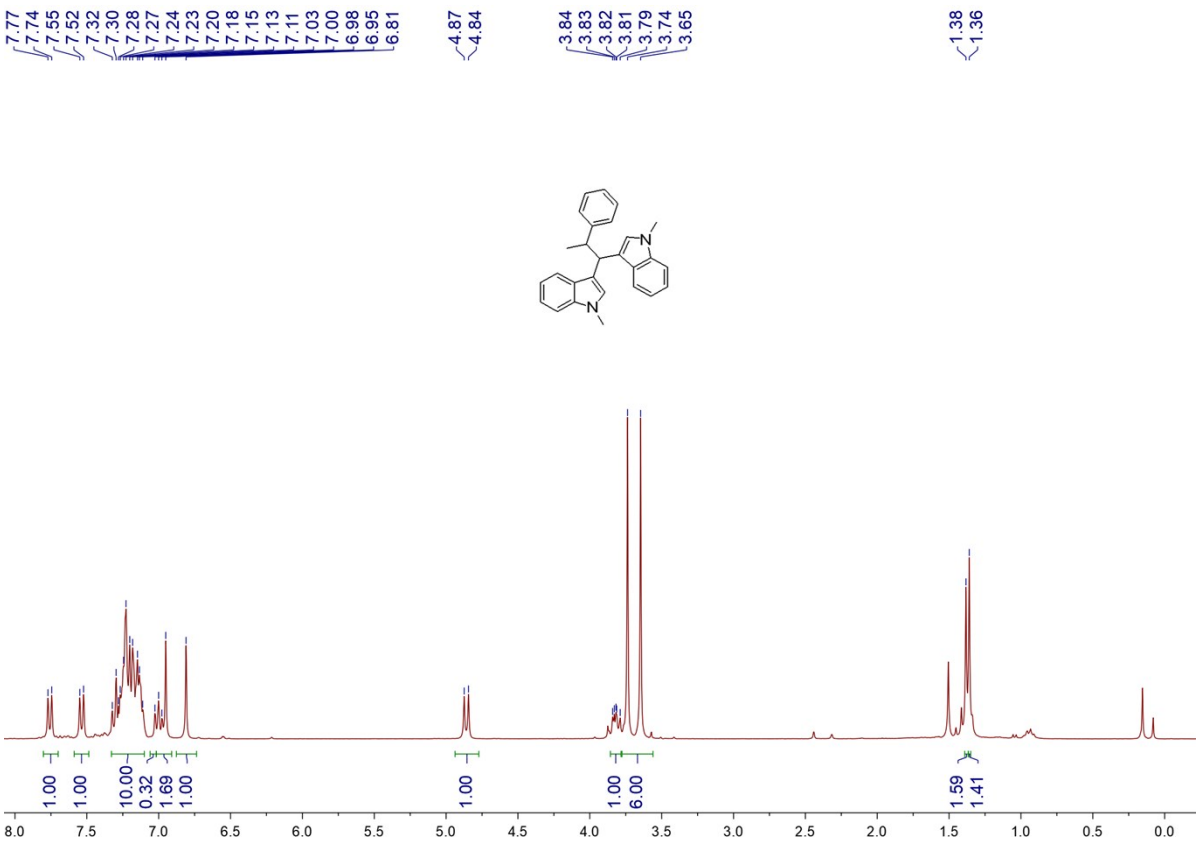
Product 4da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4.84
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3.81
3.79
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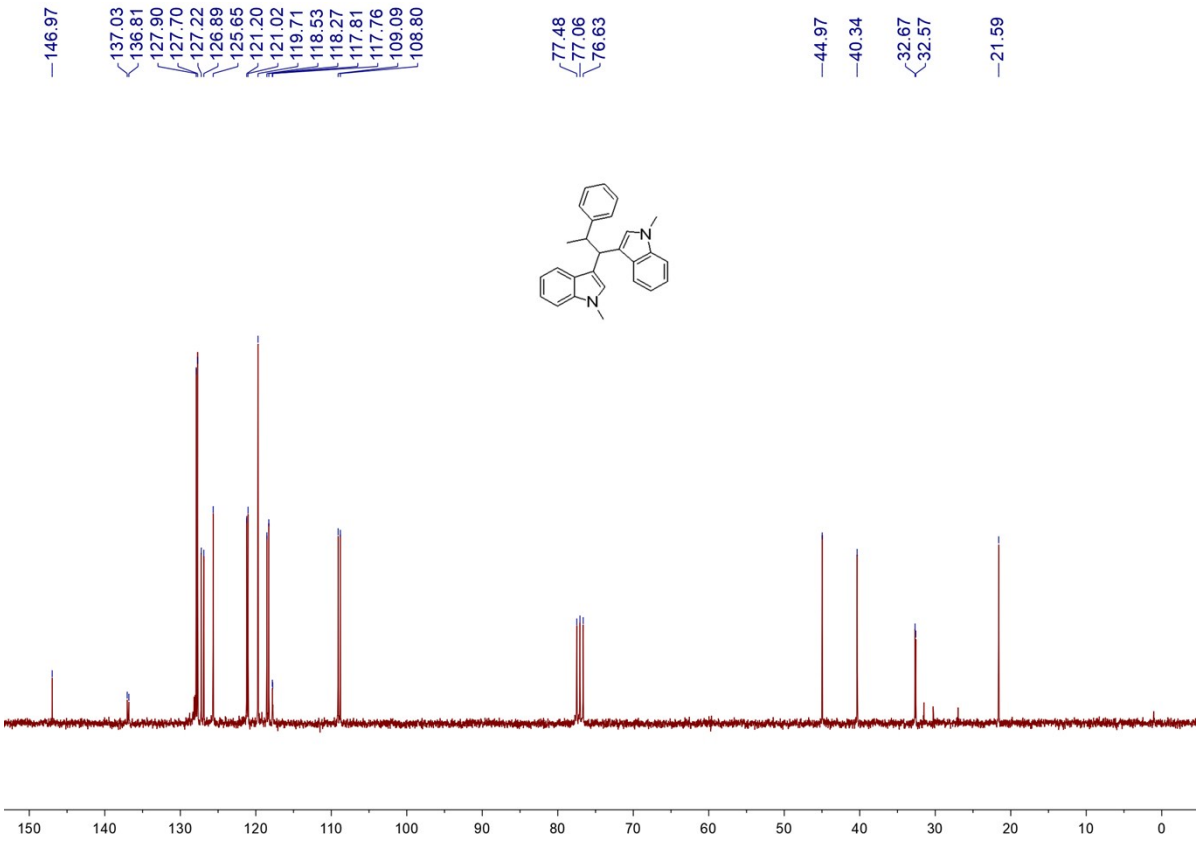
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44.97
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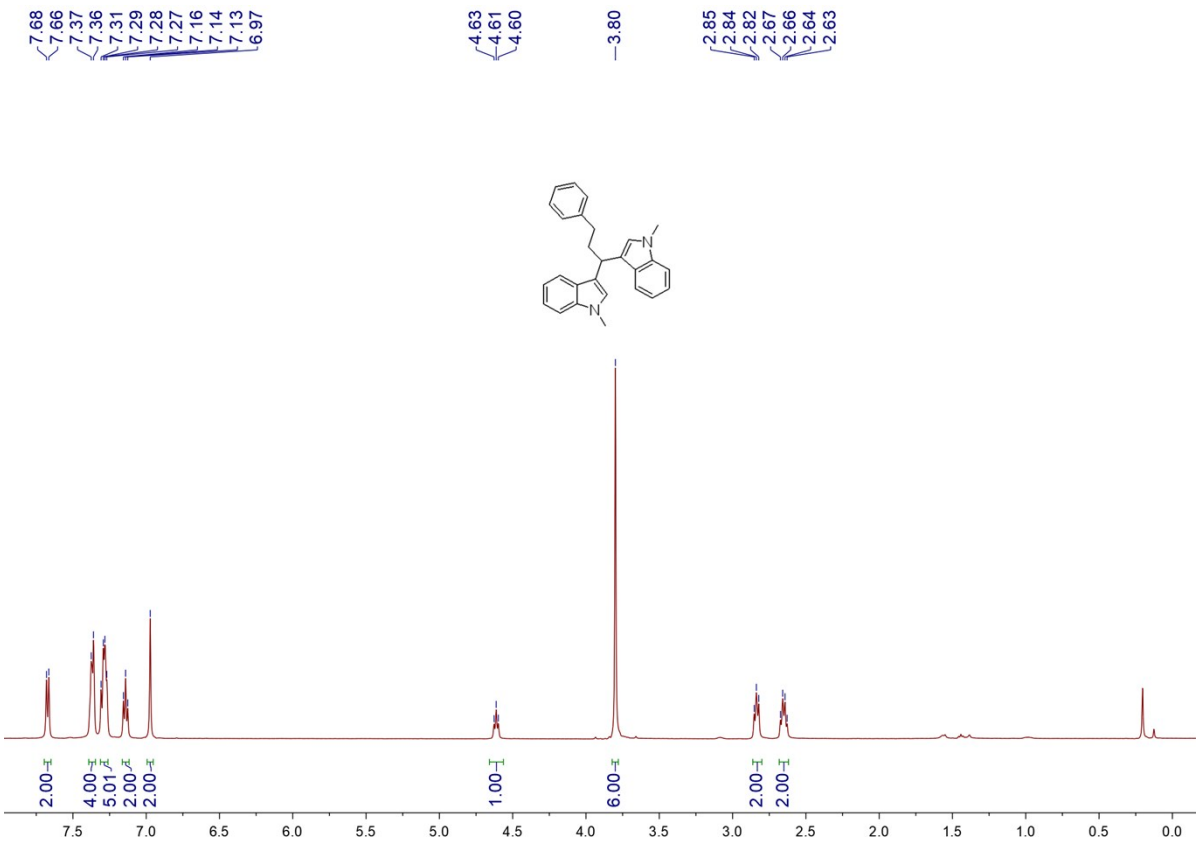
Product 4ea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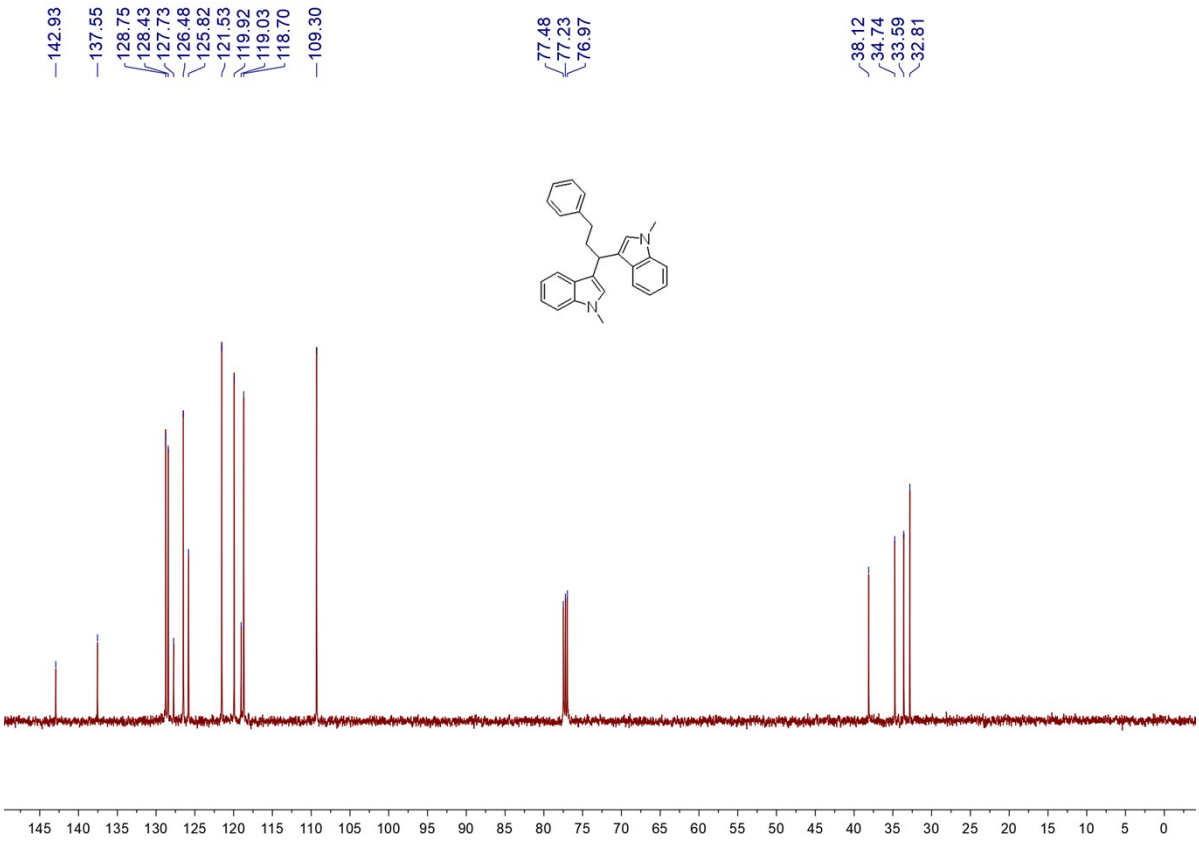
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77.23
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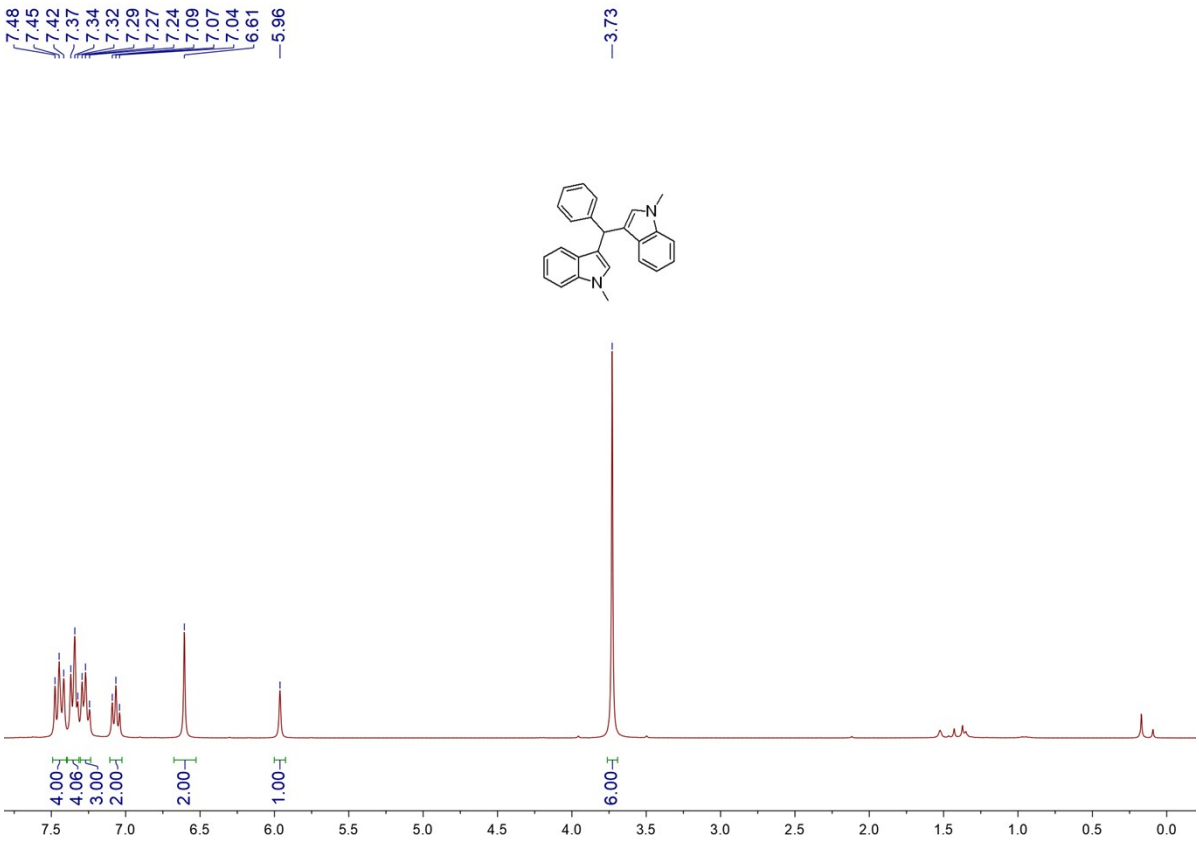
32.81
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0

Product 4fa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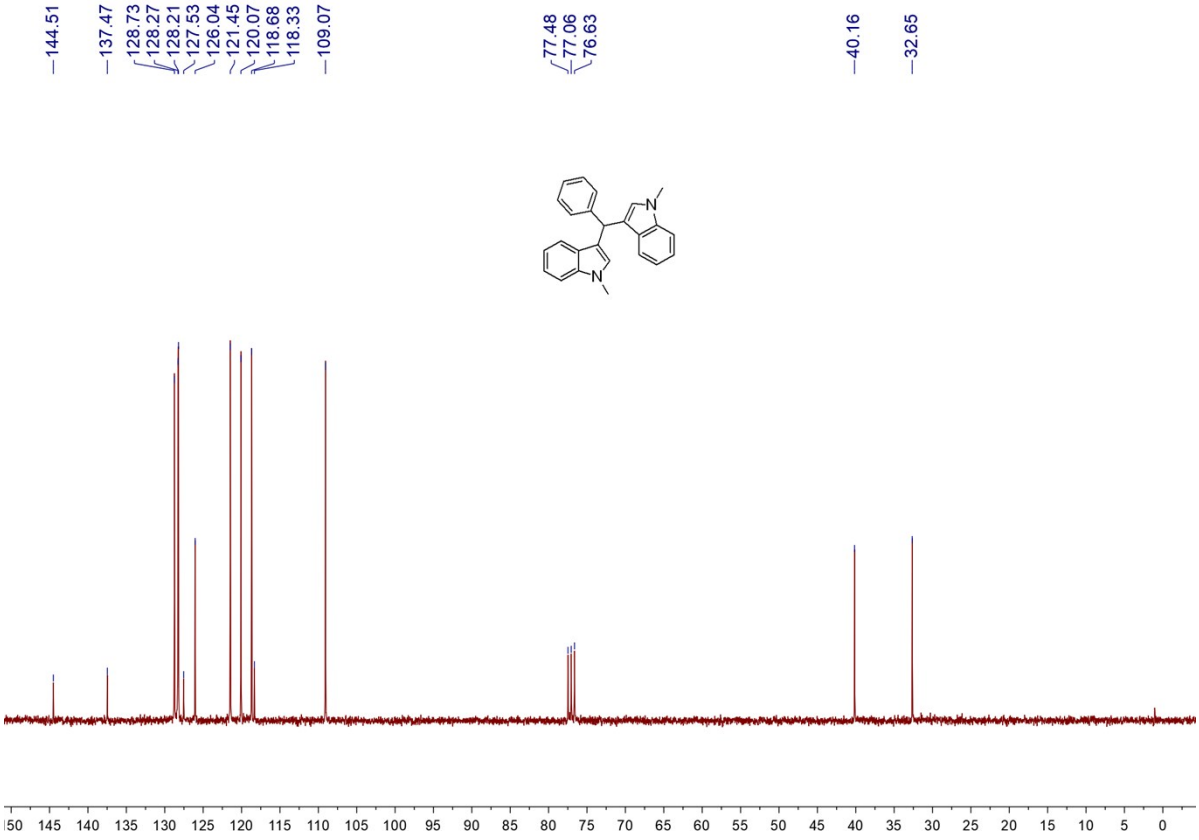
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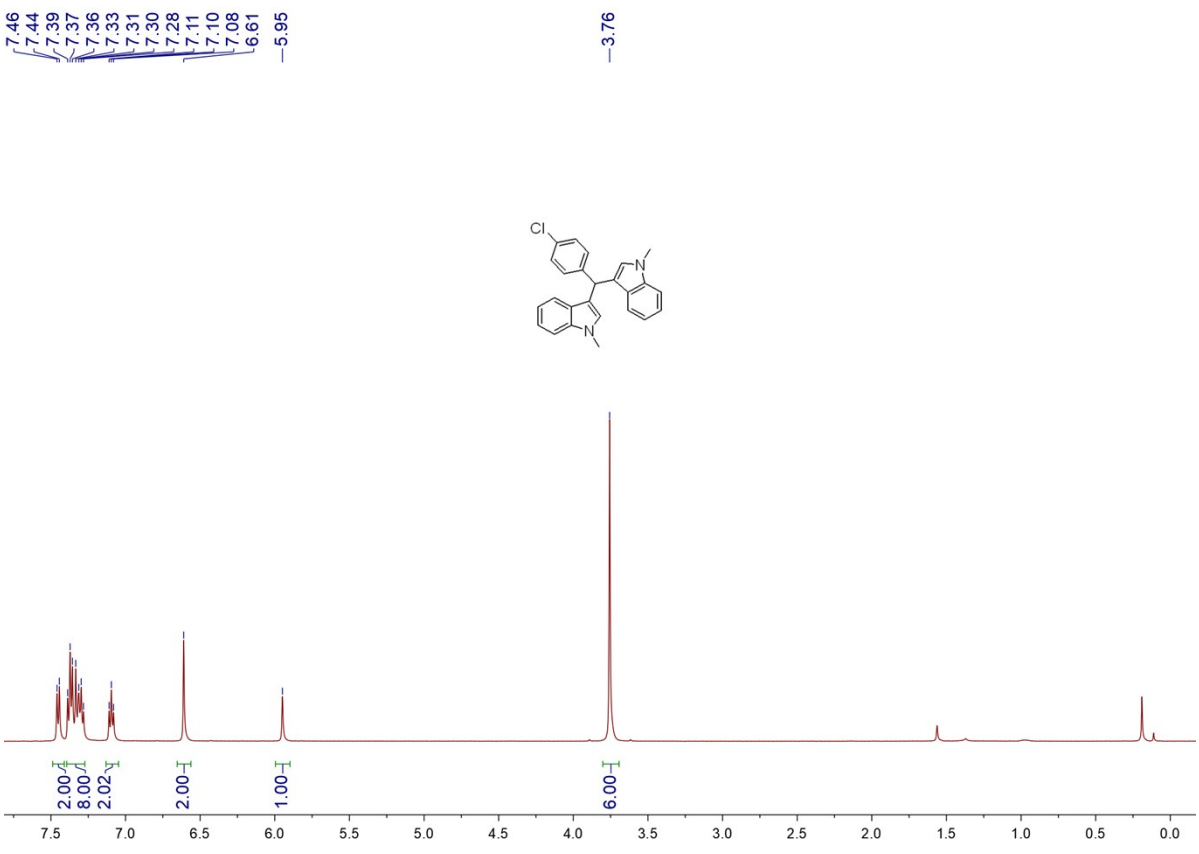
Product 4ga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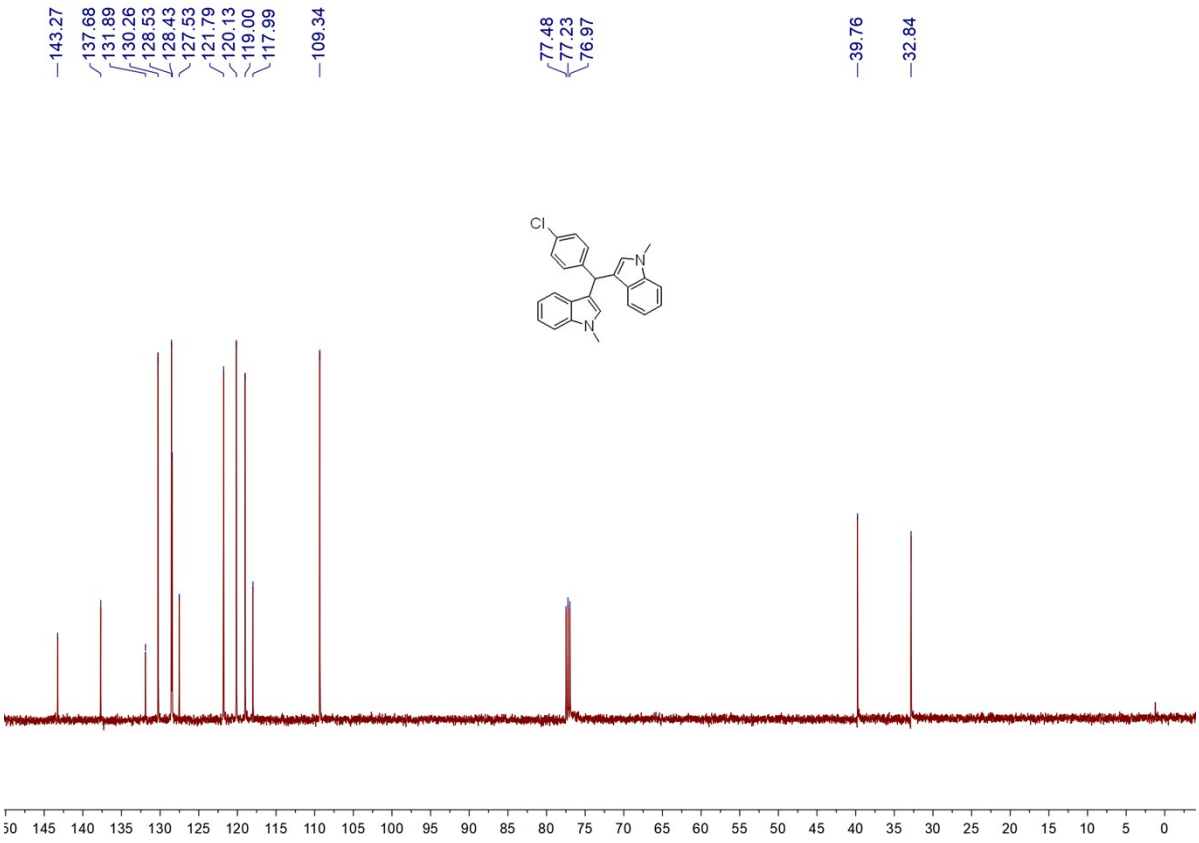
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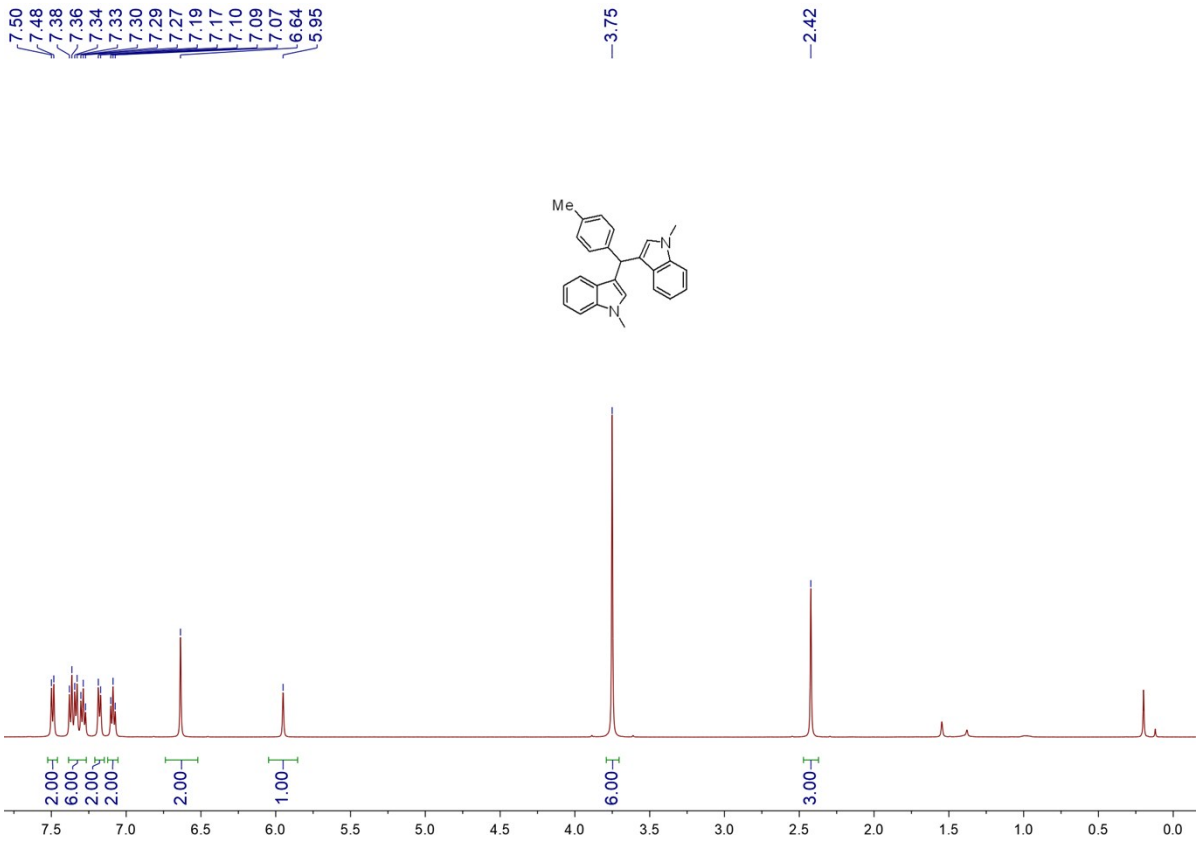
Product 4ha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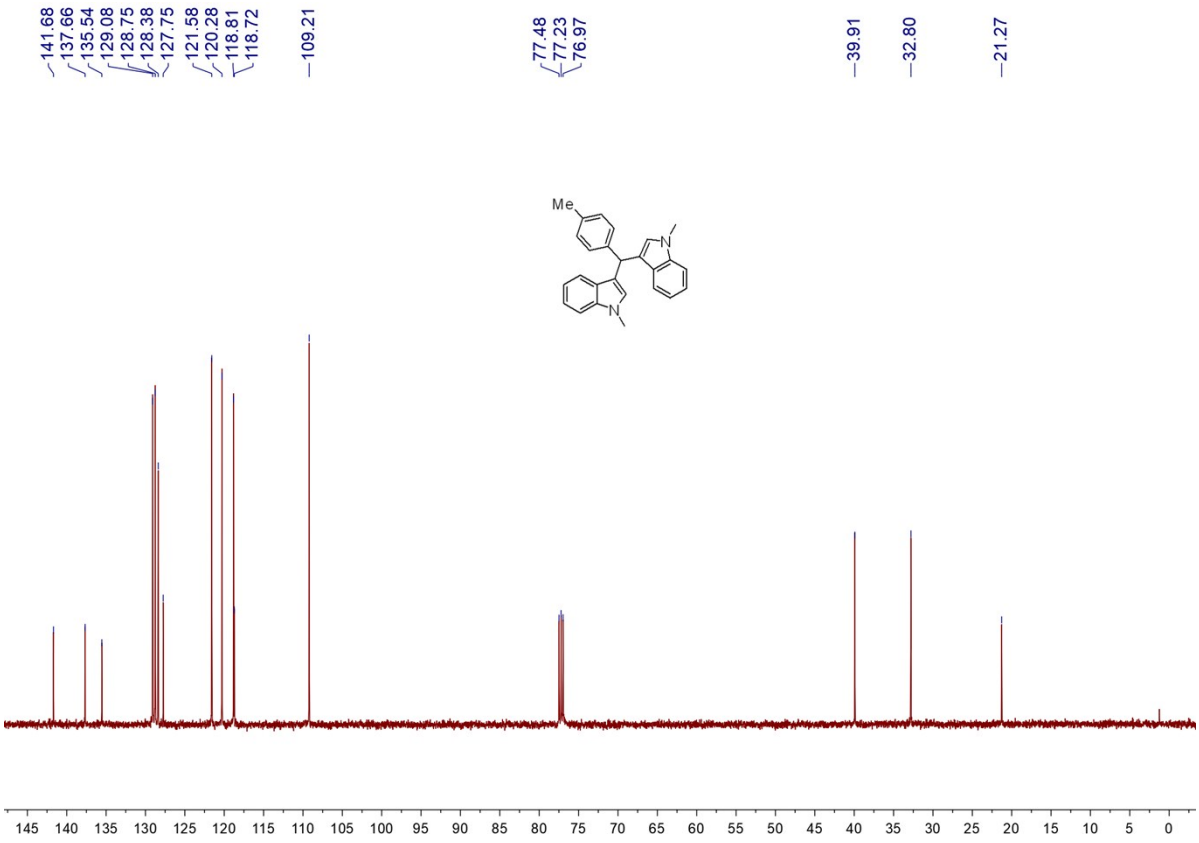
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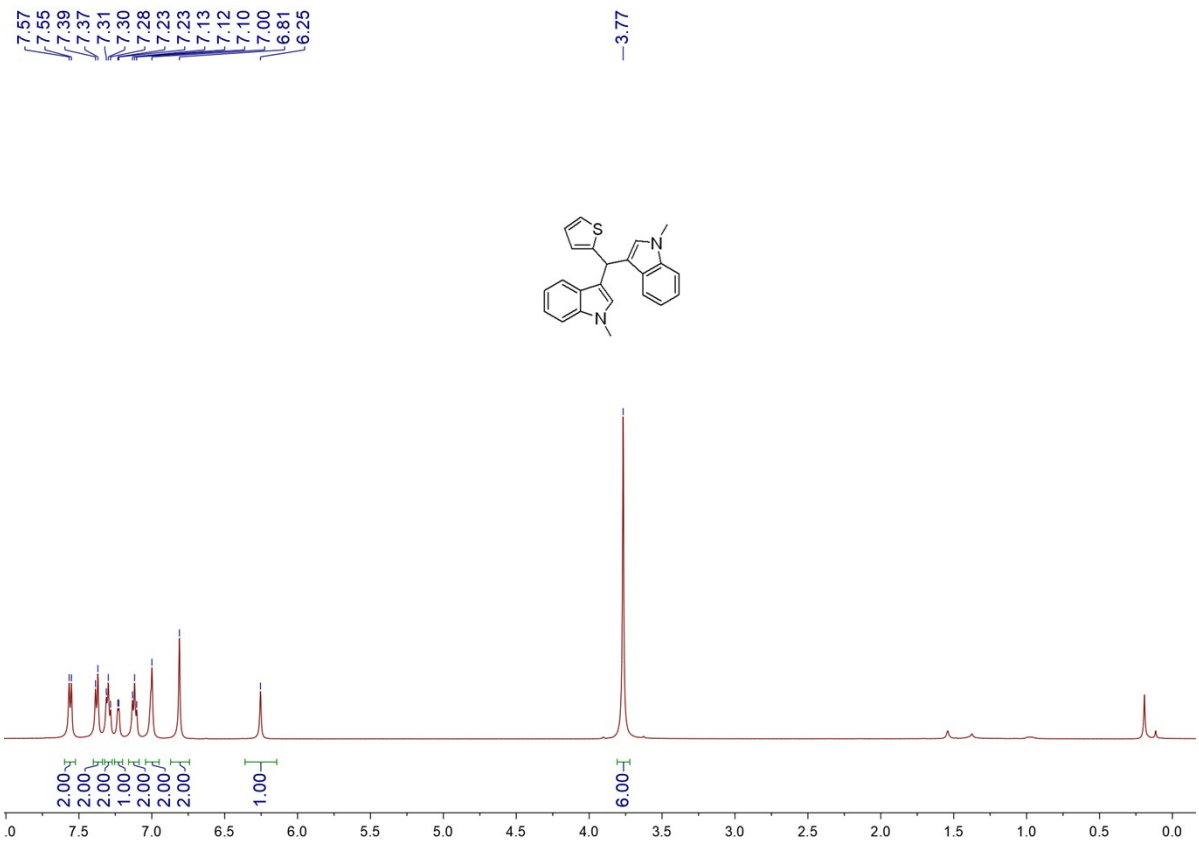
Product 4ia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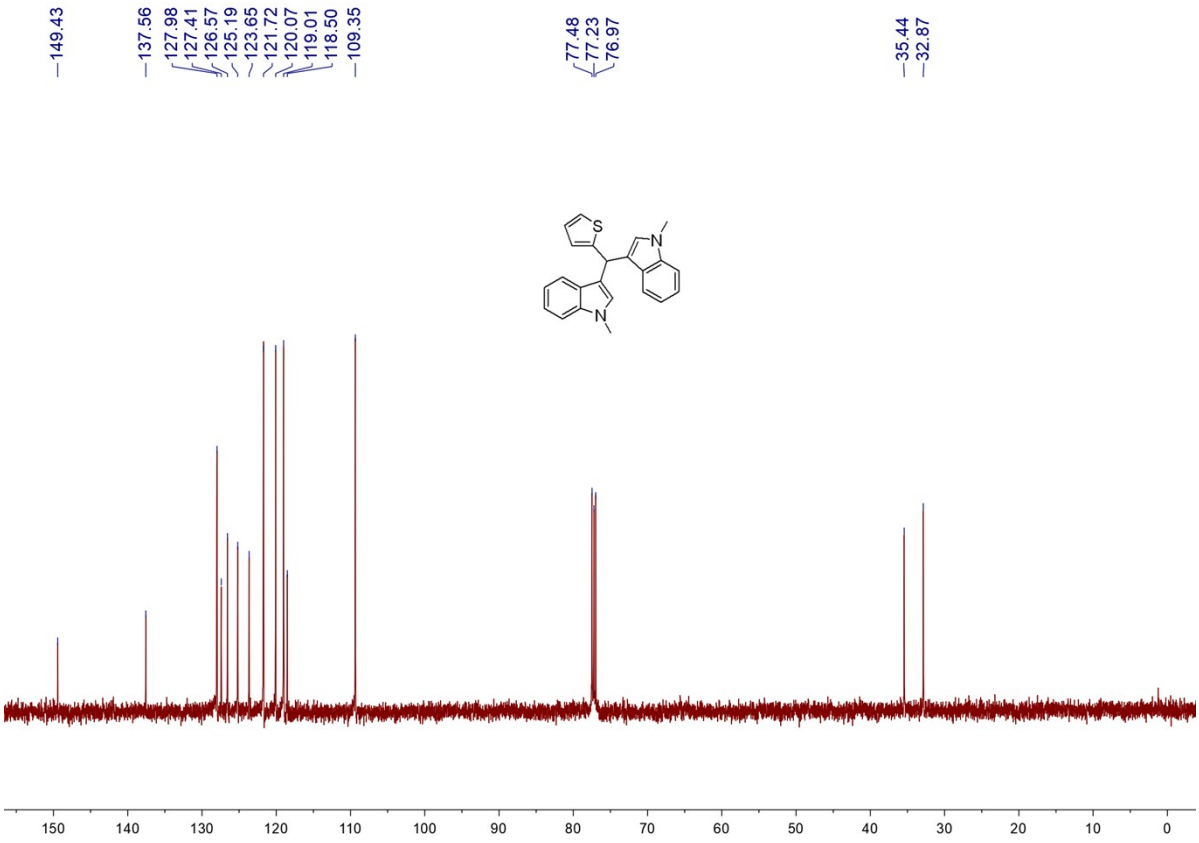
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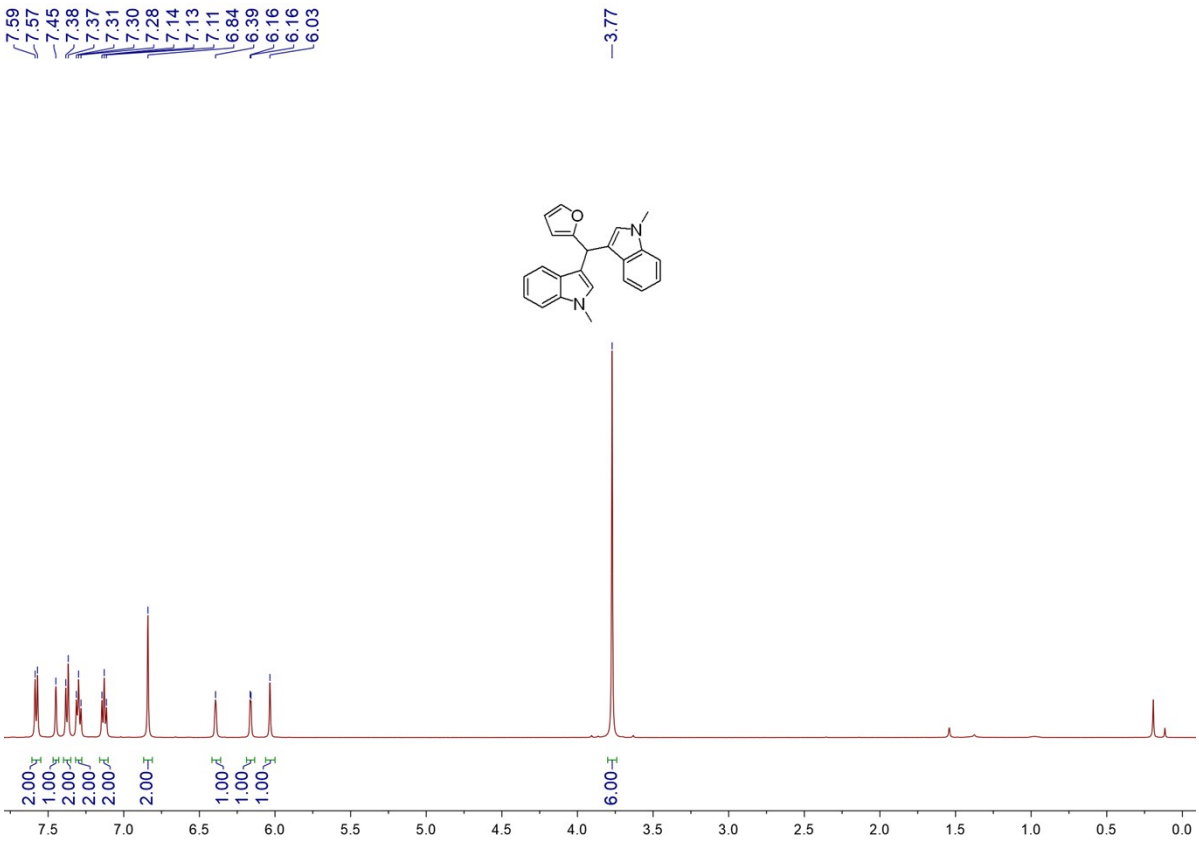
Product 4ja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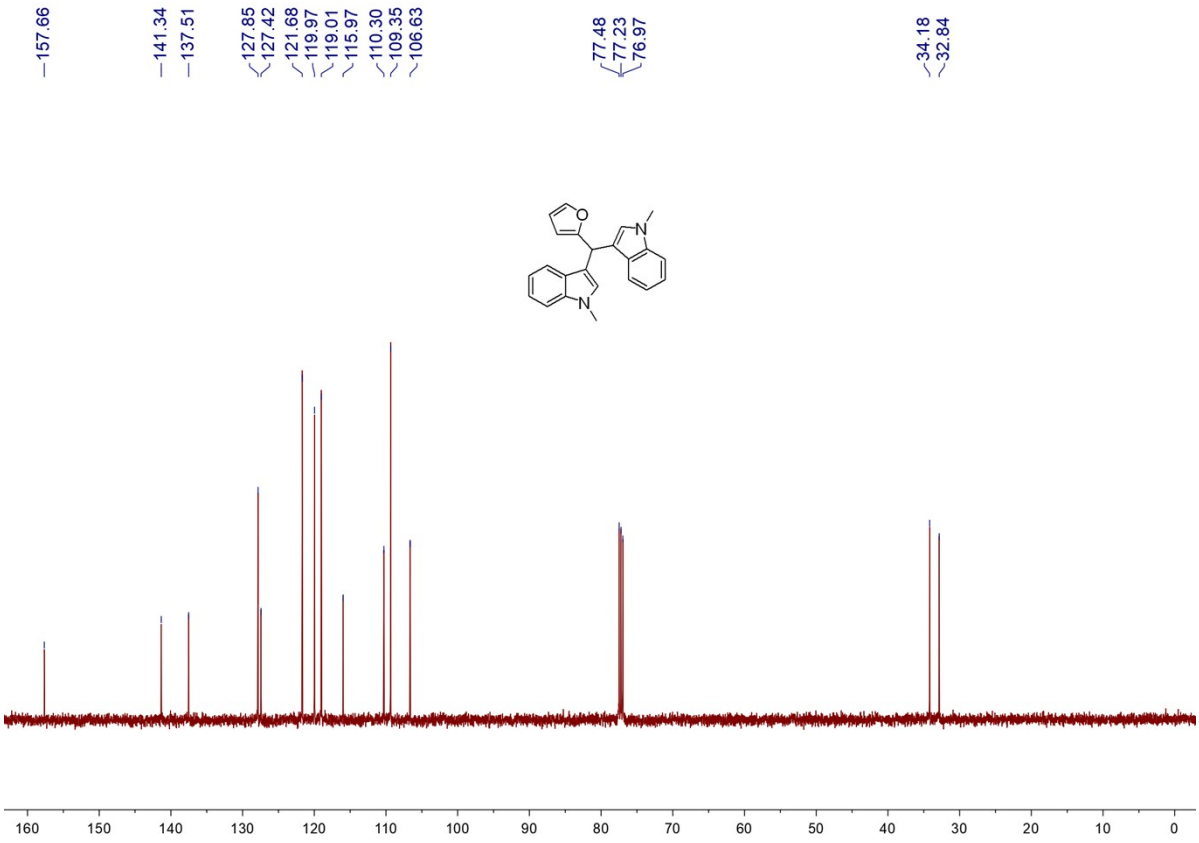
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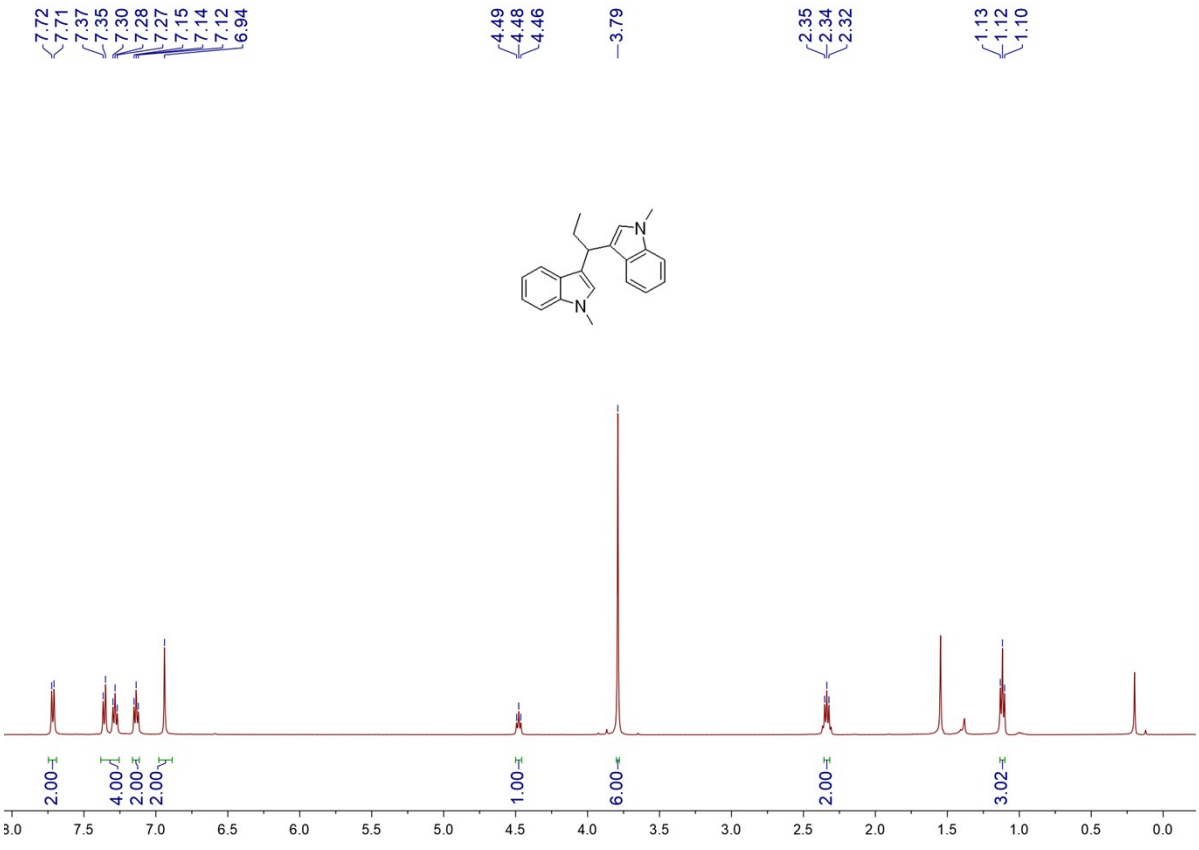
Product 4ka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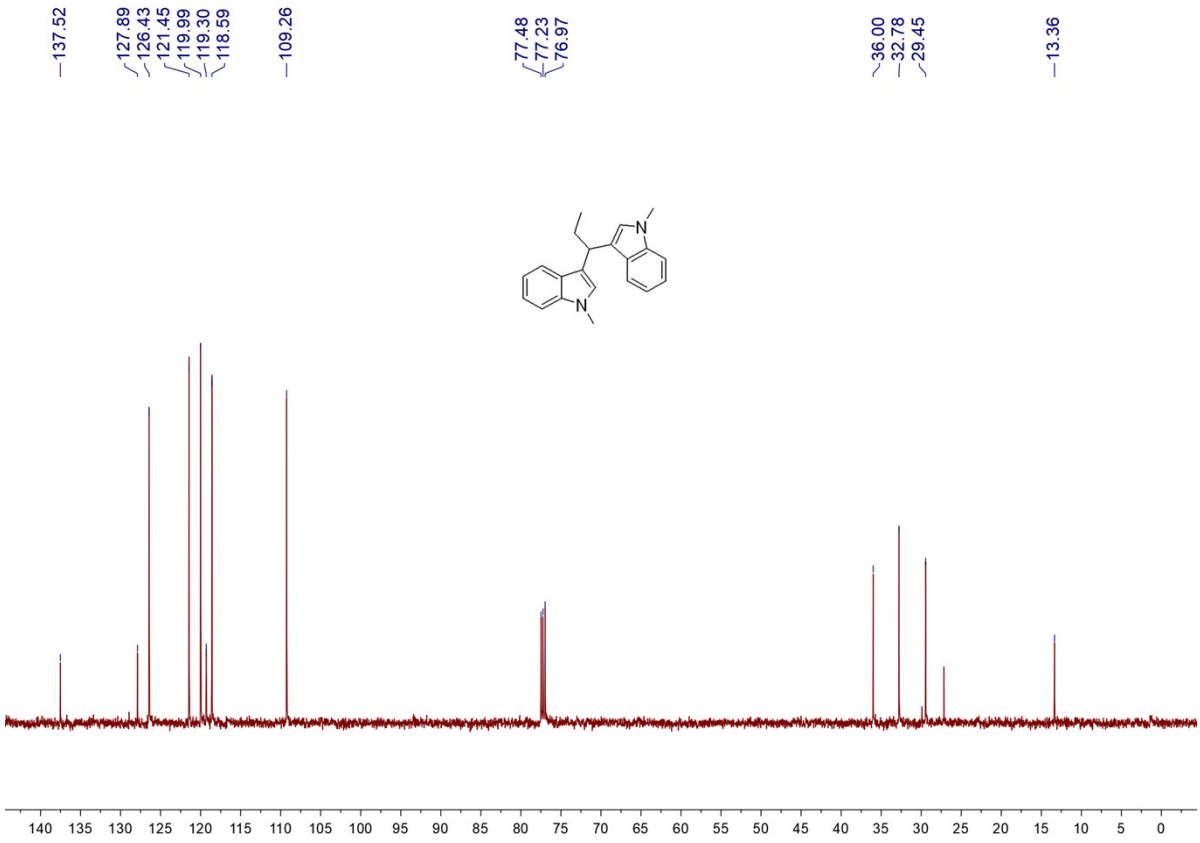
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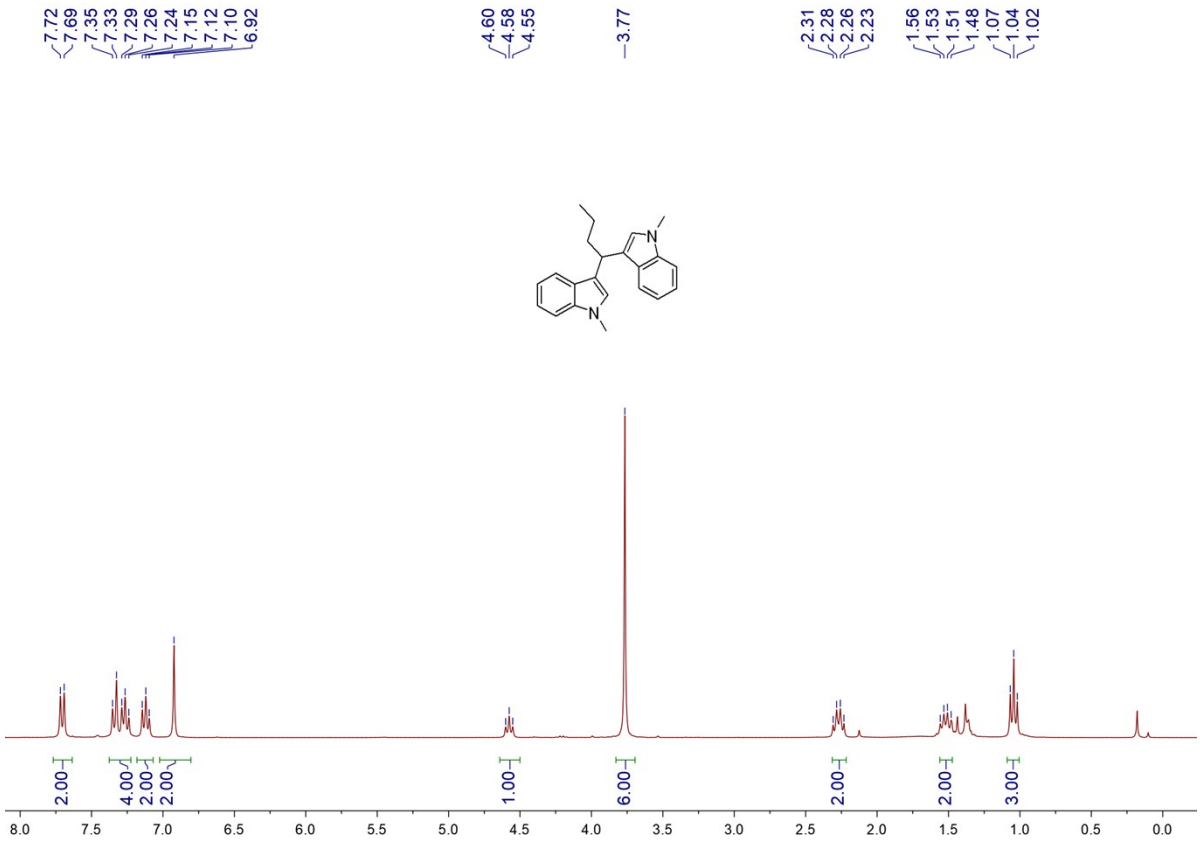
Product 4la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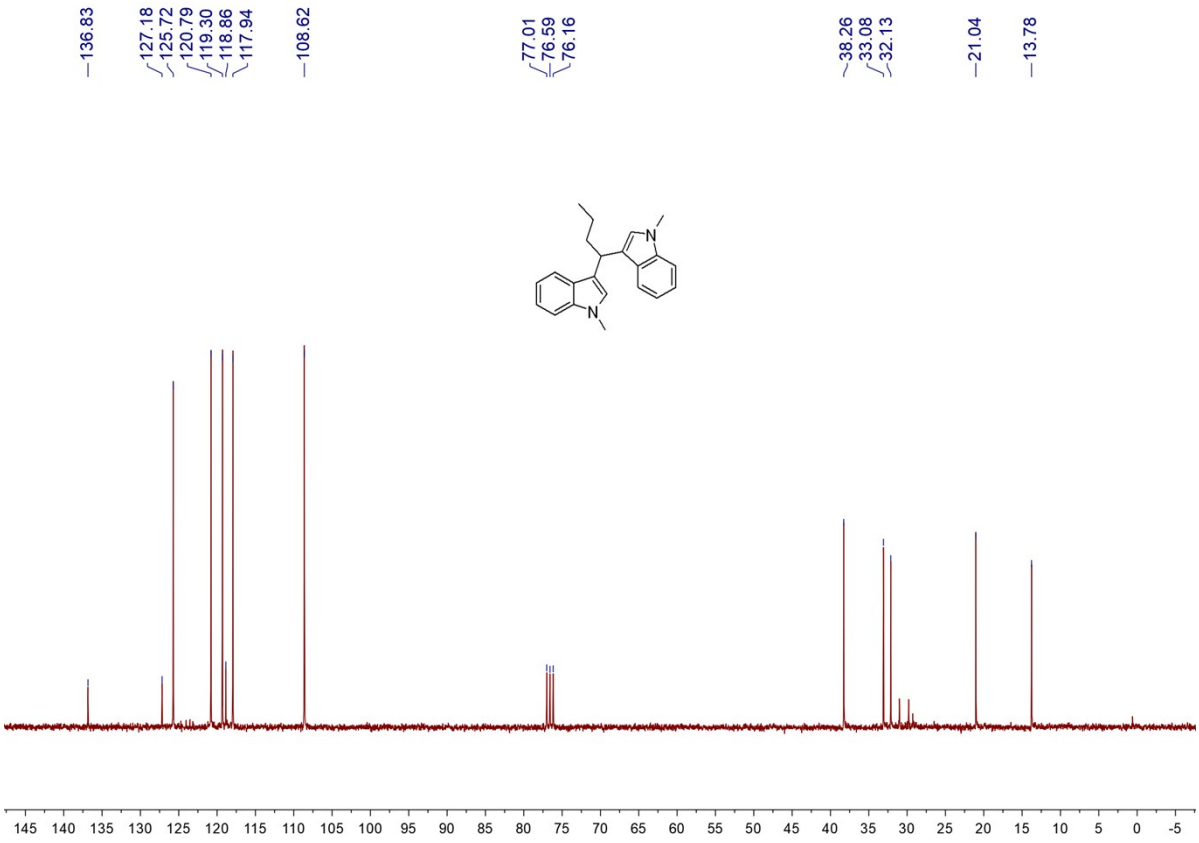
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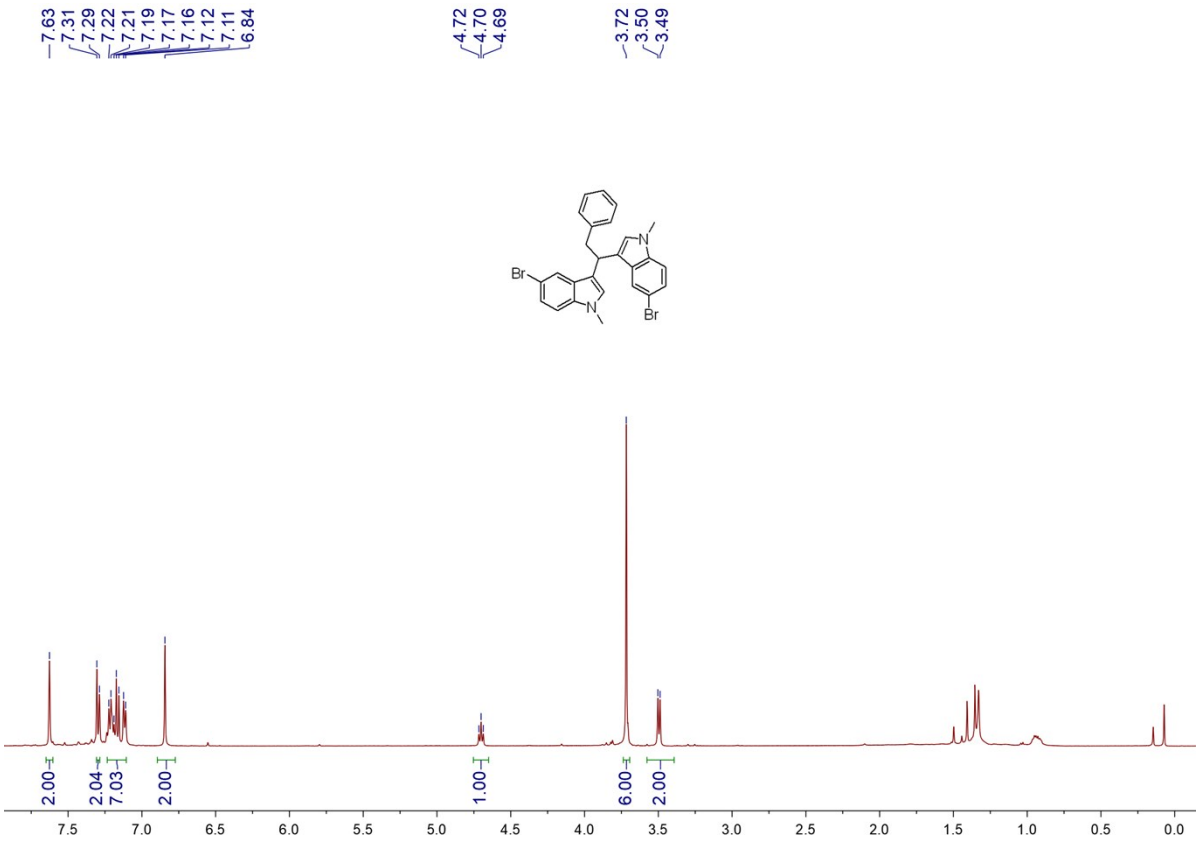
Product 4ab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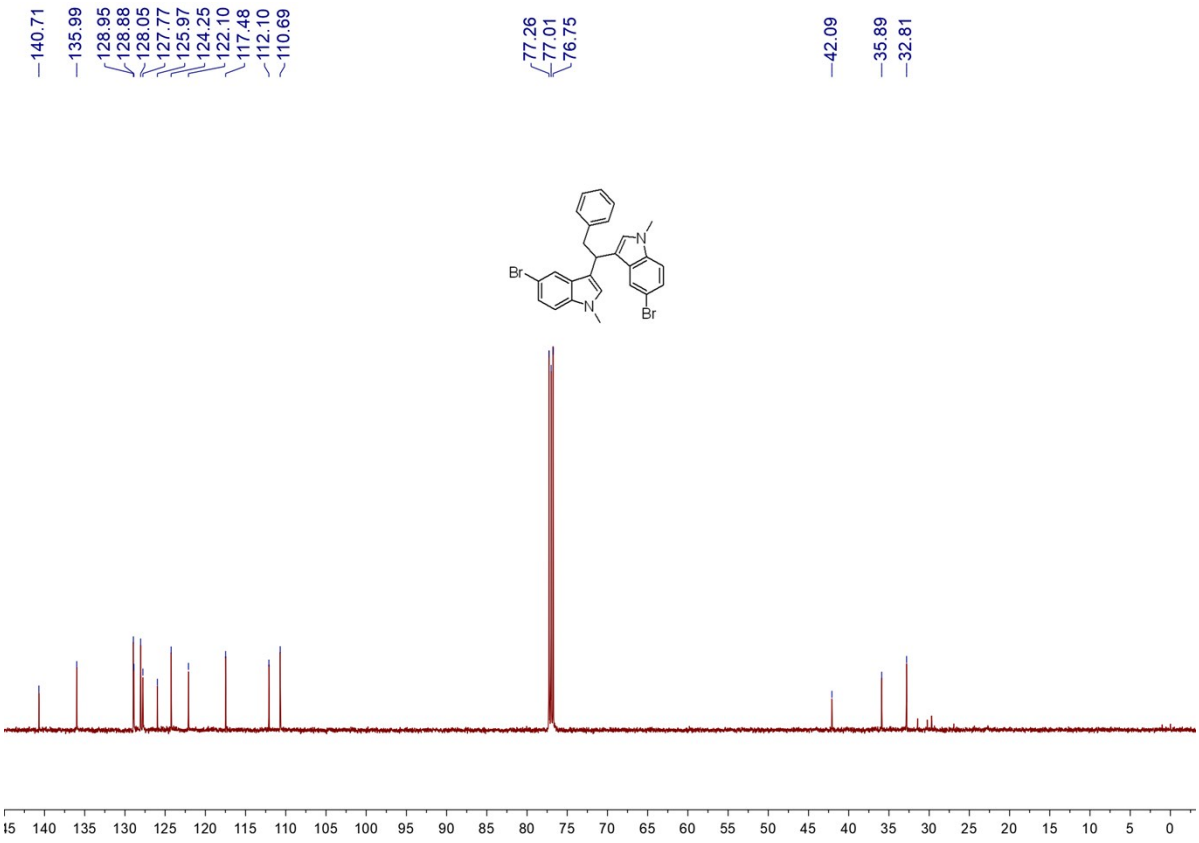
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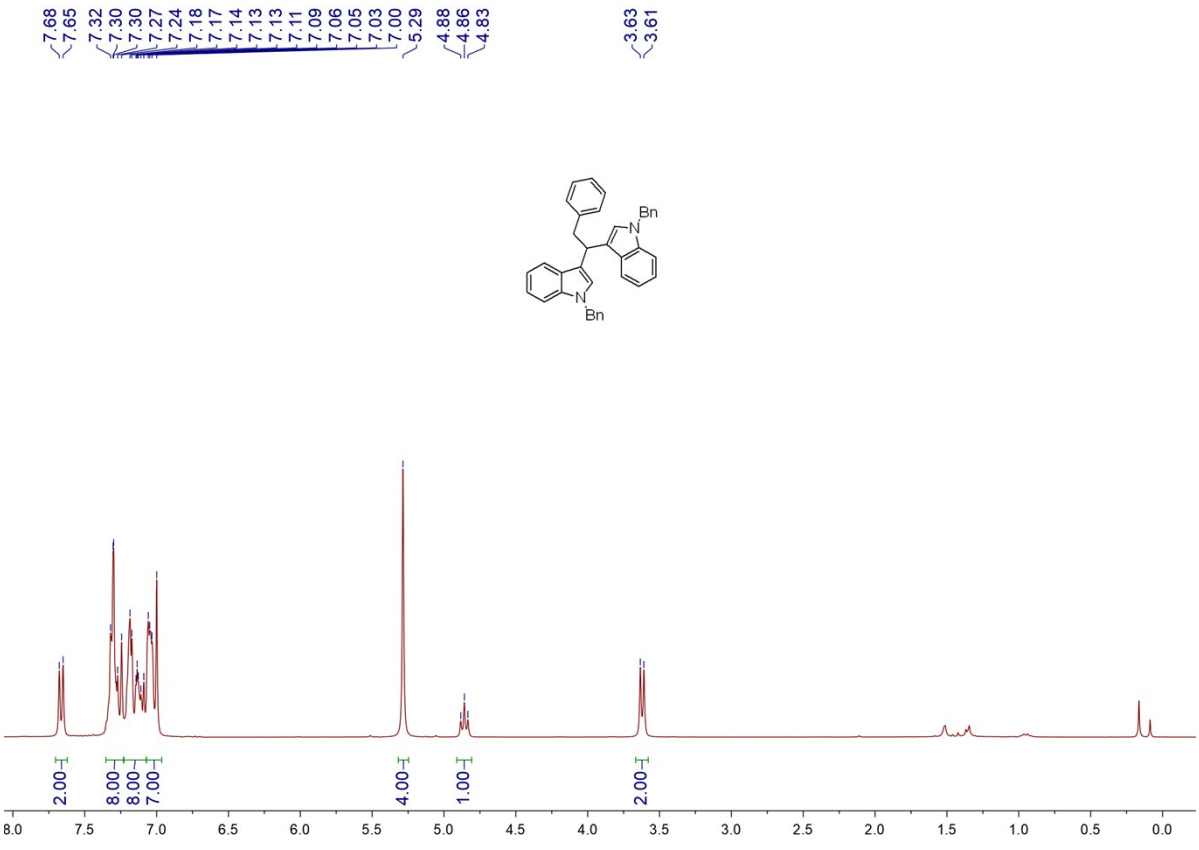
Product 4ad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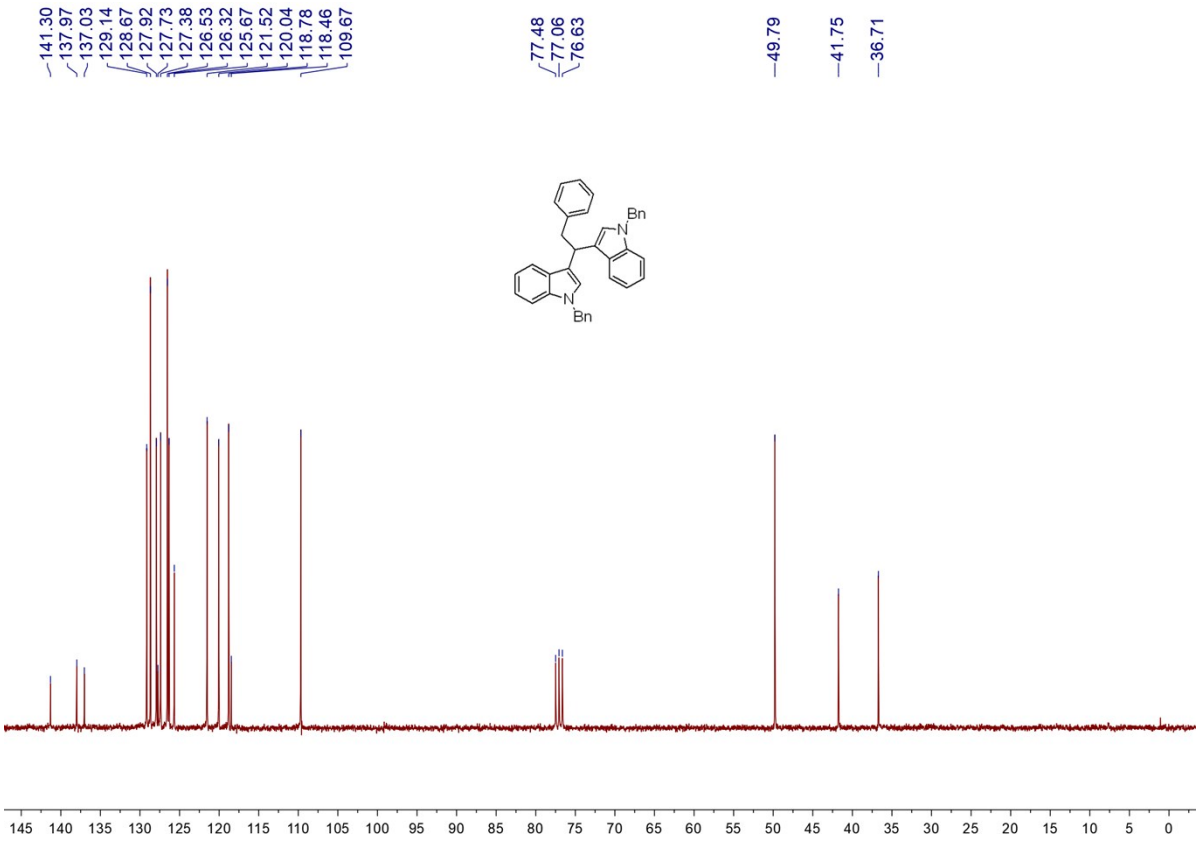
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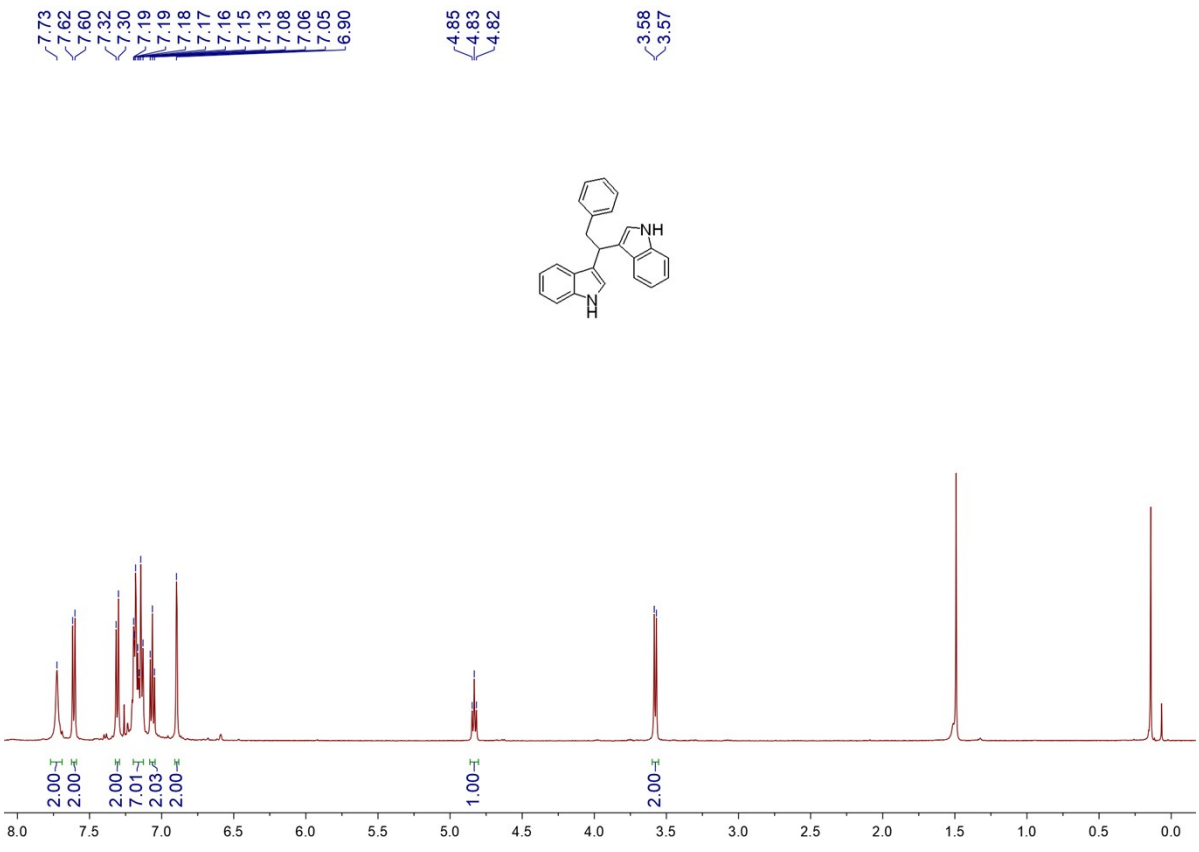
Product 4ae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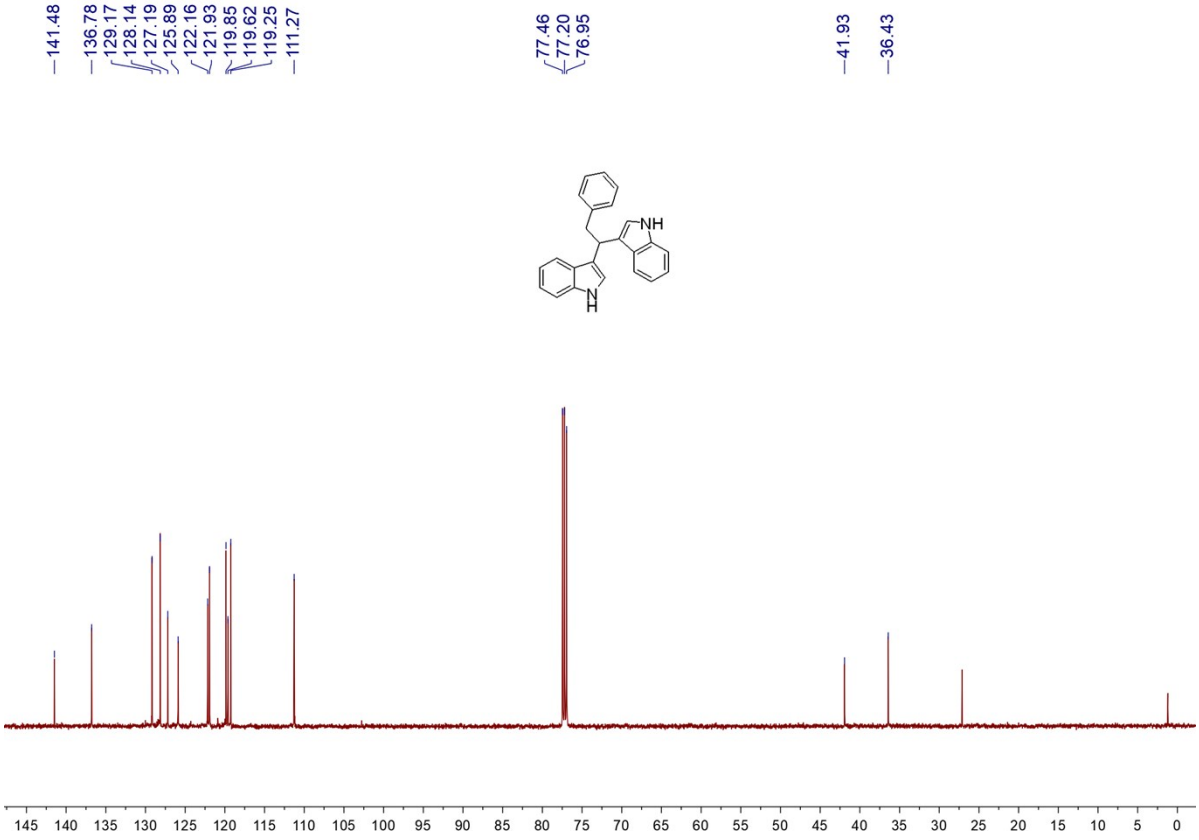
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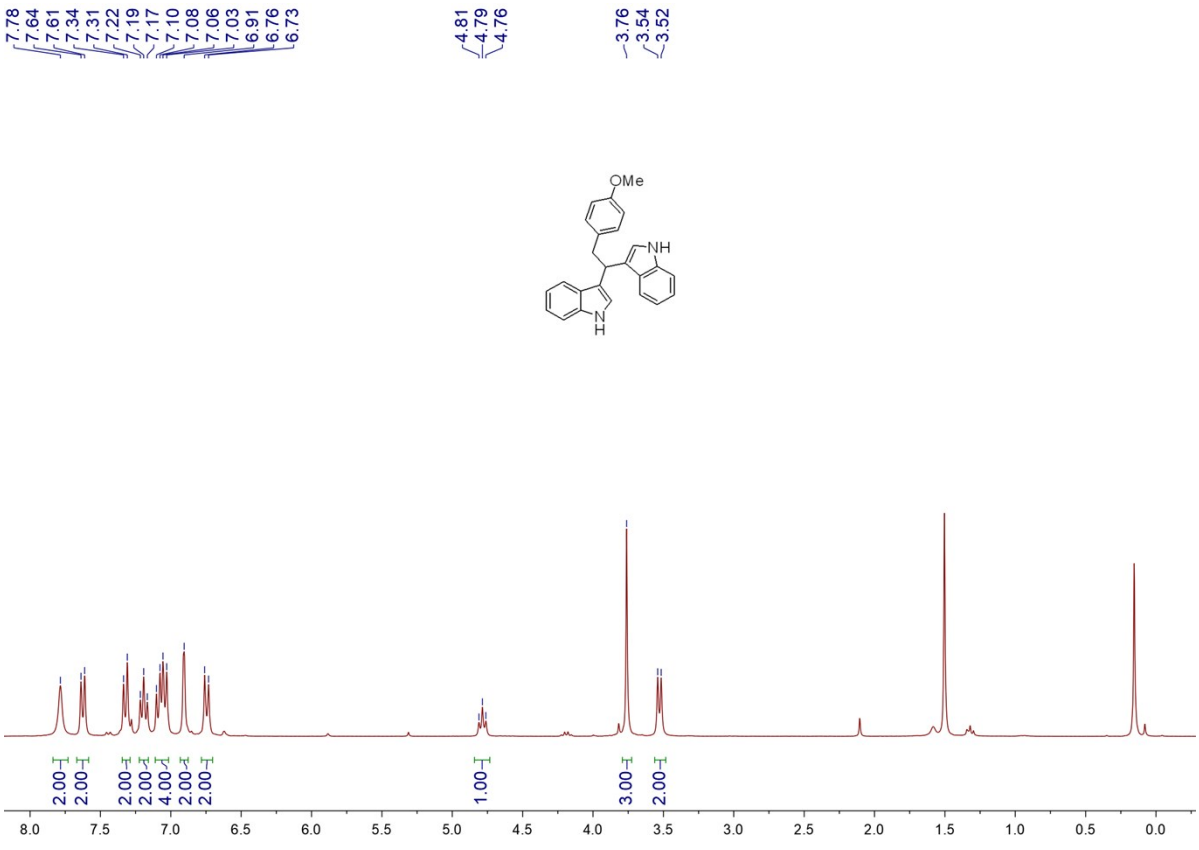
Product 4af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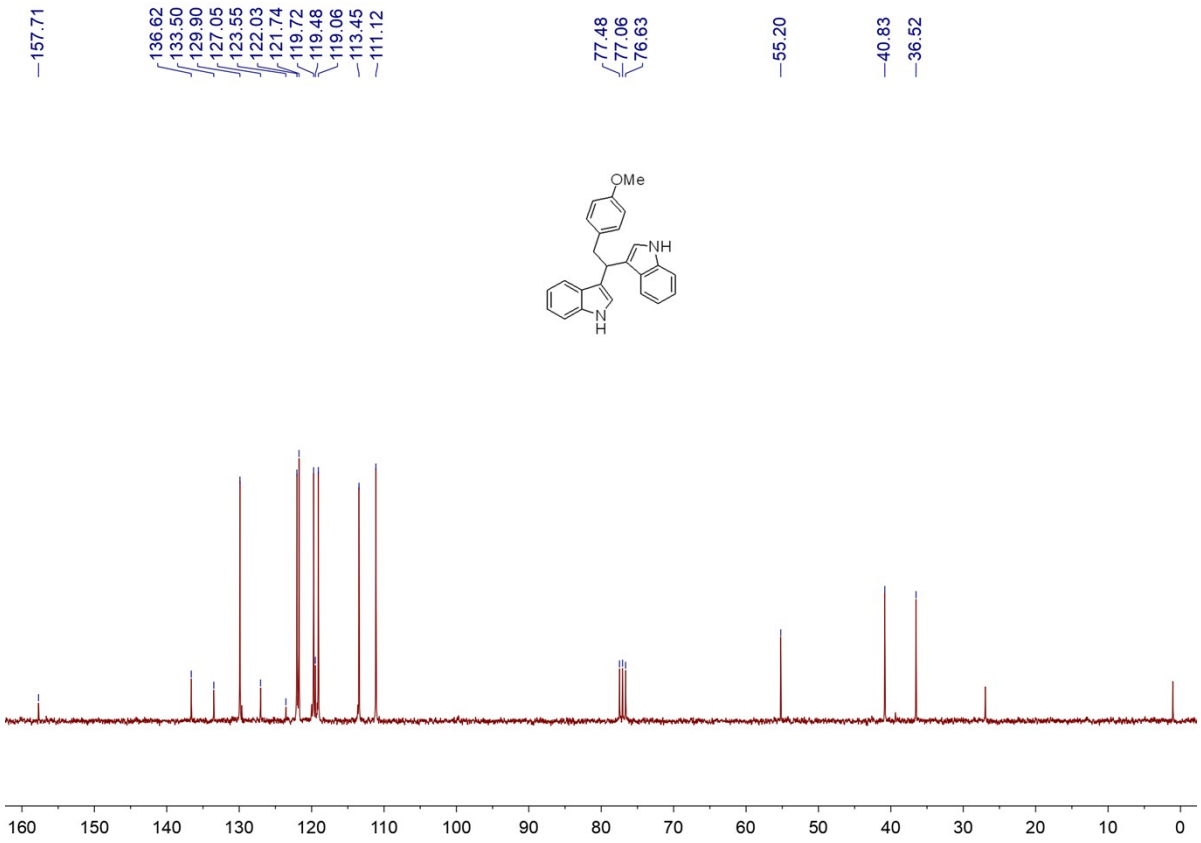
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OMe
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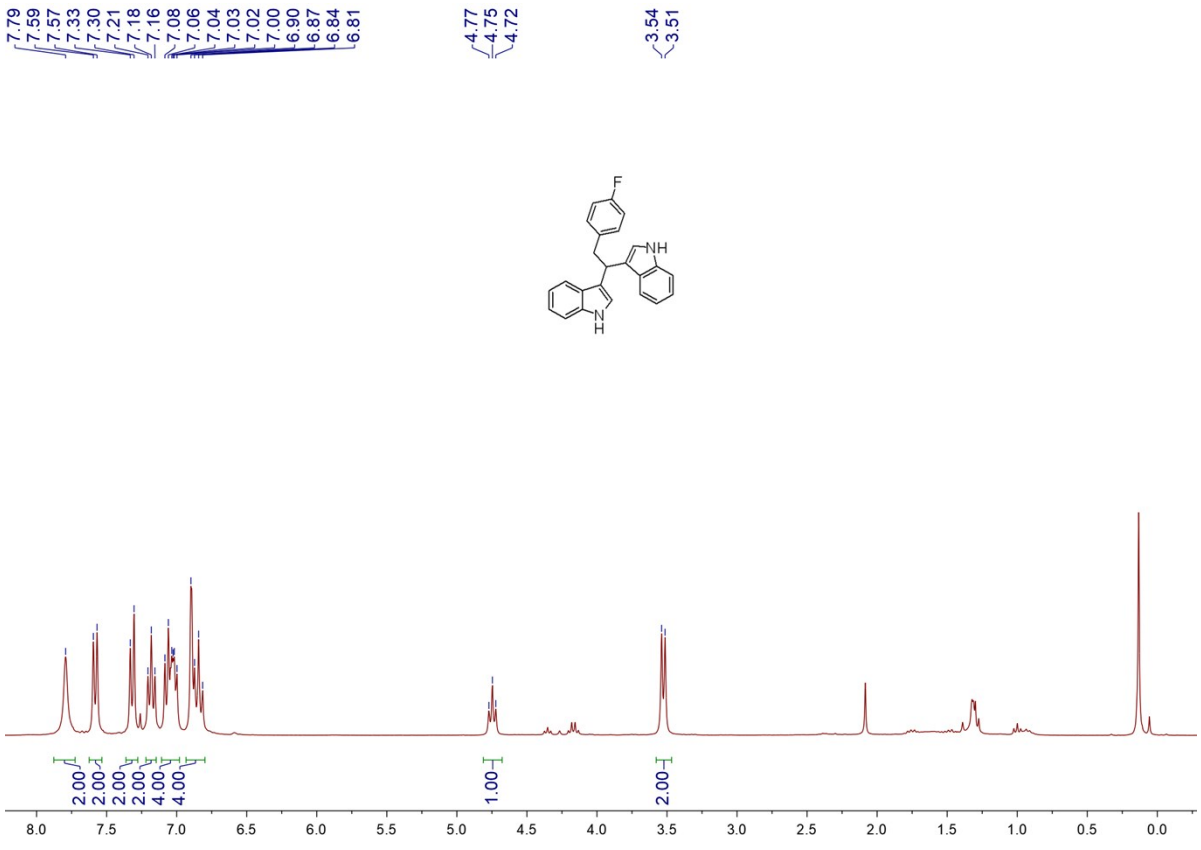
Product 4ag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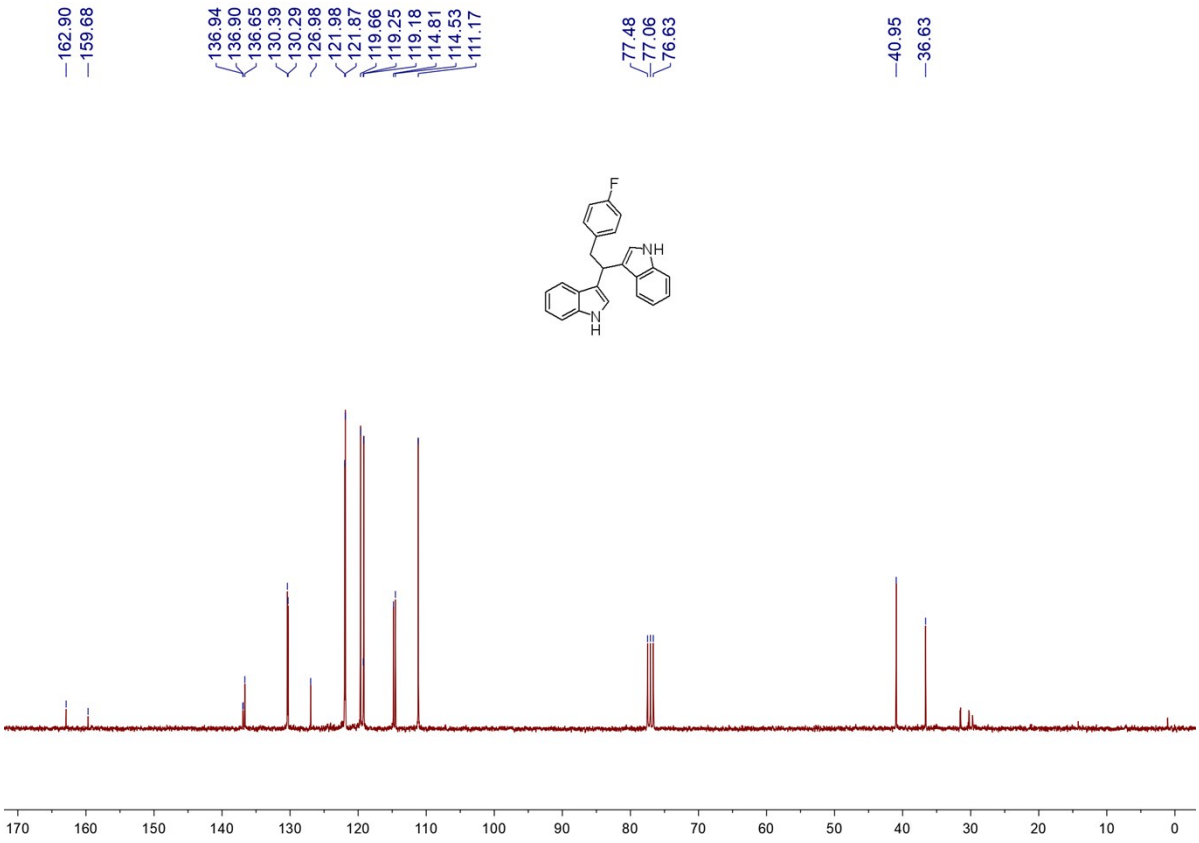
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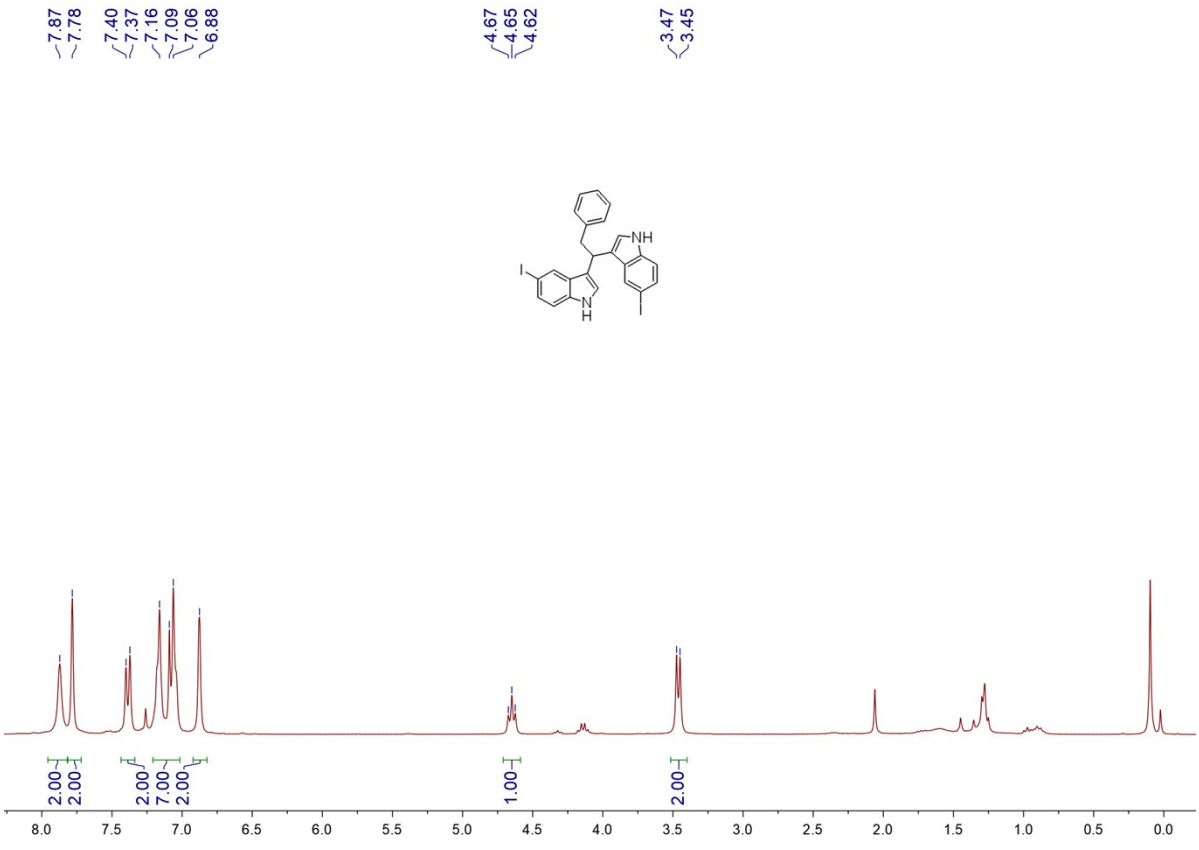
Product 4ah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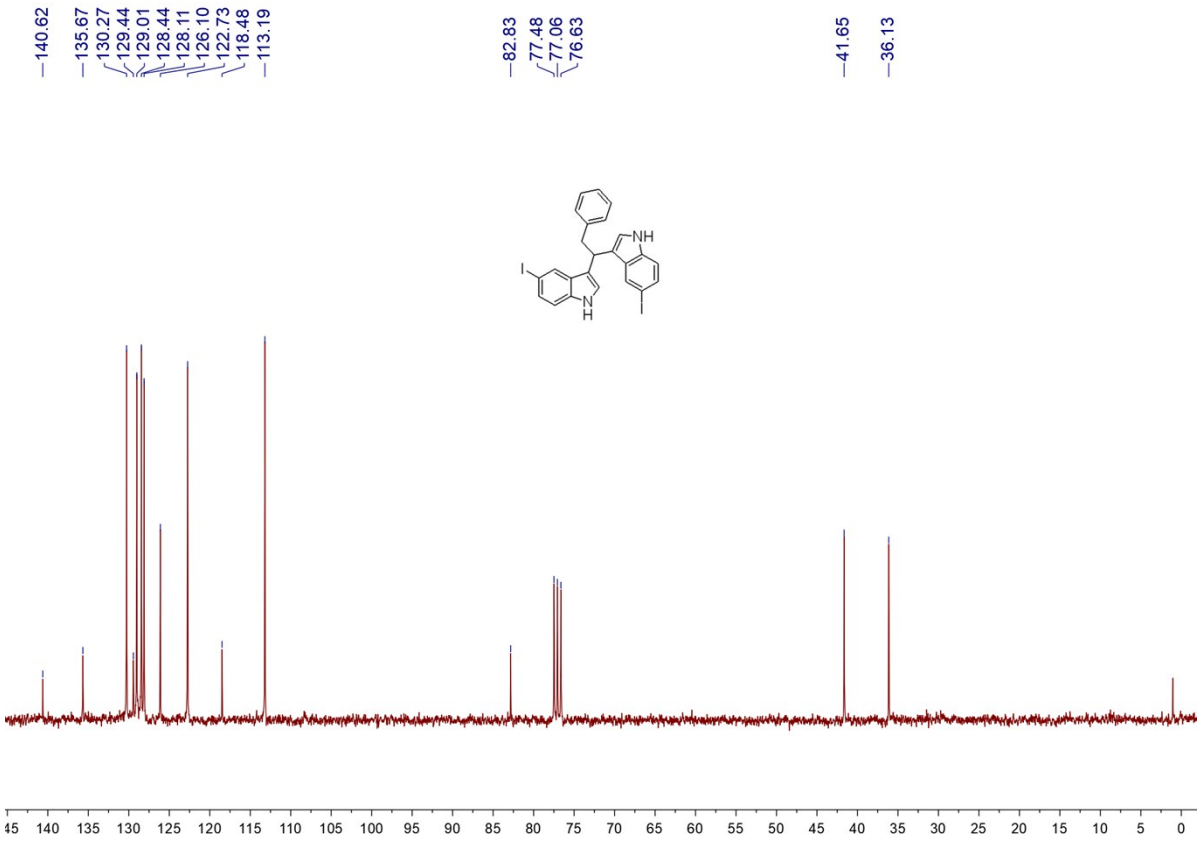
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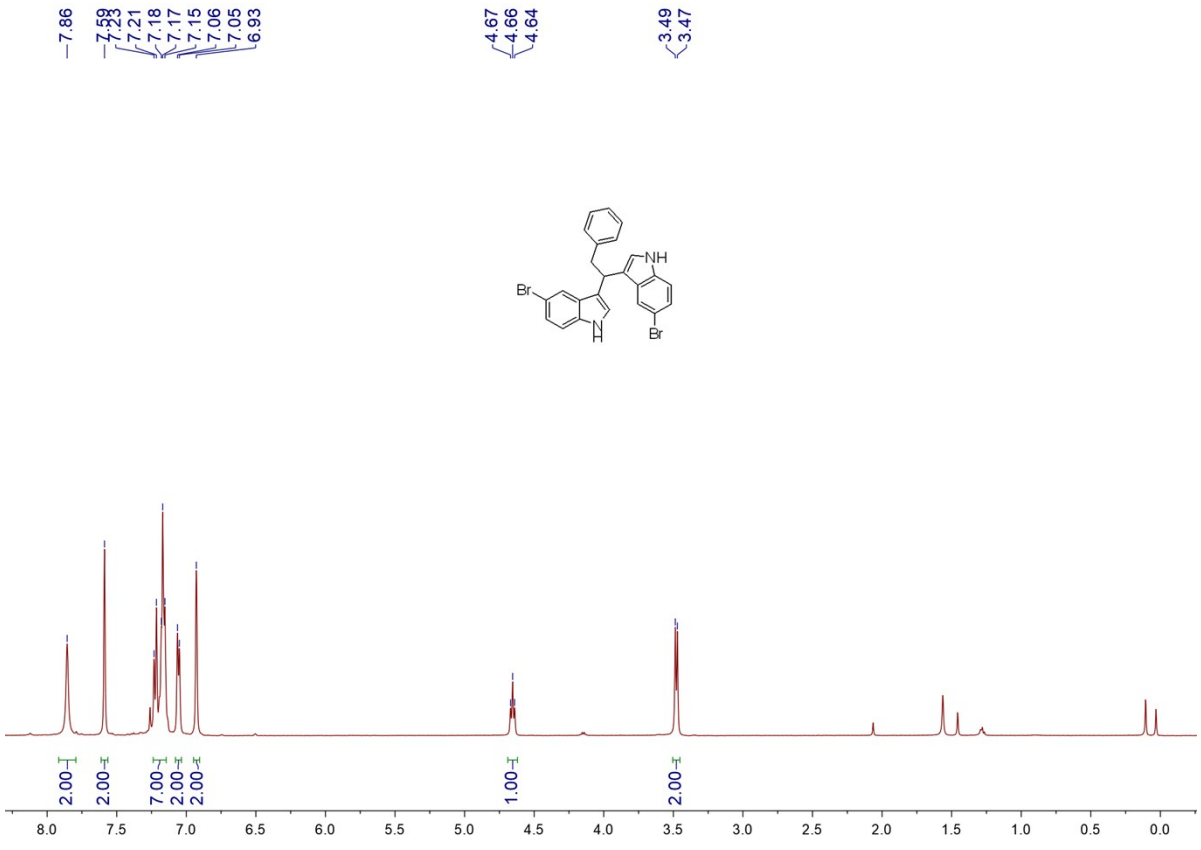
Product 4ai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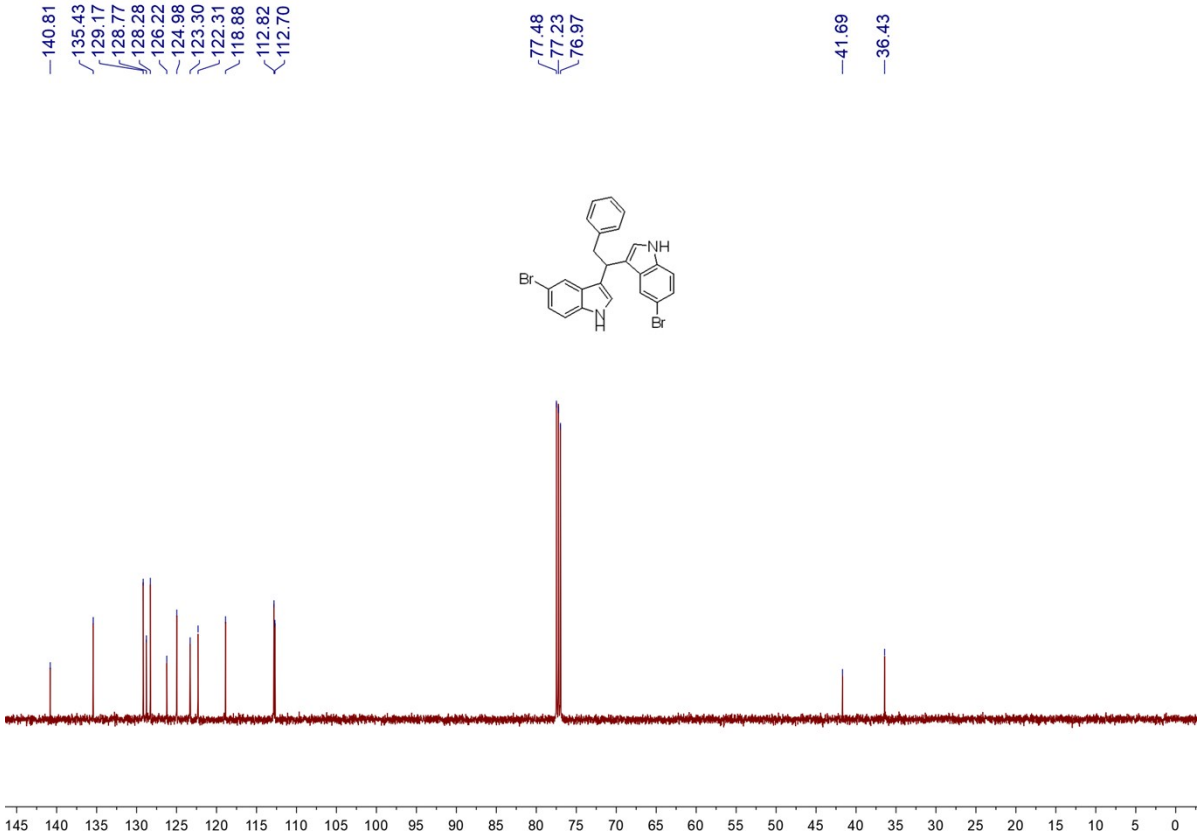
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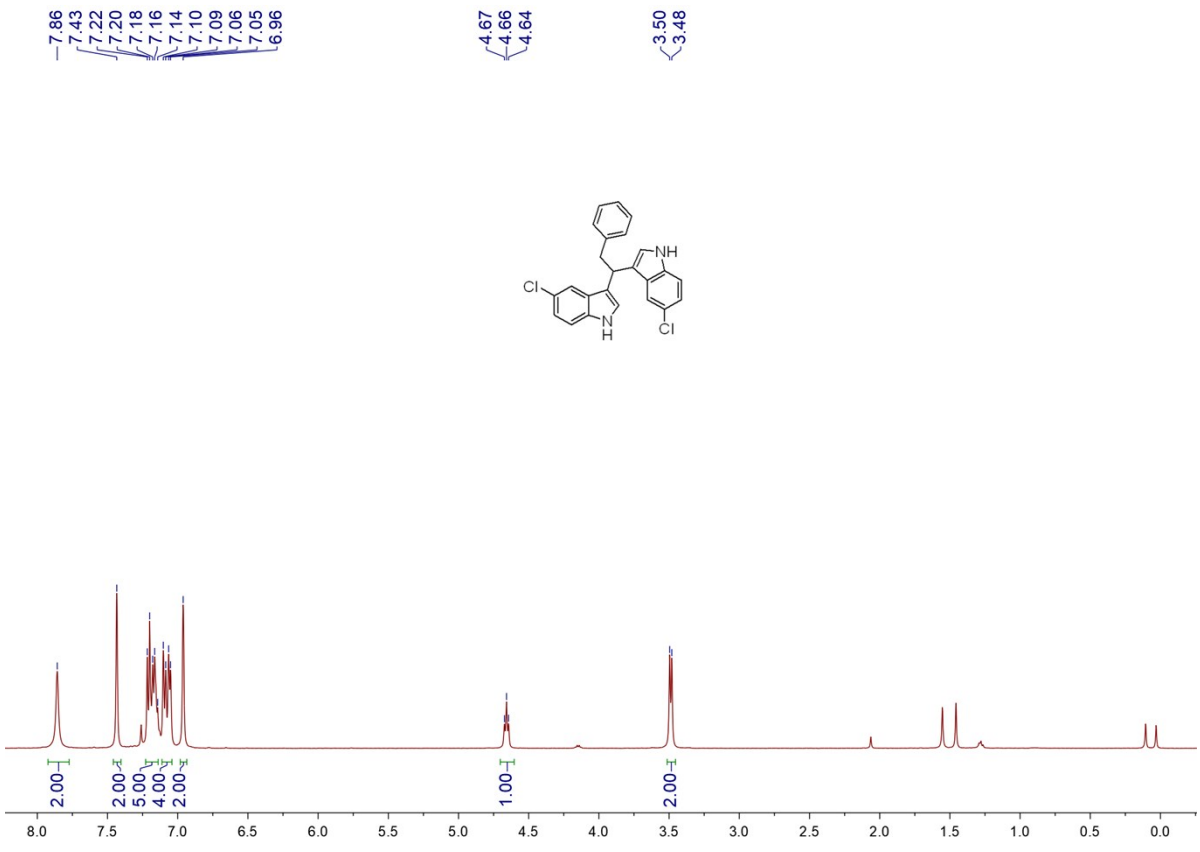
Product 4aj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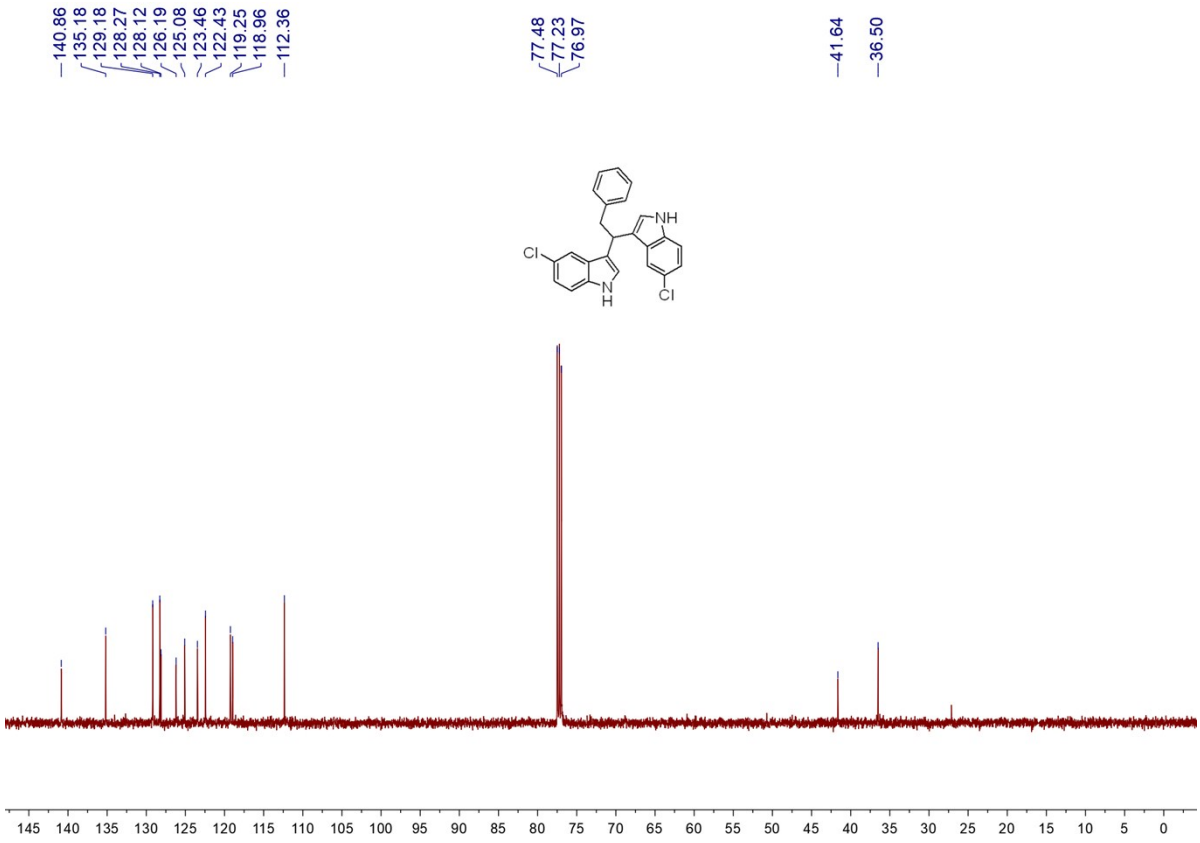
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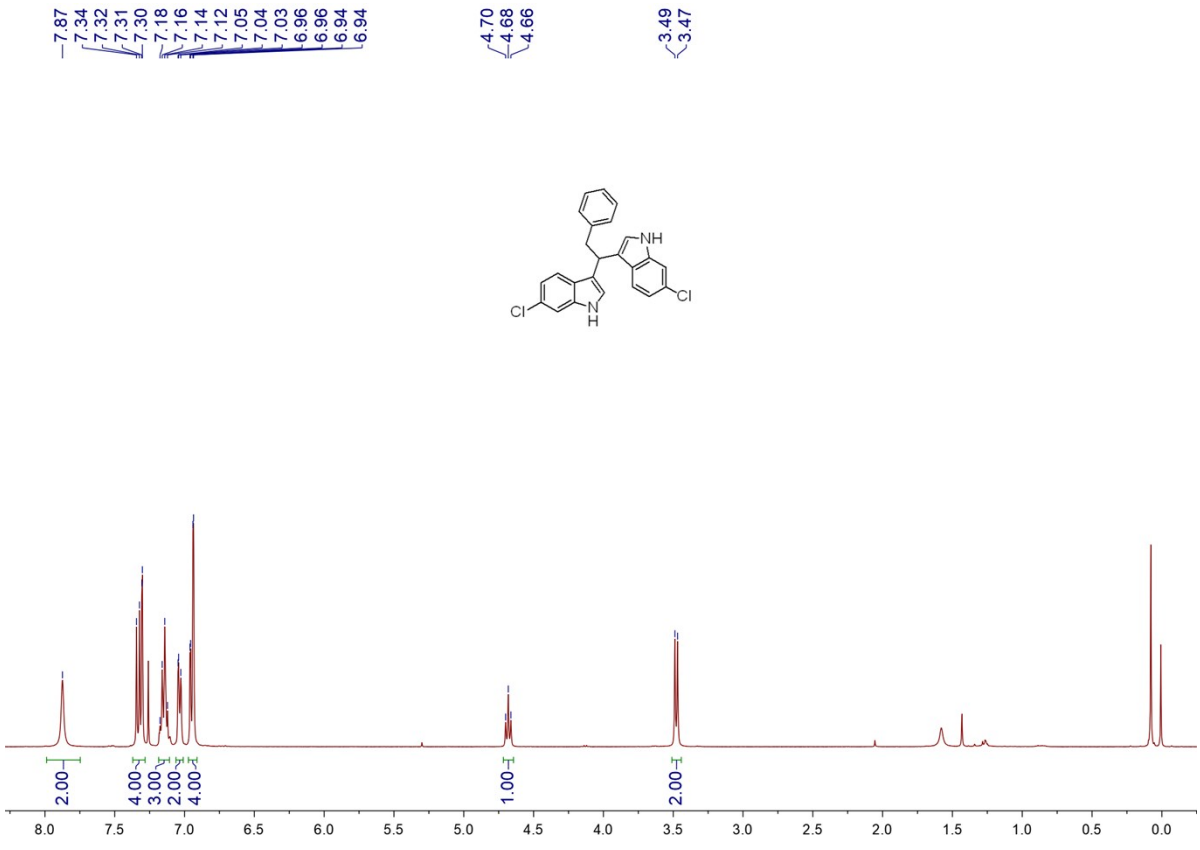
Product 4ak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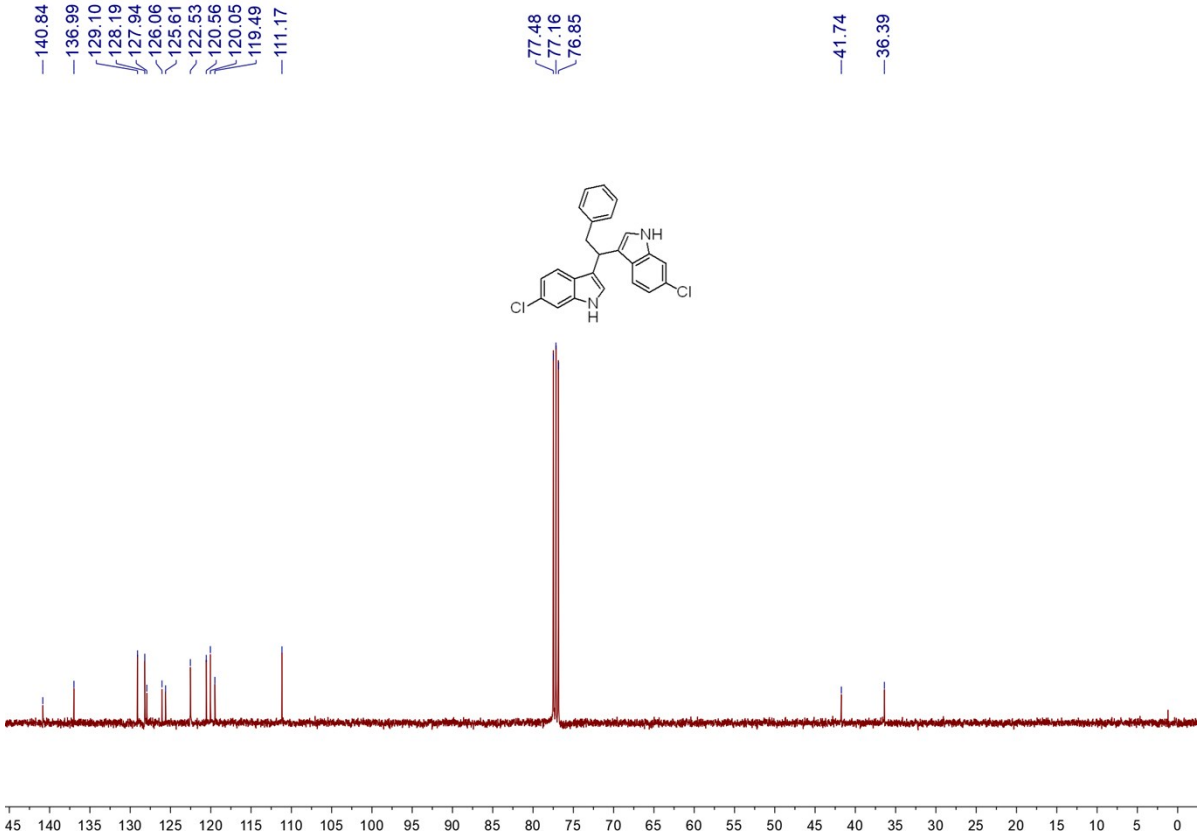
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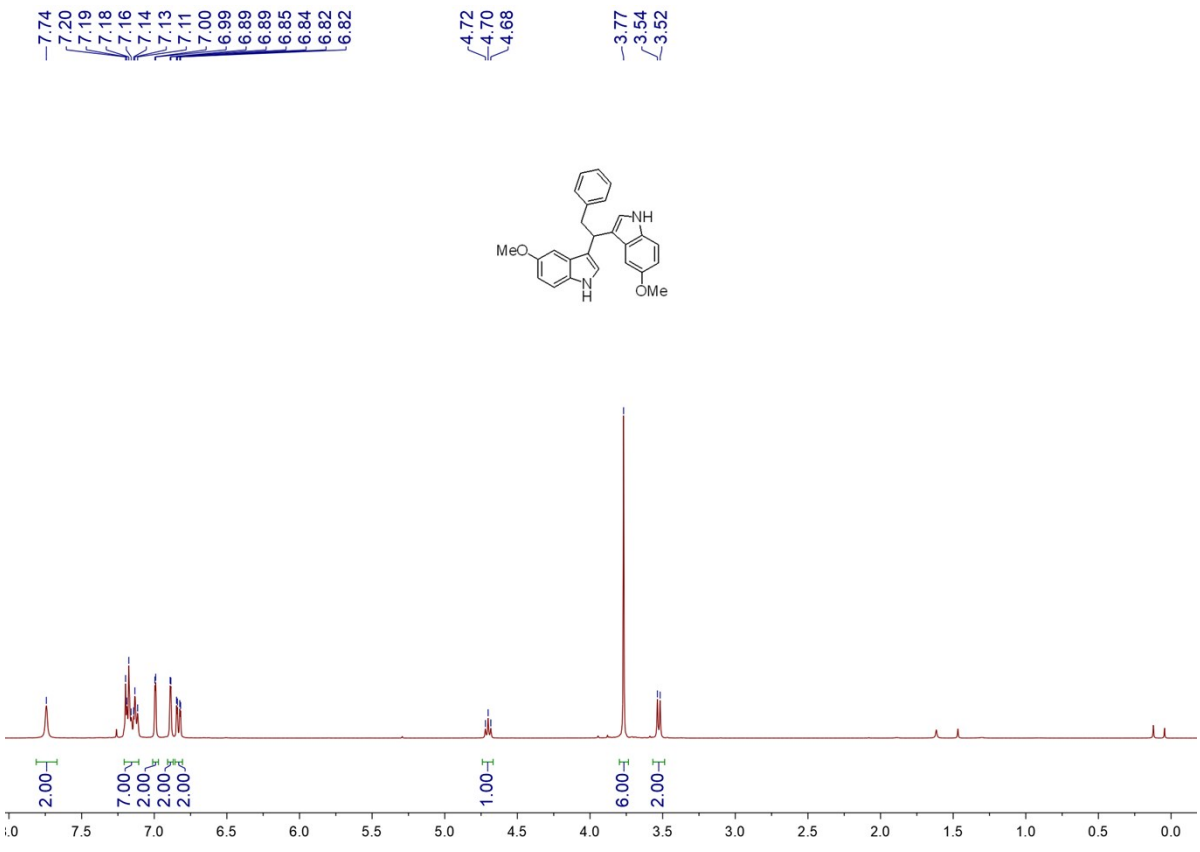
Product 4an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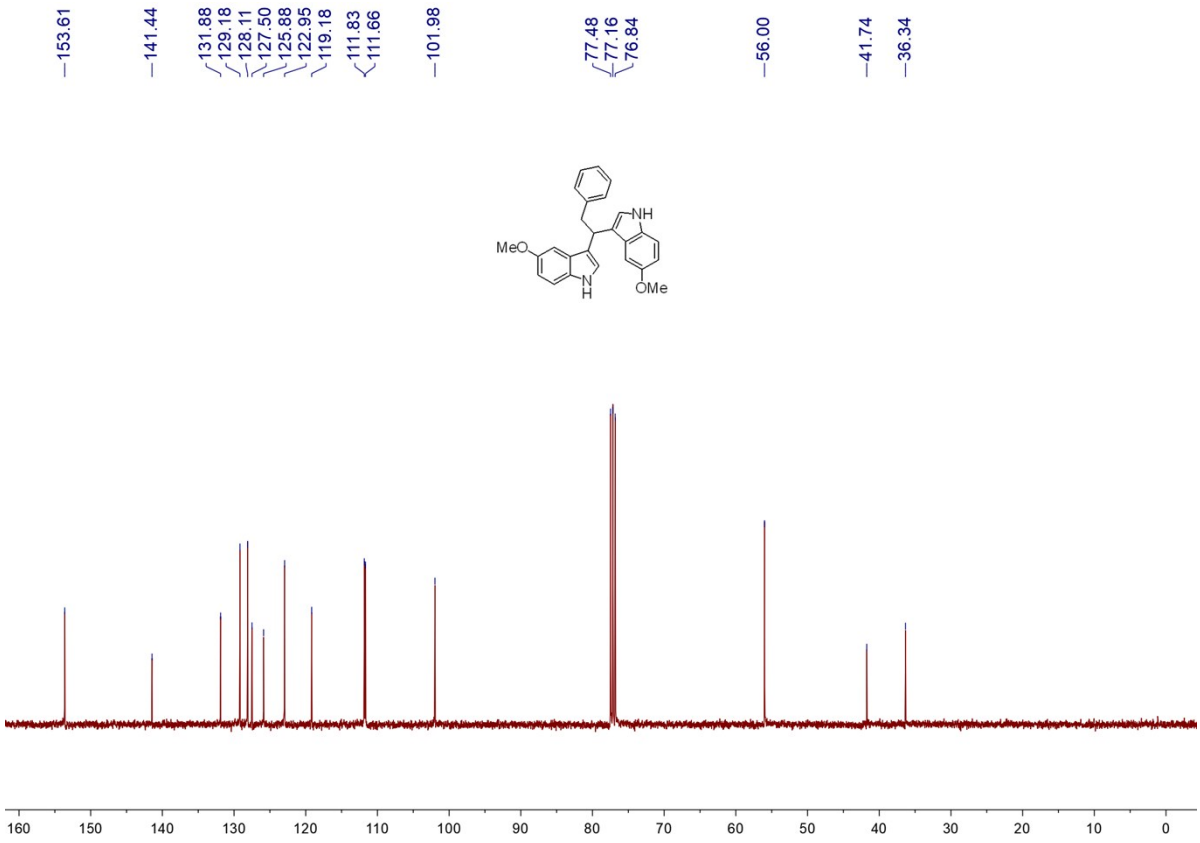
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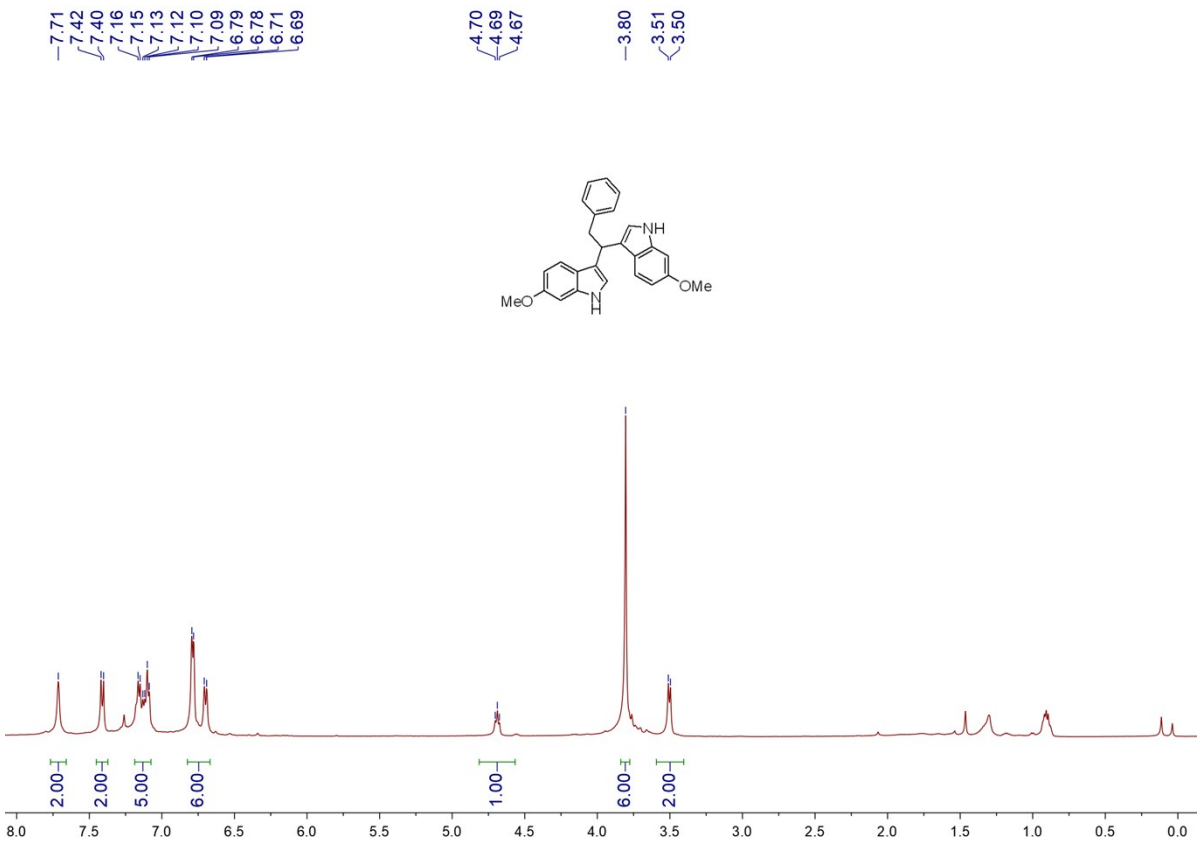
Product 4ao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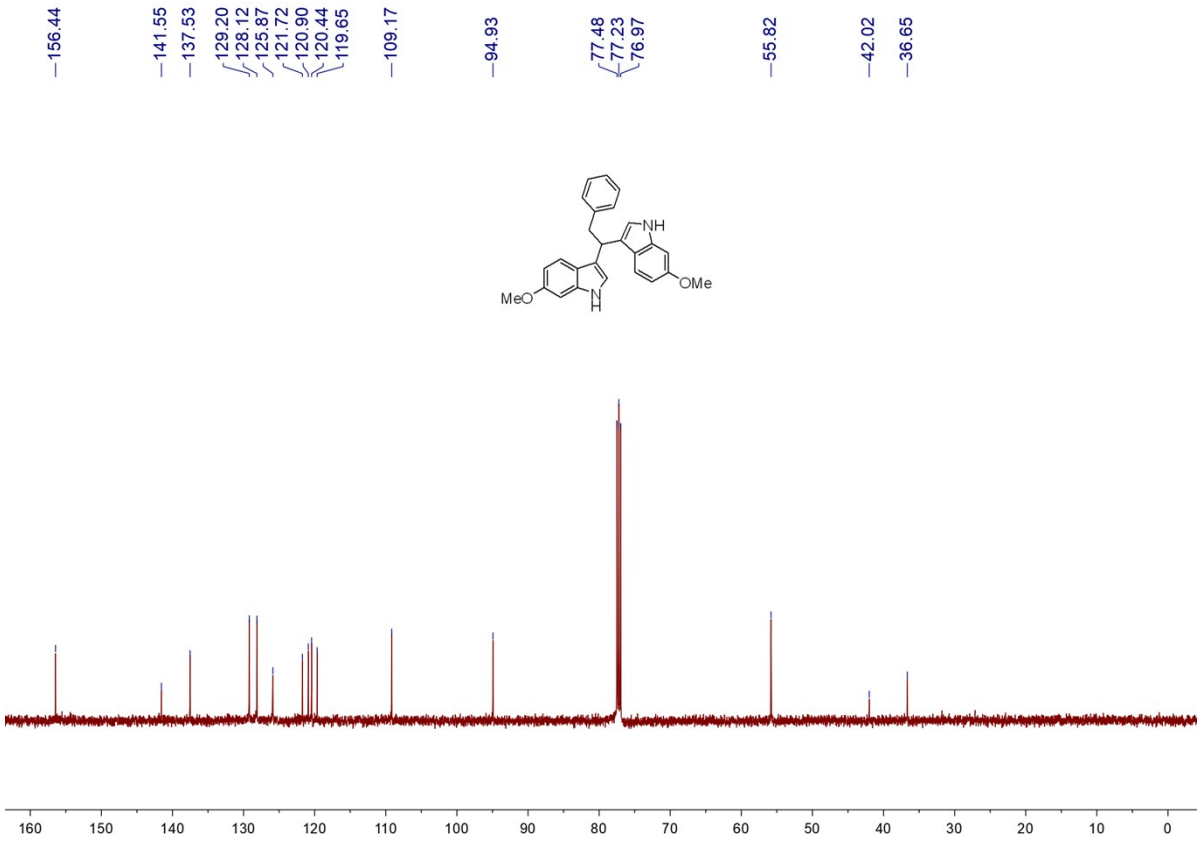
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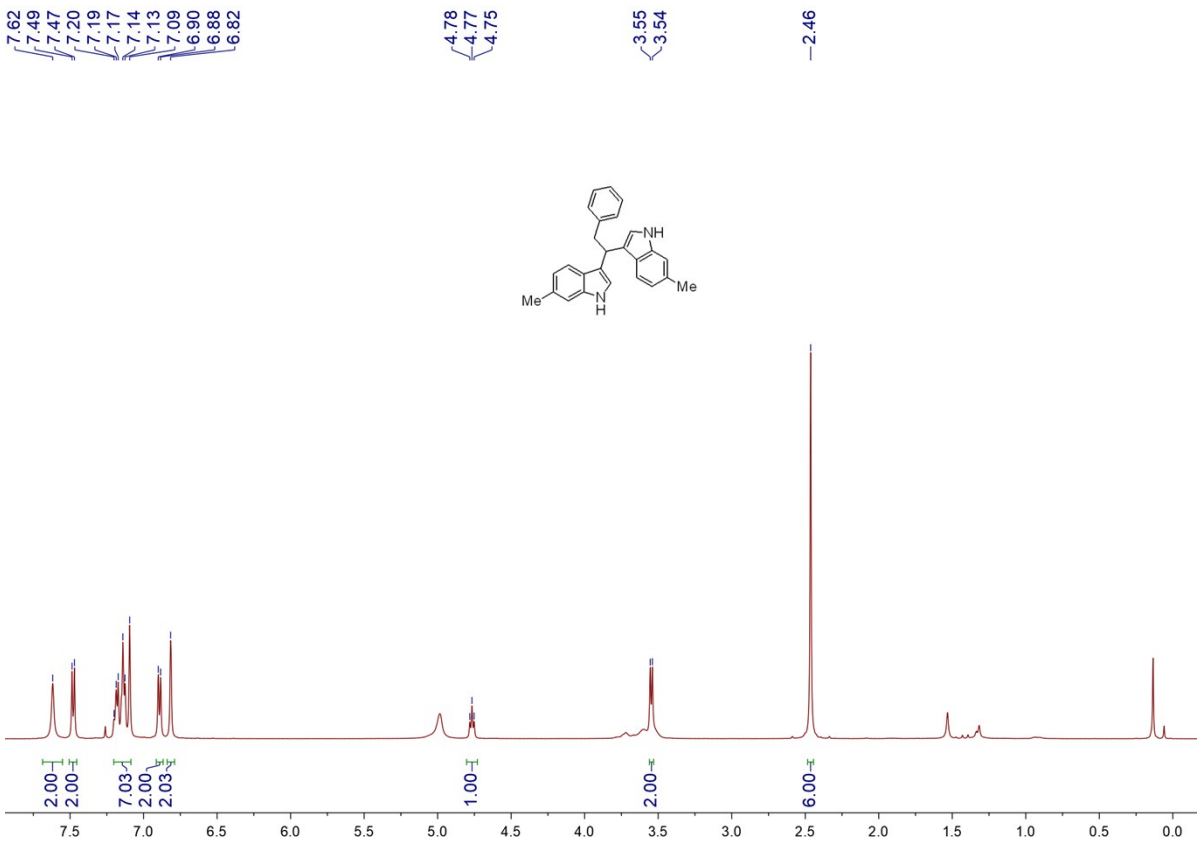
Product 4ap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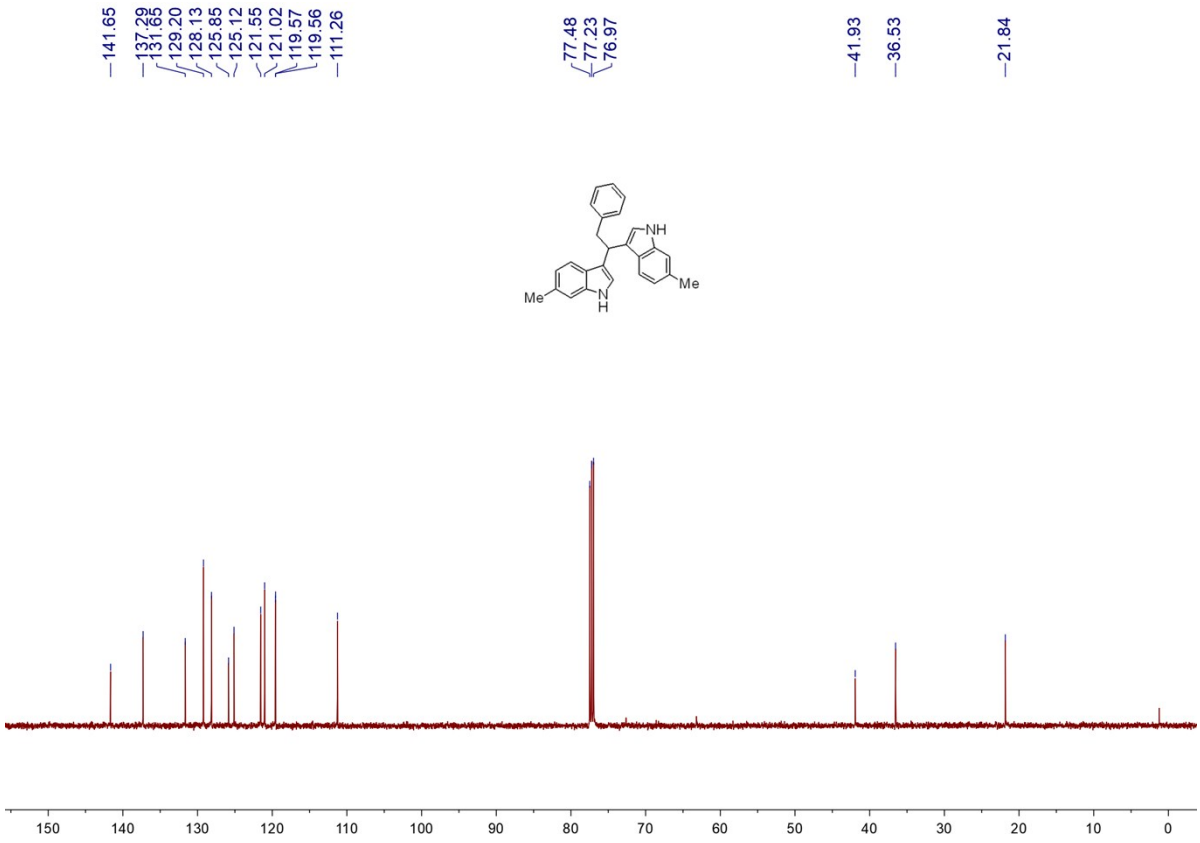
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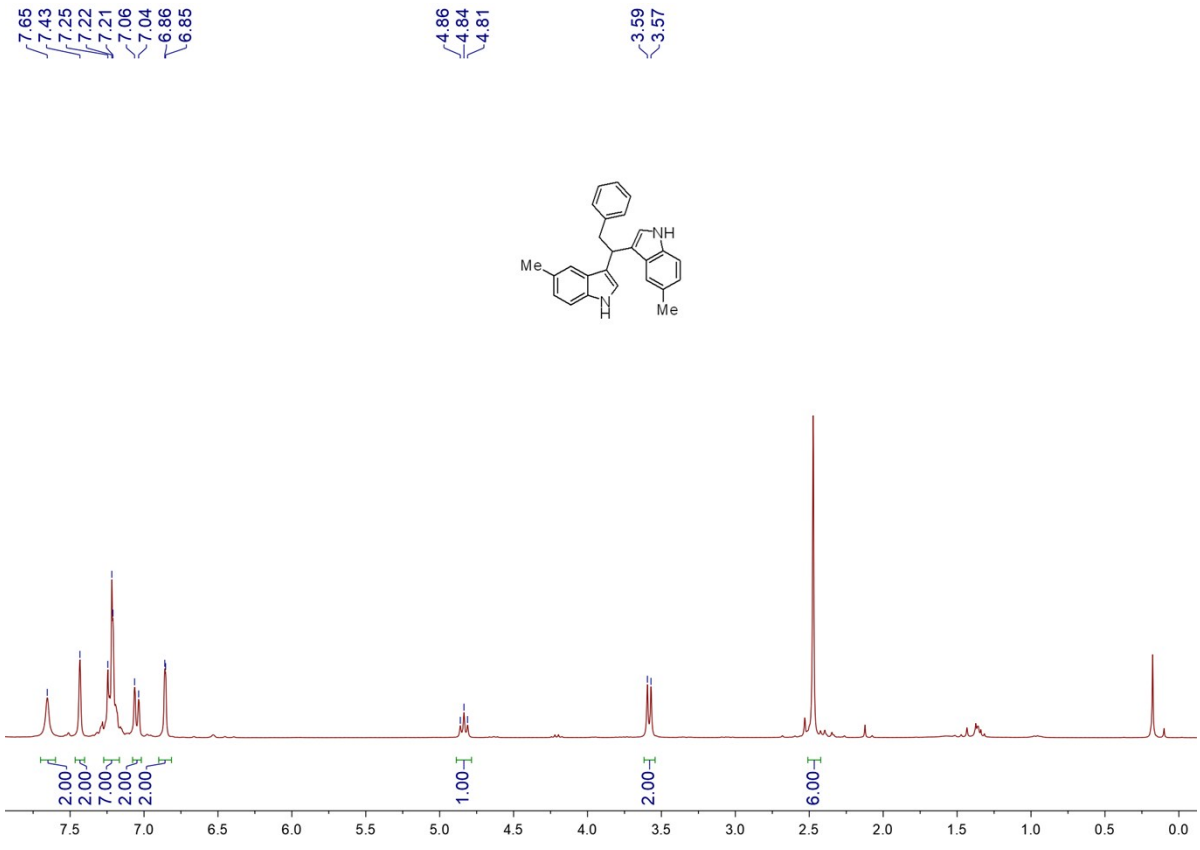
Product 4aq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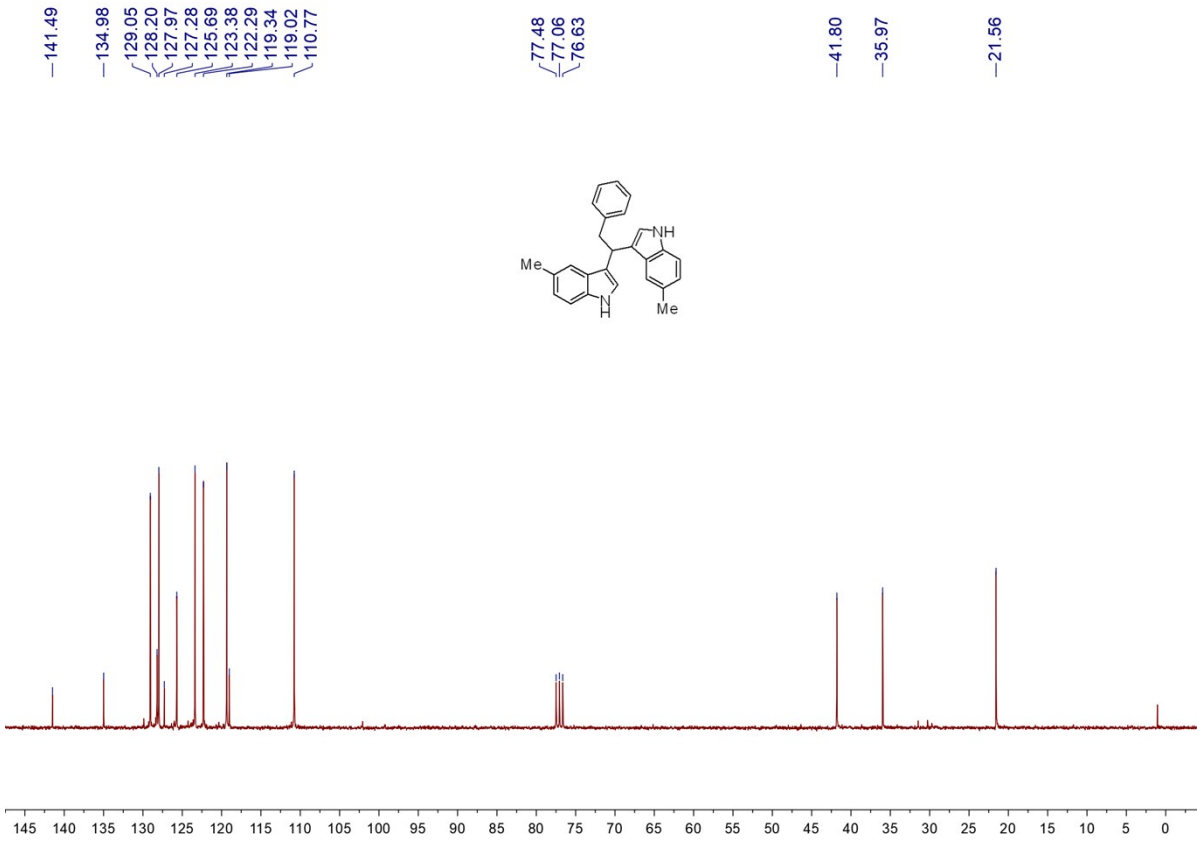
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