Supporting Information

Ligand-controlled regioselective cascade C-C/C-F cleavage/annulation of gem-DFCPs: a divergent synthesis of pyrroles

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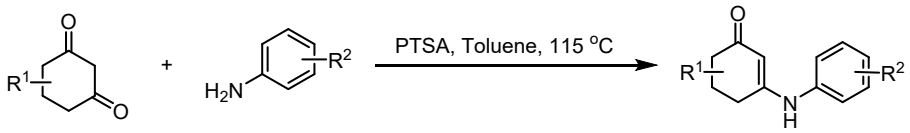
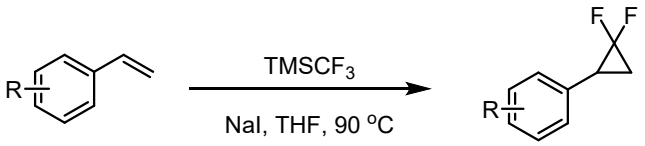
1. General Methods. Unless otherwise noted, all solvents were used directly without further purification. Palladium catalyst, ligand were obtained from Aladdin, and TCI and used directly without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker instrument (400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protic solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ, ppm). Data for HRMS were obtained by using BRUKER micrOTOF-Q III instrument with ESI source or EI source. The crystal was measured by using Agilent instrument.

2.1 General procedure for the synthesis of substrates (1a-w)[1,2]



To a 50 mL vial equipped with a magnetic stir bar was added cyclohexanedione (3.6 mmol, 1.2 equiv.) and PTSA (0.3 mmol, 10 mol%) and Toluene (1 mL). Then aniline was added, and the mixture was stirred at 115 °C (oil bath) to reflux for the indicated time on a magnetic stirrer with a hot plate. After the system was cooled to room temperature, n-hexane was added to the bottle and filtered to obtain solid.

2.2 General procedure for the synthesis of substrates (2a-n)[3-9]

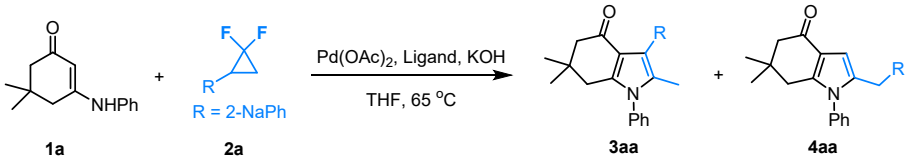


To a 250 mL Schlenk tube equipped with a magnetic stir bar was added olefin (5 mmol, 1.0 equiv.), sodium iodide (2.5 mmol, 0.5 equiv.). The tube was evacuated and back-filled with nitrogen (this process was repeated three times), THF (1 mL) was added subsequently. Then $TMSCF_3$ was added dropwise via a syringe, and the mixture was stirred at 90 °C (oil bath) to reflux until the reaction completion about 8 hours on a magnetic stirrer with a hot plate. After the system was cooled to room temperature, The mixture was filtered and concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel with PE as eluent to give gem-difluorocyclopropanes.

3. Optimization of the reaction conditions

3.1 Optimization of the ligand for template reactions

Table S1 Ligand screening for template reactions



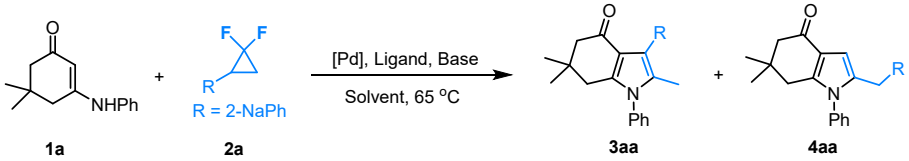
1a 2a 3aa 4aa

Entry	Ligand	3aa yield (%)[a]	4aa yield (%)[a]
1	$PtBu_3 \cdot HBF_4$	34	-
2	DPPF	57	9
3	DPPP	7	-
4	Cy_3P	39	4
5	RuPhos	18	17
6	QPhos	68	6
7	XPhos	10	25
8	(R)-BINAP	4	7
9	tBu-PPh_2	62	14
10	tBu-BrettPhos	9	9
11	tBu-XPhos	41	20

[a]Reaction conditions: 1a (0.1 mmol), 2a (0.1 mmol), $Pd(OAc)_2$ (5 mol%), Ligand (5 mol%), KOH (0.2 mmol), THF (dry, 1 mL), 65 °C, 12 h; The yields were determined by LC analysis using benzophenone as the internal standard.

3.2 Optimization of the substrate

Table S2 Optimization of the substrate



1a 2a 3aa 4aa

Entry	Ligand	[Pd]	Base	Solvent	3aa yield (%)[a]	4aa yield (%)[a]
1	QPhos	$Pd(OAc)_2$	KOH	THF	65	-
2	QPhos	$Pd(alkyl)_2Cl_2$	KOH	THF	61	-
3	QPhos	$Pd(TFA)_2$	KOH	THF	75	-

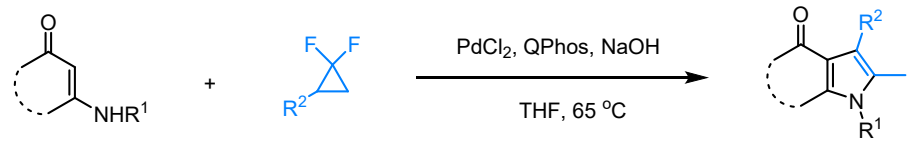
4	QPhos	$PdCl_2$	KOH	THF	74	-
5	QPhos	$Pd(MeCN)_4BF_4$	KOH	THF	65	-
6	QPhos	(NHC)Pd(allyl)Cl	KOH	THF	63	-
7	QPhos	DPPF • $PdCl_2$	KOH	THF	73	-
8	QPhos	$Pd(PhCN)_2Cl_2$	KOH	THF	59	-
9	QPhos	$Pd_2(dba)_3$	KOH	THF	61	-
10	QPhos	$PdCl_2$	Cs_2CO_3	THF	35	-
11	QPhos	$PdCl_2$	tBuONa	THF	67	-
12	QPhos	$PdCl_2$	NaOH	THF	70	-
13	QPhos	$PdCl_2$	K_3PO_4	THF	18	-
14	QPhos	$PdCl_2$	NaOH	DMF	22	-
15	QPhos	$PdCl_2$	NaOH	DCM	61	-
16	QPhos	$PdCl_2$	NaOH	DCE	31	-
17	QPhos	$PdCl_2$	NaOH	NMP	17	-
18[c]	QPhos	$PdCl_2$	NaOH	THF	80(79[b])	-
19	XPhos	$Pd(OAc)_2$	KOH	THF	-	23
20	XPhos	$Pd(alkyl)_2Cl_2$	KOH	THF	-	25
21	XPhos	$Pd(TFA)_2$	KOH	THF	-	22
22	XPhos	$PdCl_2$	KOH	THF	-	22
23	XPhos	$Pd(MeCN)_4BF_4$	KOH	THF	-	28
24	XPhos	DPPF • $PdCl_2$	KOH	THF	-	31
25	XPhos	$Pd(MeCN)_2Cl_2$	KOH	THF	-	28
26	XPhos	$Pd_2(dba)_3$	KOH	THF	-	34
27	XPhos	$Pd(MeCN)_4(OTf)_2$	KOH	THF	-	31
28	XPhos	$Pd_2(dba)_3$	KOH	DMF	-	22
29	XPhos	$Pd_2(dba)_3$	KOH	1,4-dioxane	-	25
30	XPhos	$Pd_2(dba)_3$	KOH	EtOH	-	23
31	XPhos	$Pd_2(dba)_3$	KOH	Toluene	-	31
32	XPhos	$Pd_2(dba)_3$	KOH	NMP	-	25
33	XPhos	$Pd_2(dba)_3$	K_3PO_4	THF	-	29

34	XPhos	$Pd_2(dba)_3$	Cs_2CO_3	THF	-	23
35	XPhos	$Pd_2(dba)_3$	NaOH	THF	-	34
36[d]	XPhos	$Pd_2(dba)_3$	K_2CO_3	THF	-	56[b]
37[d]	XPhos	$Pd_2(dba)_3$	K_2HPO_4	THF	-	59[b]
38[d]	XPhos	$Pd_2(dba)_3$	Na_2CO_3	THF	-	42[b]
39[d]	XPhos	$Pd_2(dba)_3$	NaH_2PO_4	THF	-	61(58[b])

[a]Reaction conditions: 1a (0.1 mmol), 2a (0.1 mmol), [Pd] (5 mol%), Ligand (10 mol%), Base (0.2 mmol), Solvent (1 mL), 65 °C, 12 h; The yields were determined by LC analysis using benzophenone as the internal standard. [b]Isolated yield. [c]Reaction time: 6h. [d]The reaction is filtered after completion, then Cs_2CO_3 (0.2 mmol), EtOH (1 mL) was added. Isolated yield.

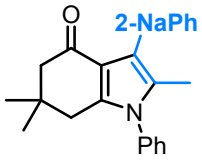
4. Characterization of new compounds

4.1 General procedure for the synthesis of substrates (3)

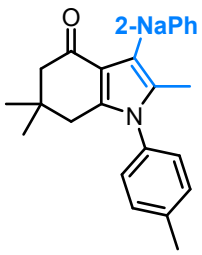


1 2 3

A 8 mL sealed tube equipped with a stir bar was charged with enaminone **1** (0.1 mmol, 1.0 equiv.), gem-difluorocyclopropane **2** (0.1 mmol, 1.0 equiv.), Qphos (7.1mg, 0.01 mmol, 0.1 equiv), $PdCl_2$ (0.9mg, 0.005mmol, 0.05 equiv.) and NaOH (0.4 mmol, 2.0 equiv.) under nitrogen. Followed by the addition of THF (1.0 mL). The flask was then sealed and the mixture was stirred at 65 °C (oil bath) for 6 hours. After the reaction was complete, the reaction mixture was cooled to room temperature, filtrated via celite and the filtrate concentrated under reduced pressure. After the solvent was removed, the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/20 to 1/5, v/v) to afford desired product **3aa-3pa, 3ab-3am**.

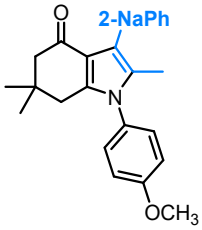


2,6,6-trimethyl-3-(naphthalen-2-yl)-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (3aa). 3aa was obtained as a white solid (30.8 mg, 81%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 222-223 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.86-7.82 (m, 4H), 7.63 (dd, *J* = 8.4 Hz, 1.6Hz, 1H), 7.58-7.50 (m, 3H), 7.45-7.42 (m, 2H), 7.32-7.30 (m, 2H), 2.47 (s, 2H), 2.40 (s, 2H), 2.06 (s, 3H), 1.10 (s, 6H).^{13}C NMR (100 MHz, Chloroform-d) δ 193.1, 143.1, 137.3, 133.3, 132.4, 132.3, 129.6, 129.6, 128.9, 128.8, 128.32, 127.9, 127.8, 127.6, 126.8, 125.5, 125.3, 120.3, 116.7, 53.2, 37.1, 35.3, 28.6, 11.2. **FT-IR (ATR):** 2956, 2923, 1655, 1598, 1498, 1443, 1427, 1057 cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{27}H_{26}NO$ [M] $^+$: 380.2014, found: 380.2002.

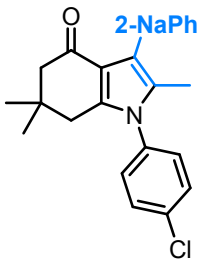


2,6,6-trimethyl-3-(naphthalen-2-yl)-1-(p-tolyl)-1,5,6,7-tetrahydro-4H-indol-4-one (3ba). Following general procedure, 3ba was obtained as a yellow solid (31.5 mg, 80%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 168-169 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.89-7.85 (m, 4H), 7.67 (dd, *J* = 8.4 Hz, 1.6Hz, 1H), 7.49-7.44 (m, 2H), 7.38-7.36 (m, 2H), 7.23-7.21 (m, 2H), 2.50 (s, 5H), 2.43 (s, 2H), 2.09 (s, 3H), 1.13 (s, 6H).^{13}C NMR (100 MHz, Chloroform-d) δ 193.1, 143.2, 138.8, 134.6, 133.3, 132.5, 132.3, 130.2, 129.6, 129.0, 128.3, 127.9, 127.6, 127.6, 126.8, 125.5, 125.3, 120.1,

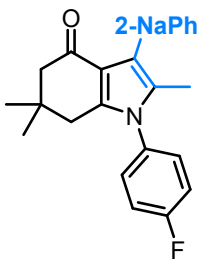
116.5, 53.2, 37.1, 35.2, 28.6, 21.3, 11.2. **FT-IR (ATR):** 2956, 2923, 1667 1513, 1402, 1050cm^{-1}. **HRMS (ESI$^+$, m/z)**: calcd for $C_{28}H_{27}NO_4Na$ [M+Na]$^+$: 416.1990, found: 416.1973.



1-(4-methoxyphenyl)-2,6,6-trimethyl-3-(naphthalen-2-yl)-1,5,6,7-tetrahydro-4H-indol-4-one (3ca). Following general procedure, 3ca was obtained as a white solid (23.7 mg, 61%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 154-155 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.86-7.82 (m, 4H), 7.65 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.46-7.41 (m, 2H), 7.23-7.20 (m, 2H), 7.06-7.02 (m, 2H), 3.89 (s, 3H), 2.47 (s, 2H), 2.40 (s, 2H), 2.06 (s, 3H), 1.11 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.1, 159.7, 143.5, 133.3, 132.5, 132.3, 129.9, 129.6, 129.2, 128.9, 128.3, 127.9, 127.6, 126.7, 125.5, 125.3, 120.0, 116.4, 114.8, 55.6, 53.2, 37.1, 35.2, 28.6, 11.2. **FT-IR (ATR):** 2955, 2943, 1666, 1510, 1440, 1421, 1246, 1179, 1033cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{28}H_{28}NO_2$ [M] $^+$: 410.2120, found: 410.2111.

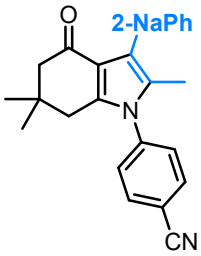


1-(4-chlorophenyl)-2,6,6-trimethyl-3-(naphthalen-2-yl)-1,5,6,7-tetrahydro-4H-indol-4-one (3da). Following general procedure, 3da was obtained as a yellow solid (24.0 mg, 58%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 176-177 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 (t, *J* = 8.0 Hz, 4H), 7.65 (t, *J* = 9.6 Hz, 1H), 7.58-7.53 (m, 2H), 7.49-7.45 (m, 2H), 7.35-7.28 (m, 2H), 2.49 (d, *J* = 5.2 Hz, 2H), 2.42 (s, 2H), 2.08 (s, 3H), 1.13 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.0, 142.9, 135.8, 134.8, 133.3, 132.3, 129.9, 129.6, 129.5, 129.1, 128.7, 128.3, 127.9, 127.6, 126.8, 125.6, 125.4, 120.6, 116.9, 53.1, 37.1, 35.3, 28.6, 11.2. **FT-IR (ATR):** 2959, 2947, 2889, 1666, 1525, 1492, 1422, 1410, 1398, 1091, 1049cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{27}H_{25}ClNO$ [M] $^+$: 414.1625, found: 414.1624.

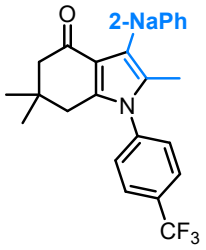


1-(4-fluorophenyl)-2,6,6-trimethyl-3-(naphthalen-2-yl)-1,5,6,7-tetrahydro-4H-indol-4-one (3ea). Following general procedure, 3ea was obtained as a white solid (29.4 mg, 74%)

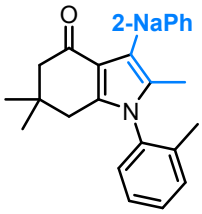
by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 192-193 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.77-7.72 (m, 4H), 7.53 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.37-7.34 (m, 2H), 7.22-7.12 (m, 4H), 2.36 (s, 2H), 2.31 (s, 2H), 1.96 (s, 3H), 1.02 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ ^{13}C NMR (101 MHz, Chloroform-d) δ 193.0, 162.4 (d, *J* = 248.1 Hz), 143.1, 133.3, 133.2 (d, *J* = 3.3 Hz), 132.3 (d, *J* = 5.2 Hz), 129.6, 129.5, 128.9, 128.3, 127.9, 127.6, 126.8, 125.6, 125.4, 120.4, 116.7 (d, *J* = 22.6 Hz), 53.1, 37.1, 35.2, 28.6, 11.2. ^{19}F NMR (376 MHz, Chloroform-d) δ-111.9. **FT-IR (ATR):** 2955, 2925, 1656, 1516, 1447, 1223, 1057cm^{-1}. **HRMS (ESI^{+}, m/z)**: calcd for $C_{27}H_{24}FNONa$ $[M+Na]^{+}$: 420.1740, found: 420.1726.



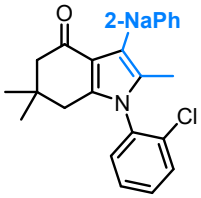
4-(2,6,6-trimethyl-3-(naphthalen-2-yl)-4-oxo-4,5,6,7-tetrahydro-1H-indol-1-yl) benzonitrile (3fa). Following general procedure, 3fa was obtained as a yellow solid (19.8 mg, 49%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 117-118 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.82-7.76 (m, 6H), 7.50 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.41-7.37 (m, 4H), 2.40 (s, 2H), 2.34 (s, 2H), 2.00 (s, 3H), 1.04 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 192.9, 142.3, 141.2, 133.6, 133.2, 132.4, 131.8, 129.3, 128.7, 128.4, 128.3, 127.9, 127.6, 126.9, 125.7, 125.5, 121.5, 112.8, 53.0, 37.2, 35.4, 28.5, 11.4. **FT-IR (ATR):** 2951, 2926, 2228, 1652, 1603, 1504, 1439, 1413, 1386, 1108, 1057cm^{-1}. **HRMS (ESI^{+}, m/z)**: calcd for $C_{28}H_{24}N_2ONa$ $[M+Na]^{+}$: 427.1786, found: 427.1775.



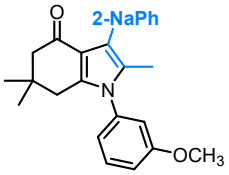
2,6,6-trimethyl-3-(naphthalen-2-yl)-1-(4-(trifluoromethyl)phenyl)-1,5,6,7-tetrahydro-4H-indol-4-one (3ga). Following general procedure, 3ga was obtained as a yellow solid (36.7 mg, 41%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 135-136 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.89-7.85 (m, 6H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.50-7.45 (m, 4H), 2.50 (s, 2H), 2.43 (s, 2H), 2.10 (s, 3H), 1.14 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ193.0, 142.7, 140.4, 133.3, 132.4, 132.1, 131.0.9 (q, *J* = 32.8 Hz), 129.4, 128.6, 128.4, 128.3, 127.9, 127.6, 126.9 (q, *J* = 2.9 Hz), 126.8, 125.7, 125.5, 125.4, 123.7 (d, *J* = 270.7 Hz), 121.0, 117.3, 53.1, 37.2, 35.4, 28.6, 11.3. ^{19}F NMR (376 MHz, Chloroform-d) δ -62.6. **FT-IR (ATR):** 2960, 2919, 2357, 1651, 1322, 1157, 1127, 1106, 1067cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{28}H_{25}F_3NO$ $[M]^{+}$: 448.1888, found: 448.1863.



2,6,6-trimethyl-3-(naphthalen-2-yl)-1-(o-tolyl)-1,5,6,7-tetrahydro-4H-indol-4-one (3ha). Following general procedure, 3ha was obtained as a white solid (27.6 mg, 70%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 145-146 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.87-7.83 (m, 4H), 7.67 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.48 -7.41 (m, 4H), 7.38 (td, *J* = 7.6, 2.8 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 2.41 (q, *J* = 16.4Hz, 3H), 2.21 (d, *J* = 16.4 Hz, 1H), 2.09 (s, 3H), 1.97 (s, 3H), 1.11 (d, *J* = 2.8 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 193.0, 142.9, 136.4, 136.3, 133.3, 132.5, 132.3, 131.2, 129.6, 129.4, 128.6, 128.4, 128.3, 127.9, 127.6, 127.2, 126.7, 125.5, 125.3, 120.2, 116.5, 53.2, 36.8, 35.2, 29.1, 28.0, 17.3, 10.7. **FT-IR (ATR):** 2955, 2868, 1656, 1524, 1496, 1440, 1385, 1351, 1057cm^{-1}. **HRMS (ESI^{+}, m/z)**: calcd for $C_{28}H_{27}NONa$ $[M+Na]^{+}$: 416.1990, found: 416.1943.

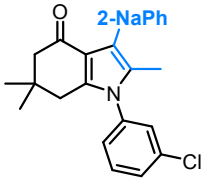


1-(2-chlorophenyl)-2,6,6-trimethyl-3-(naphthalen-2-yl)-1,5,6,7-tetrahydro-4H-indol-4-one (3ia). Following general procedure, 3ia was obtained as a white solid (29.1 mg, 70%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 144-145 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.88-7.84 (m, 4H), 7.68-7.64 (m, 2H), 7.52-7.49 (m, 2H), 7.47-7.45 (m, 2H), 7.41 (dd, *J* = 6.8 Hz, 2.4 Hz,1H), 2.47-2.36 (m, 4H), 2.02 (s, 3H), 1.14 (d, *J* = 1.2 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.1, 143.42, 133.6, 133.4, 132.4, 130.8, 130.7, 130.3, 129.7, 128.9, 128.5, 128.1, 128.0, 127.8, 126.9, 125.6, 125.4, 120.4, 53.3, 36.7, 35.4, 29.2, 28.1, 10.8. **FT-IR (ATR):** 2958, 2866, 1655, 1525, 1486, 1448,1051, 1035cm^{-1}. **HRMS (ESI^{+}, m/z)**: calcd for $C_{27}H_{24}ClNONa$ $[M+Na]^{+}$: 436.1444, found: 436.1404.

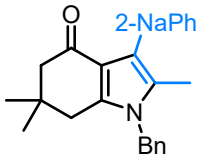


1-(3-methoxyphenyl)-2,6,6-trimethyl-3-(naphthalen-2-yl)-1,5,6,7-tetrahydro-4H-indol-4-one (3ja). Following general procedure, 3ja was obtained as a white solid (29.1 mg, 70%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 174-176 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.88-7.84 (m, 4H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.50-7.45 (m, 3H), 7.06 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 2H), 6.86(s, 1H), 3.91 (s, 3H), 2.52 (s, 2H), 2.42 (s, 2H), 2.10 (s, 3H), 1.13 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.1, 160.4, 143.0, 138.4, 133.3, 132.4, 132.3, 130.3, 129.6, 128.9, 128.3,

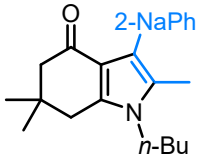
127.9, 127.6, 126.8, 125.5, 125.3, 120.2, 120.0, 116.6, 114.2, 113.8, 55.6, 53.2, 37.1, 35.2, 28.6, 11.2. **FT-IR (ATR):** 2961, 2927, 1654, 1595, 1494, 1445, 1426, 1257, 1041cm^{-1}. **HRMS (ESI$^+$, m/z)**: calcd for $C_{28}H_{27}NO_2Na$ [M+Na]$^+$: 432.1939, found: 432.1915.



1-(3-chlorophenyl)-2,6,6-trimethyl-3-(naphthalen-2-yl)-1,5,6,7-tetrahydro-4H-indol-4-one (3ka). Following general procedure, 3ka was obtained as a white solid (30.9 mg, 75%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 169-171 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.88-7.83 (m, 4H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.54 -7.50 (m, 2H), 7.48-7.44 (m, 2H), 7.37 (s, 1H), 2.50 (s, 2H), 2.42 (s, 2H), 2.09 (s, 3H), 1.14 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.0, 142.8, 138.4, 135.3, 133.3, 132.4, 132.2, 130.6, 129.5, 129.1, 128.7, 128.4, 128.2, 127.9, 127.6, 126.8, 126.2, 125.6, 125.4, 120.7, 117.0, 53.1, 37.1, 35.3, 28.6, 11.2. **FT-IR (ATR):** 2950, 2881, 1667, 1422, 1405cm^{-1}. **HRMS (ESI$^+$, m/z)**: calcd for $C_{27}H_{24}ClNONa$ [M+Na]$^+$: 436.1444, found: 436.1421.

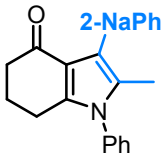


1-benzyl-2,6,6-trimethyl-3-(naphthalen-2-yl)-1,5,6,7-tetrahydro-4H-indol-4-one (3la). Following general procedure, 3la was obtained as a white solid (36.7 mg, 52%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 132-134 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.87-7.82 (m, 3H), 7.80 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.46-7.44 (m, 2H), 7.42-7.34 (m, 3H), 7.03 (d, *J* = 7.6 Hz, 2H), 5.15 (s, 2H), 2.63 (s, 2H), 2.41 (s, 2H), 2.19 (s, 3H), 1.15 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 192.8, 142.4, 136.7, 133.3, 132.6, 132.3, 129.7, 129.1, 128.4, 128.3, 127.9, 127.7, 127.6, 126.7, 125.6, 125.5, 125.3, 120.6, 52.9, 47.3, 36.4, 35.1, 28.7, 10.3. **FT-IR (ATR):** 2953, 1867, 1648, 1465, 1442, 1427, 1389, 1366cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{28}H_{28}NO$ [M] $^+$: 394.2171, found: 394.2179.

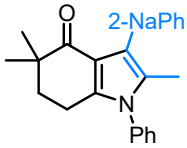


1-butyl-2,6,6-trimethyl-3-(naphthalen-2-yl)-1,5,6,7-tetrahydro-4H-indol-4-one (3ma). Following general procedure, 3ma was obtained as a yellow solid (15.3 mg, 43%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 122-123 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.86-7.83 (m, 3H), 7.77 (s, 1H), 7.58 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.47-7.42 (m, 2H), 3.86 (t, *J* = 7.6 Hz, 2H), 2.70 (s, 2H), 2.39 (s, 2H), 2.27 (s, 3H), 1.72 (q, *J* = 7.6 Hz, 2H), 1.46 (q, *J* = 7.6 Hz, 2H), 1.20 (s, 6H), 1.04 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 192.6, 141.7, 133.3, 132.8, 132.2, 129.8, 128.3, 127.8, 127.6, 127.6, 126.6, 125.4, 125.2, 120.2, 116.1, 52.9, 44.0, 36.6, 35.1, 32.9, 28.8, 20.2, 13.9, 10.3. **FT-IR (ATR):** 2955, 2932, 1646, 1599, 1445, 1365, 1039cm^{-1}. **HRMS (EI, m/z):**

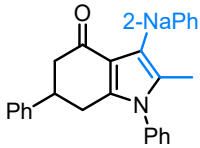
calcd for $C_{25}H_{30}NO$ [M] $^{+}$: 360.2327, found: 360.2337.



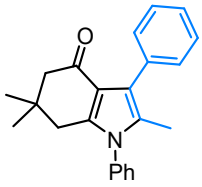
2-methyl-3-(naphthalen-2-yl)-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (3na). Following general procedure, 3na was obtained as a white solid (21.1 mg, 60%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/5 to 1/3). M.p. 194-196 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.88-7.84 (m, 4H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.60-7.52 (m, 3H), 7.48-7.45 (m, 2H), 7.37-7.35 (m, 2H), 2.64 (s, 2H), 2.55 (s, 2H), 2.15 (s, 2H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.7, 144.2, 137.3, 133.3, 132.5, 132.3, 129.6, 129.6, 128.8, 128.3, 127.9, 127.8, 127.6, 126.8, 125.6, 125.3, 125.3, 120.4, 117.8, 39.1, 23.7, 23.1, 11.2. **FT-IR (ATR):** 3042, 2945, 2917, 2874, 1657, 1597, 1496, 1455, 1426, 1069, 1006cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{25}H_{22}NO$ [M] $^{+}$: 352.1701, found: 352.1706.



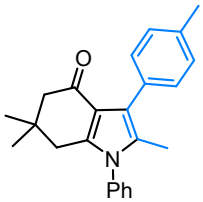
2,5,5-trimethyl-3-(naphthalen-2-yl)-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (3oa). Following general procedure, 3oa was obtained as a white solid (46.2 mg, 61%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 186-187 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.88-7.84 (m, 3H), 7.81 (s, 1H), 7.64 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.59-7.55 (m, 2H), 7.52 (d, *J* = 6.0 Hz, 1H), 7.48-7.43 (m, 2H), 7.39-7.34 (m, 2H), 2.66 (t, *J* = 6.0 Hz, 2H), 2.08 (s, 3H), 1.99 (t, *J* = 6.4 Hz, 2H), 1.23 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 198.6, 142.3, 137.3, 133.3, 132.7, 132.3, 129.7, 129.6, 129.0, 128.7, 128.2, 127.9, 127.8, 127.6, 126.7, 125.4, 125.2, 121.0, 116.1, 42.0, 37.4, 24.6, 20.1, 11.2. **FT-IR (ATR):** 3050, 2963, 2915, 1653, 1597, 1530, 1497, 1455, 1437, 1421, 1385, 1354, 1040cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{27}H_{26}NO$ [M] $^{+}$: 428.2014, found: 428.2017.



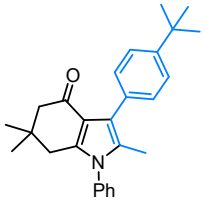
2-methyl-3-(naphthalen-2-yl)-1,6-diphenyl-1,5,6,7-tetrahydro-4H-indol-4-one (3pa). Following general procedure, 3pa was obtained as a white solid (32.4 mg, 38%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 204-206 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.91-7.86 (m, 4H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.57 -7.46 (m, 5H), 7.36-7.32 (m, 4H), 7.30-7.28 (m, 3H), 360-3.53 (m, 1H), 2.95-2.73 (m, 4H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 192.3, 143.5, 143.2, 137.1, 133.3, 132.4, 132.3, 129.7, 129.5, 129.3, 128.9, 128.7, 128.4, 127.9, 127.8, 127.7, 126.9, 126.9, 126.8, 125.6, 125.4, 120.5, 117.6, 46.1, 42.3, 31.1, 11.2. **FT-IR (ATR):** 3056, 3027, 2940, 2895, 1656, 1597, 25+8, 2563, 1427, 1412m 1353, 1057cm^{-1}. **HRMS (ESI^{+}, m/z)**: calcd for $C_{31}H_{25}NONa$ [M+Na]$^{+}$: 450.1834, found: 450.1823.



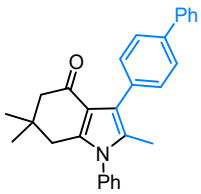
2,6,6-trimethyl-1,3-diphenyl-1,5,6,7-tetrahydro-4H-indol-4-one (3ab). Following general procedure, 3ab was obtained as a white solid (42.1 mg, 64%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 118-119 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.57-7.52 (m, 3H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.33-7.28 (m, 3H), 2.47 (s, 2H), 2.39 (s, 2H), 2.03 (s, 3H), 1.11 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.0, 142.9, 137.3, 134.6, 130.4, 129.6, 128.7, 128.6, 127.8, 127.5, 126.2, 120.4, 116.5, 53.2, 37.1, 35.2, 28.5, 11.2. **FT-IR (ATR):** 2959, 2869, 1647, 1501, 1457, 1446, 1426, 1414, 1384, 1351, 1331, 1055, 1027cm^{-1}. **HRMS (ESI^{+}, m/z)**: calcd for $C_{23}H_{23}NONa$ [M+Na]$^{+}$: 352.1667, found: 352.1672.



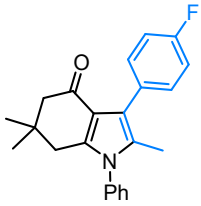
2,6,6-trimethyl-1-phenyl-3-(p-tolyl)-1,5,6,7-tetrahydro-4H-indol-4-on (3ac). Following general procedure, 3ac was obtained as a white solid (48.1 mg, 70%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 139-141 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.58-7.50 (m, 3H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.32-7.28 (m, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 2.46 (s, 2H), 2.40 (d, *J* = 4.0 Hz, 5H), 2.03 (s, 3H), 1.11 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.0, 142.8, 137.4, 135.7, 131.5, 130.3, 129.6, 128.7, 128.3, 127.8, 124.4, 120.3, 116.5, 53.2, 37.1, 35.2, 28.6, 21.3, 11.2. **FT-IR (ATR):** 2956, 2924, 1651, 1497, 1441, 1057cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{24}H_{26}NO$ [M] $^{+}$: 344.2014, found: 344.1989.



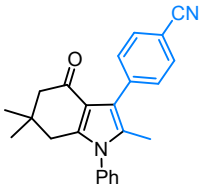
3-(4-(tert-butyl)phenyl)-2,6,6-trimethyl-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (3ad). Following general procedure, 3ad was obtained as a white solid (30 mg, 39%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p.>250 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.58-7.51 (m, 3H), 7.41 (s, 4H), 7.33-7.29 (m, 2H), 2.46 (s, 2H), 2.39 (s, 2H), 2.04 (s, 3H), 1.37 (s, 9H), 1.10 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.1, 148.7, 142.8, 137.4, 131.4, 130.0, 129.6, 128.6, 128.4, 127.8, 124.5, 120.2, 116.5, 53.3, 37.1, 35.2, 34.5, 31.4, 28.5, 11.3. **FT-IR (ATR):** 2954, 2867, 1654, 4597, 1497, 1455, 1442, 1424, 1356, 1057cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{27}H_{32}NO$ [M] $^{+}$: 386.2484, found: 386.2456.



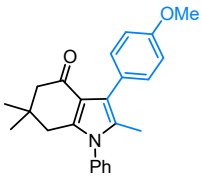
3-([1,1'-biphenyl]-4-yl)-2,6,6-trimethyl-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (3ae). Following general procedure, 3ae was obtained as a yellow solid (51 mg, 63%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 225-226 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.71-7.64 (m, 4H), 7.60-7.52 (m, 5H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.39-7.31 (m, 3H), 2.49 (s, 2H), 2.43 (s, 2H), 2.09 (s, 3H), 1.13 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.2, 143.1, 141.5, 138.9, 137.3, 133.7, 130.8, 129.6, 128.8, 128.7, 128.7, 127.8, 127.1, 126.9, 126.4, 119.9, 116.5, 53.3, 37.1, 35.2, 28.6, 11.3. **FT-IR (ATR):** 2957, 2928, 2867, 2360, 1650, 1596, 1488, 1496, 1439, 1384, 1354, 1057, 1008cm^{-1}. **HRMS (ESI^{+}, m/z)**: calcd for $C_{29}H_{27}NONa$ [M+Na]$^{+}$: 428.1990, found: 428.1863



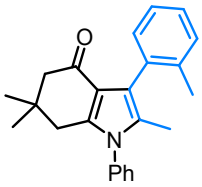
3-(4-fluorophenyl)-2,6,6-trimethyl-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (3af). Following general procedure, **3af** was obtained as a yellow solid (37.5 mg, 54%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 83-84 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.59-7.52 (m, 3H), 7.45-7.40 (m, 2H), 7.31-7.29 (m, 2H), 7.12-7.04 (m, 2H), 2.46 (s, 2H), 2.40 (s, 2H), 2.01 (s, 3H), 1.11 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.2, 161.4 (d, *J* = 243.0 Hz), 143.0, 137.2, 131.9 (d, *J* = 7.9 Hz), 130.5 (J = 3.2 Hz), 129.6, 128.8, 128.5, 127.8, 119.4, 116.4, 114.5 (J = 21.1 Hz), 53.2, 37.0, 35.2, 28.5, 11.1. ^{19}F NMR (376 MHz, Chloroform-d) δ -117.0. **FT-IR (ATR):** 2947, 2868, 1653, 1577, 1496, 1453, 1440, 1421, 1411, 1384, 1353, 1214cm^{-1}. **HRMS (ESI^{+}, m/z)**: calcd for $C_{23}H_{22}FNONa$ [M+Na]$^{+}$: 370.1583, found: 370.1548.



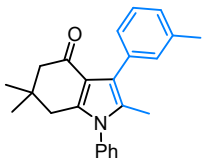
4-(2,6,6-trimethyl-4-oxo-1-phenyl-4,5,6,7-tetrahydro-1H-indol-3-yl)benzonitrile (3ag). Following general procedure, 3ag was obtained as a white solid (18.4 mg, 26%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 154-156 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.51-7.42 (m, 5H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 2H), 2.30 (s, 2H), 1.93 (s, 3H), 1.01 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.2, 143.7, 139.9, 136.8, 131.3, 131.0, 129.8, 129.5, 129.1, 127.7, 119.6, 118.8, 116.2, 109.5, 53.1, 37.0, 35.3, 28.5, 11.2. **FT-IR (ATR):** 3056, 2958, 2924, 2224, 1654, 1597, 1529, 1497, 1440, 1423, 1386, 1356cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{24}H_{23}N_2O$ [M] $^{+}$: 355.1810, found: 355.1812.



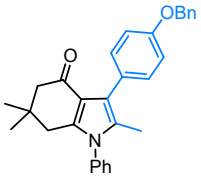
3-(4-methoxyphenyl)-2,6,6-trimethyl-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (3ah). Following general procedure, 3ah was obtained as a white solid (49.6 mg, 69%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 132-133 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.58-7.50 (m, 3H), 7.42-7.37 (m, 2H), 7.32-7.29 (m, 2H), 6.97-6.93 (m, 2H), 3.86 (s, 3H), 2.46 (s, 2H), 2.39 (s, 2H), 2.02 (s, 3H), 1.10 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.1, 158.1, 142.8, 137.4, 131.5, 130.4, 129.6, 128.7, 128.2, 127.8, 126.9, 116.5, 113.1, 55.2, 53.2, 37.1, 35.2, 28.5, 11.1. **FT-IR (ATR):** 2953, 2913, 1649, 1522, 1497, 1454, 1442, 1421, 1285, 1177, 1029cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{24}H_{26}NO_2$ [M] $^{+}$: 360.1964, found: 360.1963.



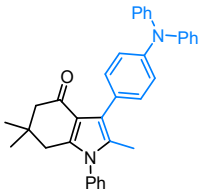
2,6,6-trimethyl-1-phenyl-3-(o-tolyl)-1,5,6,7-tetrahydro-4H-indol-4-one (3ai). Following general procedure, 3ai was obtained as a white solid (48.1 mg, 54%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 105-106 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.59-7.50 (m, 3H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.26-7.19 (m, 4H), 2.48 (d, *J* = 1.2 Hz, 2H), 2.35 (s, 2H), 2.21 (s, 3H), 1.86 (s, 3H), 1.10 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 192.9, 142.3, 140.8, 137.8, 137.4, 134.9, 130.6, 129.5, 128.6, 128.17, 127.8, 126.8, 125.1, 119.4, 117.7, 52.8, 37.0, 35.3, 28.8, 28.2, 20.1, 10.7. **FT-IR (ATR):** 2957, 2944, 1668, 1523, 1495, 1408, 1053cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{24}H_{26}NO$ [M] $^{+}$: 344.2014, found: 344.1993.



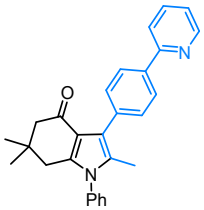
2,6,6-trimethyl-1-phenyl-3-(m-tolyl)-1,5,6,7-tetrahydro-4H-indol-4-one (3aj). Following general procedure, 3aj was obtained as a brown solid (52.2 mg, 76%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 131-132 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.57-7.48 (m, 3H), 7.29-7.27 (m, 3H), 7.26-7.21 (m, 2H), 7.08 (d, *J* = 6.8 Hz, 1H), 2.43 (s, 2H), 2.39 (s, 3H), 2.37 (s, 2H), 2.00 (s, 3H), 1.08 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.0, 142.9, 137.3, 136.9, 134.4, 131.1, 129.6, 128.7, 128.5, 127.8, 127.5, 127.5, 127.1, 120.4, 116.5, 53.2, 37.1, 35.2, 28.5, 21.6, 11.2. **FT-IR (ATR):** 2943, 1866, 1650, 1596, 1519, 1497, 1451, 1411, 1055cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{24}H_{26}NO$ [M] $^{+}$: 344.2014, found: 344.2004.



3-(4-(benzyloxy)phenyl)-2,6,6-trimethyl-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (3ak). Following general procedure, 3ak was obtained as a white solid (48.7 mg, 56%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 164-165 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.59-7.48 (m, 5H), 7.45-7.38 (m, 4H), 7.36 (d, *J* = 6.4 Hz, 1H), 7.32-7.29 (m, 2H), 7.06-7.01 (m, 2H), 5.12 (s, 2H), 2.46 (s, 2H), 2.39 (s, 2H), 2.02 (s, 3H), 1.10 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.1, 157.4, 142.8, 137.4, 137.4, 131.5, 129.6, 128.7, 128.6, 128.2, 127.9, 127.8, 127.6, 127.2, 119.9, 116.5, 114.0, 70.0, 53.2, 37.1, 35.2, 28.5, 11.2. **FT-IR (ATR):** 2958, 2922, 2865, 1651, 1496, 1454, 1443, 1421, 1367, 1280, 1237, 1170 cm^{-1}. **HRMS (ESI$^+$, m/z)**: calcd for $C_{30}H_{29}NO_2Na$ $[M+Na]^+$: 458.2096, found: 458.2057.

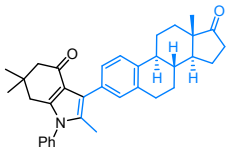


3-(4-(diphenylamino)phenyl)-2,6,6-trimethyl-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (3al). Following general procedure, 3al was obtained as a yellow solid (74 mg, 75%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 192-194 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.60-7.49 (m, 3H), 7.39-7.34 (m, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.29-7.24 (m, 4H), 7.20-7.19 (m, 4H), 7.13-7.10 (m, 2H), 7.05-6.98 (m, 2H), 2.47 (s, 2H), 2.41 (s, 2H), 2.06 (s, 3H), 1.11 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.3, 148.0, 145.7, 142.9, 137.3, 131.2, 129.6, 129.1, 129.0, 128.7, 128.4, 127.8, 124.2, 123.2, 122.4, 120.1, 116.5, 53.3, 37.1, 35.2, 28.6, 11.4. **FT-IR (ATR):** 2951, 2868, 2360, 1654, 1588, 1492, 1438, 1407, 1315, 1289, 1271cm^{-1}. **HRMS (ESI$^+$, m/z)**: calcd for $C_{35}H_{32}NONa$ $[M+Na]^+$: 519.2412, found: 519.2419.



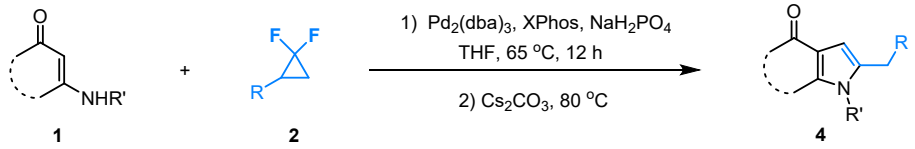
2,6,6-trimethyl-1-phenyl-3-(4-(pyridin-2-yl)phenyl)-1,5,6,7-tetrahydro-4H-indol-4-one (3am). Following general procedure, 3am was obtained as a yellow solid (39.8 mg, 49%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 218-220 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.71 (d, *J* = 4.8 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.81-7.73 (m, 2H), 7.62-7.48 (m, 5H), 7.34 -7.29 (m, 2H), 7.25-7.19 (m, 1H), 2.47 (s, 2H), 2.42 (s, 2H), 2.06 (s, 3H), 1.12 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.1, 157.7, 149.5, 143.1, 137.2, 137.1, 136.7, 135.6, 130.8, 129.6, 129.0, 128.8, 127.8, 126.2, 121.8, 120.5, 119.9, 116.4, 53.2, 37.1, 35.2, 28.5, 11.3. **FT-IR (ATR):** 2956, 2867, 1650, 1585, 1495, 1465, 1455, 1441, 1426, 1410, 1385, 1354, 1058cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{28}H_{27}N_2O$

[M] $^{+}$: 407.2123, found: 407.2123.

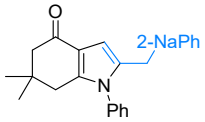


2,6,6-trimethyl-3-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one(3an). Following general procedure, 3an was obtained as a yellow solid (48.5 mg, 48%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 210-212 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.56-7.48 (m, 3H), 7.31-7.28 (m, 2H), 7.24-7.19 (m, 2H), 7.07 (d, *J* = 4.5 Hz, 1H), 3.00-2.93 (m, 2H), 2.53-2.42 (m, 4H), 2.36 (s, 2H), 2.14-1.95 (m, 7H), 1.70-1.60 (m, 5H), 1.08 (s, 6H), 0.93 (s, 3H), 0.90-0.85 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.09, 142.88, 135.40, 131.86, 130.92, 129.57, 128.69, 127.87, 127.83, 124.55, 53.24, 50.62, 48.09, 44.51, 38.16, 37.10, 35.94, 35.17, 31.69, 31.60, 29.49, 28.52, 26.71, 25.63, 22.66, 21.64, 14.13, 13.91, 11.27. **FT-IR (ATR):** 2922, 2866, 1735, 1657, 1598, 1497, 1445, 1053cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{28}H_{27}N_2O$ [M] $^{+}$: 506.3059, found: 506.3059.

General procedure for the synthesis of substrates (4)

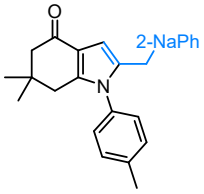


A 8 mL sealed tube equipped with a stir bar was charged with enaminone **1** (0.1 mmol, 1.0 equiv.), gem-difluorocyclopropane **2** (0.1 mmol, 1.0 equiv.), Xphos (4.8 mg, 0.01 mmol, 0.1 equiv), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 0.025 equiv.) and NaH_2PO_4 (24 mg, 0.4 mmol, 2.0 equiv.) under nitrogen. Followed by the addition of THF (1 mL). The flask was then sealed and the mixture was stirred at 65 °C (oil bath) for 12 hours. After the reaction was complete, the reaction mixture was cooled to room temperature, filtrated via celite and the filtrate concentrated under reduced pressure. Then Cs_2CO_3 (65.2 mg, 2.0 equiv.) was added under Ar atmosphere. Followed by the addition of EtOH (1 mL). The flask was then sealed and the mixture was stirred at 80 °C (oil bath) for 12 hours. After the reaction was complete, the reaction mixture was cooled to room temperature, filtrated via celite and the filtrate concentrated under reduced pressure. After the solvent was removed, the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/20 to 1/10, v/v) to afford desired product **4aa-4ka, 4ab-4ai**.

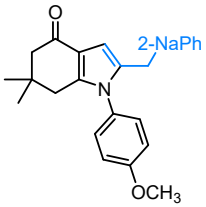


6,6-dimethyl-2-(naphthalen-2-ylmethyl)-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (4aa). Following general procedure, 4aa was obtained as a white solid (63.1 mg, 80%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 175-176 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.82-7.78 (m, 1H), 7.70 (d, *J* = 8.4 Hz,

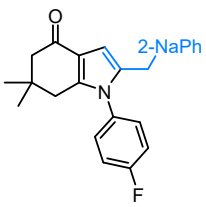
1H), 7.68-7.63 (m, 1H), 7.48-7.38 (m, 5H), 7.30 (s, 1H), 7.5 (d, *J* = 8.4 Hz, 1H), 7.10-7.07 (m, 1H), 6.46 (s, 1H), 3.90 (s, 2H), 2.38 (d, *J* = 2.4 Hz, 4H), 1.08 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.8, 144.0, 136.9, 135.9, 134.8, 133.4, 132.1, 129.4, 128.8, 128.0, 127.9, 127.6, 127.5, 127.1, 127.0, 125.9, 125.4, 119.1, 104.6, 52.1, 36.6, 35.6, 33.4, 28.6. **FT-IR (ATR):** 2959, 2929, 1645, 1495, 1459, 1431, 1408, 1365, 1209, 1118cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{28}H_{28}NO$ [M] $^{+}$: 3180.2014, found: 380.2000.



6,6-dimethyl-2-(naphthalen-2-ylmethyl)-1-(p-tolyl)-1,5,6,7-tetrahydro-4H-indol-4-one (4ba). Following general procedure, 4ba was obtained as a white solid (63.1 mg, 80%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 195-196 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.78-7.75 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.65-7.64 (m, 1H), 7.44-7.39 (m, 2H), 7.29 (s, 1H), 7.18 (d, *J* = 8 Hz, 2H), 7.14 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 6.97-6.90 (m, 2H), 6.40 (s, 1H), 3.85 (s, 2H), 2.41 (s, 3H), 2.35 (s, 4H), 1.05 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.8, 144.1, 138.8, 136.0, 134.9, 134.3, 133.4, 132.1, 130.0, 127.9, 127.7, 127.6, 127.5, 127.2, 127.1, 125.9, 125.4, 118.9, 104.4, 52.1, 36.6, 35.6, 33.3, 28.6, 21.2. **FT-IR (ATR):** 2955, 2931, 2867, 1648, 1515, 1459, 1431, 1410, 1366, 1245, 1212, 1178, 1112cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{28}H_{28}NO$ [M] $^{+}$: 394.2171, found: 394.2146.

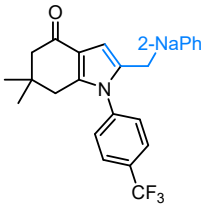


1-(4-methoxyphenyl)-6,6-dimethyl-2-(naphthalen-2-ylmethyl)-1,5,6,7-tetrahydro-4H-indol-4-one (4ca). Following general procedure, 4ca was obtained as a yellow solid (45.0 mg, 55%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 141-142 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.78-7.75 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.66-7.63 (m, 2H), 7.44-7.39 (m, 2H), 7.29 (s, 1H), 7.14 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.96-6.92 (m, 2H), 6.88-6.84 (m, 2H), 6.41 (s, 1H), 3.85 (s, 2H), 3.83 (s, 3H), 2.34 (d, *J* = 5.6 Hz, 4H), 1.05 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.8, 159.6, 144.3, 136.0, 135.0, 133.4, 132.1, 129.5, 129.0, 127.9, 127.6, 127.5, 127.2, 127.0, 125.9, 125.4, 118.8, 114.4, 104.3, 55.5, 52.1, 36.6, 35.6, 33.3, 28.6. **FT-IR (ATR):** 3054, 2954, 2932, 1639, 1514, 1461, 1439, 1244, 1199, 1179, 1030cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{28}H_{28}NO$ [M] $^{+}$: 410.2120, found: 410.2116.

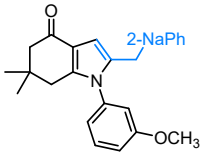


1-(4-fluorophenyl)-6,6-dimethyl-2-(naphthalen-2-ylmethyl)-1,5,6,7-tetrahydro-4H-

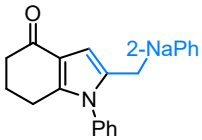
indol-4-one (4da). Following general procedure, 4da was obtained as a yellow solid (29.4 mg, 37%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/20 to 1/10). M.p. 154-155 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.78-7.76 (m, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.66-7.60 (m, 1H), 7.46-7.38 (m, 2H), 7.26 (s, 1H), 7.11 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.07-7.05 (m, 2H), 7.03-6.97 (m, 2H), 6.46 (s, 1H), 3.86 (s, 2H), 2.34 (d, *J* = 16.0 Hz, 4H), 1.06 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.8, 162.4 (d, *J* = 247.7 Hz), 152.1, 146.1, 144.1, 135.8, 134.7, 133.4, 132.1, 129.8 (d, *J* = 8.7 Hz), 128.0, 127.6, 127.5, 127.0 (d, *J* = 1.9 Hz), 126.0, 125.5, 119.1, 116.3 (d, *J* = 22.8 Hz), 104.8, 100.4, 52.0, 36.6, 35.6, 33.3, 28.6. ^{19}F NMR (376 MHz, Chloroform-d) δ -62.66. **FT-IR (ATR):** 2940, 2855, 1653, 1593, 1497, 1462, 1430, 1408, 1355, 1209, 1169, 1119cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{27}H_{25}FNO$ [M] $^{+}$: 398.1920, found: 398.1919.



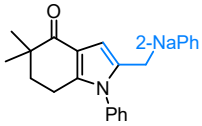
6,6-dimethyl-2-(naphthalen-2-ylmethyl)-1-(4-(trifluoromethyl)phenyl)-1,5,6,7-tetrahydro-4H-indol-4-one (4ea). Following general procedure, 4ea was obtained as a yellow oil (37.6 mg, 42%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.77-7.74 (m, 1H), 7.68-7.58 (m, 4H), 7.45-7.40 (m, 2H), 7.20 (s, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.09 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.50 (s, 1H), 3.89 (s, 2H), 2.37 (s, 2H), 2.34 (s, 2H), 1.06 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.7, 143.6, 140.1, 135.4, 134.5, 133.3, 132.1, 131.0 (*J* = 33.0 Hz), 128.5, 128.1, 127.6, 127.4, 127.0, 126.8, 126.5 (q, *J* = 3.7 Hz), 126.1, 125.6, 123.6 (q, *J* = 270.9 Hz), 119.6, 105.4, 52.0, 36.6, 35.7, 33.4, 28.6. ^{19}F NMR (376 MHz, Chloroform-d) δ -111.9. **FT-IR (ATR):** 2928, 2859, 1657, 1613, 1524, 1459, 1410, 1266, 1168, 1128, 1067cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{28}H_{25}F_3NO$ [M] $^{+}$: 448.1888, found: 448.1876.



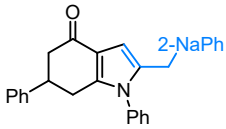
1-(3-methoxyphenyl)-6,6-dimethyl-2-(naphthalen-2-ylmethyl)-1,5,6,7-tetrahydro-4H-indol-4-one (4fa). Following general procedure, 4fa was obtained as a yellow oil (35.2 mg, 43%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 175-176 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.79-7.73 (m, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.65-7.63 (m, 1H), 7.46-7.36 (m, 2H), 7.32-7.27 (m, 2H), 7.14 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.95 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.47 (t, *J* = 2.4 Hz, 1H), 6.43 (s, 1H), 3.88 (s, 2H), 3.56 (s, 3H), 2.36 (d, *J* = 4.8 Hz, 4H), 1.06 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.8, 160.2, 143.9, 137.9, 136.0, 134.7, 133.4, 132.1, 130.0, 127.9, 127.5, 127.5, 127.2, 127.1, 125.9, 125.4, 120.1, 119.0, 114.8, 113.5, 104.6, 55.2, 52.1, 36.6, 35.6, 33.4, 28.6. **FT-IR (ATR):** 2946, 2833, 1652, 1604, 1490, 1458, 1430, 1276, 1240, 1204, 1154, 1048cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{28}H_{28}NO$ [M] $^{+}$: 410.2120, found: 410.2116.



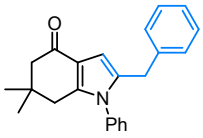
2-(naphthalen-2-ylmethyl)-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (4ga). Following general procedure, 4ga was obtained as a yellow oil (44.9 mg, 64%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/5 to 1/3). M.p. 150-151 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.77-7.74 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.64-7.62 (m, 1H), 7.44-7.36 (m, 5H), 7.12 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.09-7.06 (m, 2H), 6.45 (s, 1H), 3.88 (s, 2H), 2.49 (td, *J* = 6.8, 1.6 Hz, 4H), 2.08 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 194.5, 145.1, 136.9, 135.9, 134.6, 133.4, 132.1, 129.4, 128.8, 127.9, 127.9, 127.6, 127.5, 127.1, 127.0, 125.9, 125.4, 120.2, 104.8, 37.9, 33.3, 23.8, 22.6. **FT-IR (ATR):** 2940, 2856, 1654, 1594, 1462, 1430, 1408, 1356, 1209, 2269, 1119cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{25}H_{22}NO$ [M] $^{+}$: 352.1701, found: 352.1668.



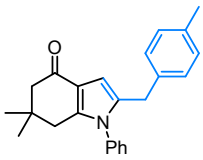
5,5-dimethyl-2-(naphthalen-2-ylmethyl)-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (4ha). Following general procedure, 4ha was obtained as a yellow oil (31.1 mg, 41%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 184-185 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.79-7.71 (m, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.64-7.60 (m, 1H), 7.46-7.33 (m, 5H), 7.28 (s, 1H), 7.12 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.09-7.06 (m, 2H), 6.43 (s, 1H), 3.87 (s, 2H), 2.50 (t, *J* = 6.0 Hz, 2H), 1.91 (t, *J* = 6.4 Hz, 2H), 1.19 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 199.2, 143.2, 136.9, 136.0, 134.8, 133.4, 132.1, 129.3, 128. 7, 127.9, 127.9, 127.6, 127.5, 127.2, 127.0, 125.9, 125.4, 118.6, 105.4, 41.6, 37.7, 33.3, 24.6, 19.8. **FT-IR (ATR):** 3052, 2923, 2853, 1652, 1598, 1529, 1497, 1458, 1266, 1154cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{27}H_{26}NO$ [M] $^{+}$: 380.2014, found: 380.1993.



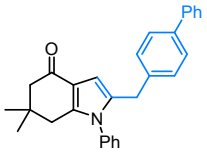
2-(naphthalen-2-ylmethyl)-1,6-diphenyl-1,5,6,7-tetrahydro-4H-indol-4-one (4ia). Following general procedure, 4ia was obtained as a yellow oil (41.0 mg, 48%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 141-142 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.79-7.72 (m, 1H), 7.71-7.59 (m, 2H), 7.46-7.16 (m, 10H), 7.12 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.06 (s, 2H), 6.50 (s, 1H), 3.89 (s, 2H), 3.48 (tt, *J* = 11.6, 4.7 Hz, 1H), 2.85-2.63 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.1, 144.2, 143.4, 136.7, 135.8, 135.2, 133.4, 132.2, 129.4, 128.9, 128.7, 128.0, 127.9, 127.6, 127.5, 127.1, 127.0, 127.0, 126.8, 126.0, 125.5, 120.0, 104.9, 45.0, 42.6, 33.3, 30.7. **FT-IR (ATR):** 3054, 2926, 1654. 1599, 1497, 1461, 1414, 1264, 1193, 1079cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{31}H_{26}NO$ [M] $^{+}$: 428.2014, found: 428.2012.



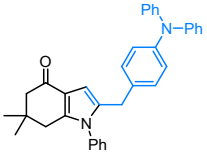
2-benzyl-6,6-dimethyl-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (4ab). Following general procedure, 4ab was obtained as a white solid (25.7 mg, 39%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 126-128 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.43 (s, 3H), 7.16 (s, 3H), 7.06 (s, 2H), 6.93 (s, 2H), 6.36 (s, 1H), 3.70 (s, 2H), 2.35 (s, 4H),1.05 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.8, 143.9, 138.4, 136.9, 135.0, 129.4, 128.7, 128.6, 128.3, 127.9, 126.2, 119.0, 104.5, 52.1, 36.62, 35.6, 33.2, 28.6. **FT-IR (ATR):** 3058, 2956, 2928, 2870, 1654, 1598, 1524, 1496, 1459, 1408, 1267, 1206. 1121cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{28}H_{27}N_2O$ [M] $^{+}$: 330.1858, found: 330.1850.



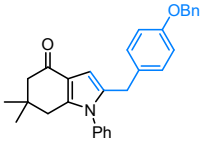
6,6-dimethyl-2-(4-methylbenzyl)-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (4ac). Following general procedure, 4ac was obtained as a white solid (48.0 mg, 70%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 109-110 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.46-7.42 (m, 3H), 7.12 -7.05 (m, 2H), 6.98 (d, J = 7.6 Hz, 2H), 6.83 (d, J = 7.6 Hz, 2H), 6.33 (s, 1H), 3.65 (s, 2H), 2.35 (s, 4H), 2.28 (s, 3H), 1.05 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.8, 143.8, 137.0, 135.7, 135.4, 135.3, 129.4, 129.0, 128.7, 128.5, 127.9, 119.0, 104.3, 52.1, 36.6, 35.6, 32.7, 28.6, 21.0. **FT-IR (ATR):** 2961, 2924, 2833, 1647, 1596, 1496, 1462, 1453, 1430, 1409, 1266, 1209cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{24}H_{26}NO$ [M] $^{+}$: 344.2014, found: 344.1996.



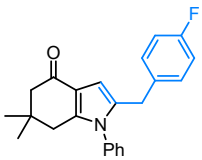
2-([1,1'-biphenyl]-4-ylmethyl)-6,6-dimethyl-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (4ad). Following general procedure, 4ad was obtained as a white solid (52.7 mg, 65%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 113-114 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.58-7.50 (m, 1H), 7.48-7.43 (m, 3H), 7.42-7.39 (m, 4H), 7.34-7.30(m, 1H), 7.13-7.05 (m, 2H), 7.00 (d, *J* = 6.4 Hz, 2H), 3.74 (s, 2H), 2.36 (s, 4H), 1.06 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.8, 143.9, 140.9, 139.2, 137.6, 136.9, 134.9, 129.4, 129.1, 128.8, 128.7, 128.0, 127.1, 127.0, 126.9, 119.0, 104.5, 52.1, 36.6, 35.6, 32.8, 28.6. **FT-IR (ATR):** 2947, 2900, 2861, 2837, 1652, 1593, 1492, 1457, 1428, 1404, 1209, 1118cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{29}H_{28}NO$ [M] $^{+}$: 406.2171, found: 406.2162.



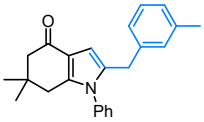
2-(4-(diphenylamino)benzyl)-6,6-dimethyl-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (4ae). Following general procedure, 4ae was obtained as a yellow solid (36.7 mg, 37%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 146-148 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.45-7.42 (m, 3H), 7.25-7.19 (t, *J* = 6.8 Hz, 4H), 7.11-7.07 (m, 2H), 7.04-7.02 (m, 4H), 6.98 (t, *J* = 6.8 Hz, 2H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.80 (d, *J* = 6.4 Hz, 2H), 6.39 (s, 1H), 3.67 (s, 2H), 2.36 (s, 4H), 1.06 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.9, 147.9, 146.0, 144.0, 137.0, 135.2, 132.9, 129.6, 129.4, 129.2, 128.7, 127.9, 124.4, 123.8, 122.5, 119.0, 104.4, 52.1, 36.7, 35.6, 32.7, 28.6. **FT-IR (ATR):** 2956, 2916, 1650, 1593, 1489, 1463, 1275, 1176cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{35}H_{33}N_2O$ [M] $^+$: 497.2593, found: 497.2593.



2-(4-(benzyloxy)benzyl)-6,6-dimethyl-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (4af). Following general procedure, 4af was obtained as a yellow solid (47.9 mg, 55%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 129-130 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.46-7.39 (m, 5H), 7.38-7.35 (m, 2H), 7.34-7.29 (m, 1H), 7.08-7.02 (m, 2H), 6.86-6.76 (m, 4H), 6.34 (s, 1H), 5.01 (s, 2H), 3.64 (s, 2H), 2.35 (d, *J* = 2.0 Hz, 4H), 1.05 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.8, 157.3, 143.9, 137.1, 136.9, 135.4, 130.8, 129.6, 129.4, 128.7, 128.6, 127.9, 127.5, 118.9, 114.7, 104.2, 70.0, 52.1, 36.6, 35.6, 32.3, 28.6. **FT-IR (ATR):** 2957, 2894, 2835, 1653, 1603, 1499, 1457, 1238, 1210, 1170, 1045cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{28}H_{27}N_2O$ [M] $^+$: 436.2277, found: 436.2250.

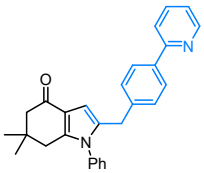


2-(4-fluorobenzyl)-6,6-dimethyl-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (4ag). Following general procedure, 4ag was obtained as a white solid (58.3 mg, 84%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 142-144 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.45-7.40 (m, 3H), 7.07-7.01 (m, 2H), 6.88-6.80 (m, 4H), 6.36 (s, 1H), 3.68 (s, 2H), 2.35 (d, *J* = 3.6 Hz, 4H), 1.05 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.8, 161.4 (d, *J* = 242.9 Hz), 144.0, 136.9, 134.8, 134.1 (d, *J* = 3.3 Hz), 129.9 (d, *J* = 7.8 Hz), 129.4, 128.8, 127.9, 119.0, 115.0 (d, *J* = 21.2 Hz), 104.5, 52.1, 36.6, 35.6, 32.4, 28.6. ^{19}F NMR (376 MHz, Chloroform-d) δ -117.0. **FT-IR (ATR):** 2950, 2920, 2868, 1643, 1598, 1504, 1497, 1460, 1405, 1264, 1216, 1139cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{23}H_{23}FNO$ [M] $^+$: 348.1764, found: 348.1754.

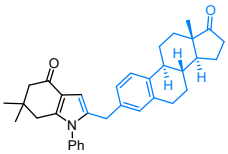


6,6-dimethyl-2-(3-methylbenzyl)-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one (4ah). Following general procedure, 4ah was obtained as a yellow solid (52.8 mg, 77%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 129-

130 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.46-7.40 (m, 3H), 7.10-7.02 (m, 3H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.76-6.70 (m, 2H), 6.35 (s, 1H), 3.65 (s, 2H), 2.35 (s, 4H), 2.23 (s, 3H), 1.05 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.8, 143.8, 138.3, 137.8, 135.2, 129.5, 129.3, 128.7, 128.2, 128.0, 127.0, 125.7, 119.0, 118.3, 104.3, 52.1, 36.6, 35.6, 33.1, 28.6, 21.3. **FT-IR (ATR):** 2957, 2927, 1651, 1596, 1524, 1494, 1460, 1385, 1265, 1212, 1121cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{28}H_{27}N_2O$ [M] $^{+}$: 344.2014, found: 344.1992.

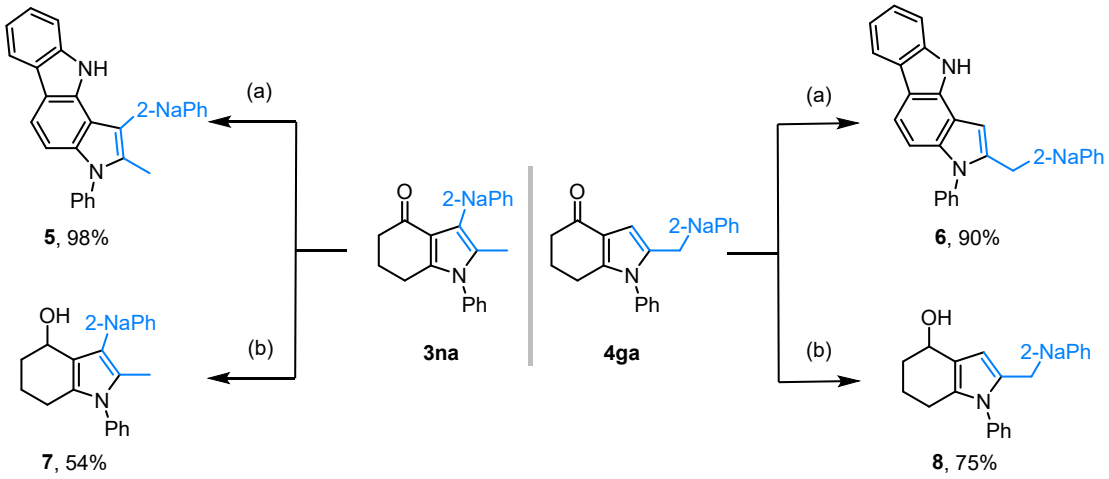


6,6-dimethyl-1-phenyl-2-(4-(pyridin-2-yl)benzyl)-1,5,6,7-tetrahydro-4H-indol-4-one (4ai). Following general procedure, 4ai was obtained as a yellow solid (56.1 mg, 69%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 128-129 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.67 (d, *J* = 4.8 Hz, 1H), 7.84-7.77 (m, 2H), 7.79-7.70 (m, 1H), 7.69-7.66 (m, 1H), 7.48-7.37 (m, 3H), 7.24-7.19 (m, 1H), 7.11-7.04 (m, 2H), 7.03 (d, *J* = 6.8 Hz, 2H), 6.44 (s, 1H), 3.77 (s, 2H), 2.36 (d, *J* = 2.4 Hz, 4H), 1.06 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.9, 172.7, 157.2, 149.5, 144.0, 139.5, 137.3, 136.9, 134.6, 129.4, 129.0, 128.8, 127.9, 126.8, 122.0, 120.5, 119.0, 104.6, 52.1, 36.6, 35.6, 32.9, 28.6. **FT-IR (ATR):** 2956, 2836, 1588, 1496, 1458, 1432, 1405, 1210, 1117cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{28}H_{27}N_2O$ [M] $^{+}$: 407.2123, found: 407.2113.



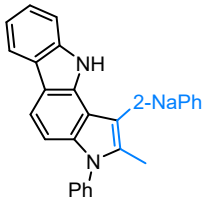
6,6-dimethyl-2-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)methyl)-1-phenyl-1,5,6,7-tetrahydro-4H-indol-4-one(4an). Following general procedure, 4ai was obtained as a yellow solid (40.4 mg, 40%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 122-124 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.50-7.43 (m, 3H), 7.16-7.10 (m, 3H), 6.78-6.66 (m, 2H), 6.28 (s, 1H), 3.61 (s, 2H), 2.86-2.75 (m, 2H), 2.50 (dd, J = 18.8, 8.6 Hz, 1H), 2.35 (d, J = 7.1 Hz, 4H), 2.19-1.93 (m, 5H), 1.76-1.51 (m, 6H), 1.48-1.33 (m, 4H), 1.29 (s, 2H), 1.05 (s, 6H), 0.92 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 193.9, 143.8, 137.8, 136.4, 135.7, 135.6, 129.4, 128.8, 128.0, 126.2, 125.3, 119.0, 116.8, 104.2, 52.0, 50.5, 48.0, 44.3, 38.2, 36.6, 35.9, 35.6, 32.7, 31.6, 31.4, 30.2, 29.3, 28.6, 26.5, 25.7, 21.6, 13.9. **FT-IR (ATR):** 2926, 2865, 1734, 1653, 1601, 1497, 1456, 1265cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{28}H_{27}N_2O$ [M] $^{+}$: 506.3059, found: 506.3061.

5. Transformation of 3ca and 4fa



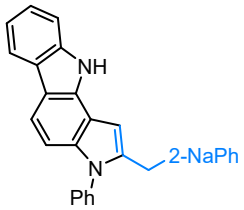
General Procedure A: A 10 mL sealed tube equipped with a stir bar was charged with 3ca or 4fa (0.1 mmol, 1.0 equiv.), $ZnCl_2$ (0.15 mmol, 1.5 equiv.) under nitrogen. Followed by the addition of AcOH (0.25 mL) and then $PhNHNH_2$ (0.1 mmol, 1.0 equiv.). The flask was then sealed and the mixture was stirred at 140 °C (oil bath) for 24 hours. After the reaction was complete, the reaction mixture was cooled to room temperature, saturated sodium bicarbonate was added and exact with ethyl acetate for three times. After drying the combined organic layers over anhydrous sodium sulfite and filtering the mixture, the solvent was removed under reduced pressure. Purify by flash column chromatography (SiO_2, ethyl acetate/petroleum ether = 1/40 to 1/20, v/v) to afford desire product **5a** or **8a**.

General Procedure B: A 10 mL sealed equipped with a stir bar was charged with 3ca or 4fa (0.1 mmol, 1.0 equiv.) under nitrogen. Followed by the addition of MeOH (1 mL), then $AlLiH_4$ was added slowly. The flask was then sealed and the mixture was stirred at room temperature for 1h. After the reaction was complete, the reaction mixture was filtrated via celite and the filtrate concentrated under reduced pressure. After the solvent was removed, the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1/20 to 1/10, v/v) to afford desired product **7a or 10a**.



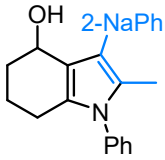
2-methyl-1-(naphthalen-2-yl)-3-phenyl-3,10-dihydropyrrolo[3,2-a] carbazole (5). According to the general procedure A, 5a was obtained as a yellow solid (41.4 mg, 98%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/40 to 1/20). M.p. 96-97 °C. 1H NMR (400 MHz, Chloroform-d) δ 8.00-7.91 (m, 4H), 7.88-7.86 (m, 1H), 7.84-7.81 (m, 1H), 7.72 (dd, J = 8.8, 2.0 Hz, 2H), 7.49-7.44 (m, 4H), 7.40-7.37 (m, 3H), 7.18-7.13 (m, 2H), 7.12-7.08 (m, 1H), 6.95 (d, J = 8.4 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 138.30, 138.26, 136.82, 134.08, 133.98, 132.51, 132.41, 132.32, 129.66, 129.38, 128.72, 128.56, 128.37, 128.14, 127.97, 127.88, 126.69, 126.00, 124.21, 123.66,

119.35, 119.17, 116.30, 114.38, 114.27, 112.28, 110.65, 103.83, 11.88. **FT-IR (ATR):** 3454, 3052, 2923, 1628, 1596, 1455, 1430, 1381, 1324, 1262, 1226cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{31}H_{23}N_2$ [M] $^+$: 423.1861, found: 423.1838.



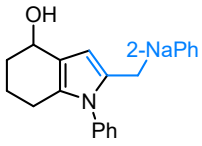
2-(naphthalen-2-ylmethyl)-3-phenyl-3,10-dihydropyrrolo[3,2-a] carbazole (6).

According to the general procedure A, 8a was obtained as a yellow solid (38.0 mg, 90%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/20 to 1/10). M.p. 137-138 °C. 1H NMR (400 MHz, Chloroform-d) δ 8.28 (s, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.84-7.78 (m, 1H), 7.77-7.75 (m, 1H), 7.75-7.66 (m, 2H), 7.53-7.40 (m, 7H), 7.35-7.30 (m, 3H), 7.39-7.26 (m, 1H), 7.24-7.20 (m, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.54 (s, 1H), 4.19 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 138.62, 138.55, 138.01, 137.93, 136.28, 133.48, 132.45, 132.20, 129.45, 128.54, 128.16, 127.95, 127.61, 127.58, 127.43, 127.28, 125.99, 125.49, 124.75, 123.56, 119.37, 119.28, 115.59, 114.19, 110.54, 112.74, 103.84, 99.03, 34.01. **FT-IR (ATR):** 3416, 3054, 2924, 2853, 1635, 1596, 1497, 1456, 1382, 1325, 1264, 1231cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{31}H_{23}N_2$ [M] $^+$: 423.1861, found: 423.1850.



2-methyl-3-(naphthalen-2-yl)-1-phenyl-4,5,6,7-tetrahydro-1H-indol-4-ol (7).

According to the general procedure C, 7a was obtained as a yellow solid (19.1 mg, 54%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/20 to 1/10). M.p. 72-73 °C. 1H NMR (400 MHz, Chloroform-d) δ 7.97 (s, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.85 (dd, J = 6.9, 2.8 Hz, 2H), 7.72 (dd, J = 8.4, 1.6 Hz, 1H), 7.52-7.47 (m, 3H), 7.46-7.45 (m, 1H), 7.44-7.42 (m, 1H), 7.43-7.39 (m, 1H), 7.32-7.29 (m, 2H), 5.01 (s, 1H), 2.46-2.36 (m, 2H), 2.14 (s, 3H), 2.06-1.93 (m, 2H), 1.91-1.73 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 138.29, 133.81, 133.76, 131.87, 129.81, 129.25, 128.40, 128.06, 127.90, 127.84, 127.74, 127.66, 126.16, 125.92, 125.31, 120.04, 118.65, 62.89, 32.56, 26.96, 22.88, 18.22, 11.63. **FT-IR (ATR):** 3051, 2929, 2856, 1723, 1629, 1597, 1535, 1498, 1421, 1403, 1363, 1264cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{25}H_{22}NONa$ [M] $^+$: 376.1677, found: 376.1661.

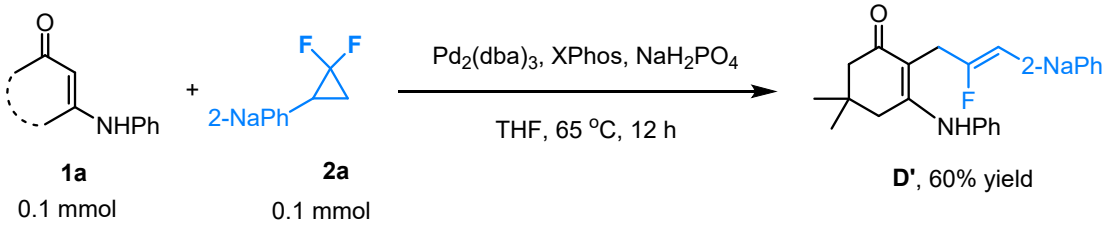


2-(naphthalen-2-ylmethyl)-1-phenyl-4,5,6,7-tetrahydro-1H-indol-4-ol (8).

According to the general procedure C, 10a was obtained as a yellow solid (26.5 mg, 75%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/20 to 1/10). M.p. 72-73 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.77-7.71 (m, 1H), 7.68-7.62 (m, 2H), 7.41-7.36 (m, 2H), 7.35-7.30 (m, 4H), 7.20-7.16 (m, 1H), 7.12-7.05 (m, 2H), 5.99 (s, 1H), 4.78 (t, J = 4.0 Hz, 1H), 3.87 (s, 2H), 2.33-2.19 (m, 2H), 1.92-1.77 (m, 4H), 1.69 (m, 1H). ^{13}C NMR

(100 MHz, Chloroform-d) δ 138.18, 137.11, 133.52, 132.20, 132.12, 130.40, 129.09, 128.23, 127.87, 127.79, 127.61, 127.59, 127.56, 127.05, 125.83, 125.29, 119.89, 105.96, 64.67, 33.59, 32.97, 22.66, 19.19. **FT-IR (ATR):** 3052, 2928, 2854, 1692, 1639, 1597, 1498, 1455, 1431, 1264, 1172, 1057, 1010cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{25}H_{22}NONa$ $[M]^+$: 376.1677, found: 376.1640.

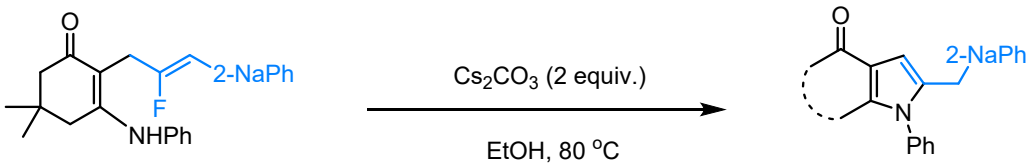
6. Control experiments



1a
0.1 mmol

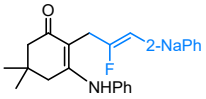
2a
0.1 mmol

D', 60% yield



D'
0.1 mmol

4aa, 95% yield



(Z)-2-(2-fluoro-3-(naphthalen-2-yl)allyl)-5,5-dimethyl-3-(phenylamino)cyclohex-2-en-1-one (D'). Following general procedure, D' was obtained as a brown solid (47.9 mg, 60%) by a column chromatography on silica gel (eluents: ethyl acetate/petroleum ether = 1/10 to 1/5). M.p. 136-137 °C. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.87 (s, 1H), 7.78-7.75 (m, 3H), 7.63 (dd, J = 8.6, 1.7 Hz, 1H), 7.44-7.41 (m, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 7.05 (d, J = 7.6 Hz, 2H), 6.92 (s, 1H), 5.78 (d, J = 40.1 Hz, 1H), 3.60 (d, J = 15.4 Hz, 2H), 2.39 (s, 2H), 2.32 (s, 2H), 1.04 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-d) δ 194.7, 160.4 (J = 266.2 Hz), 158.4, 157.8 (J = 266.2 Hz), 138.4, 133.5, 132.3, 131.2 (J = 2.5 Hz), 131.1 (J = 2.5 Hz), 129.4, 128.0 (J = 10.7 Hz), 127.9 (J = 10.7 Hz), 127.6, 127.3 (J = 7.2 Hz), 127.2 (J = 7.2 Hz), 126.7 (J = 7.4 Hz), 126.6 (J = 7.4 Hz), 126.1, 125.8, 125.7, 125.1, 106.3, 106.2, 106.1 (J = 2.3 Hz), 50.3, 40.7, 32.7, 28.3, 26.9 (J = 27.9 Hz), 26.7 (J = 27.9 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ -98.12. **FT-IR (ATR):** 3275, 2960, 1682, 1551, 1494, 1389, 1314, 1264, 1214, 1151, 1118, 1043cm^{-1}. **HRMS (EI, m/z):** calcd for $C_{27}H_{26}FNO$ [M] $^{+}$: 400.2077, found: 400.2075.

7. References

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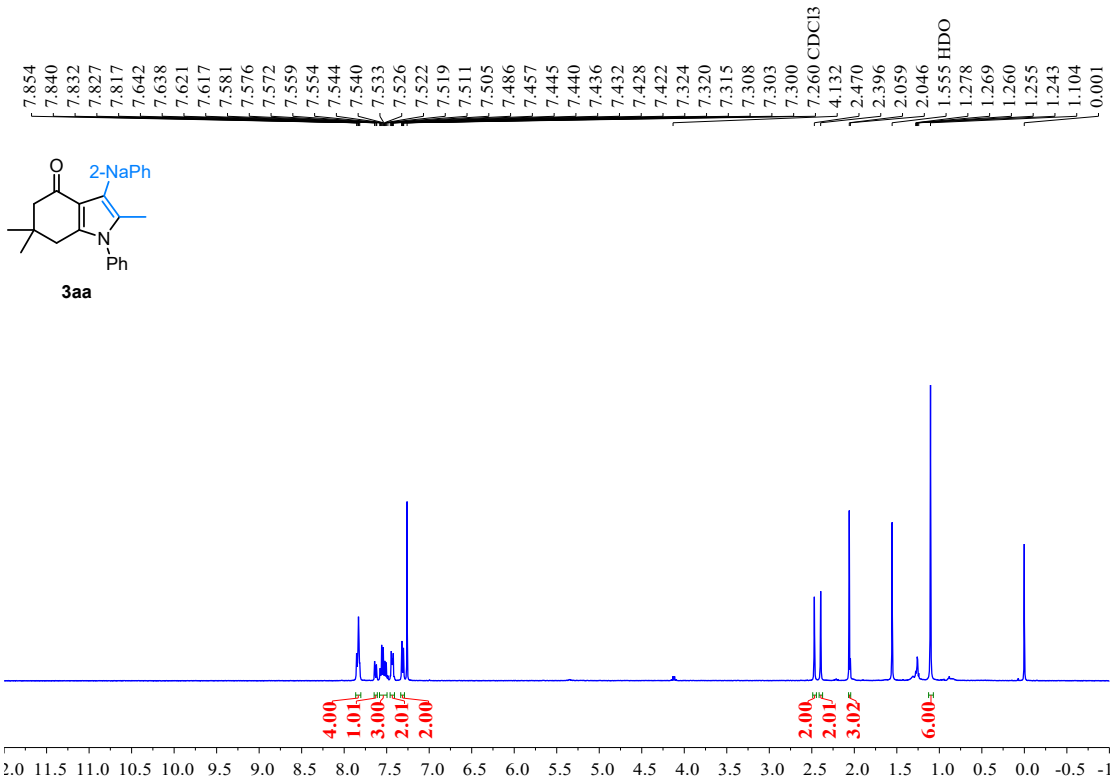
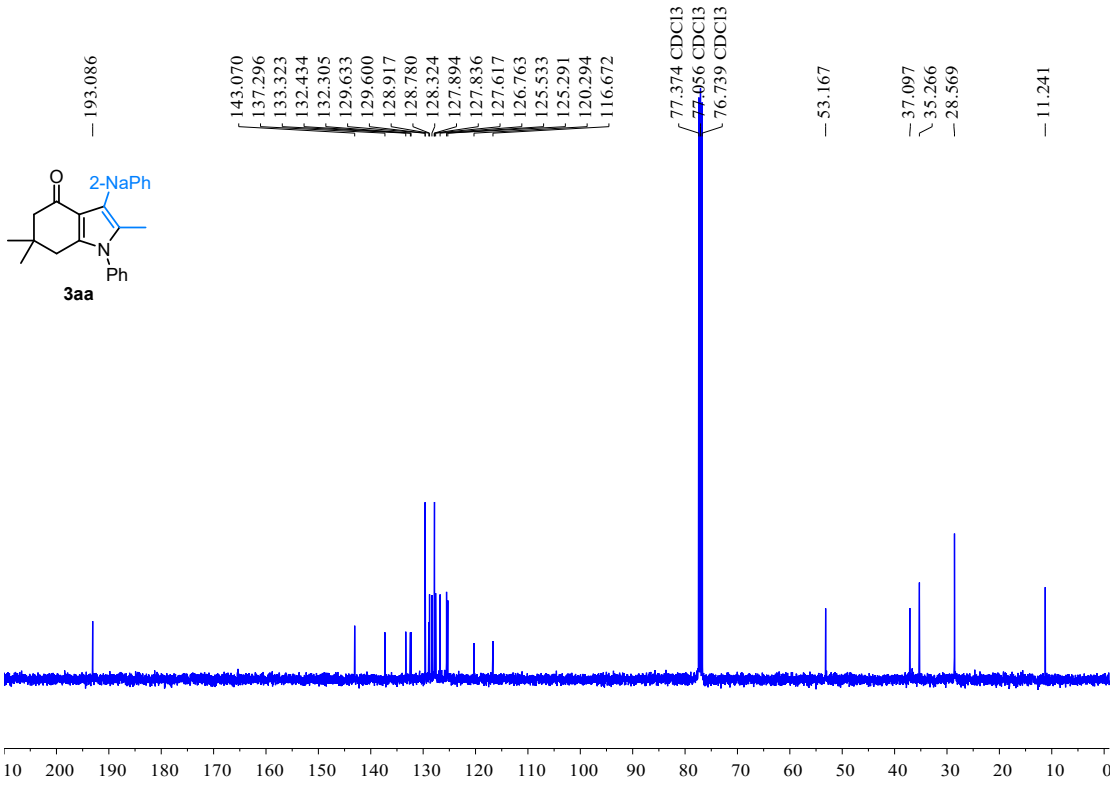
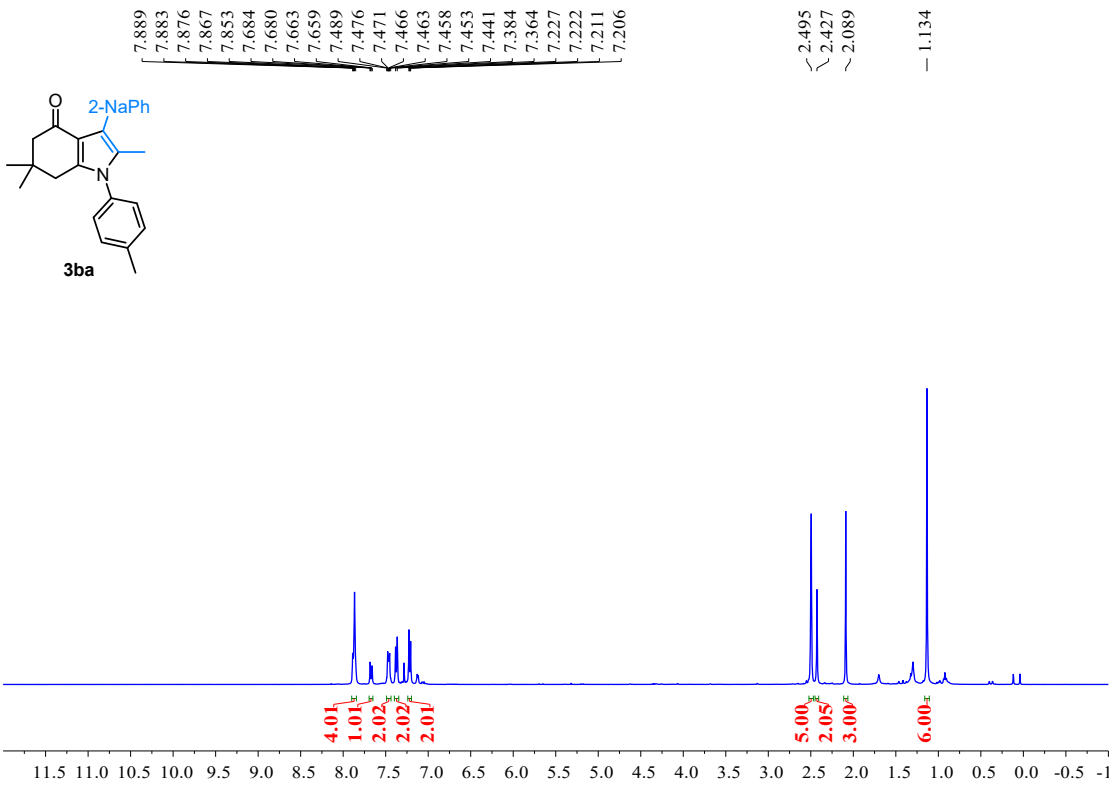
8. Copies of NMR spectra



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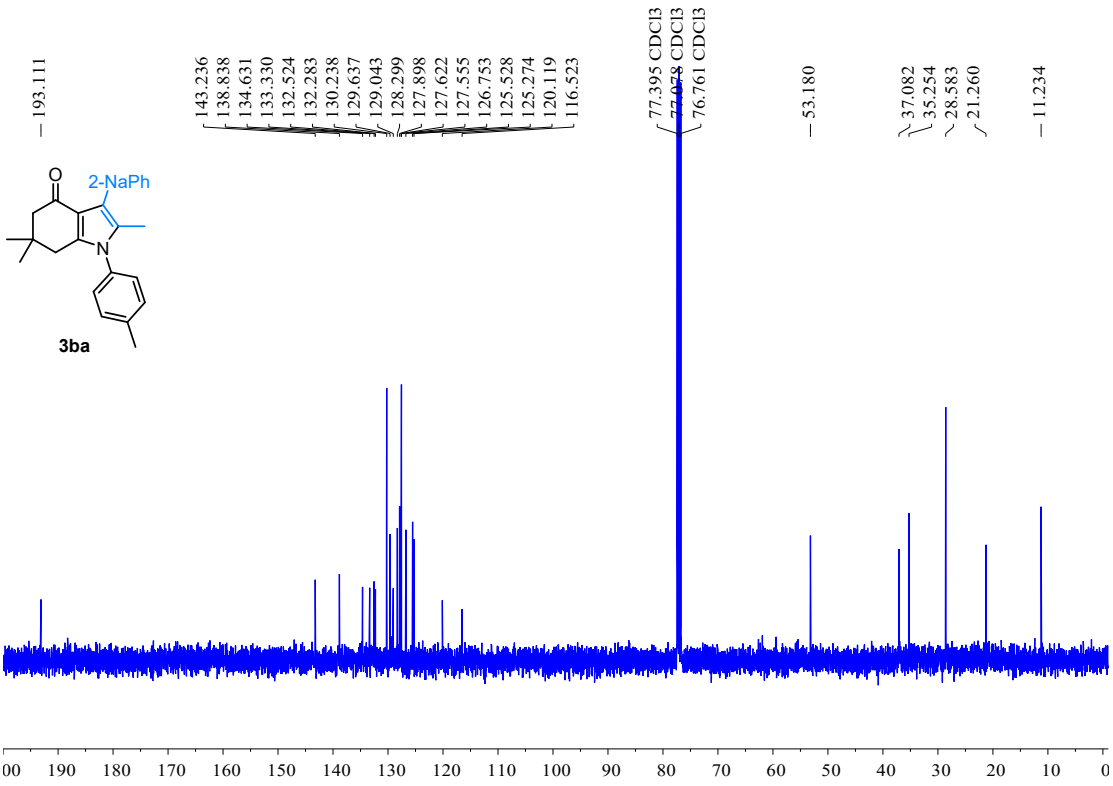
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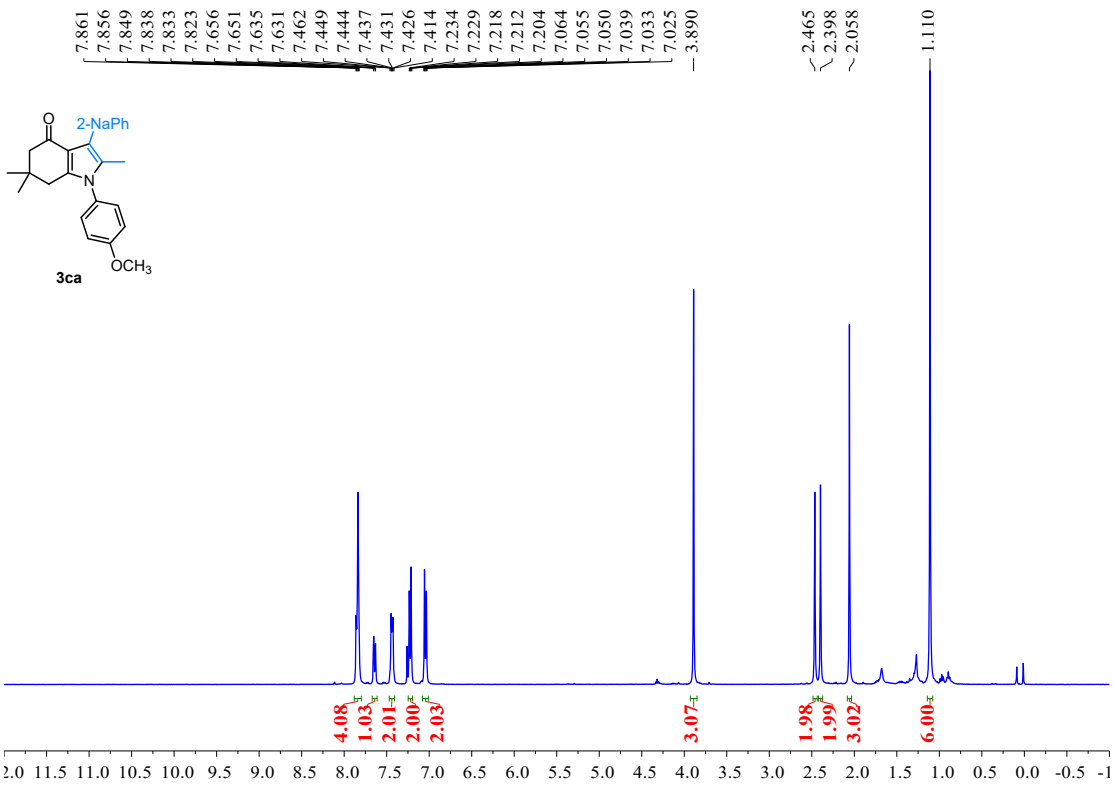
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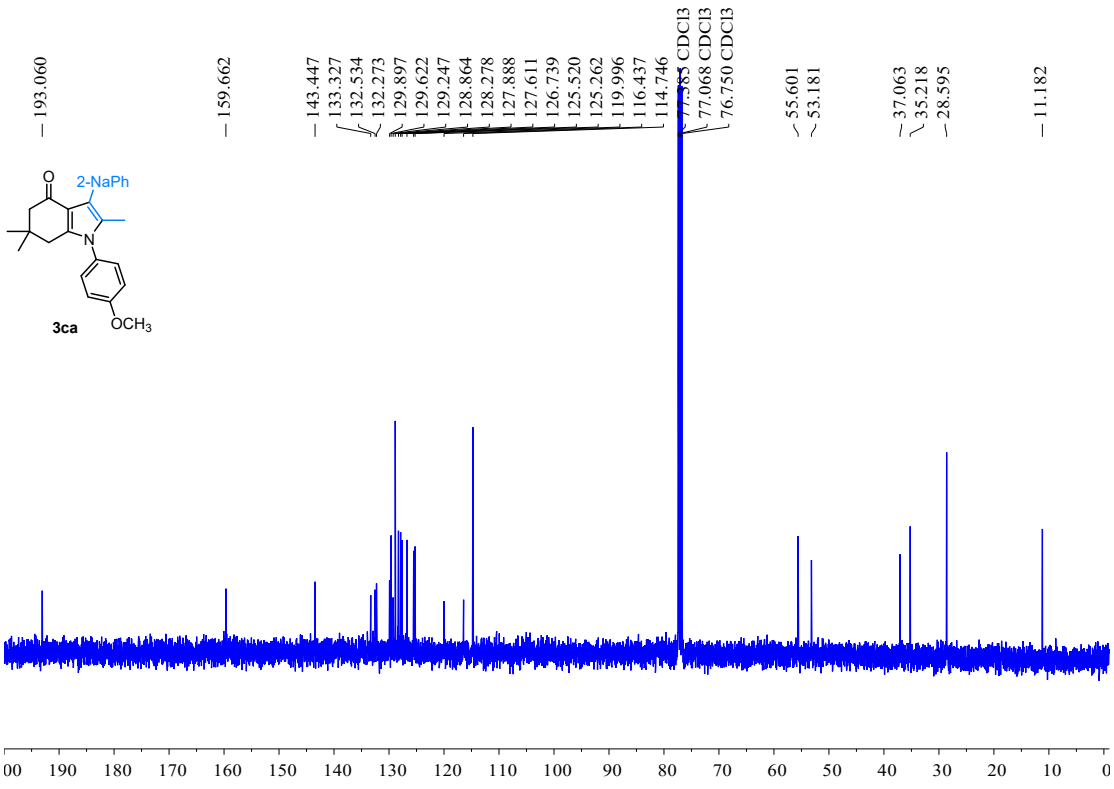
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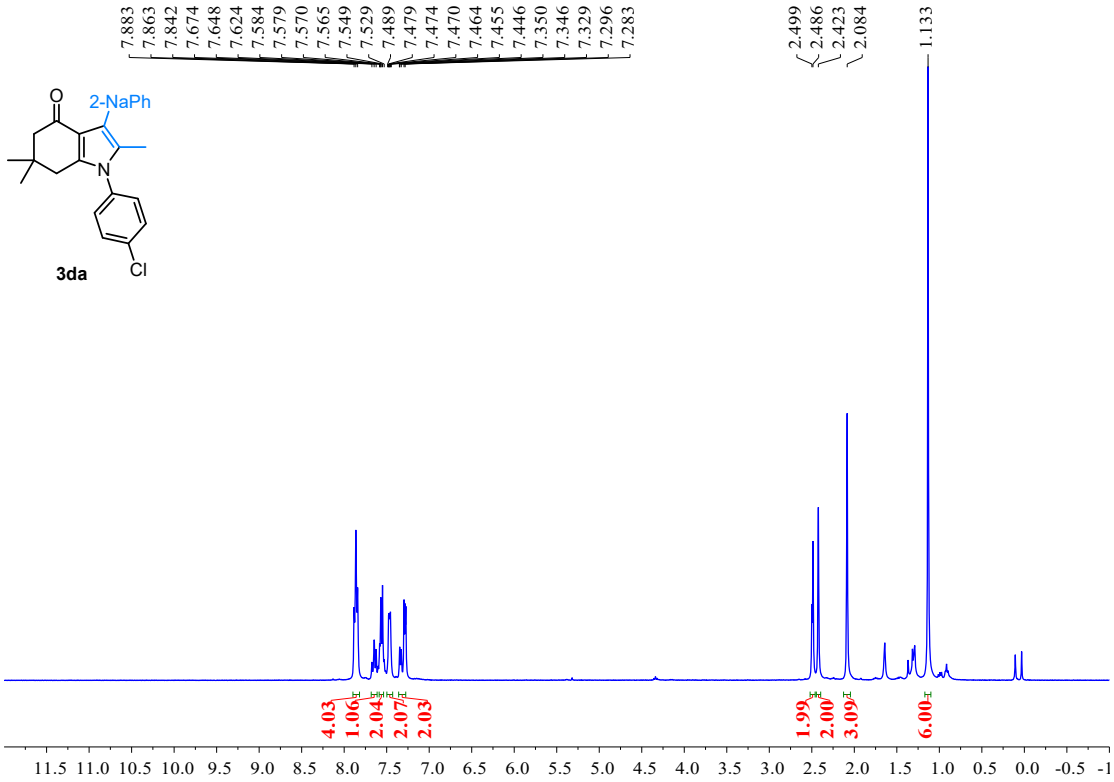
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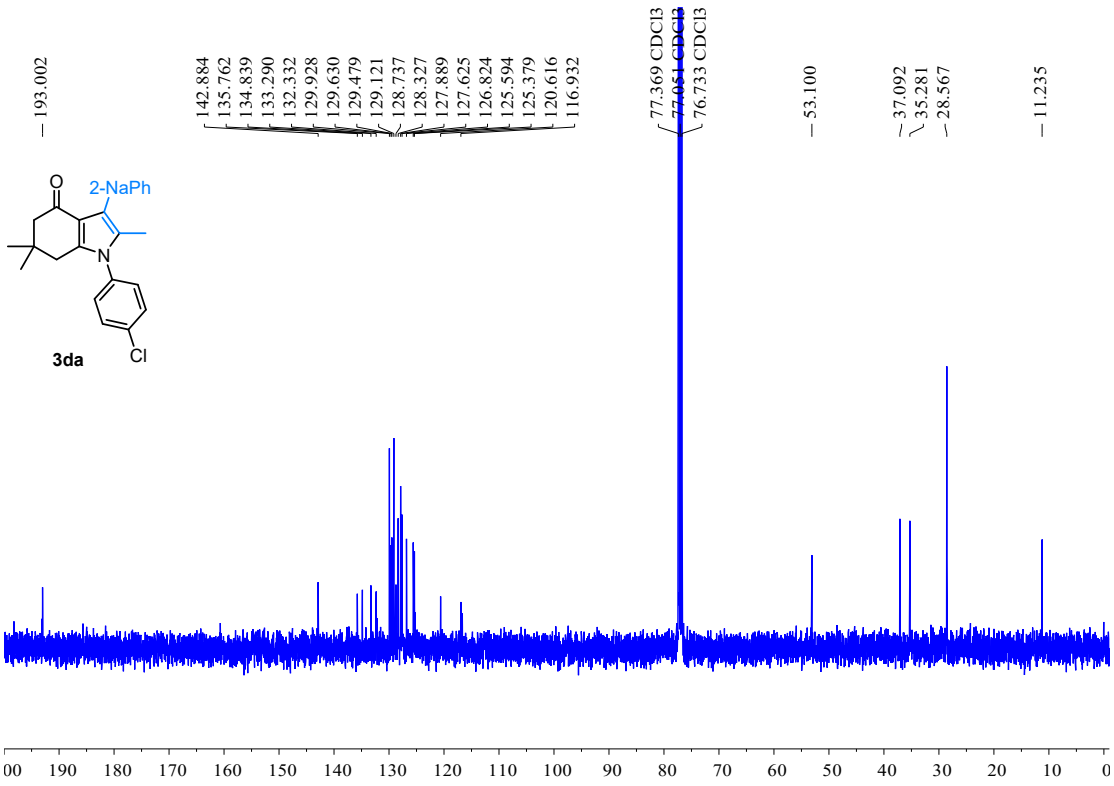
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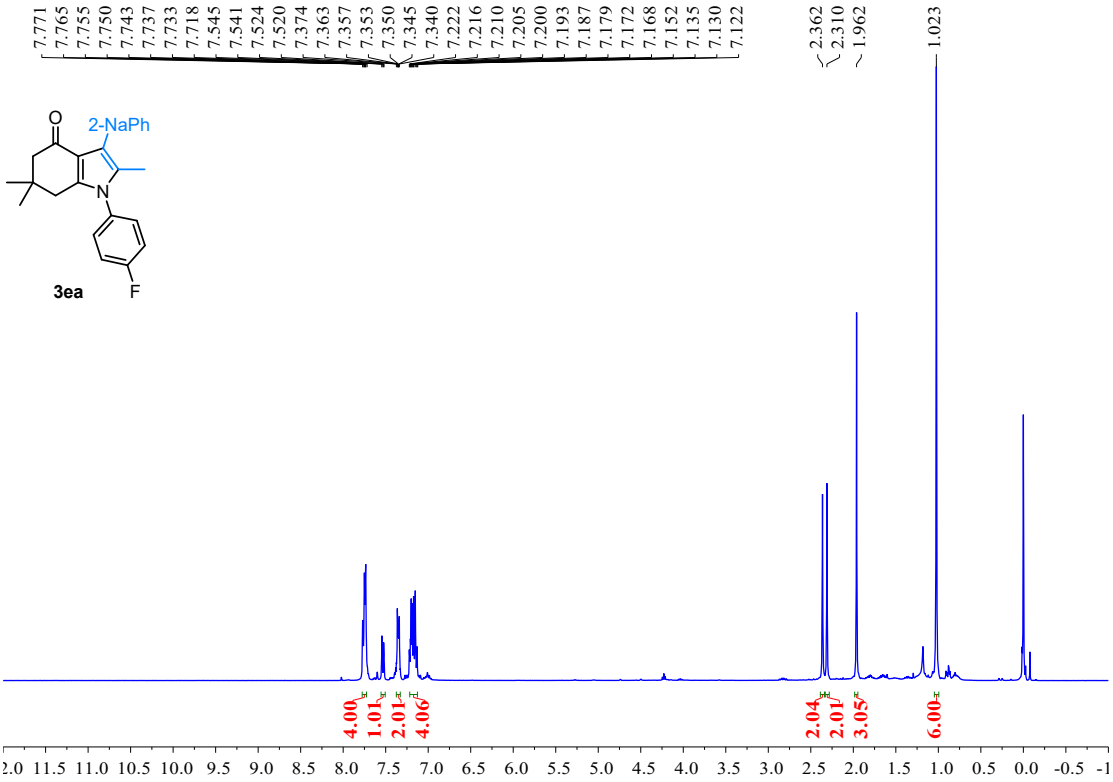
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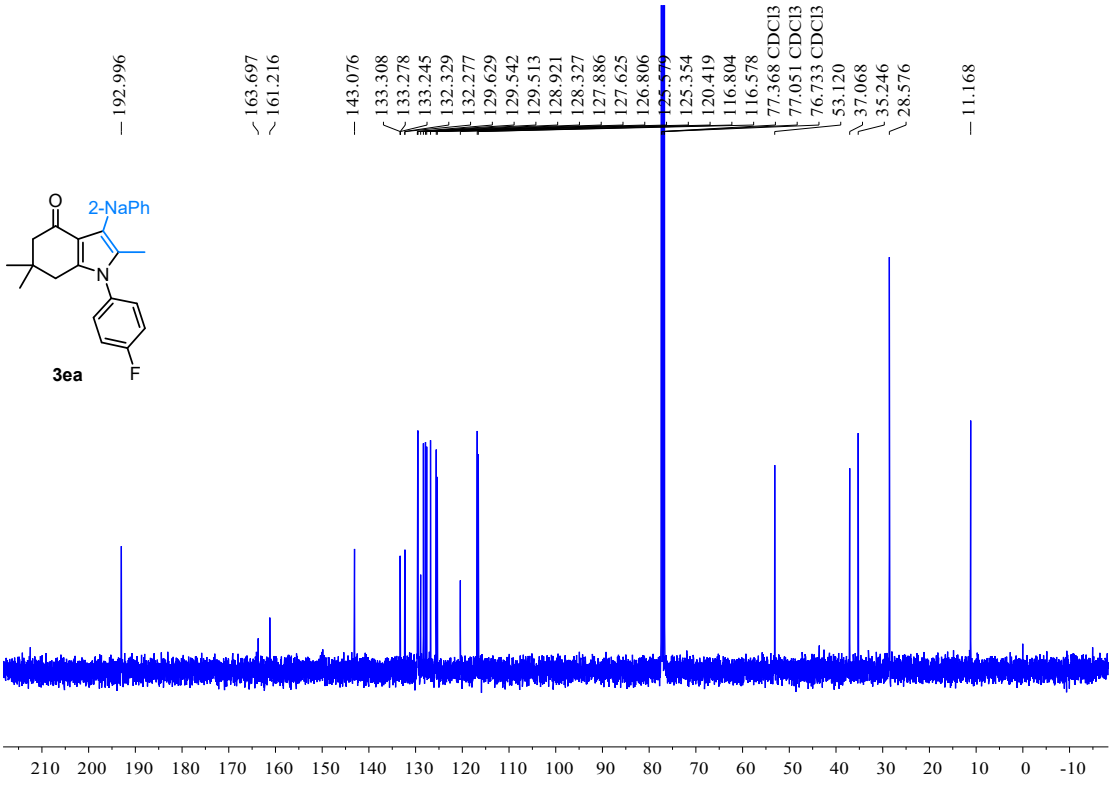
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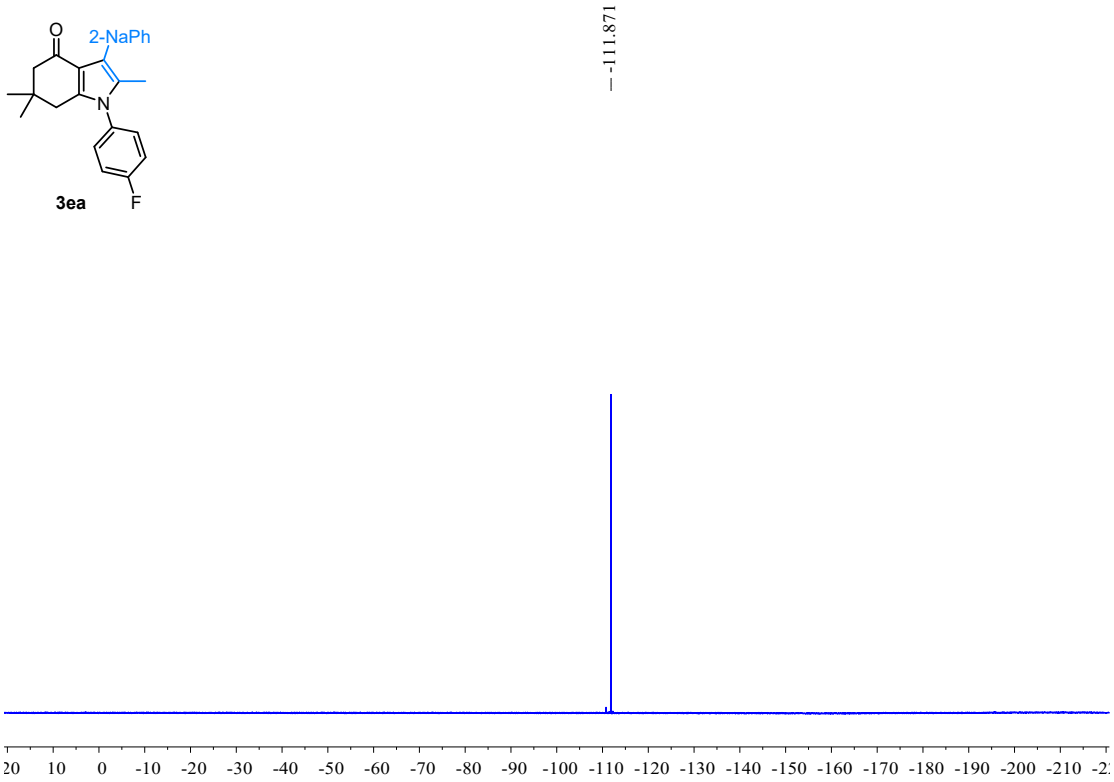
F

3ea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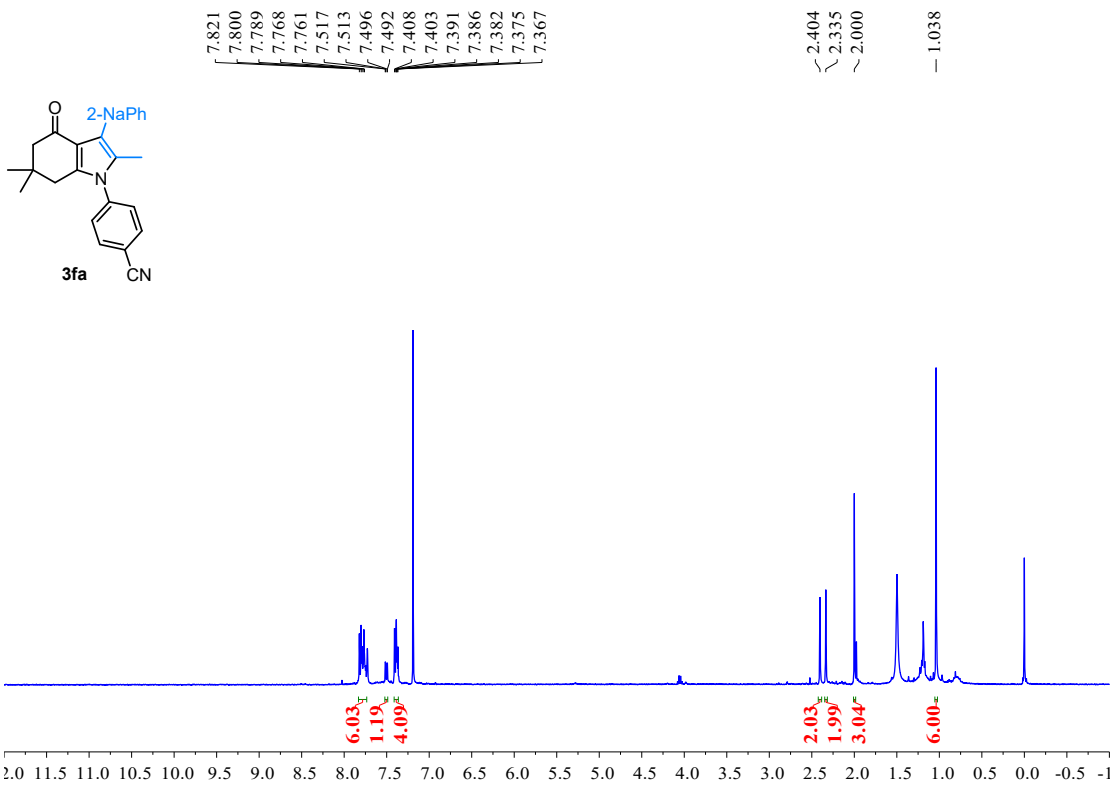
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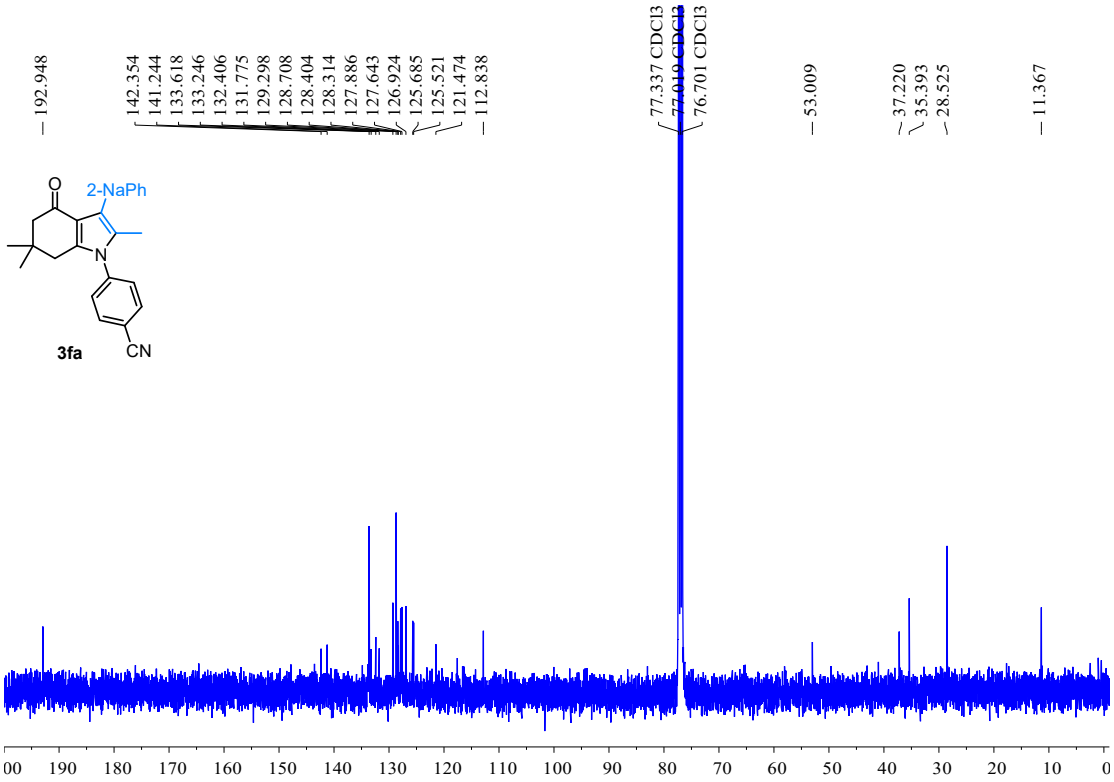
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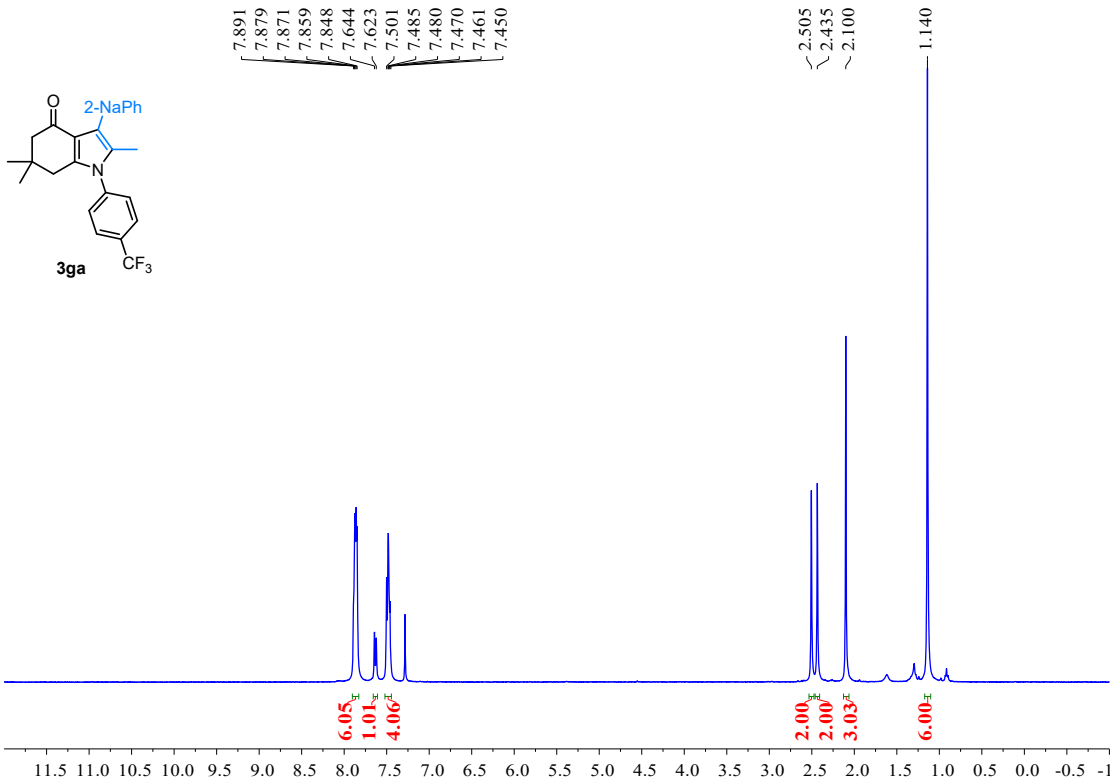
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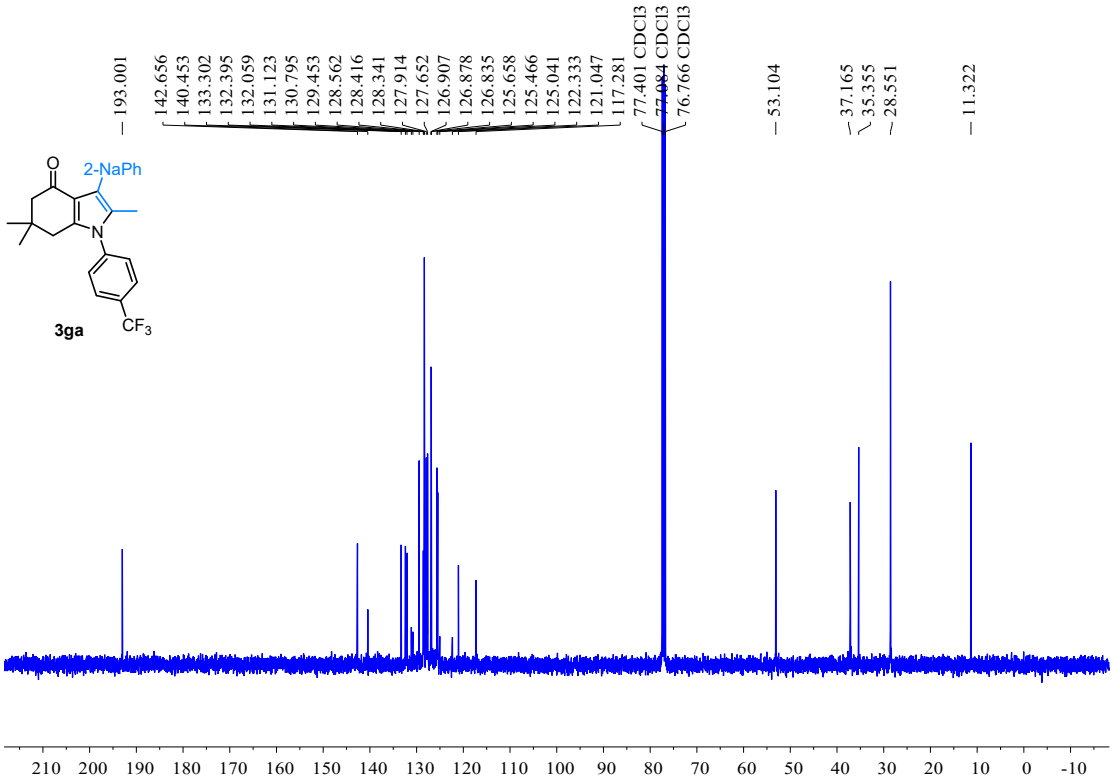
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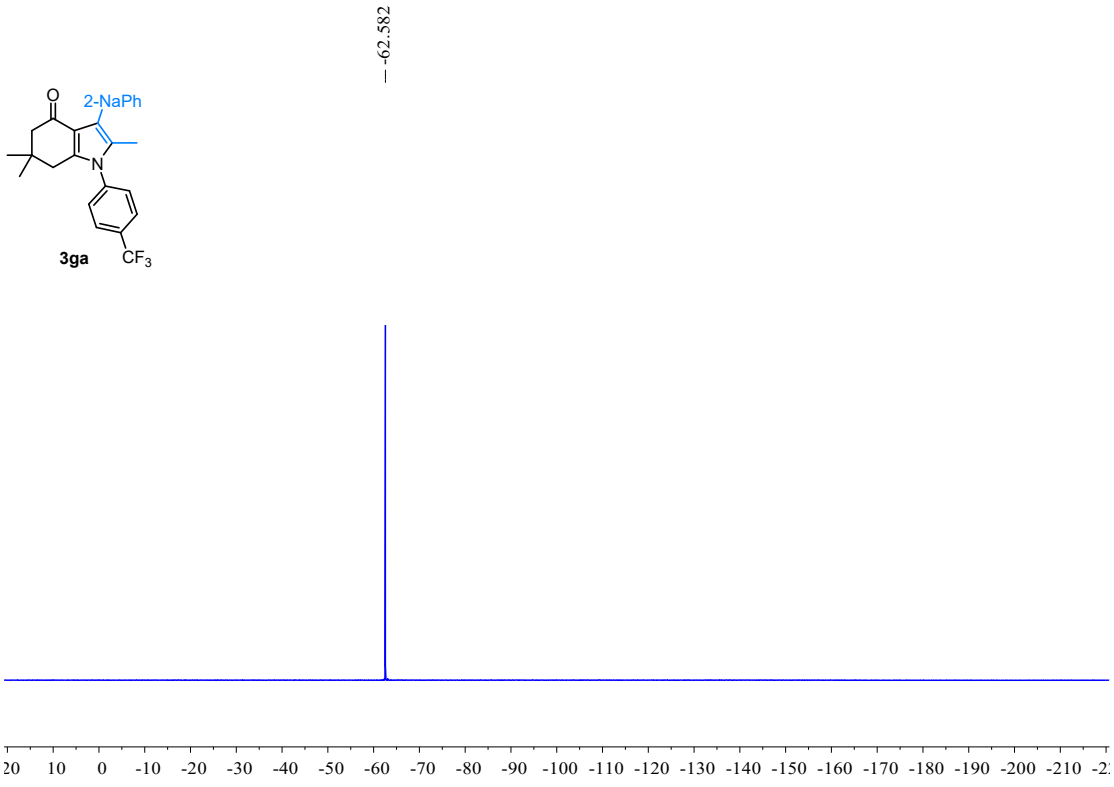
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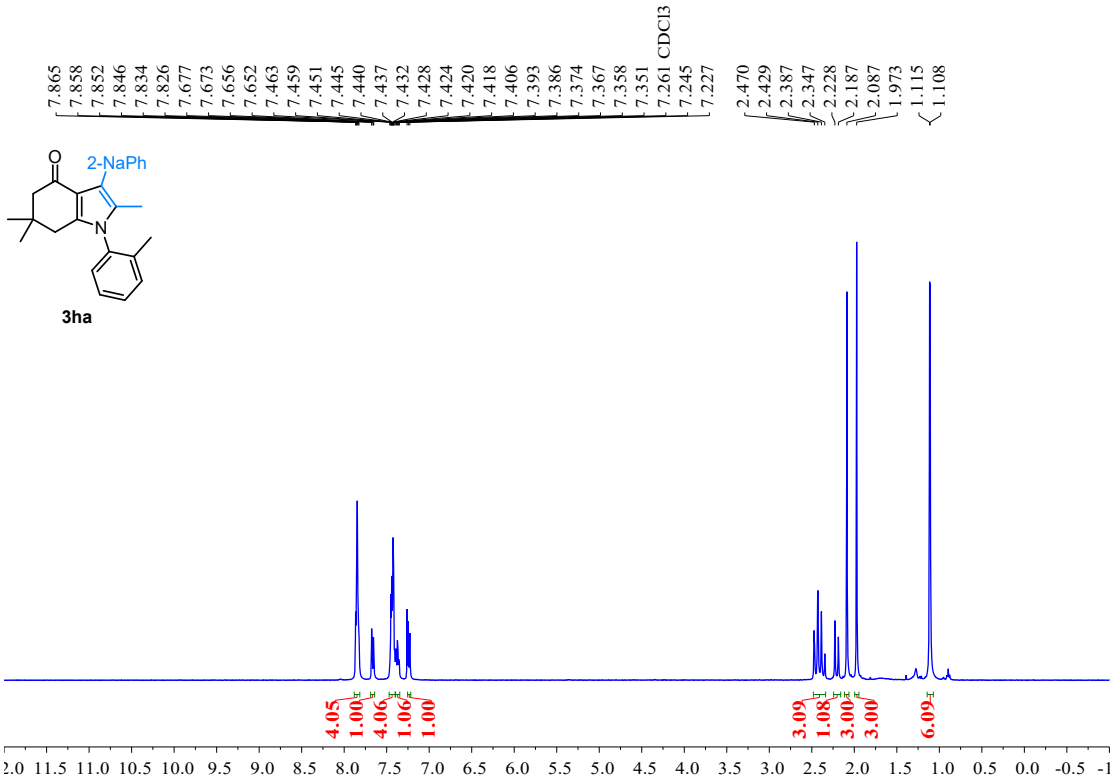
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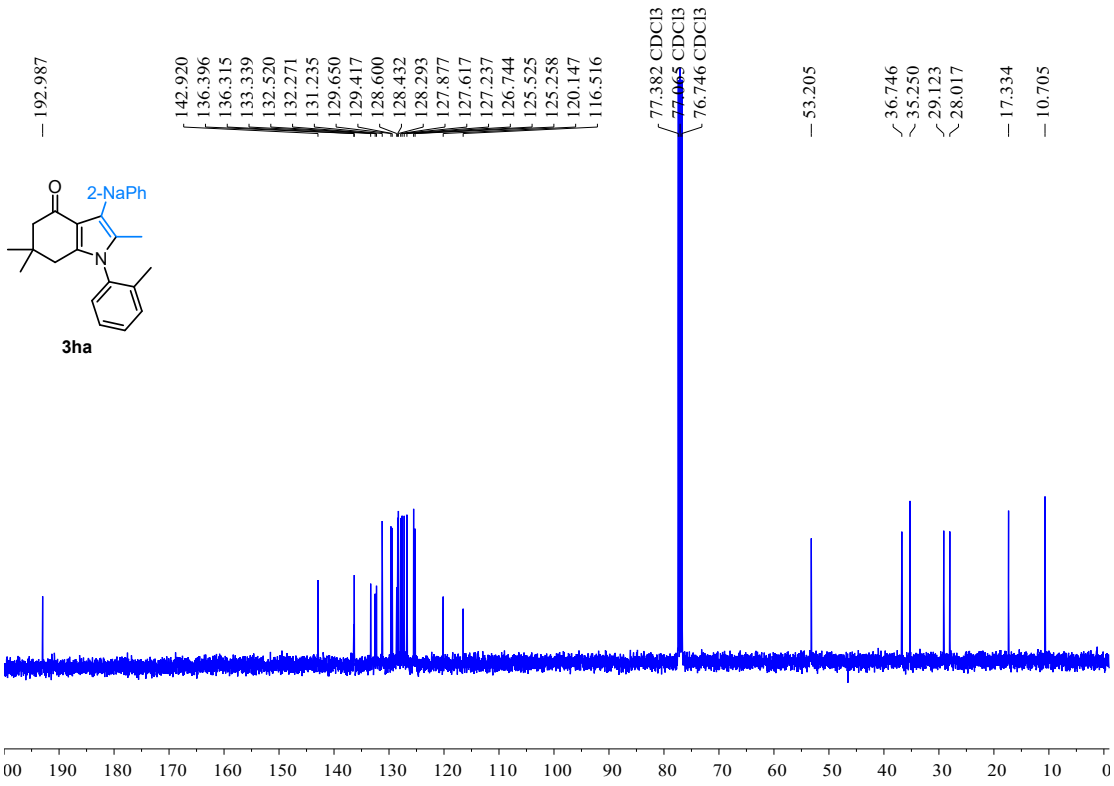
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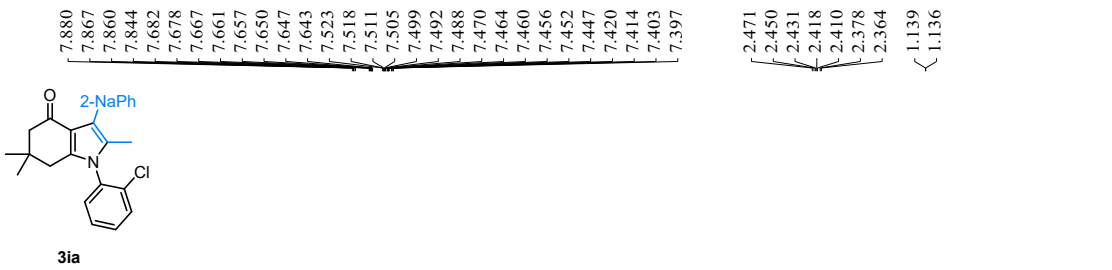
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N
Cl

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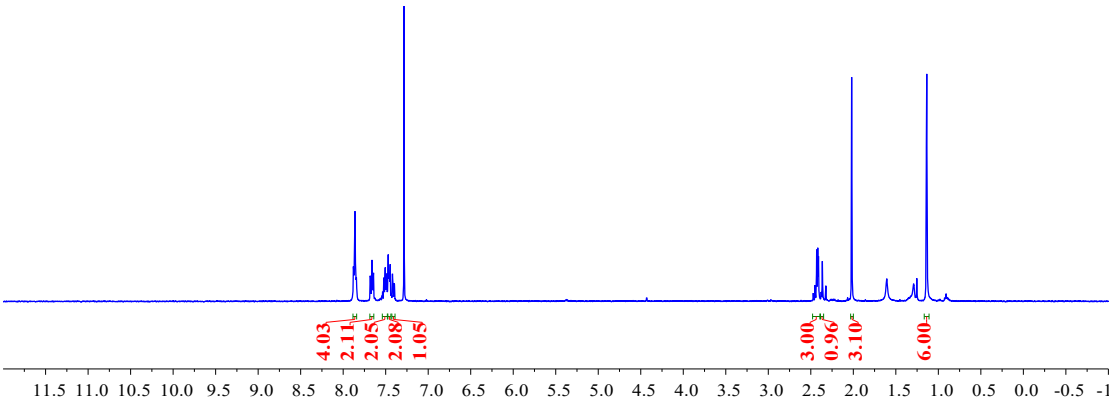
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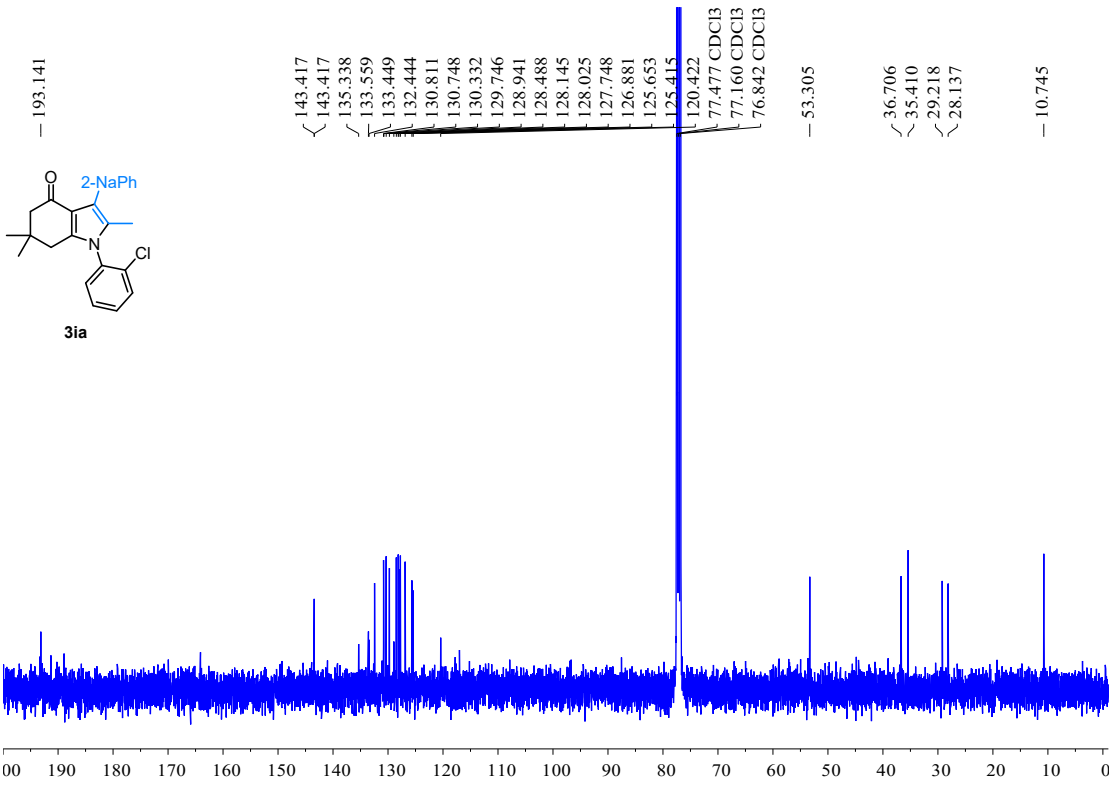
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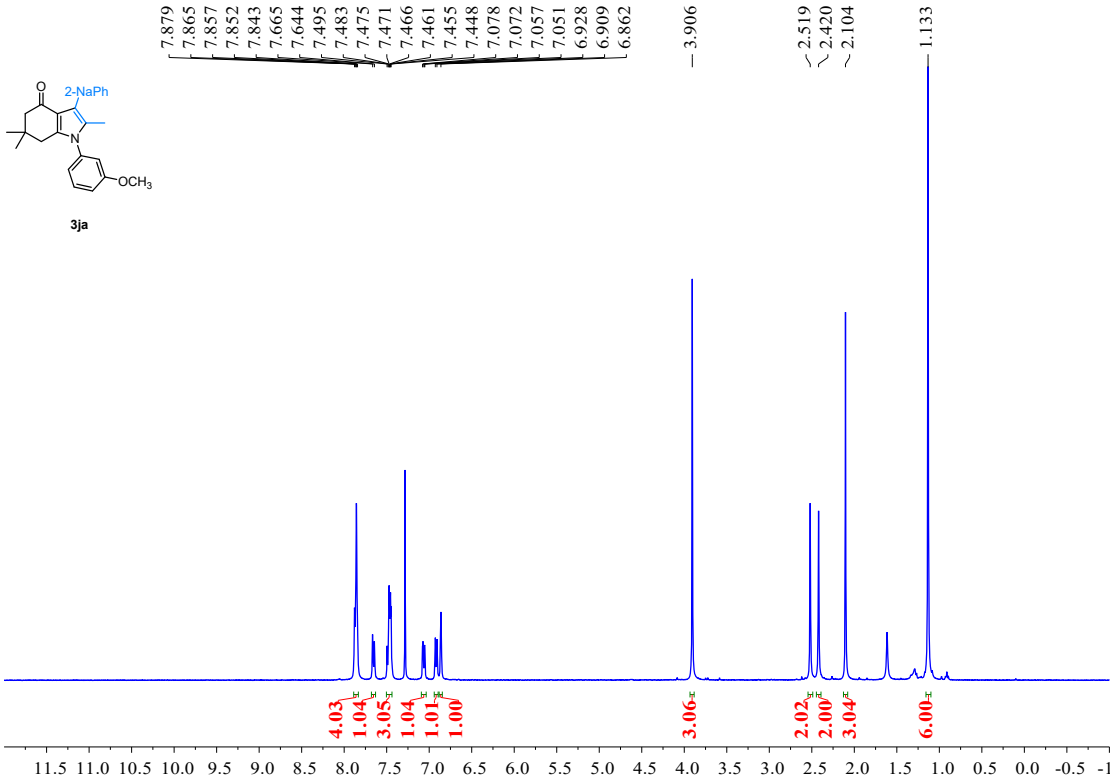
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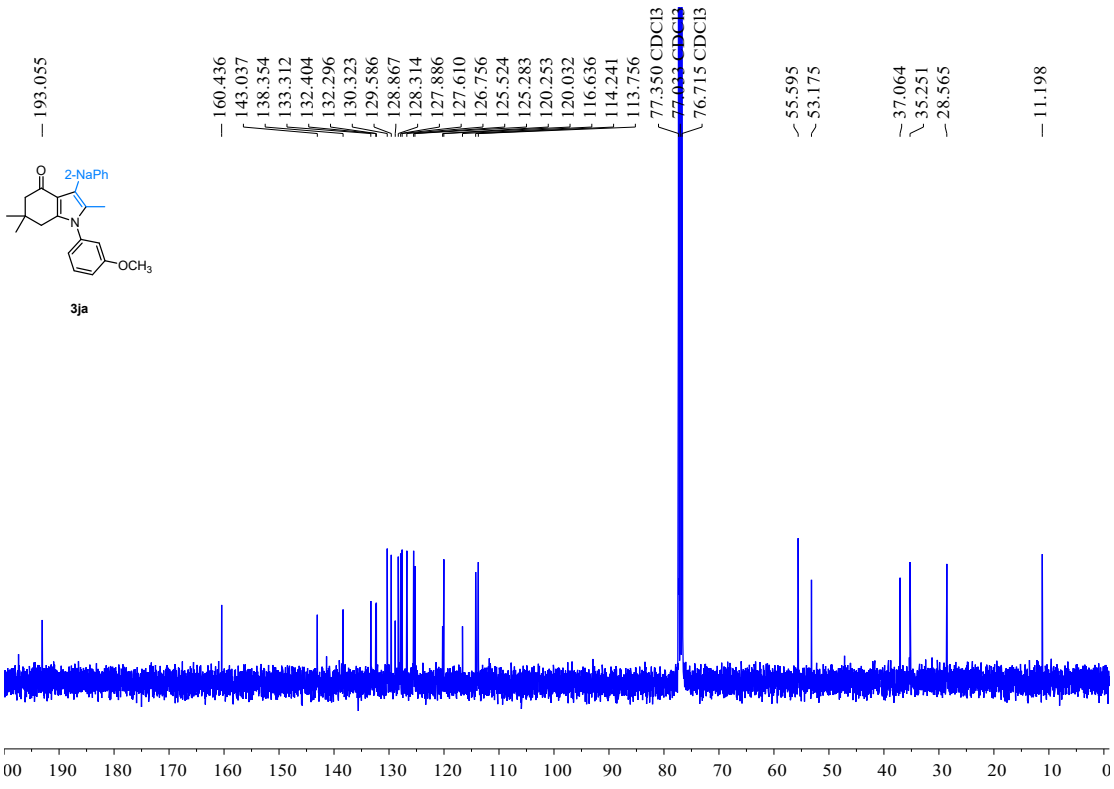
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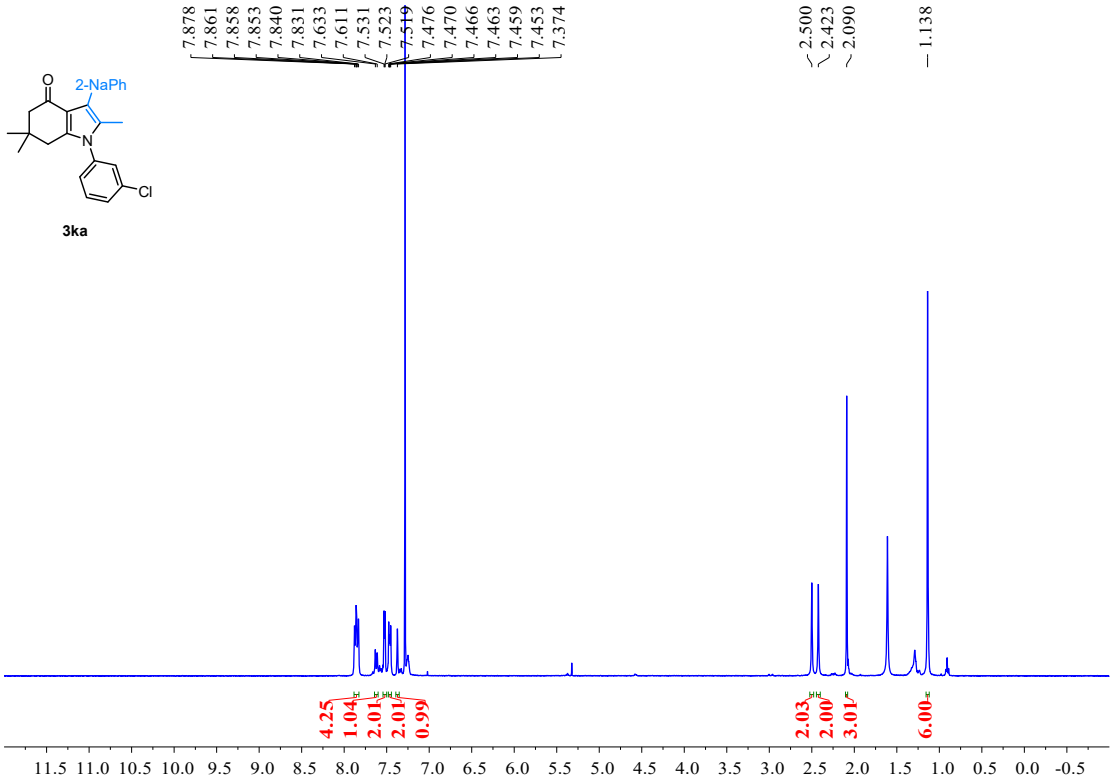
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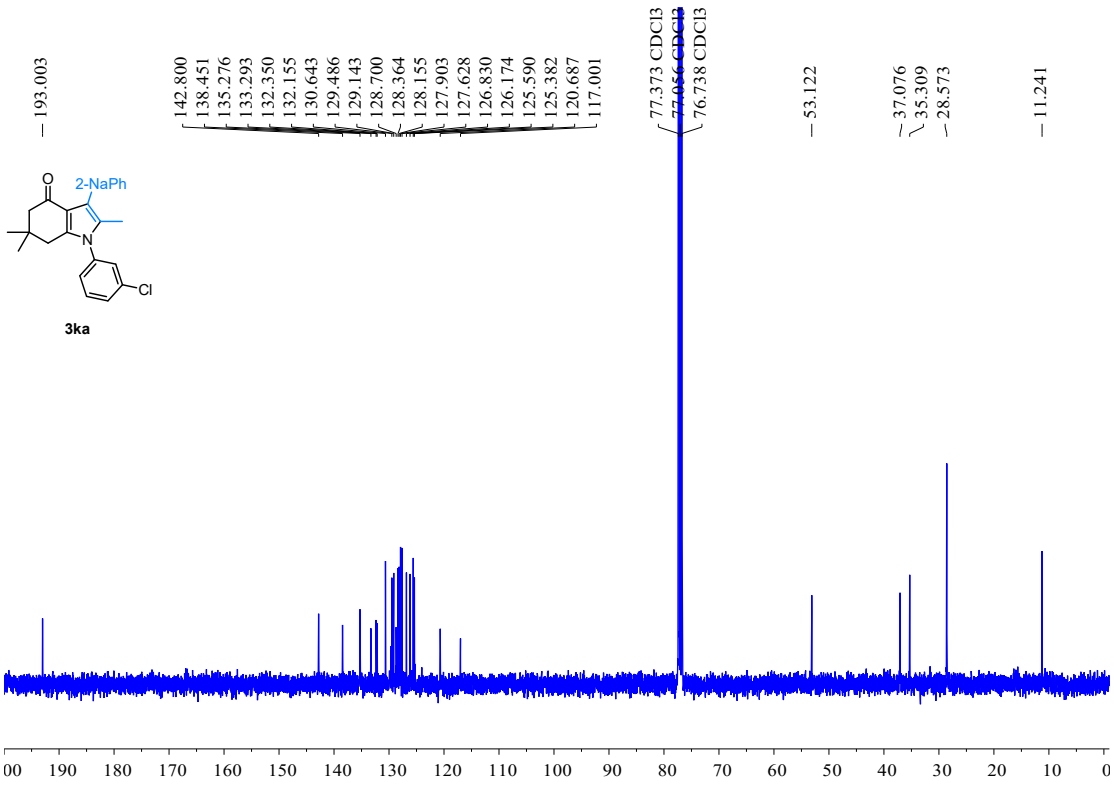
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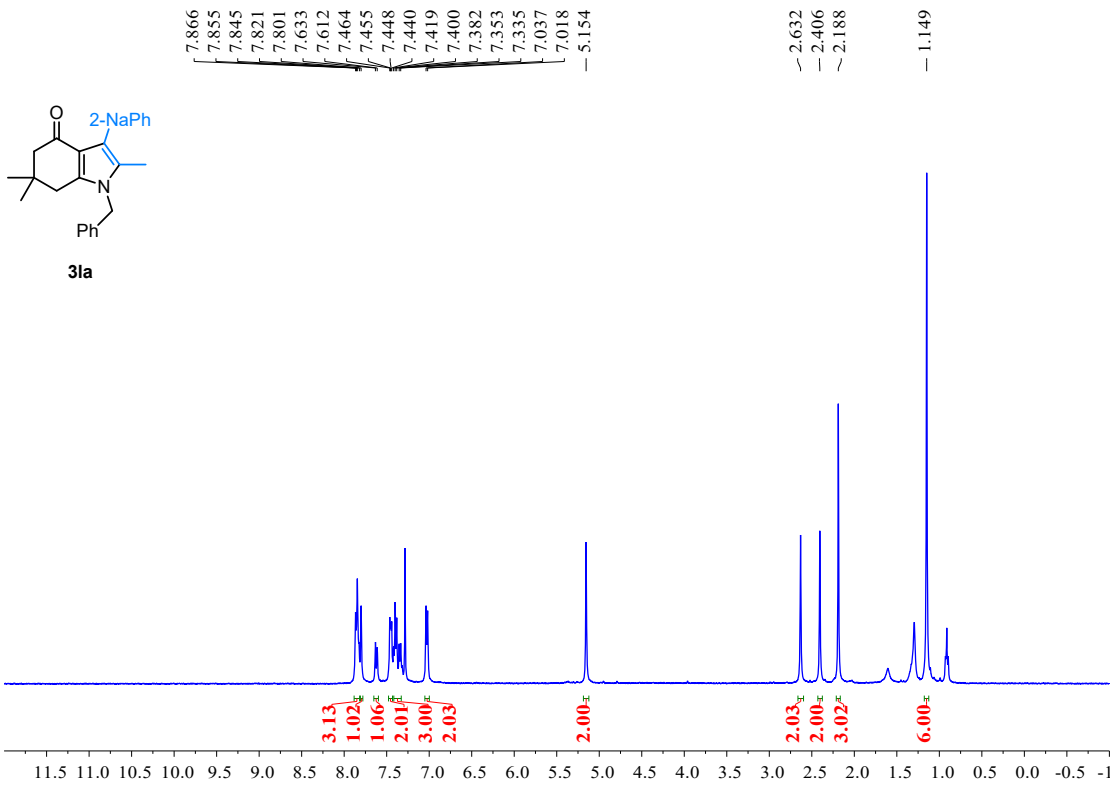
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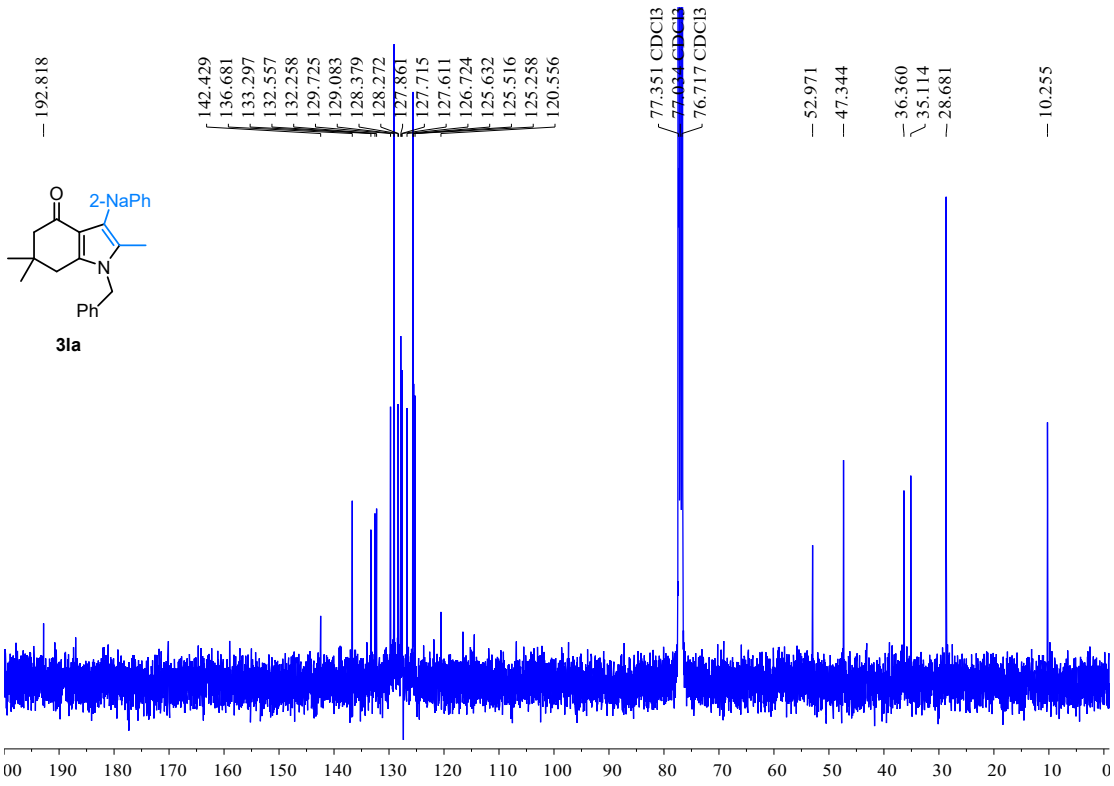
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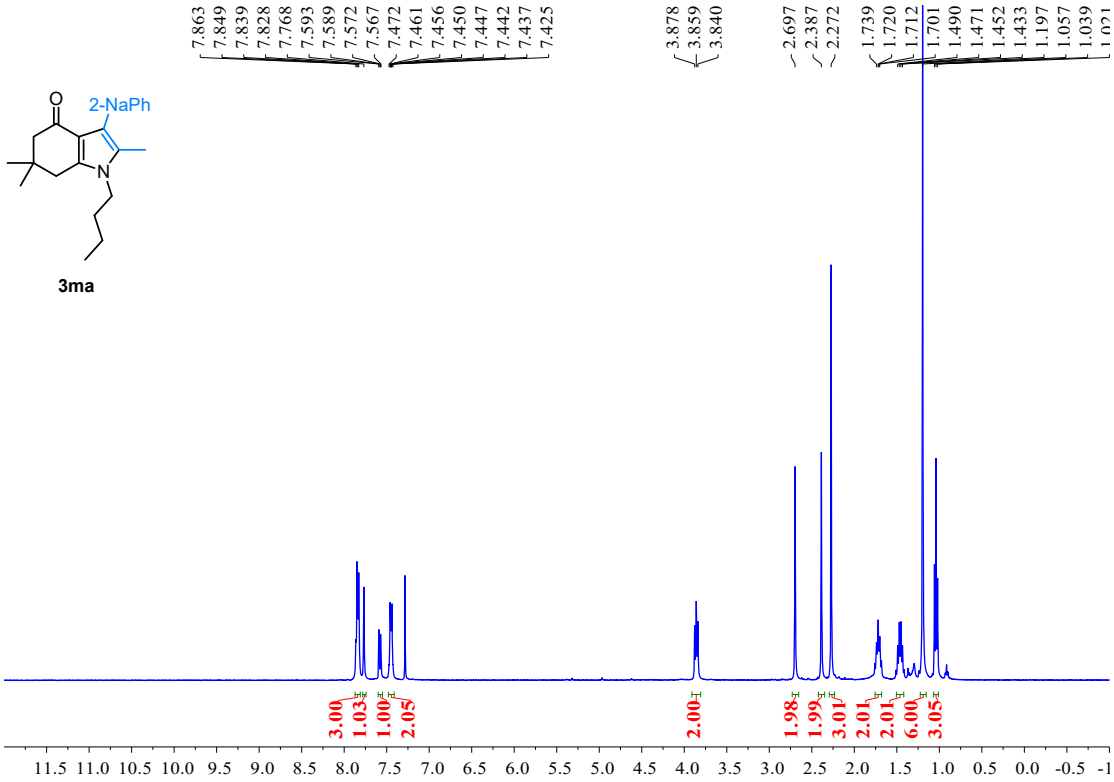
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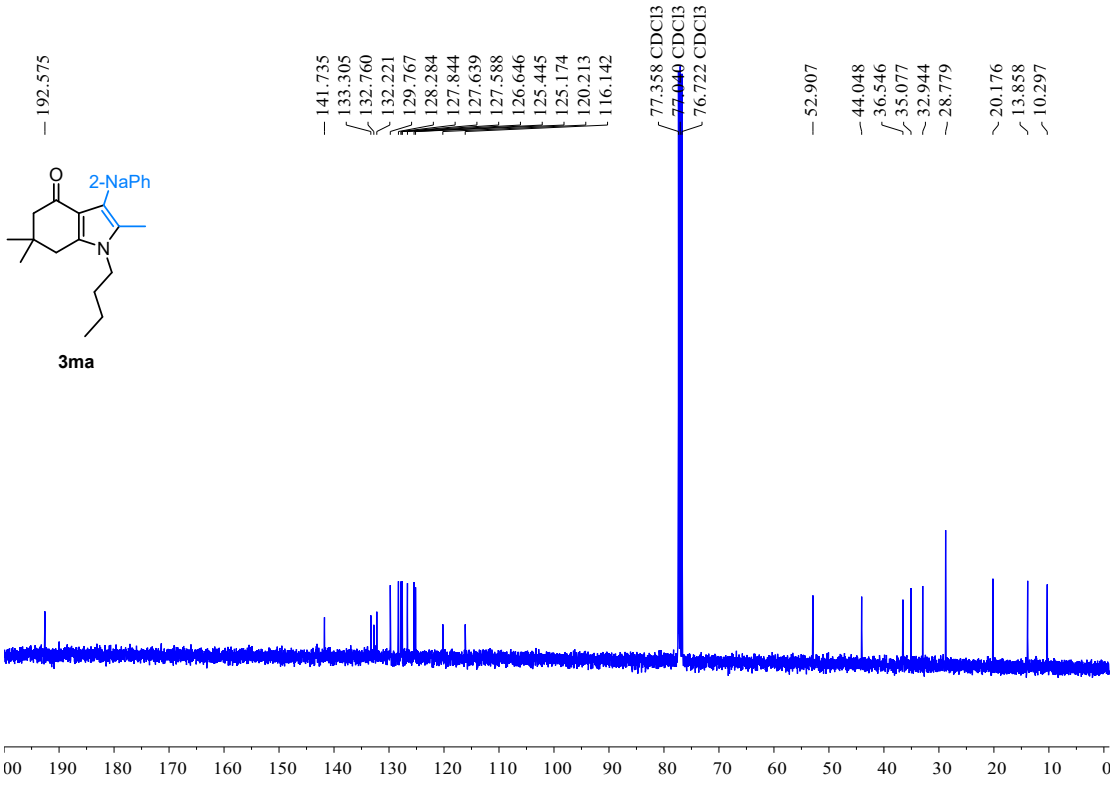
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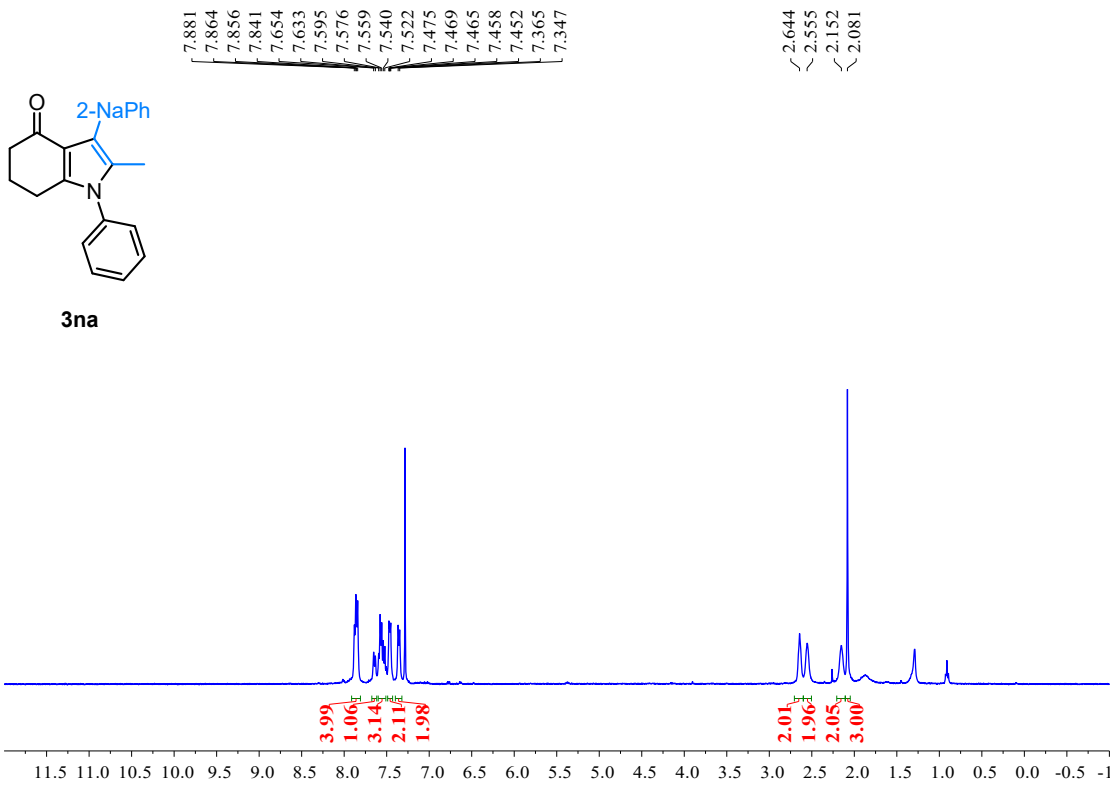
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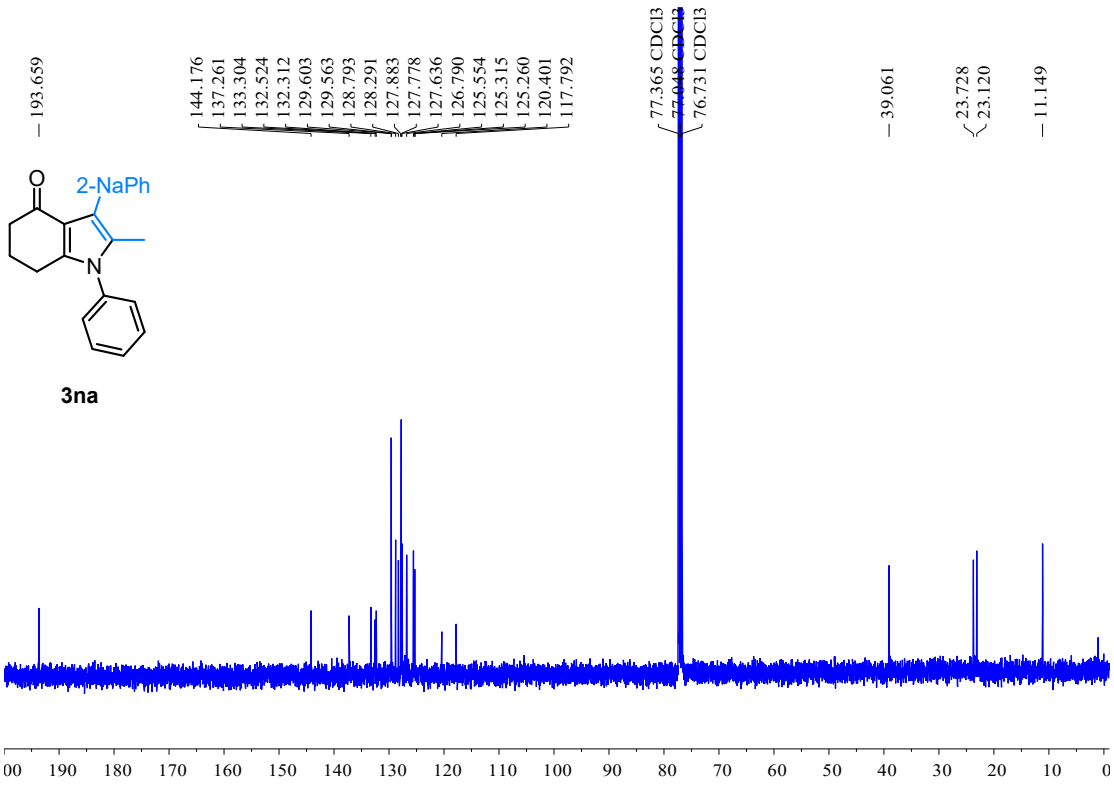
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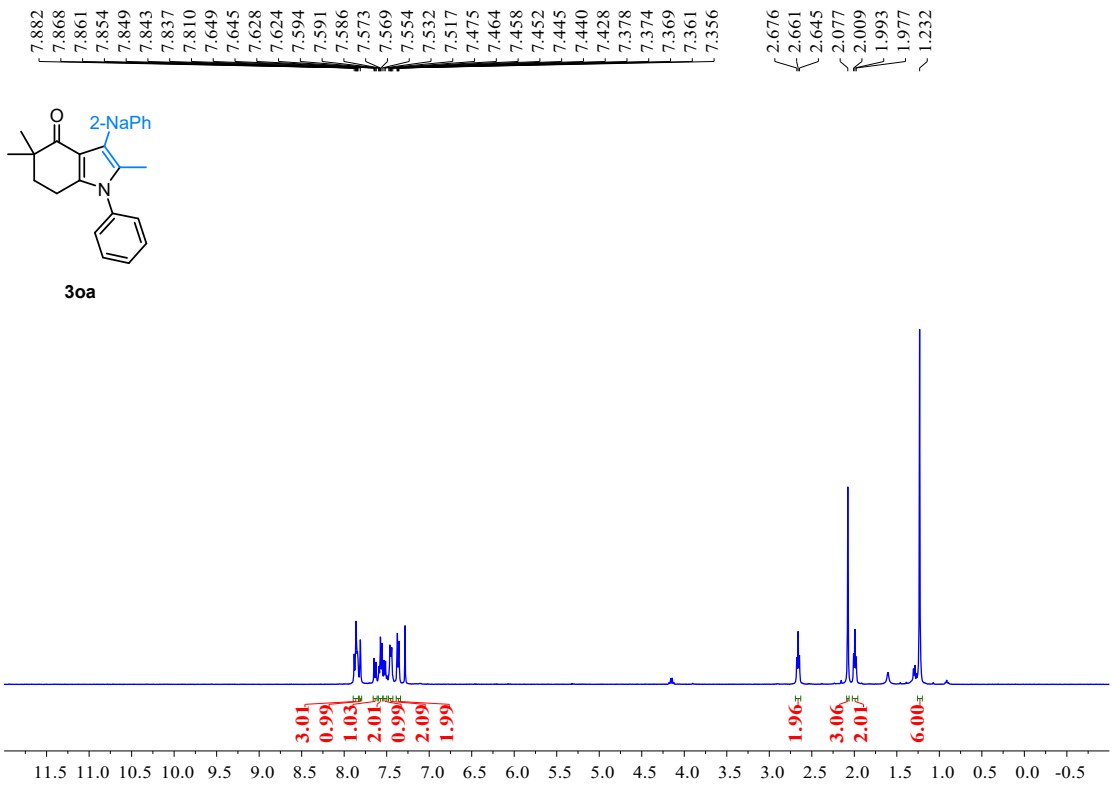
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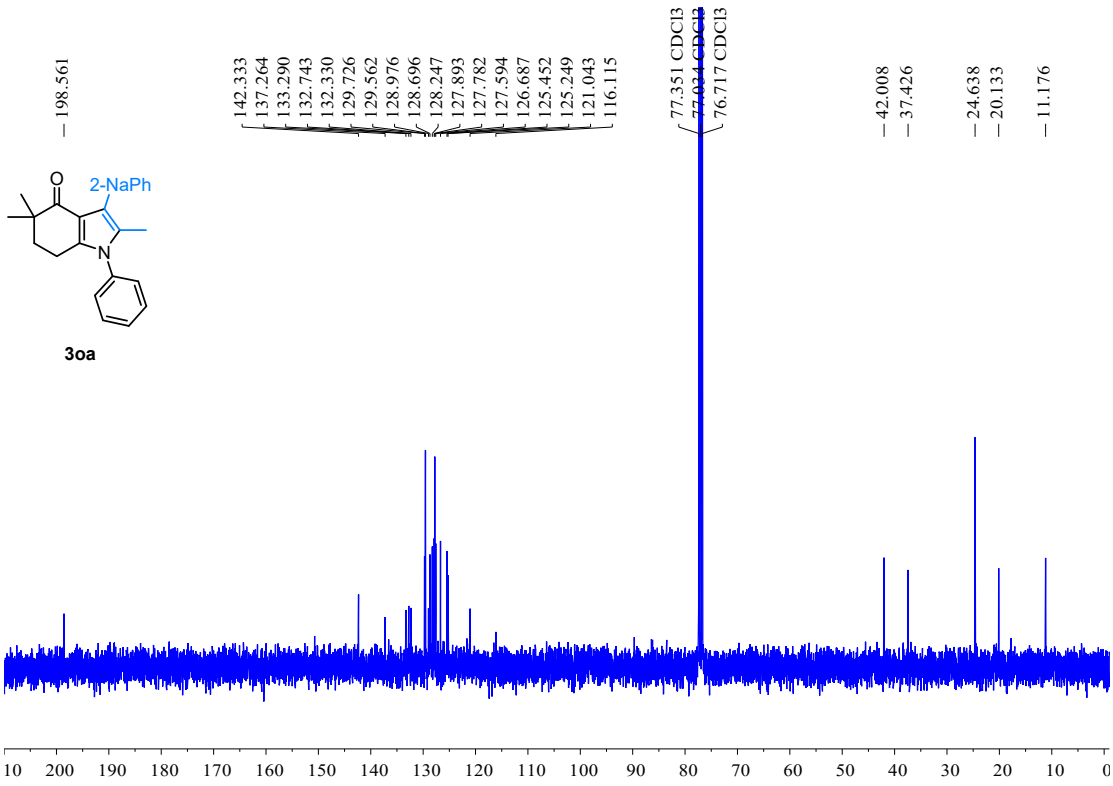
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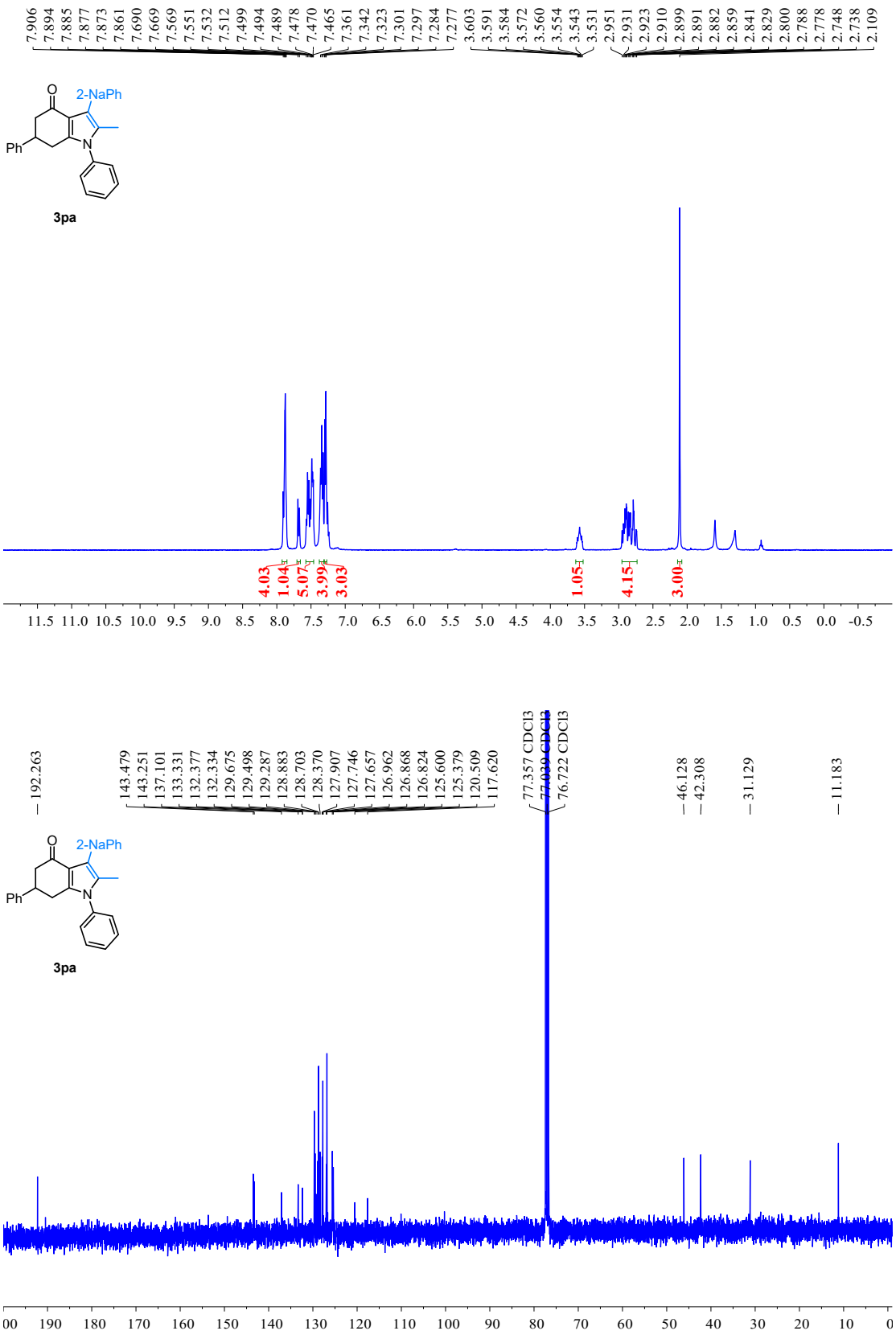
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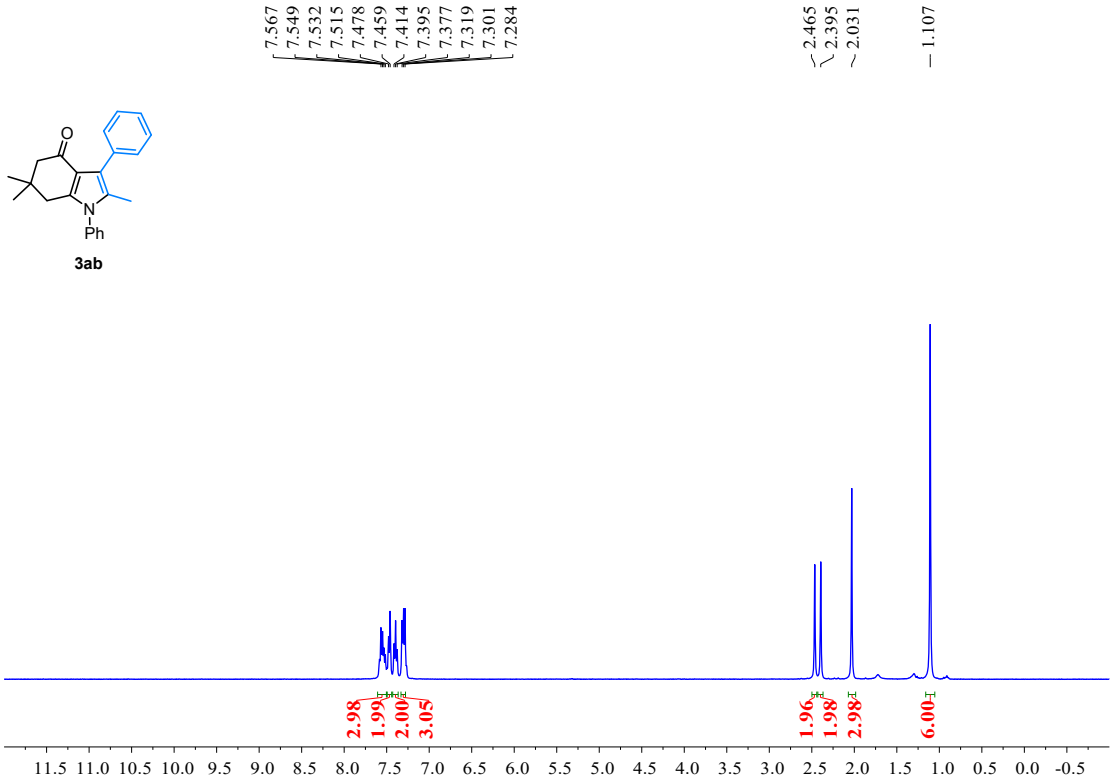
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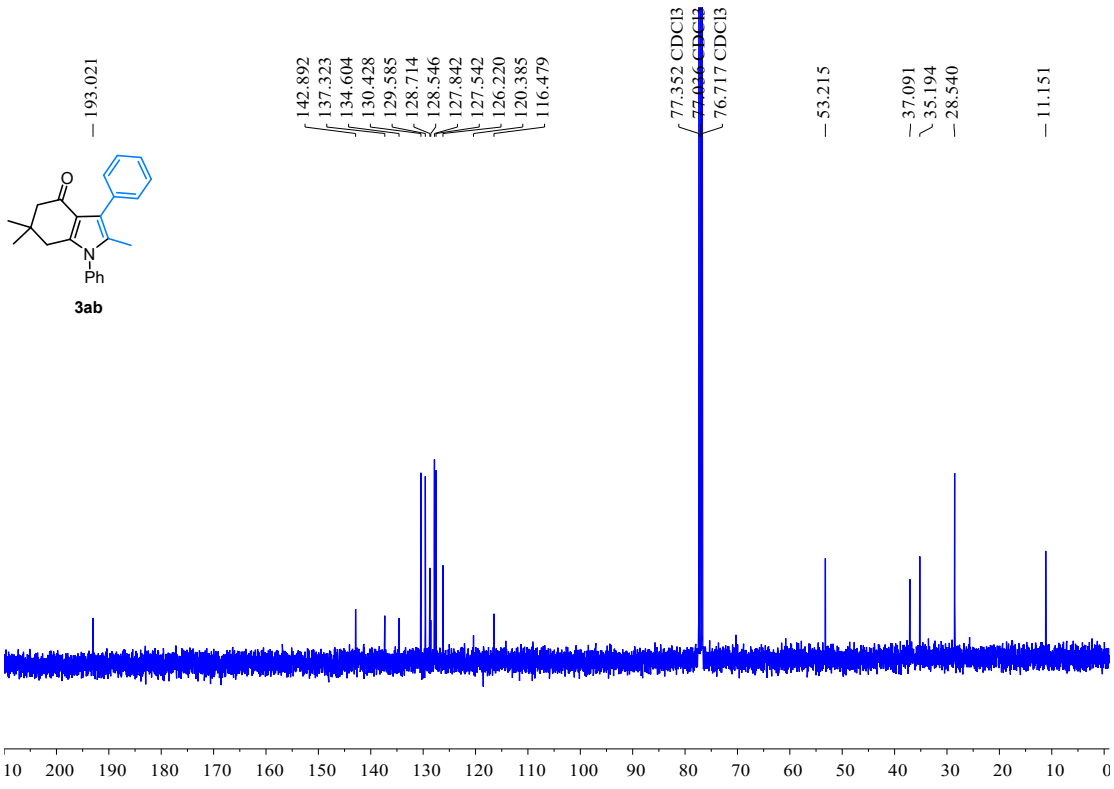
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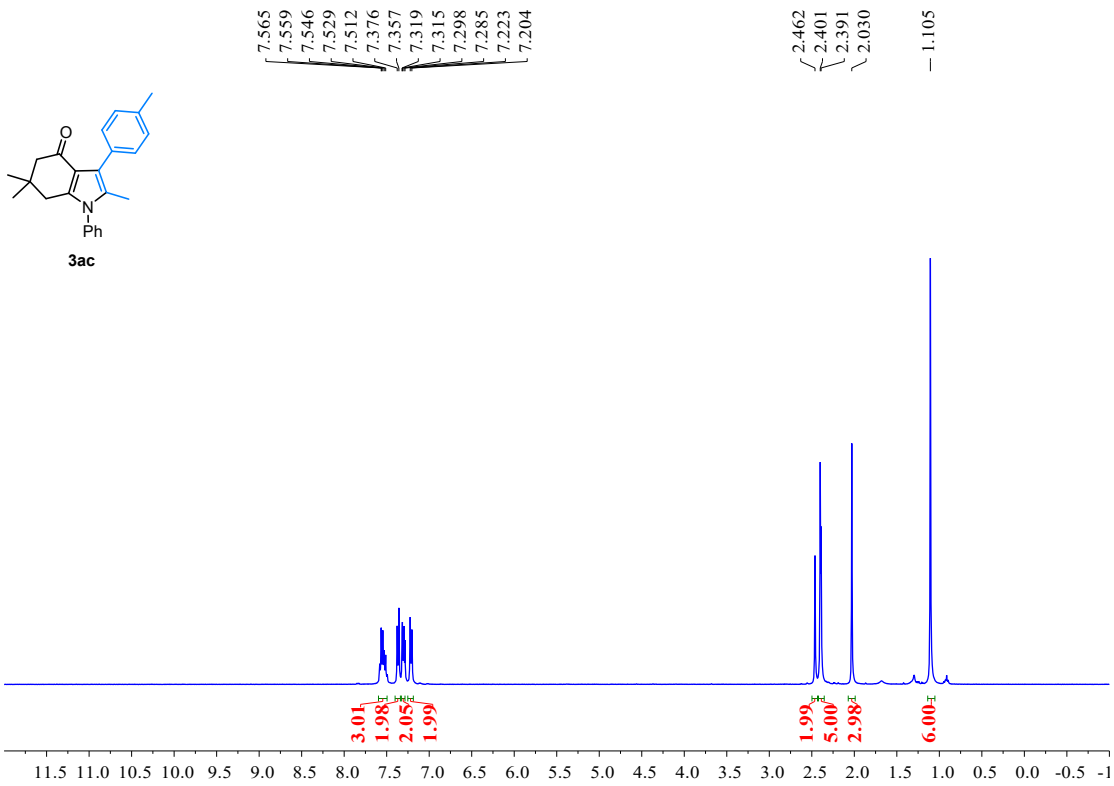
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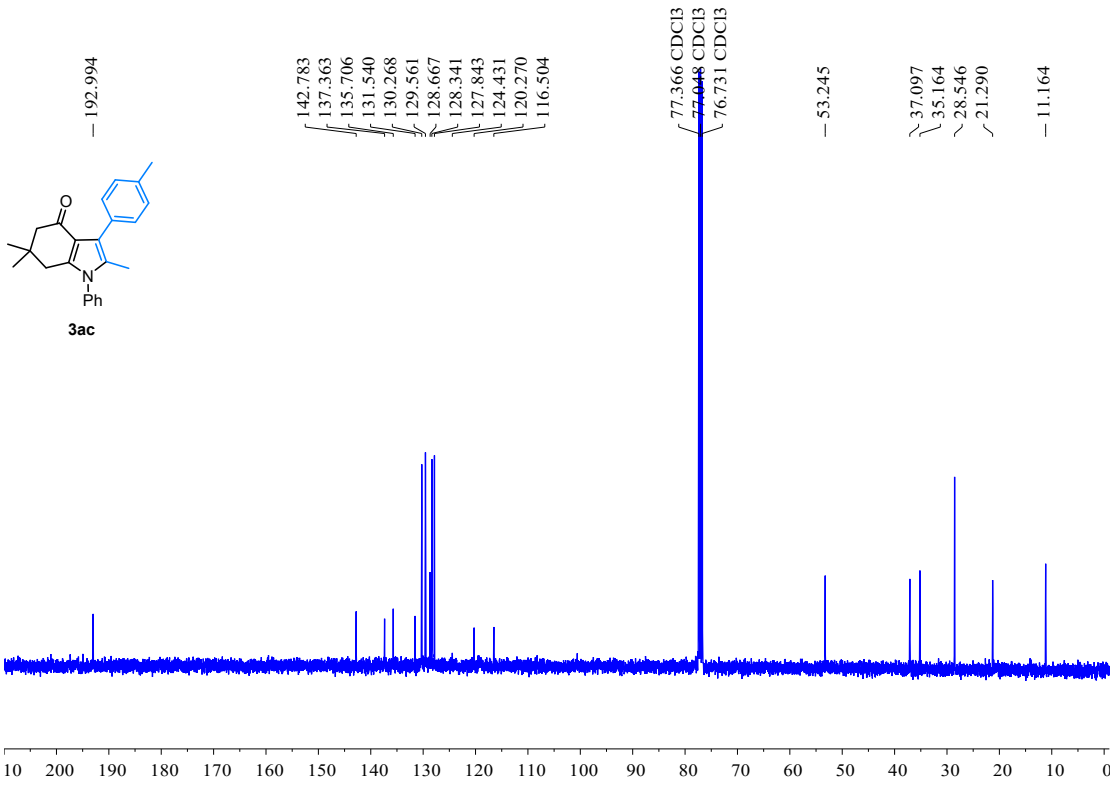
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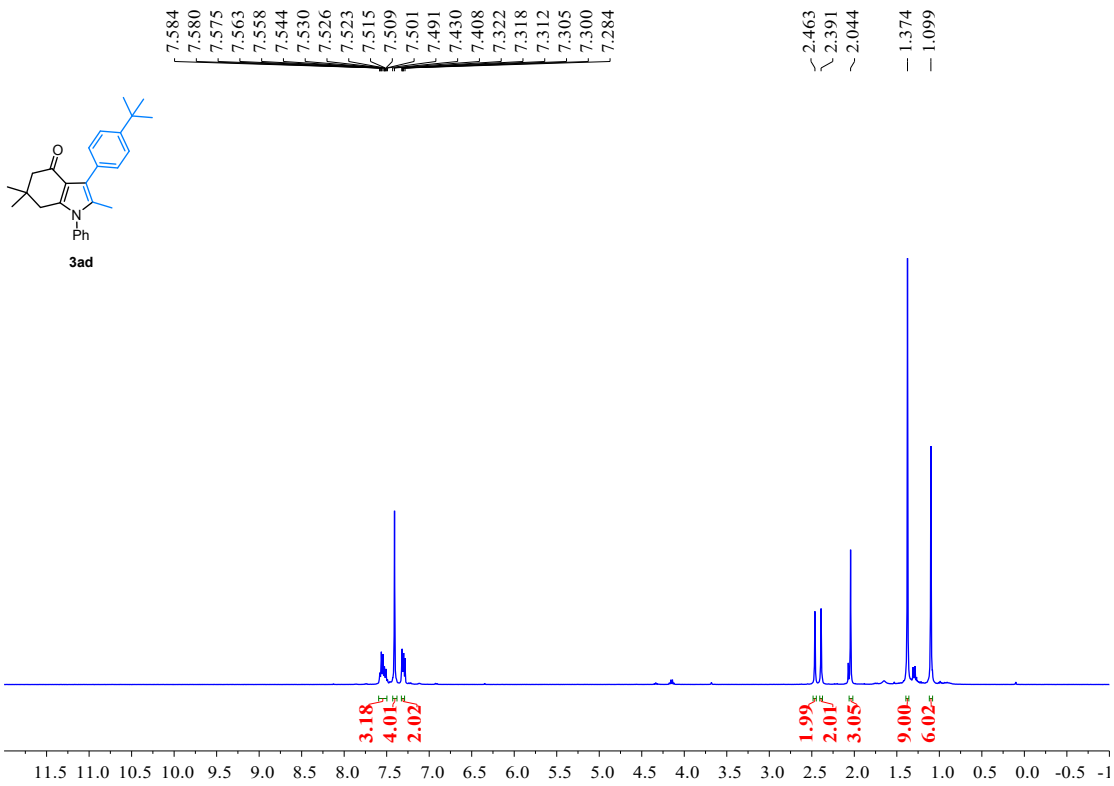
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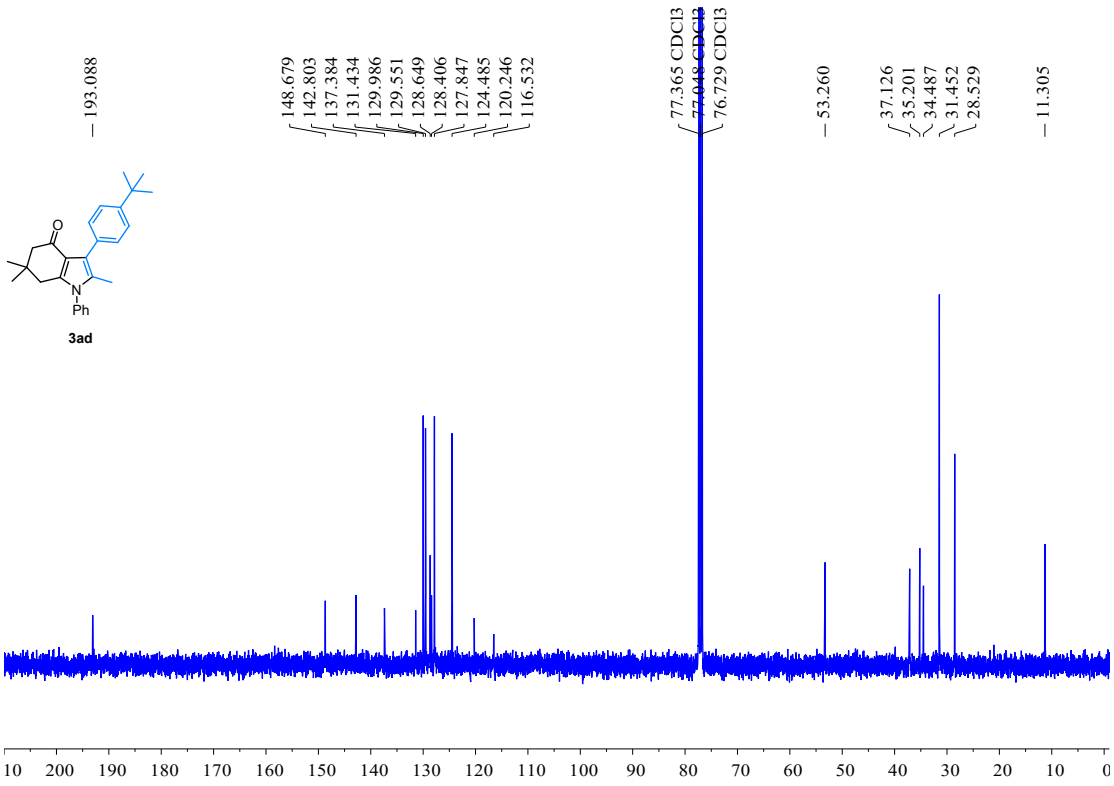
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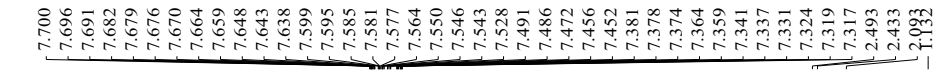
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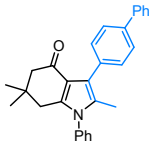
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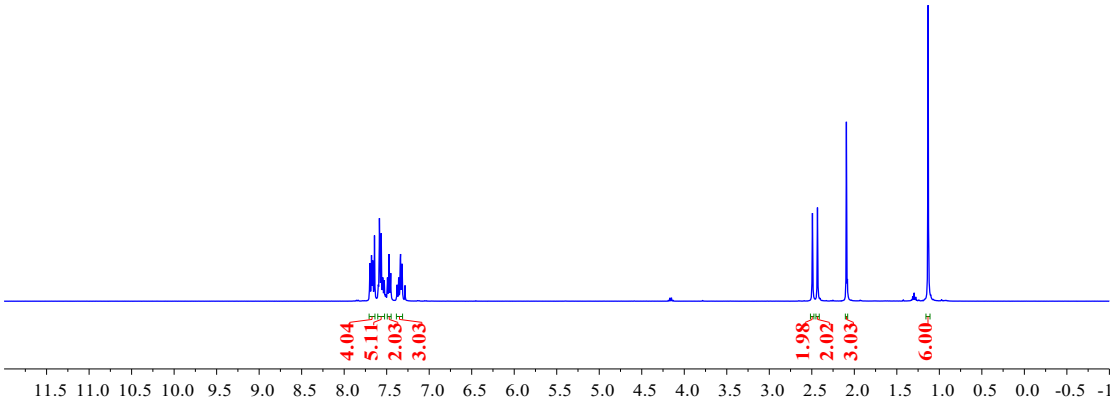
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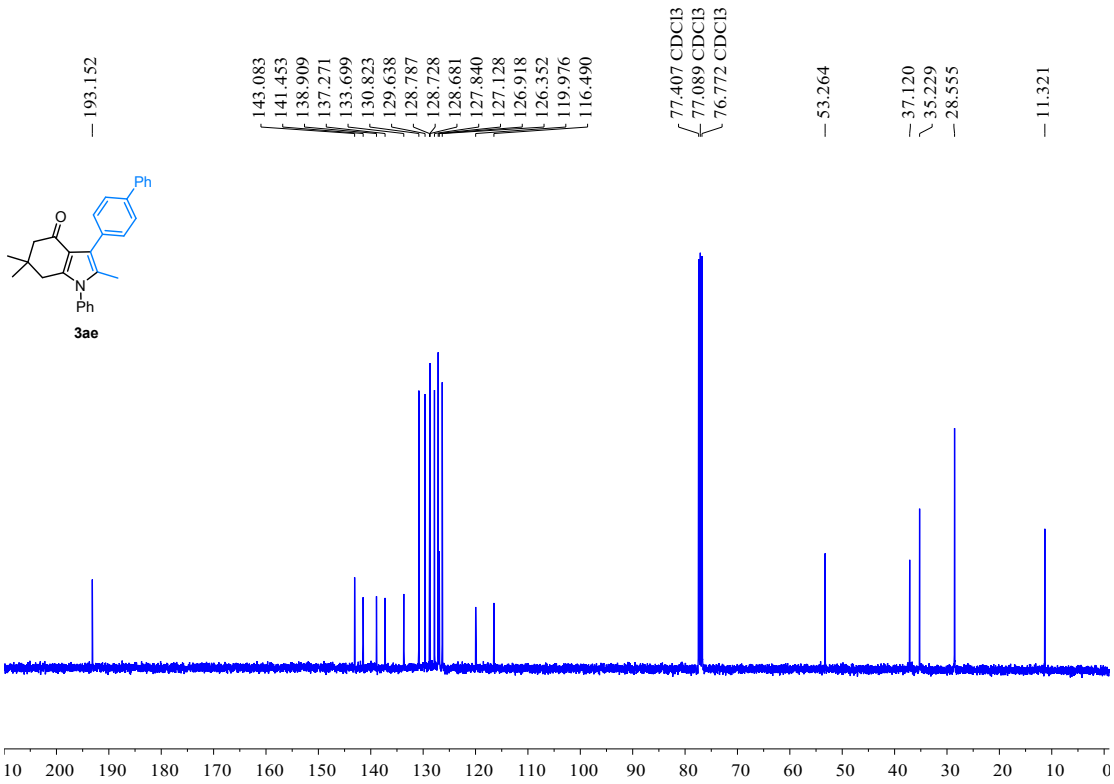
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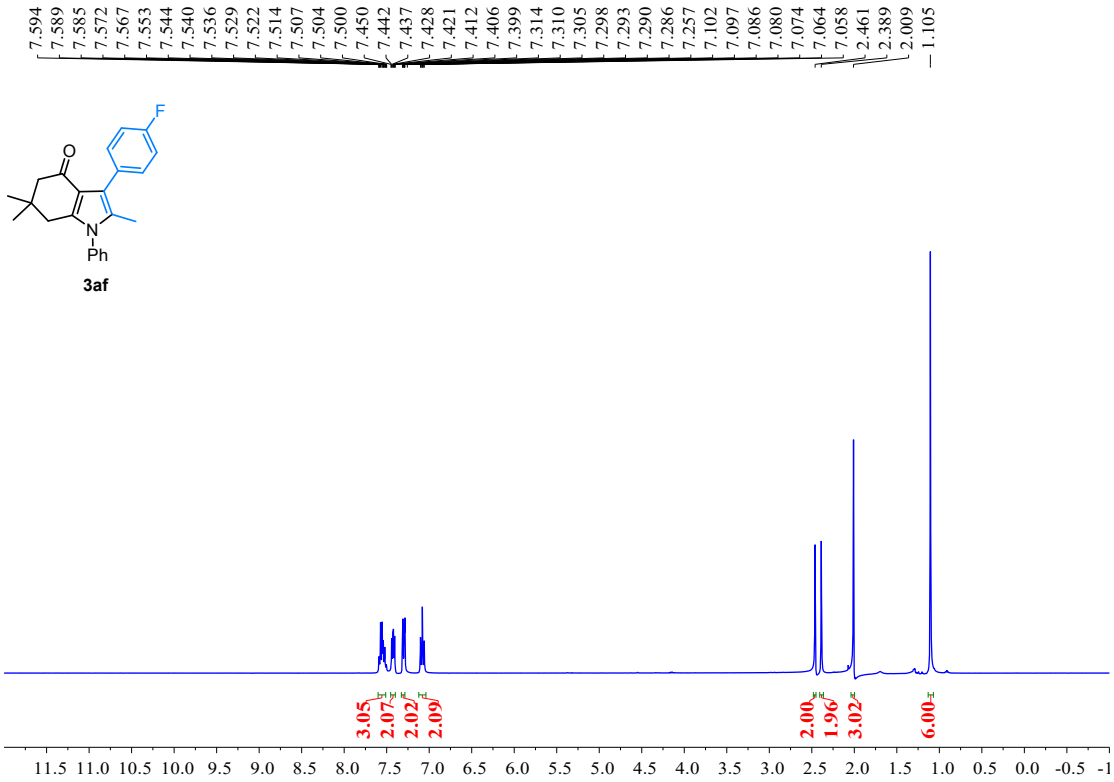
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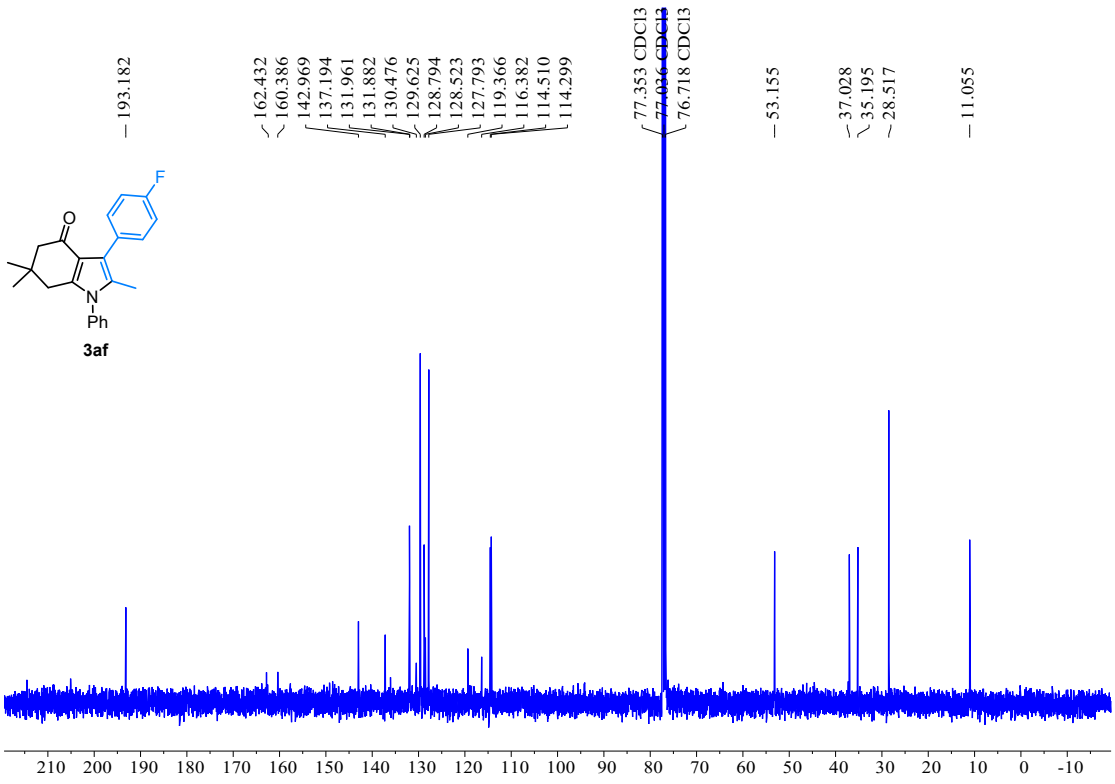
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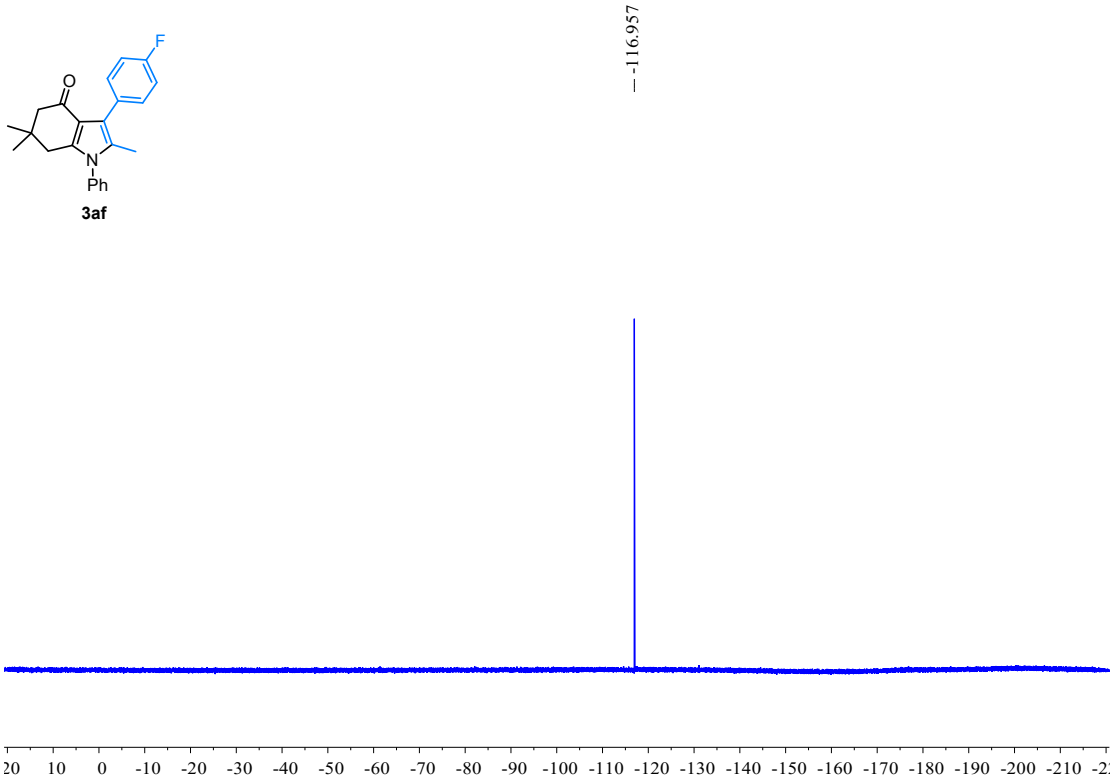
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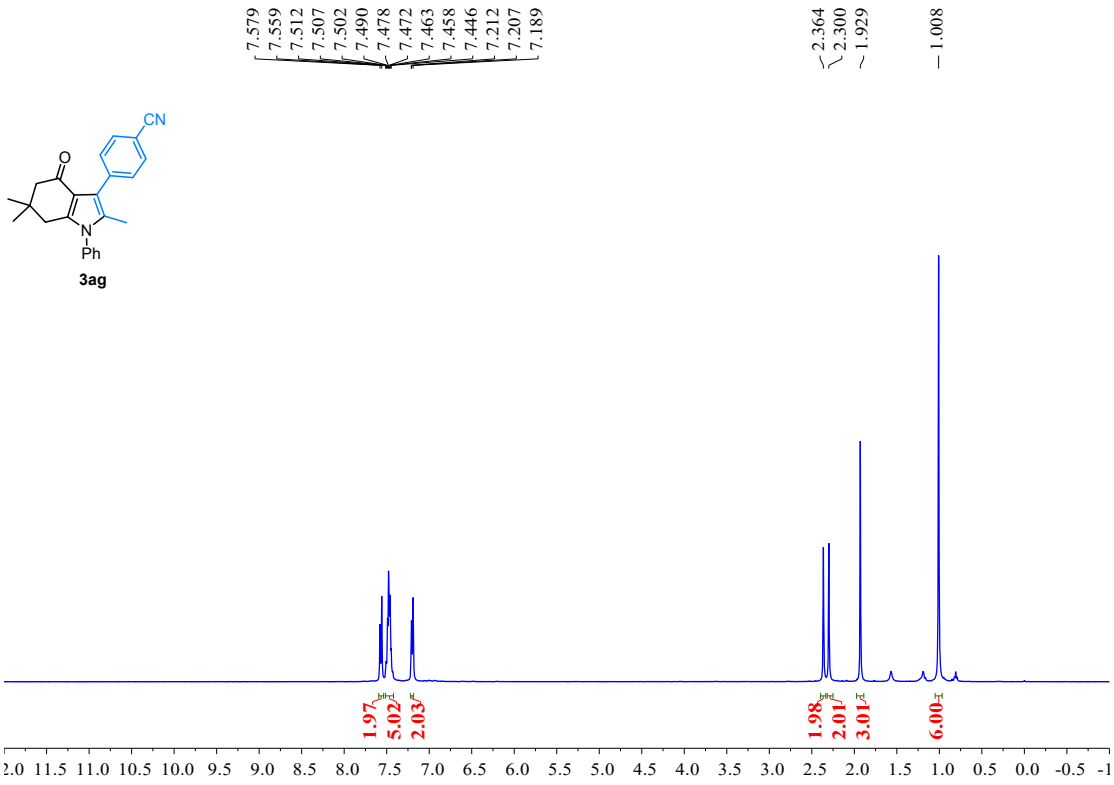
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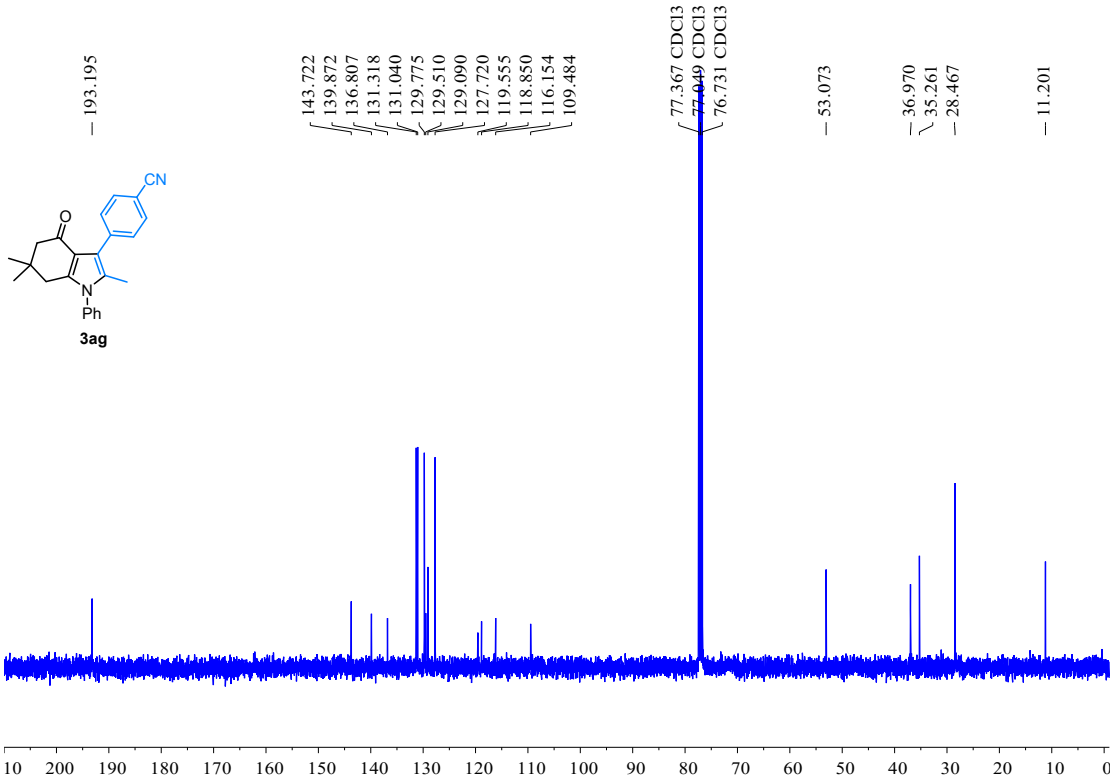
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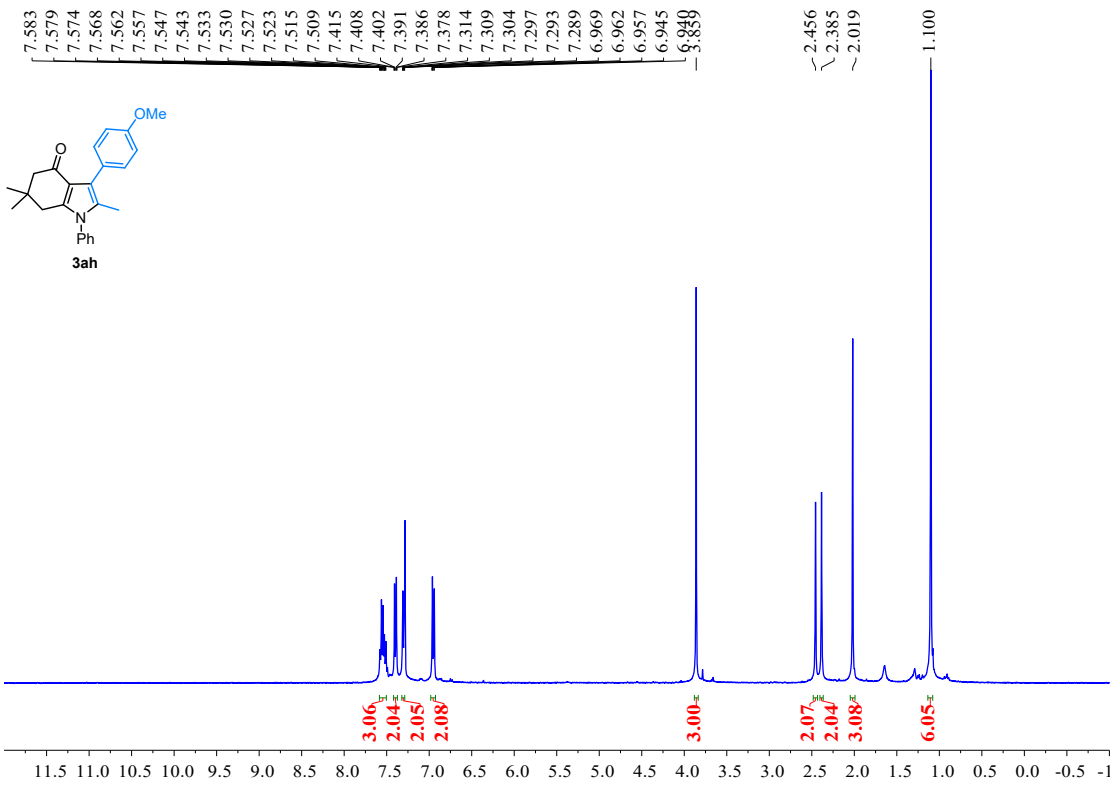
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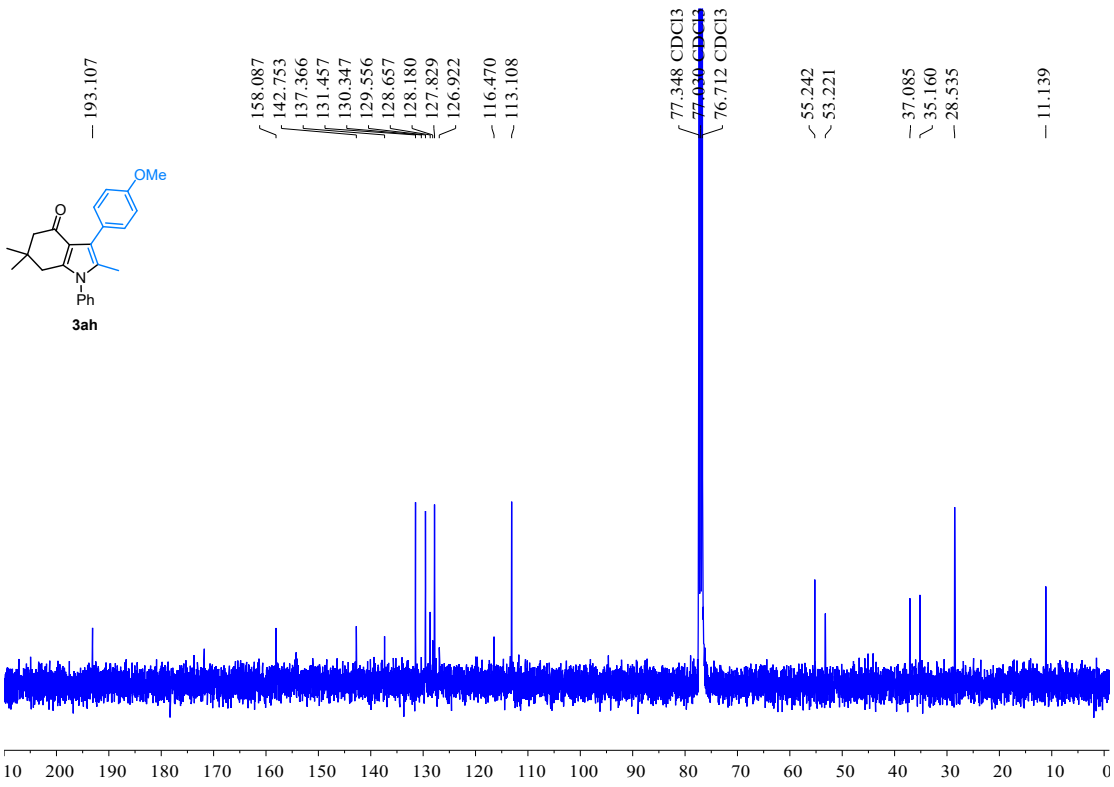
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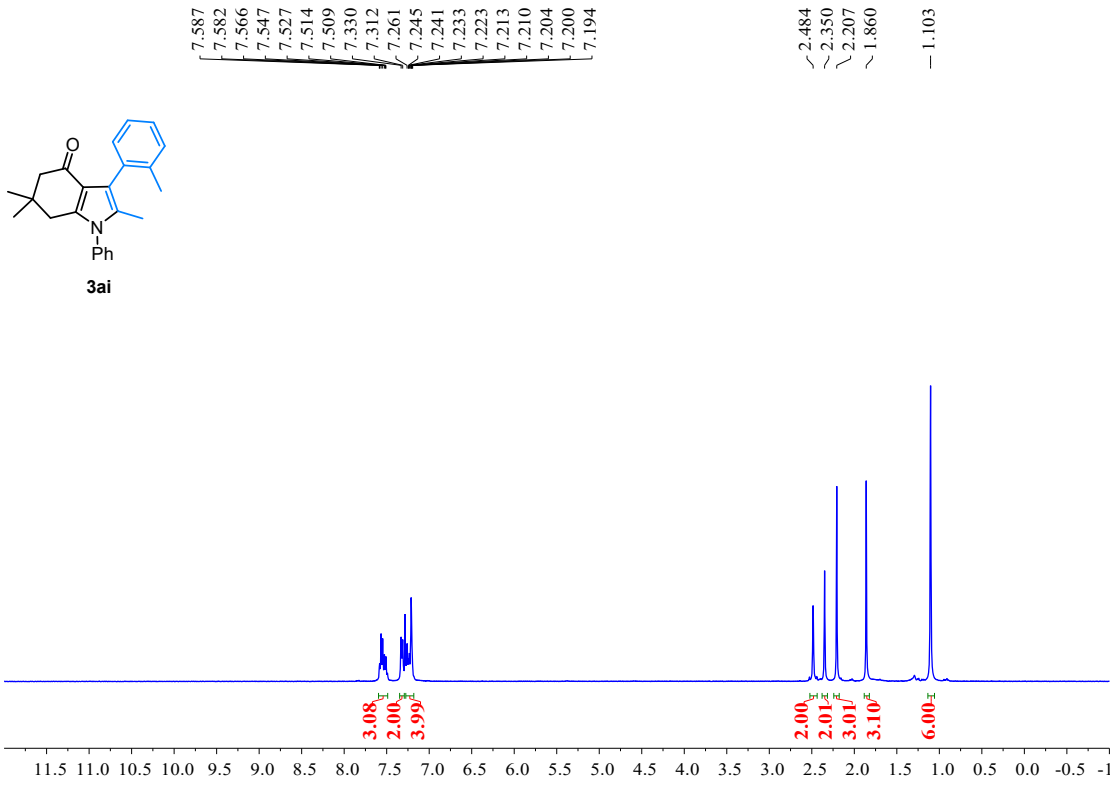
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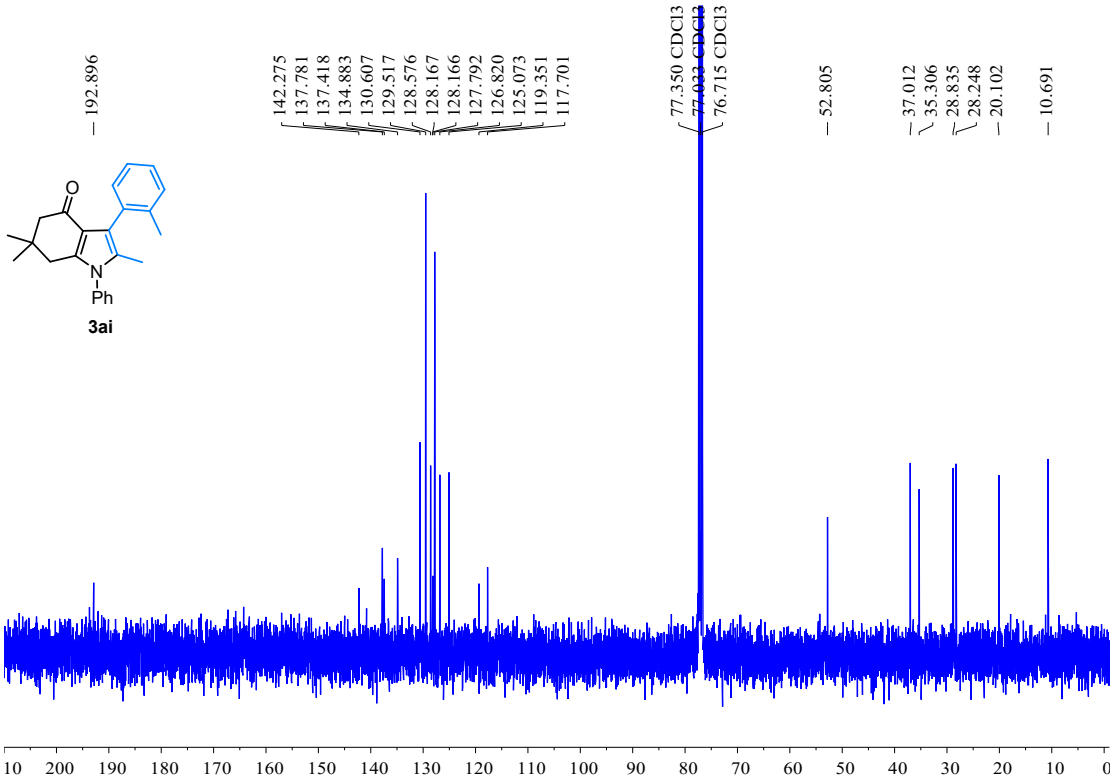
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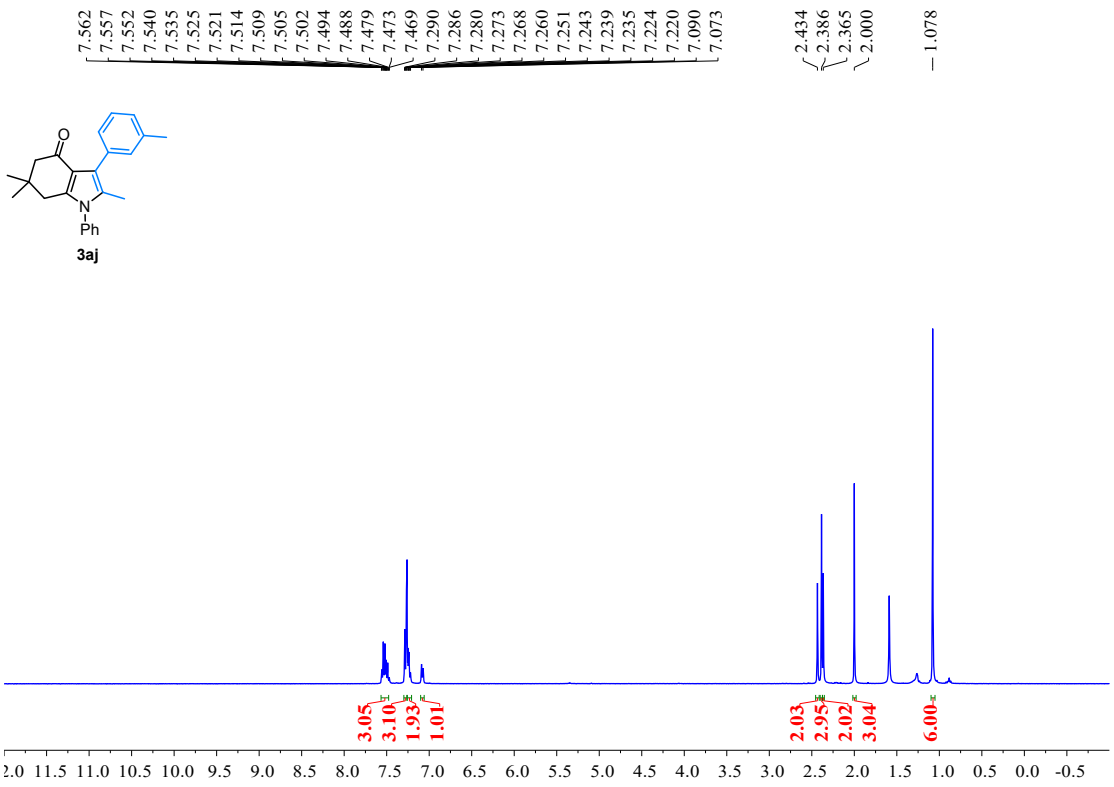
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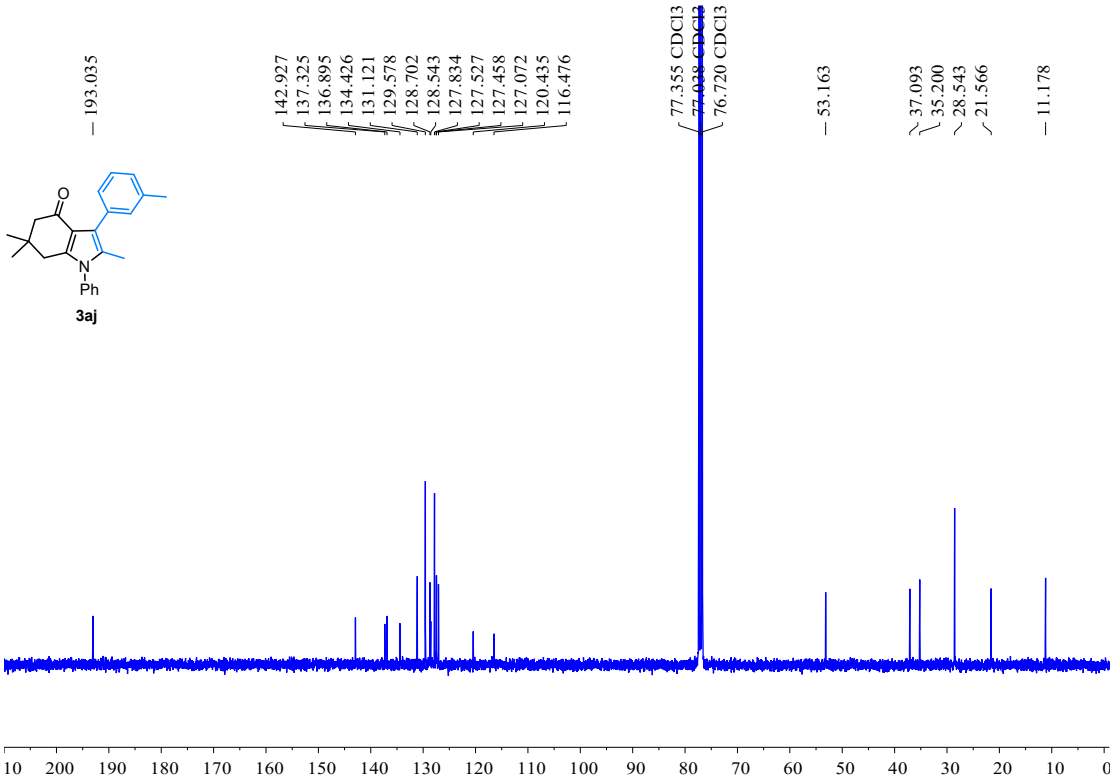
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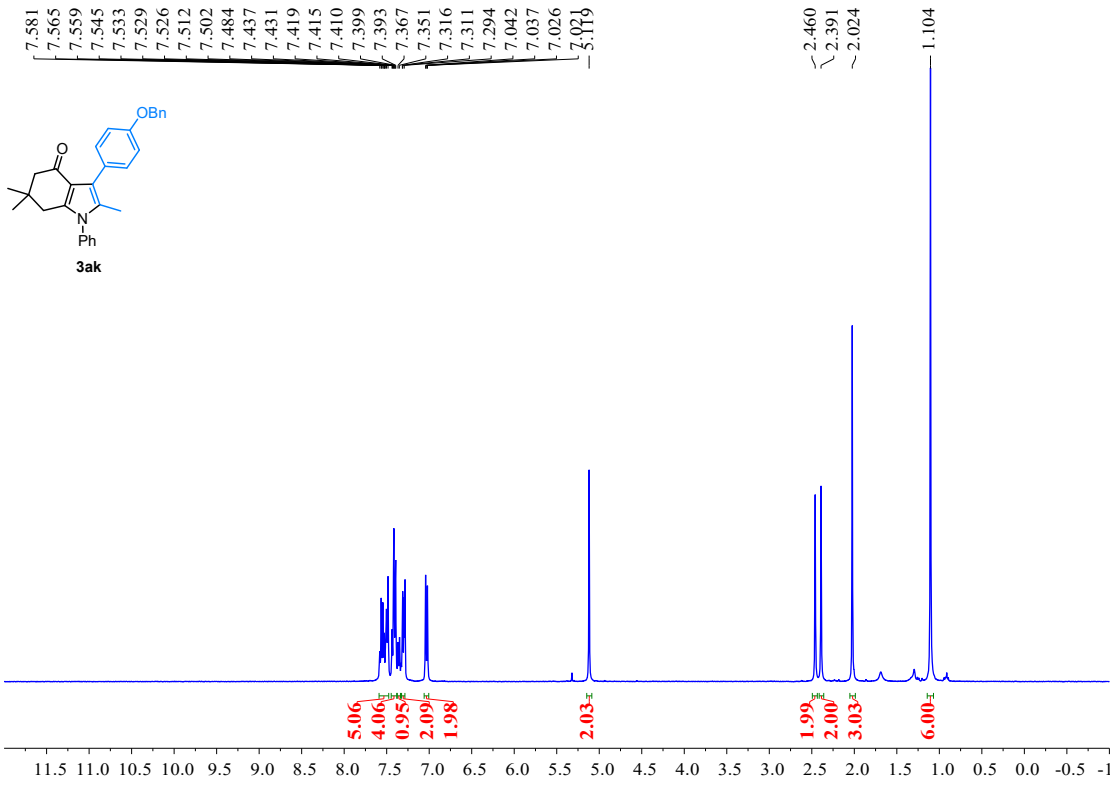
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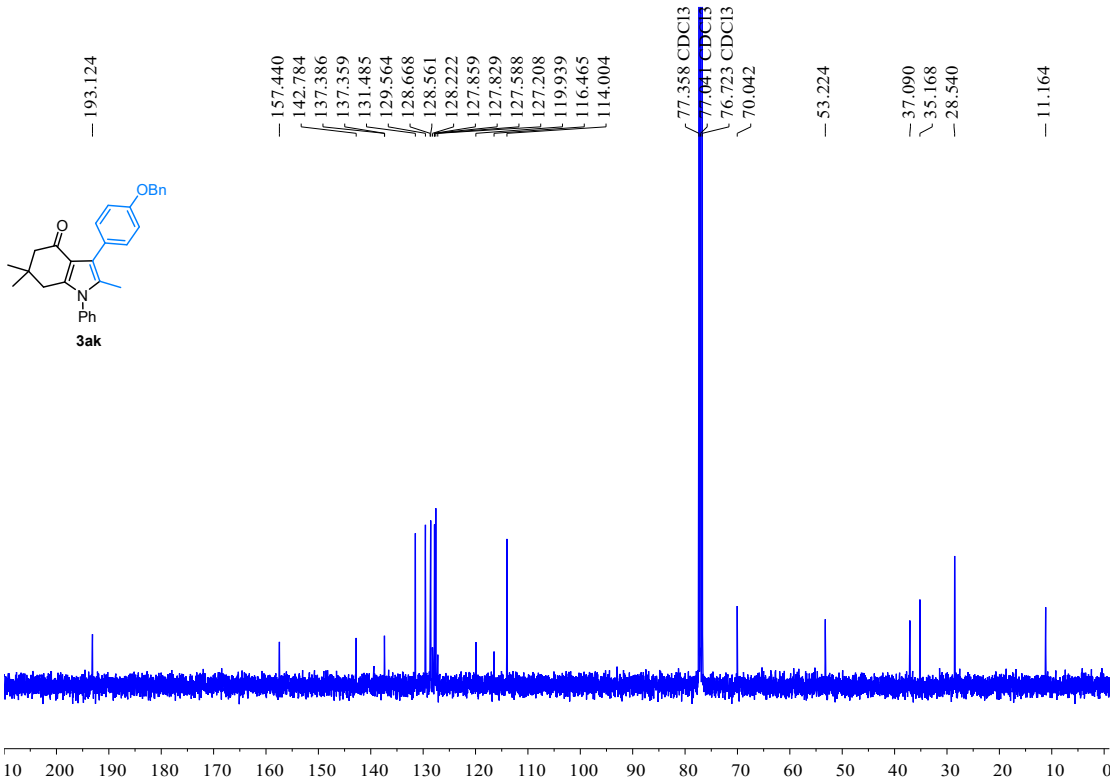
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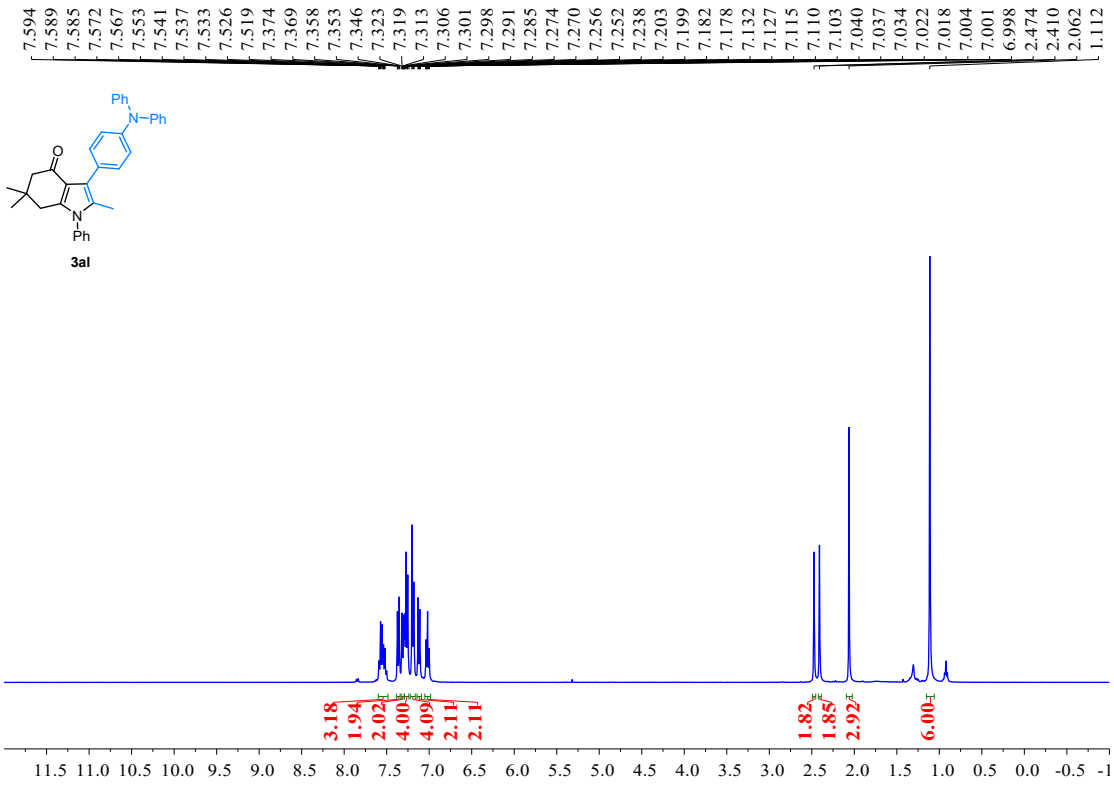
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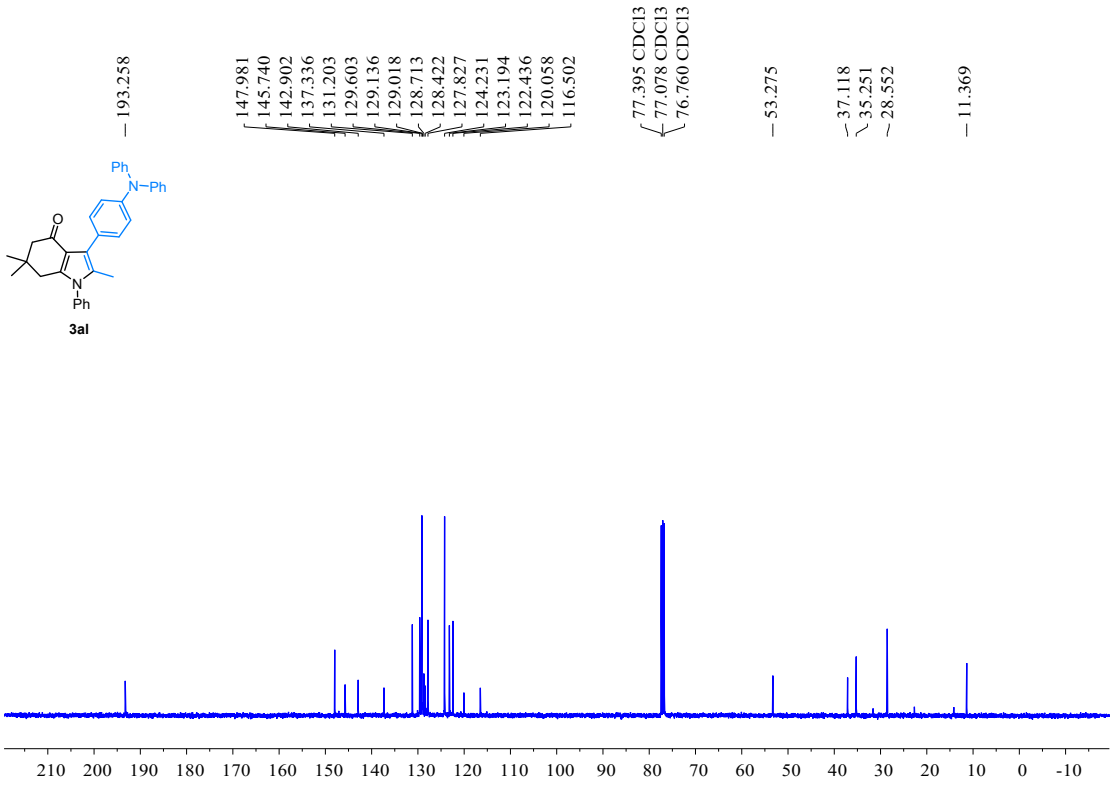
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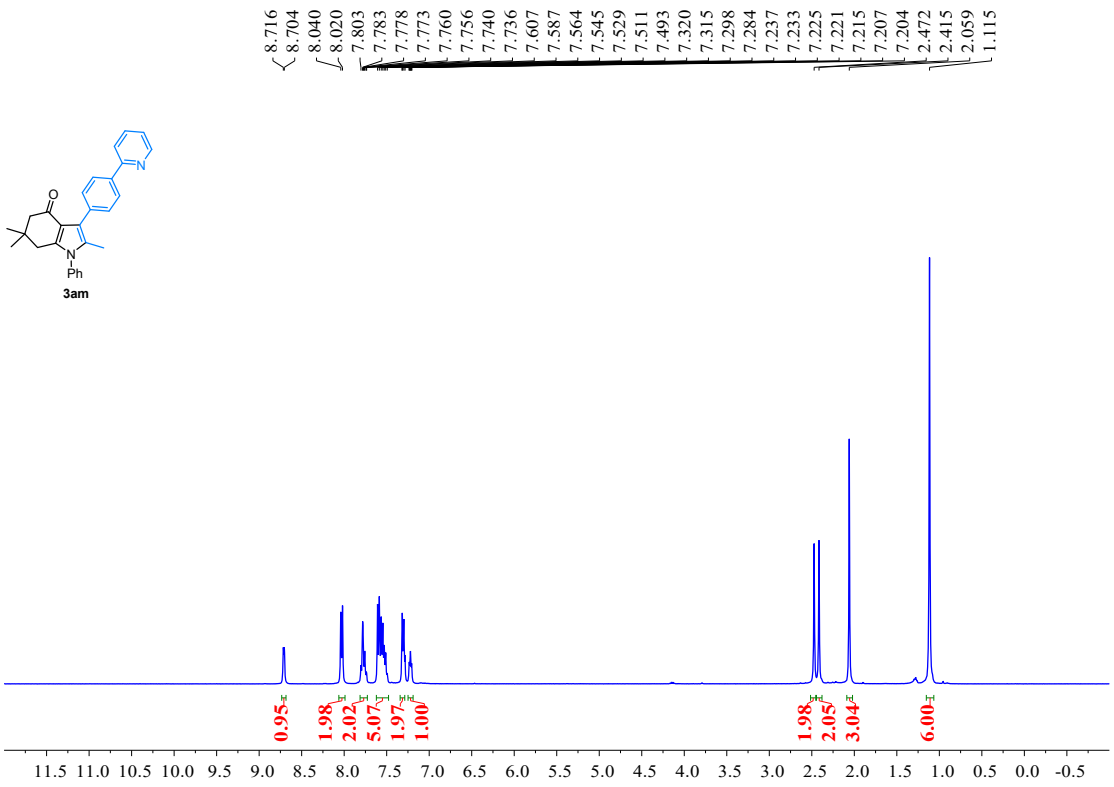
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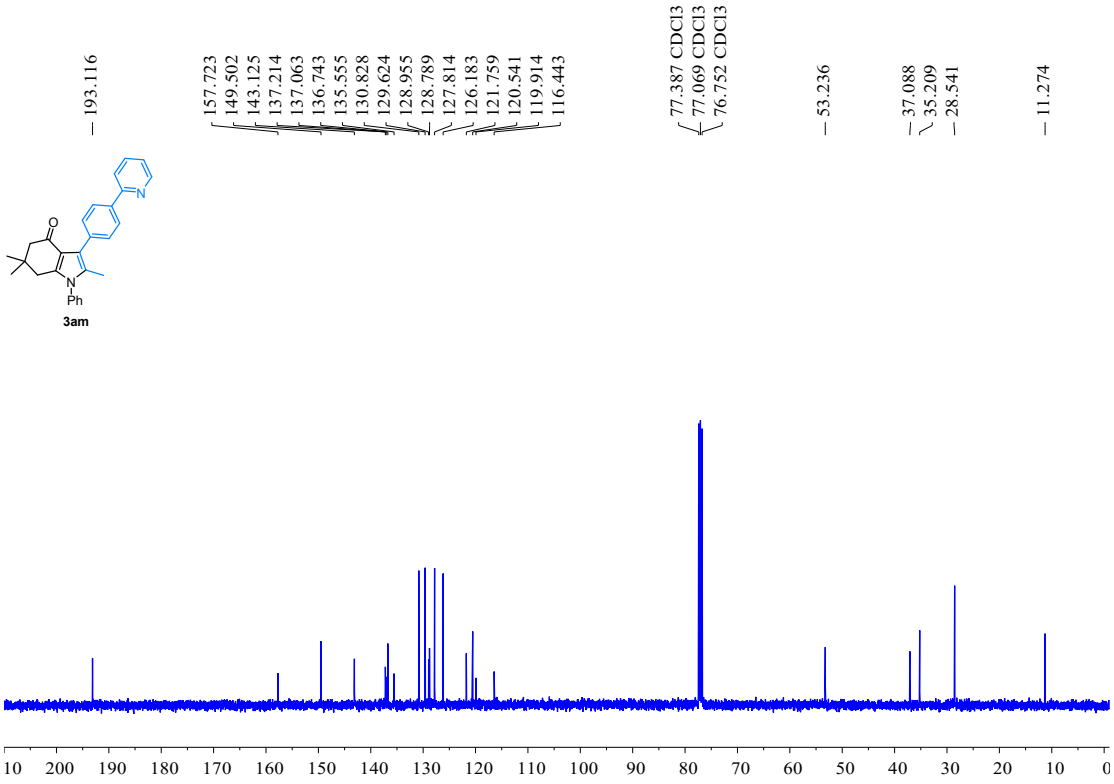
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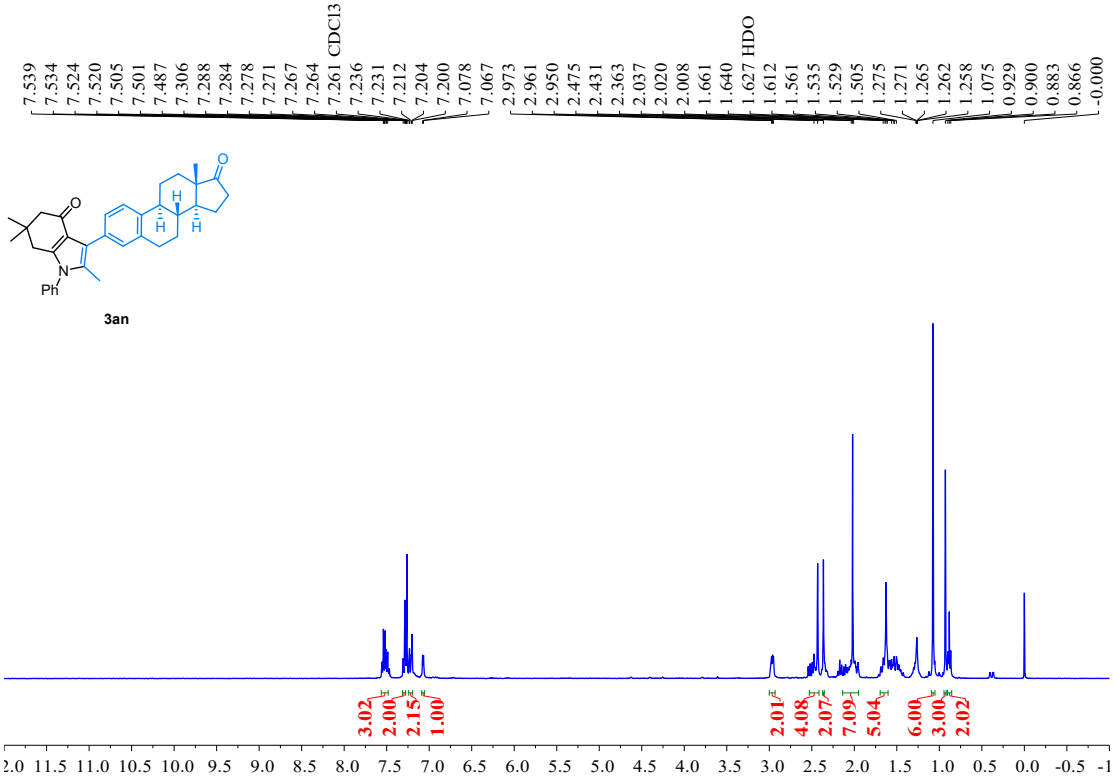
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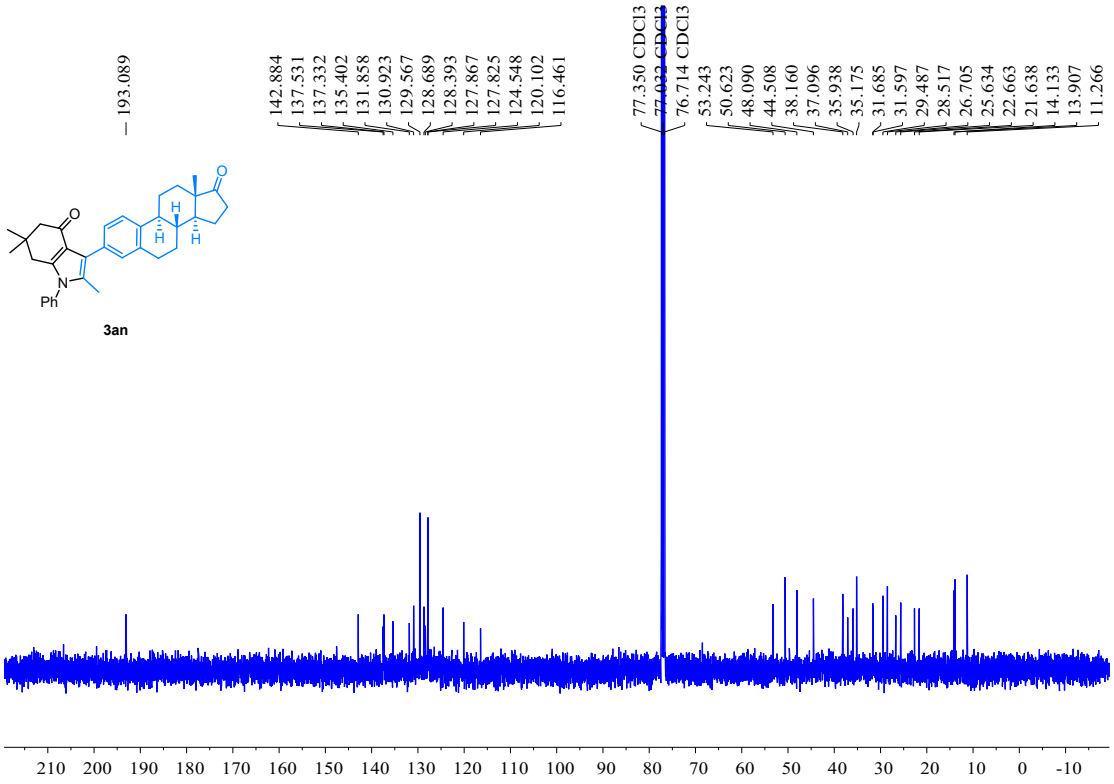
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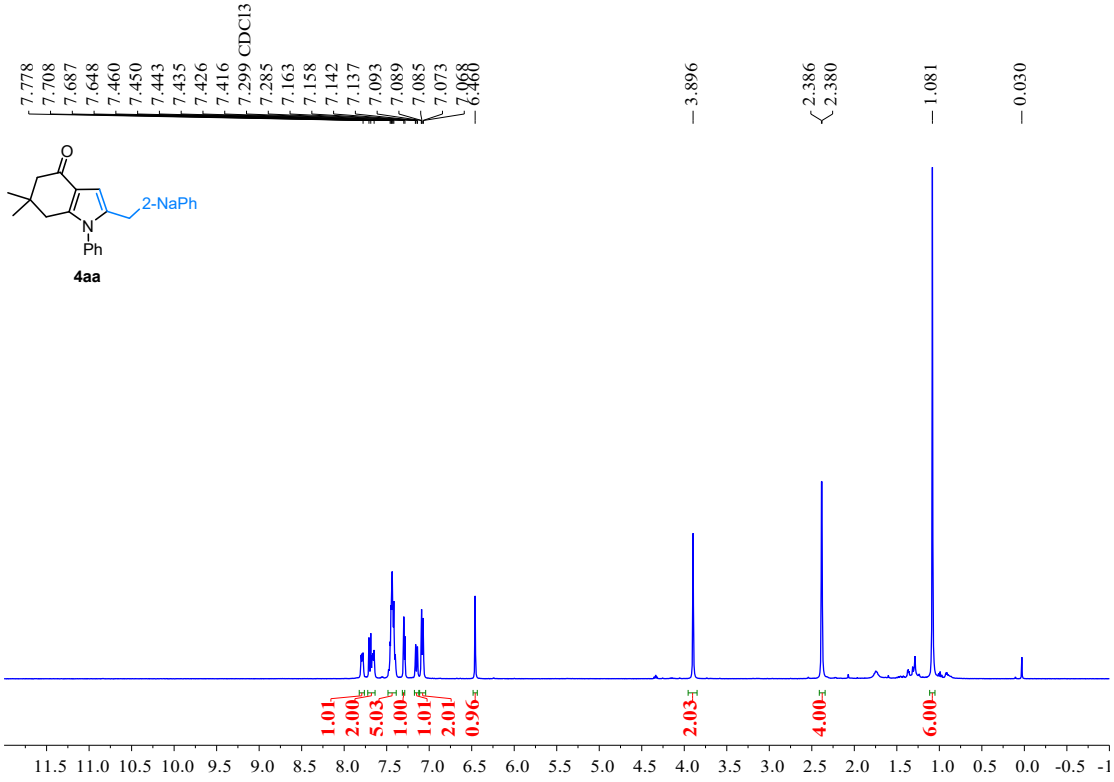
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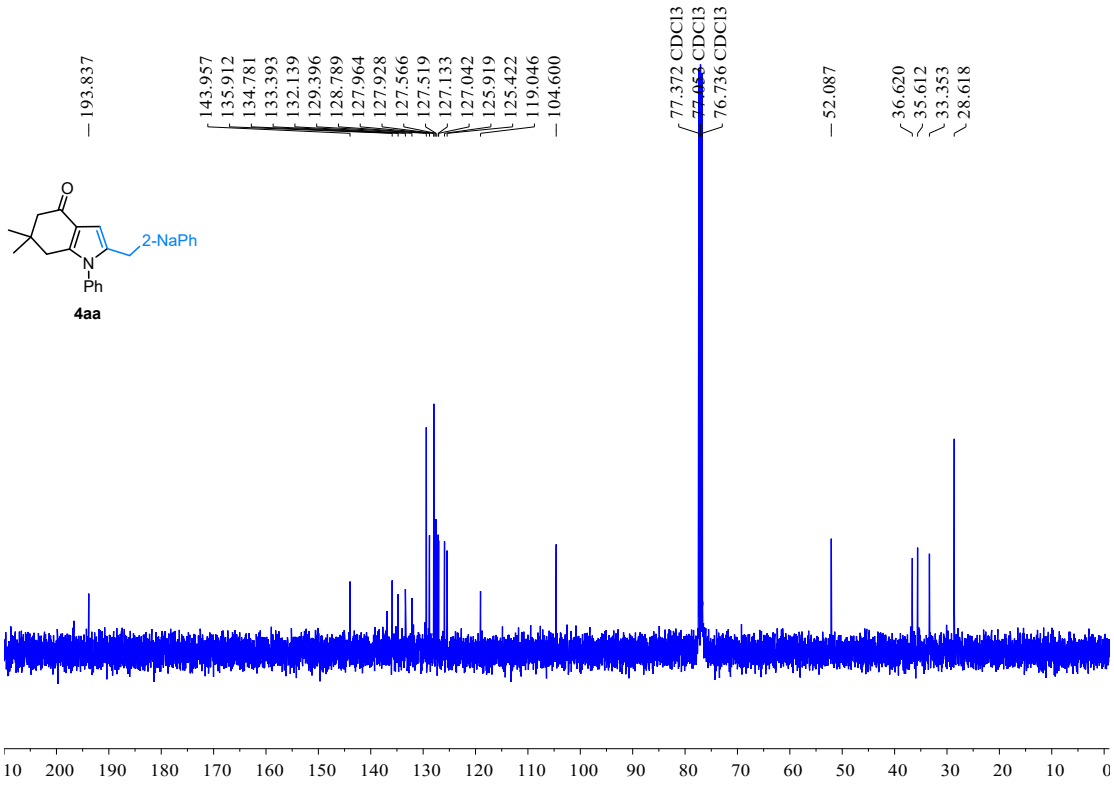
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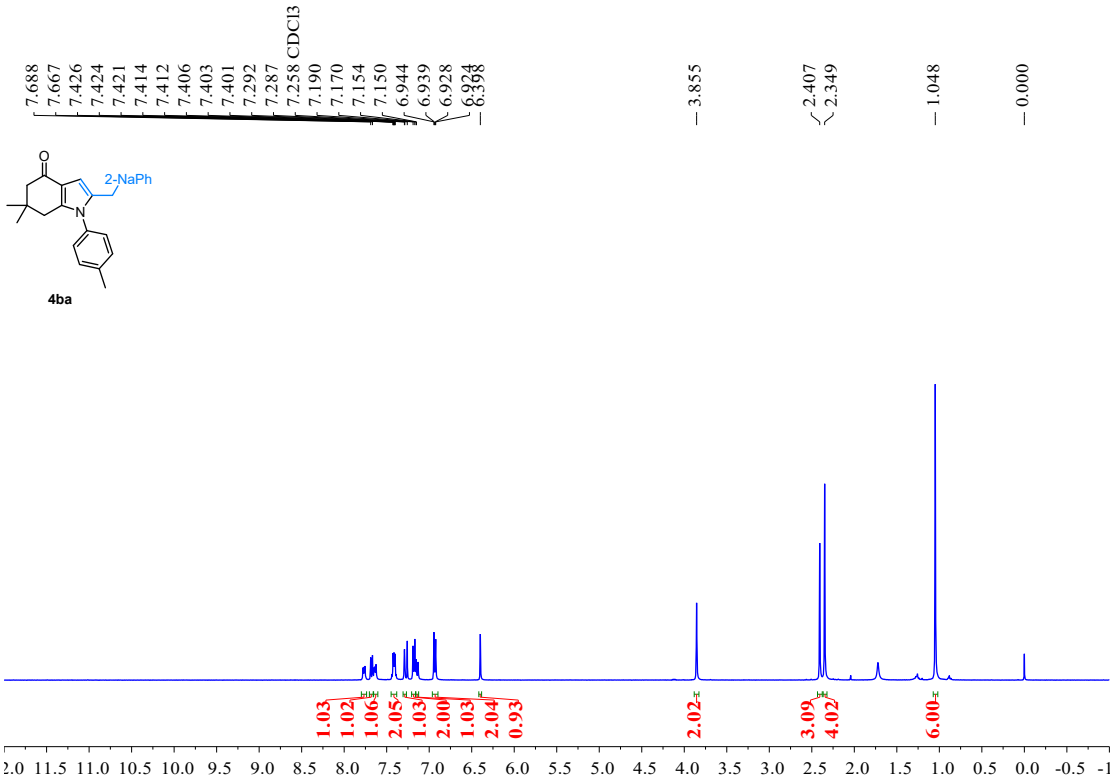
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2.04
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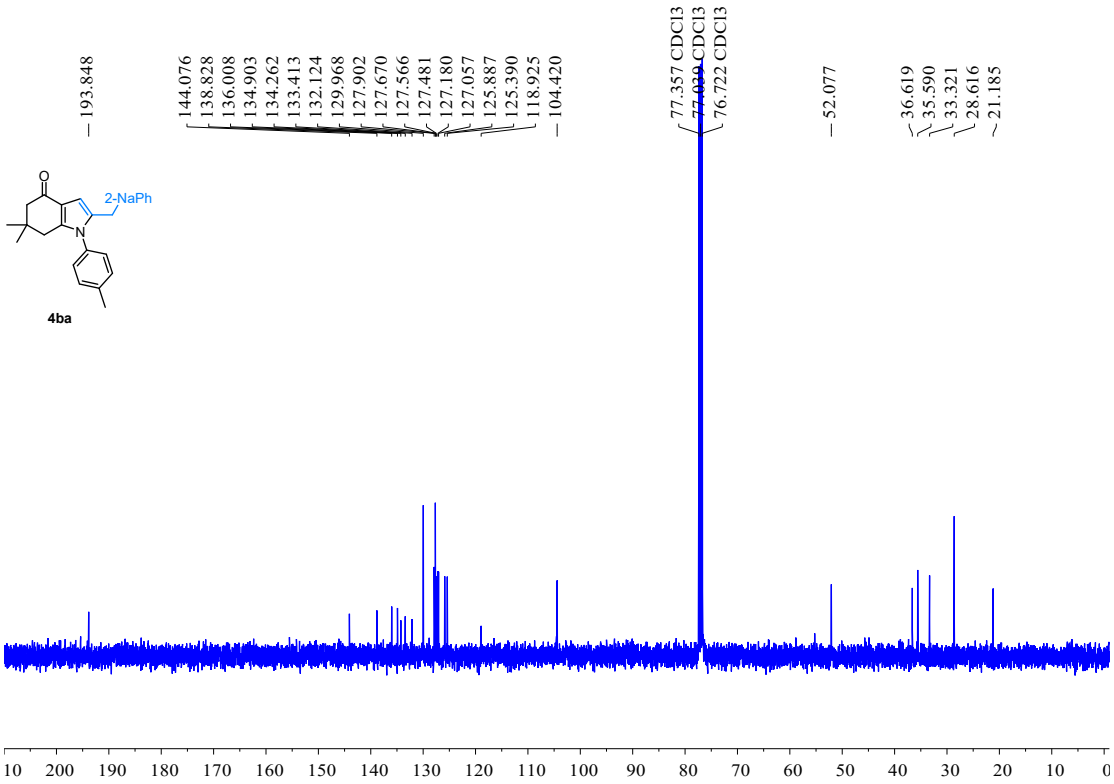
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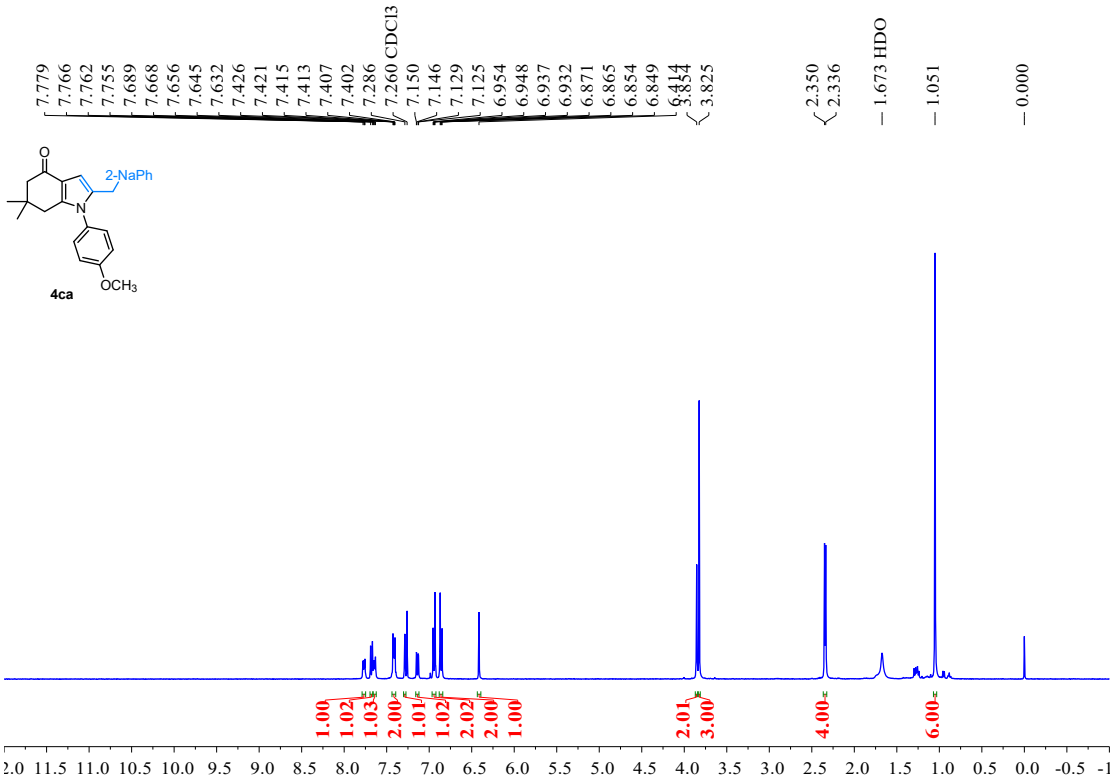
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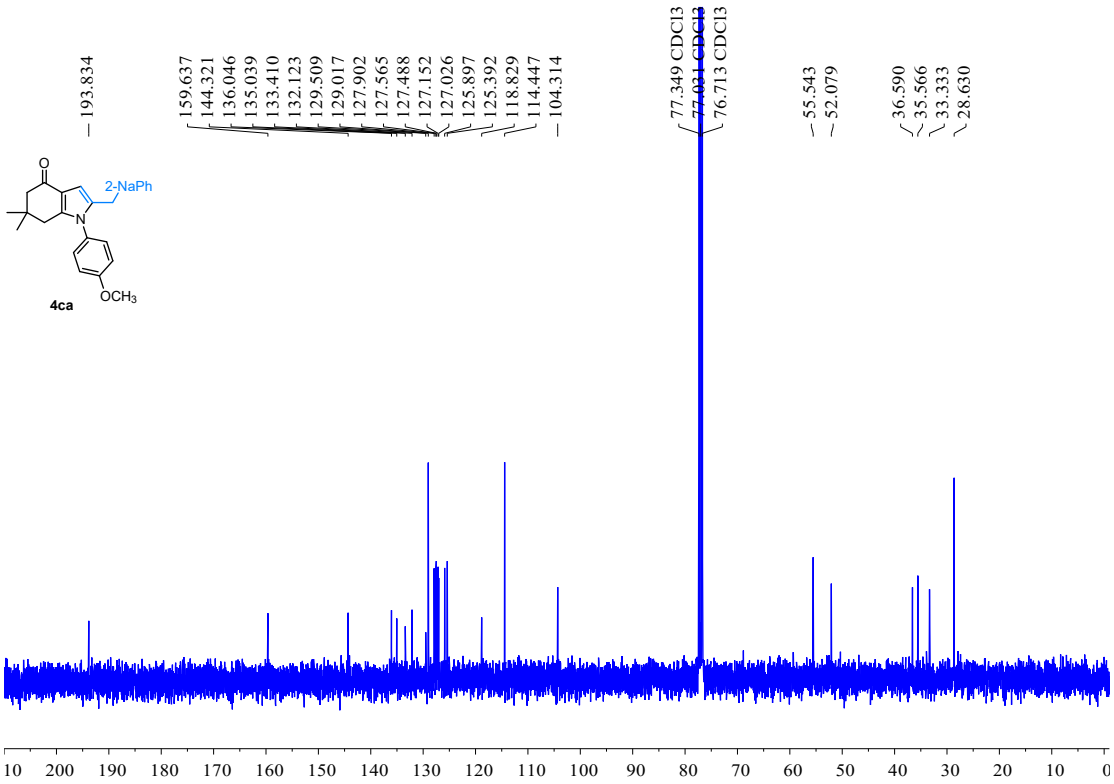
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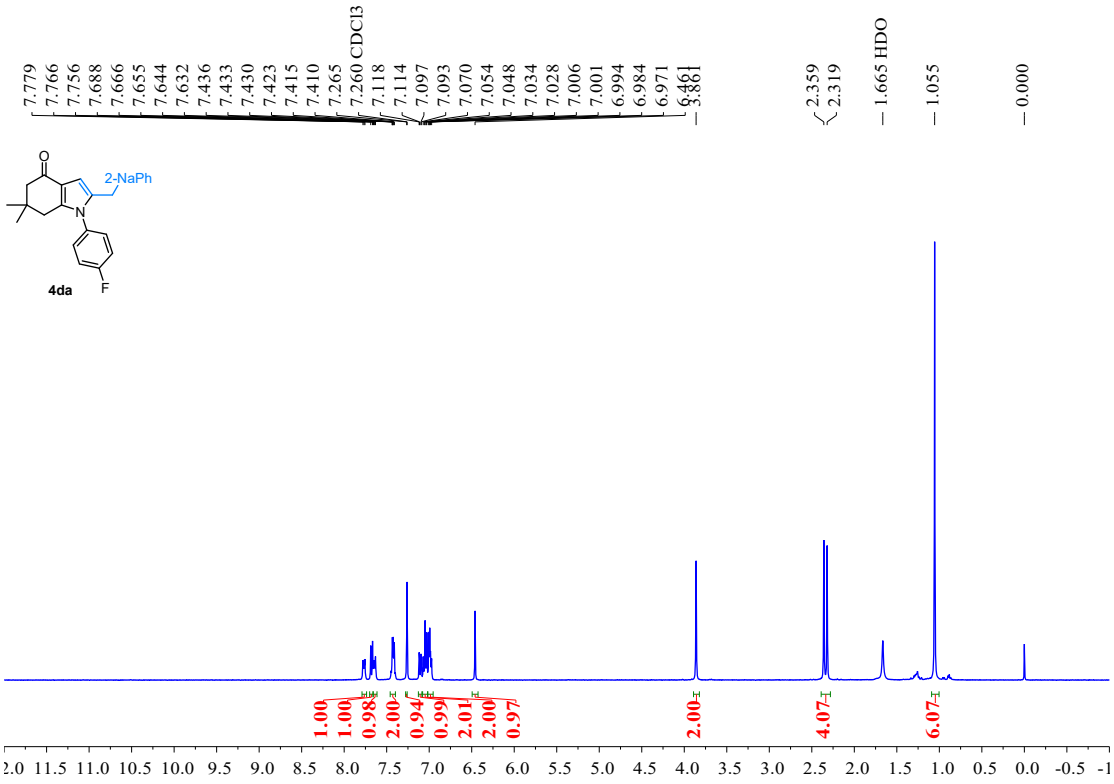
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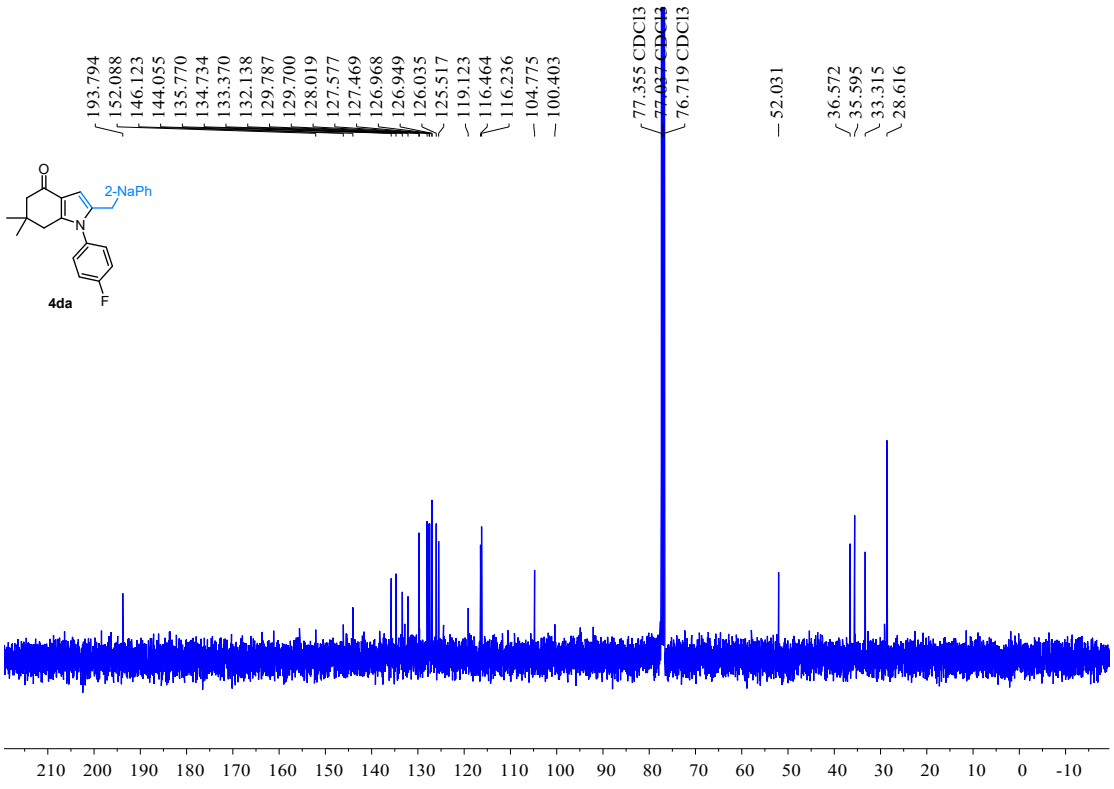
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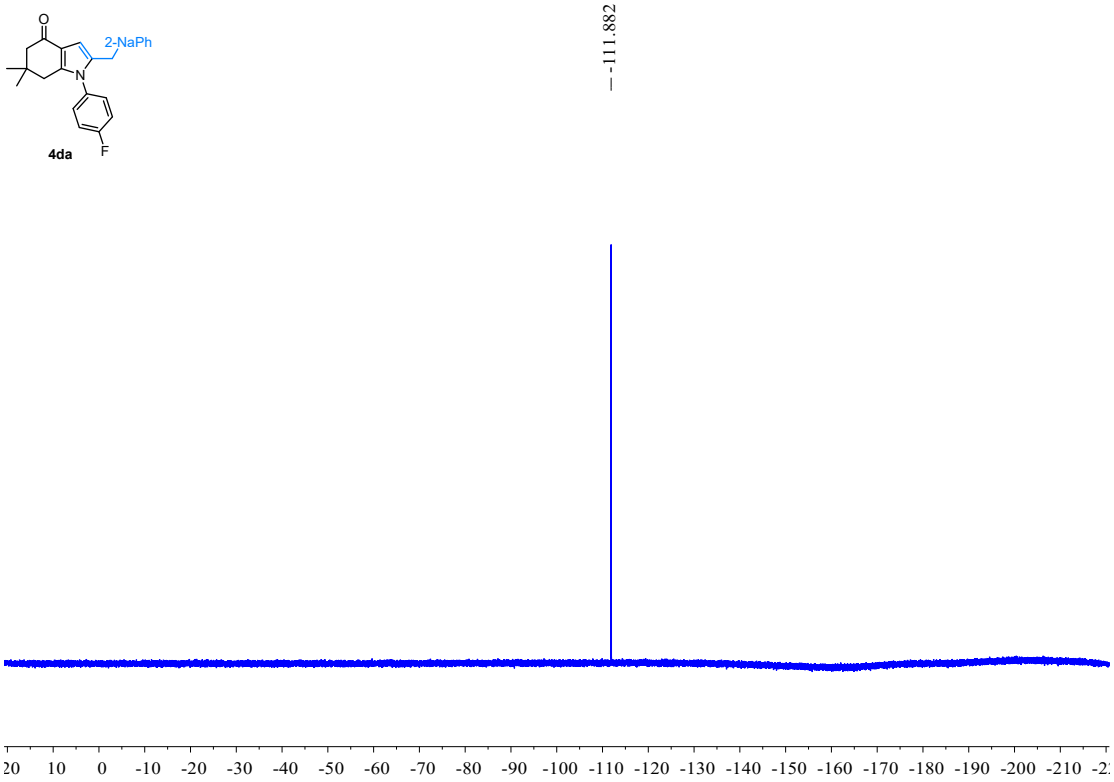
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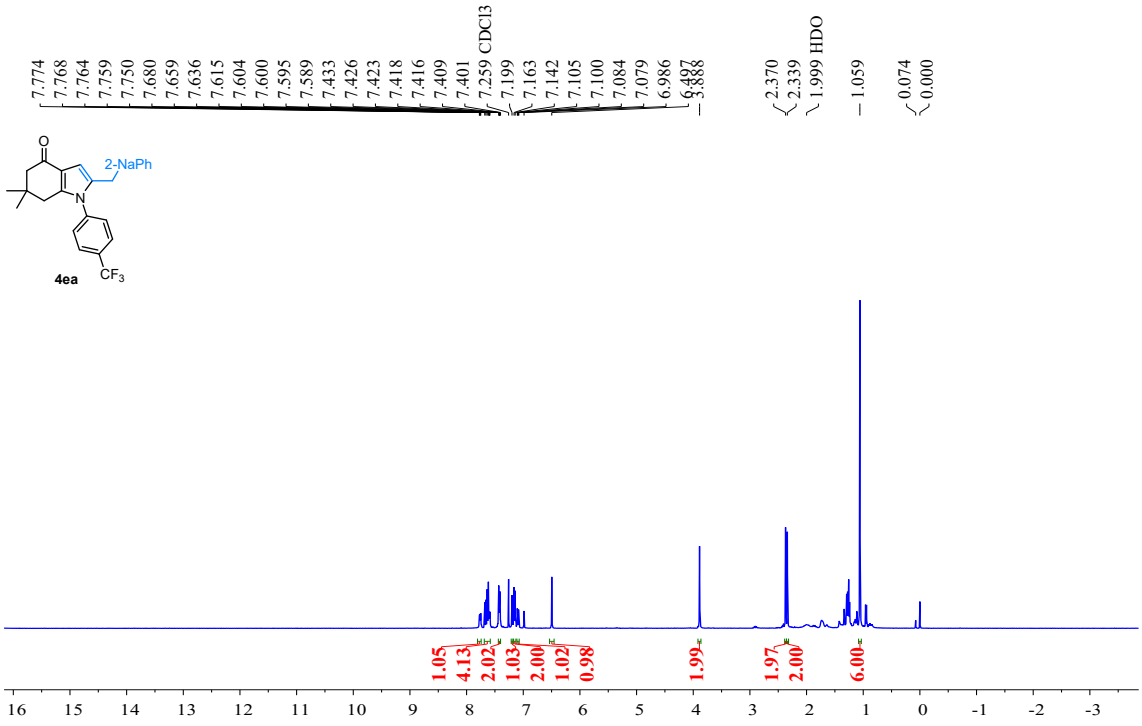
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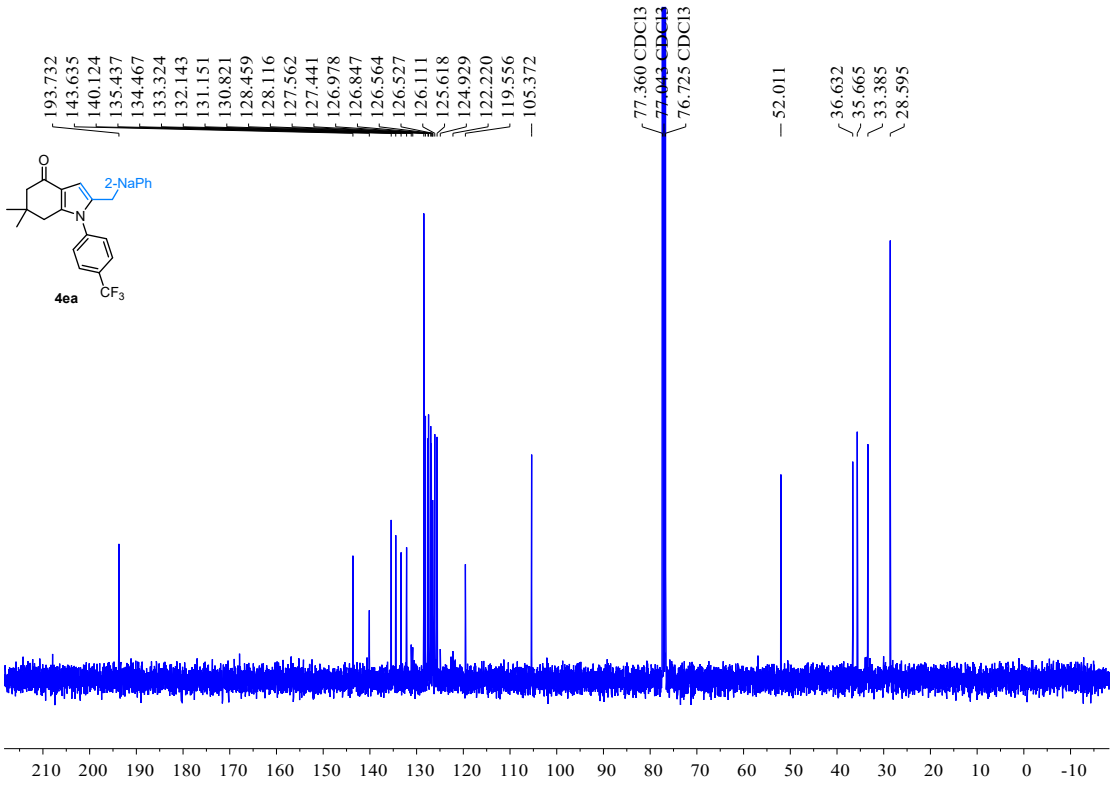
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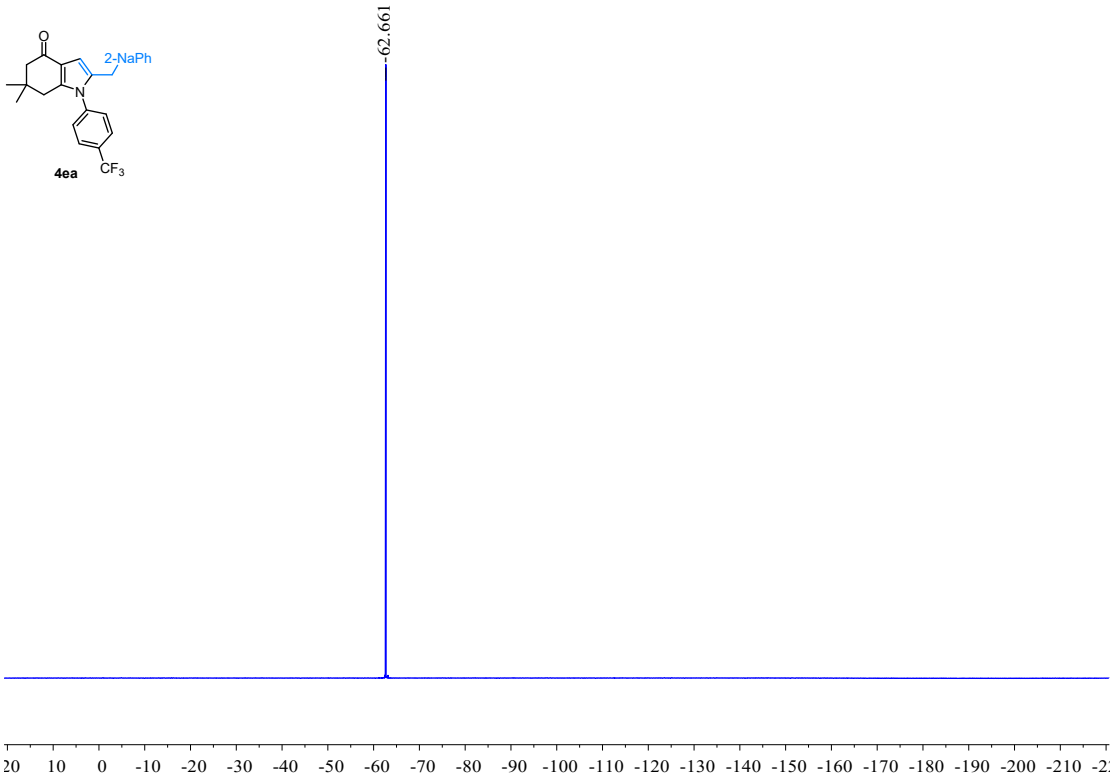
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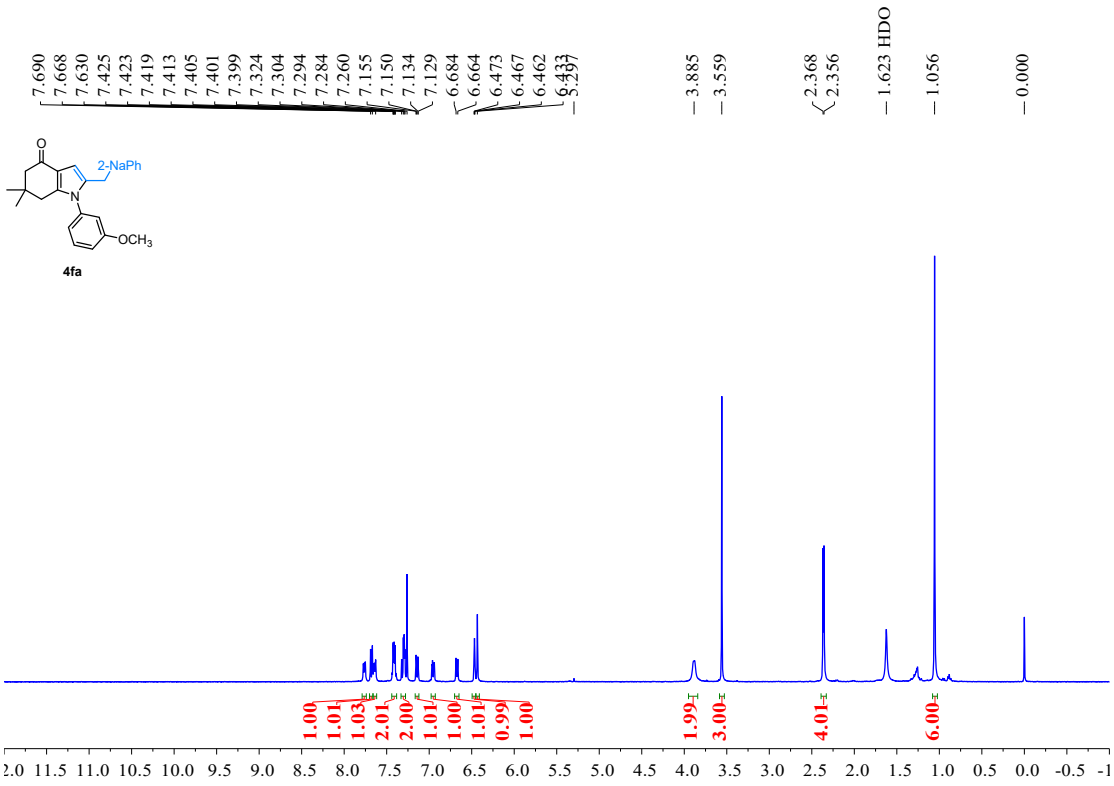
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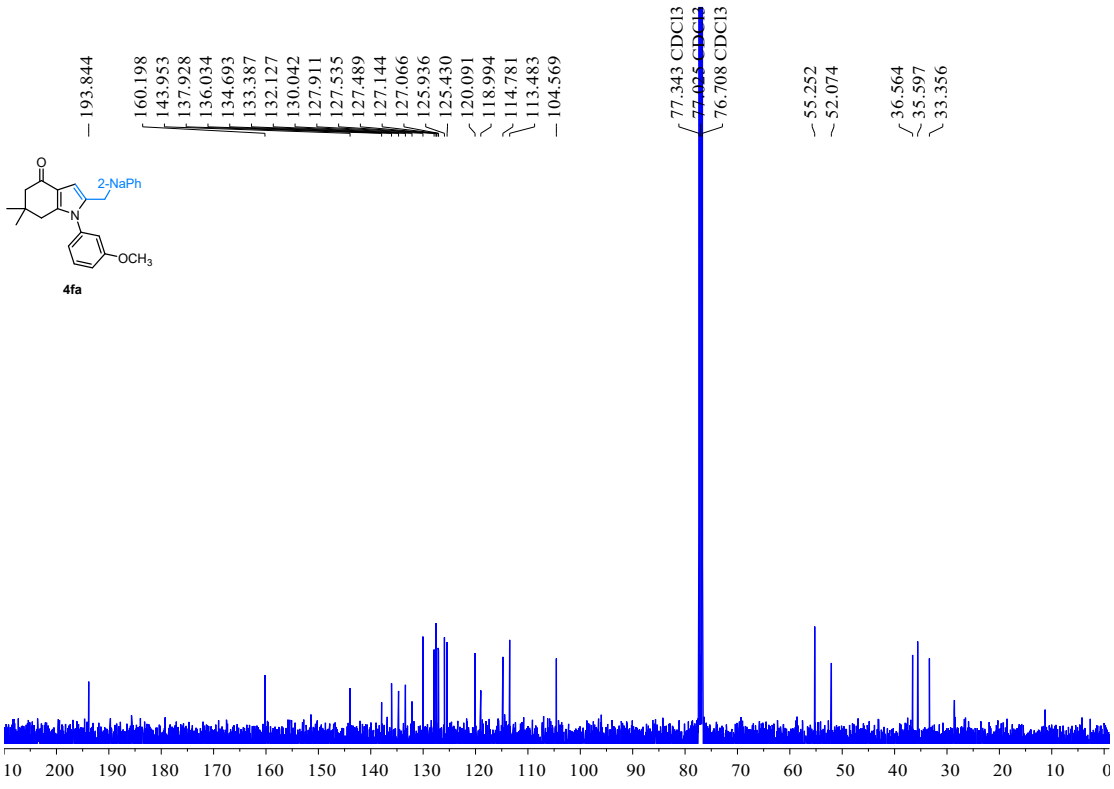
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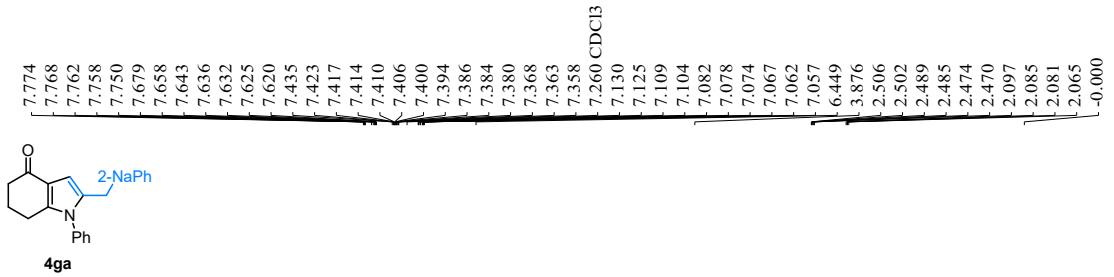
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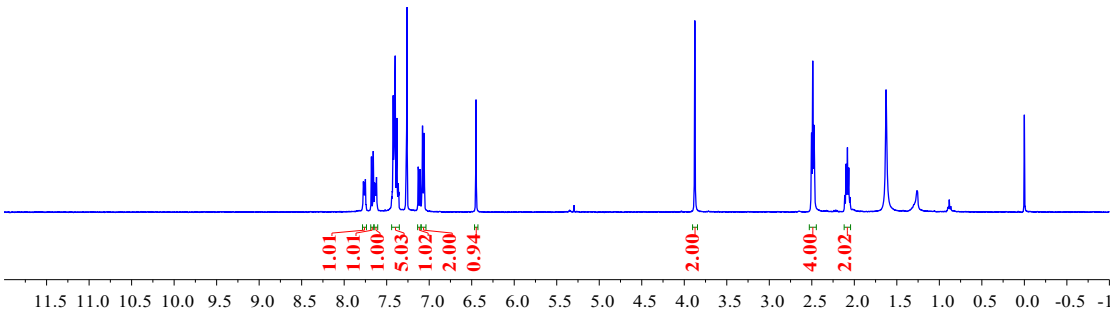
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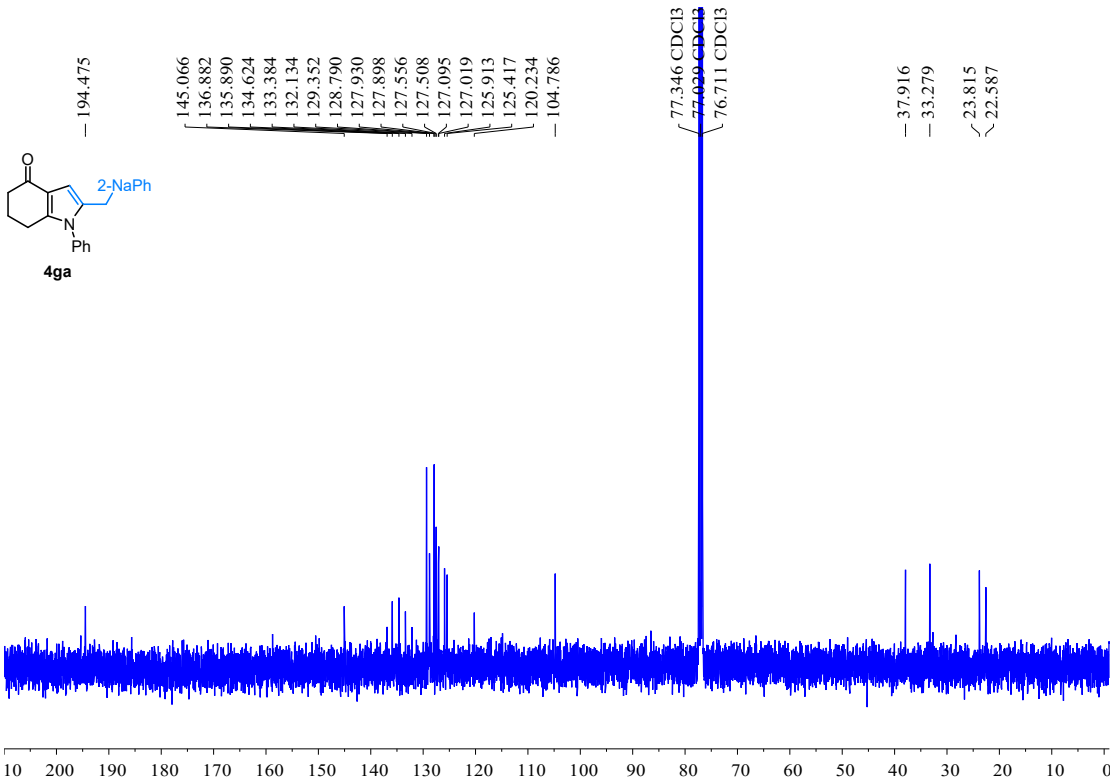
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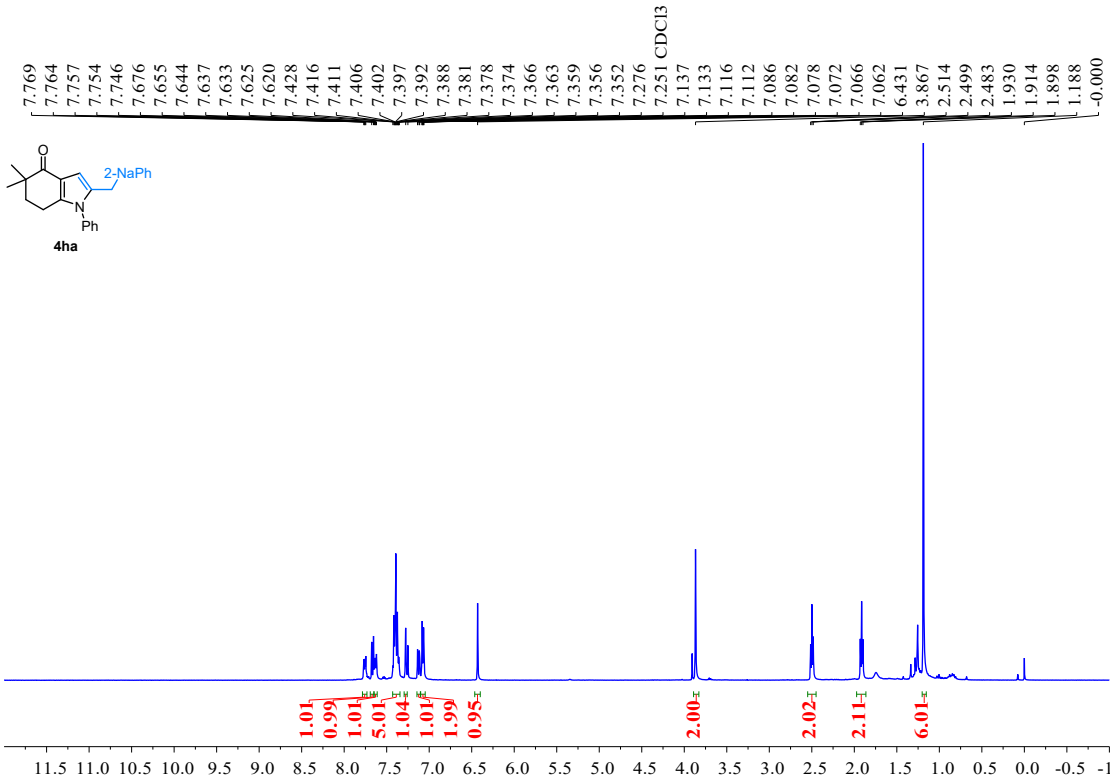
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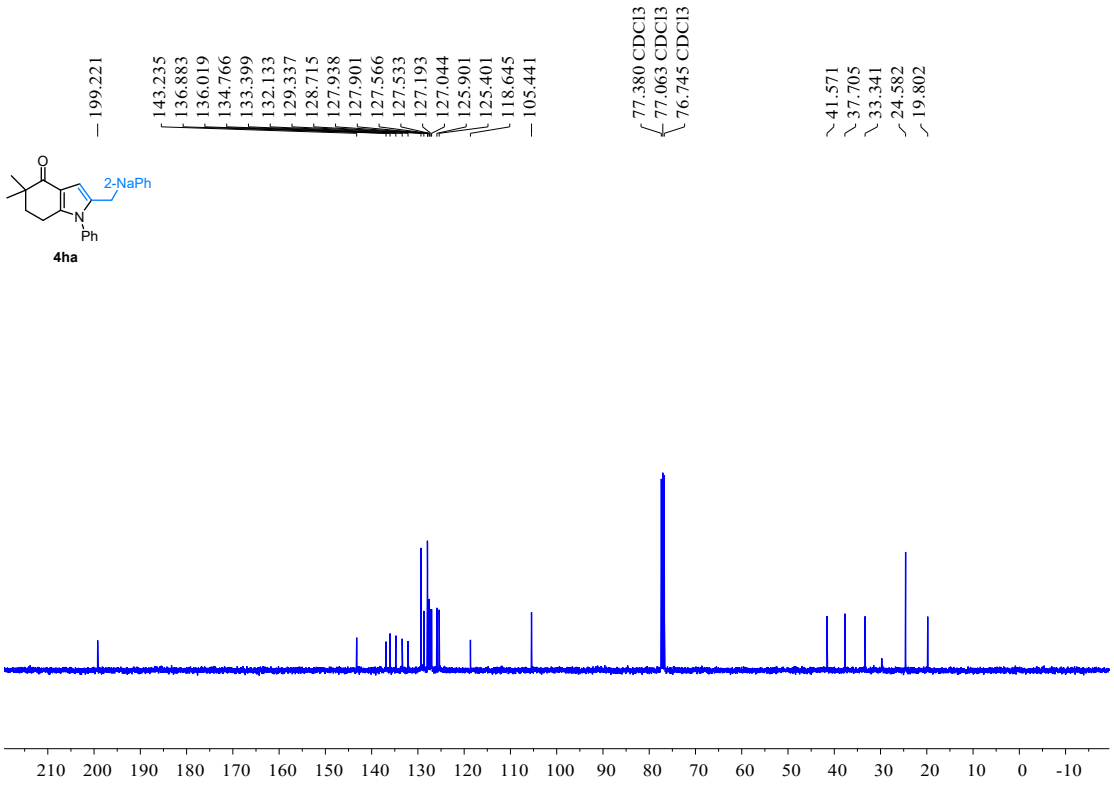
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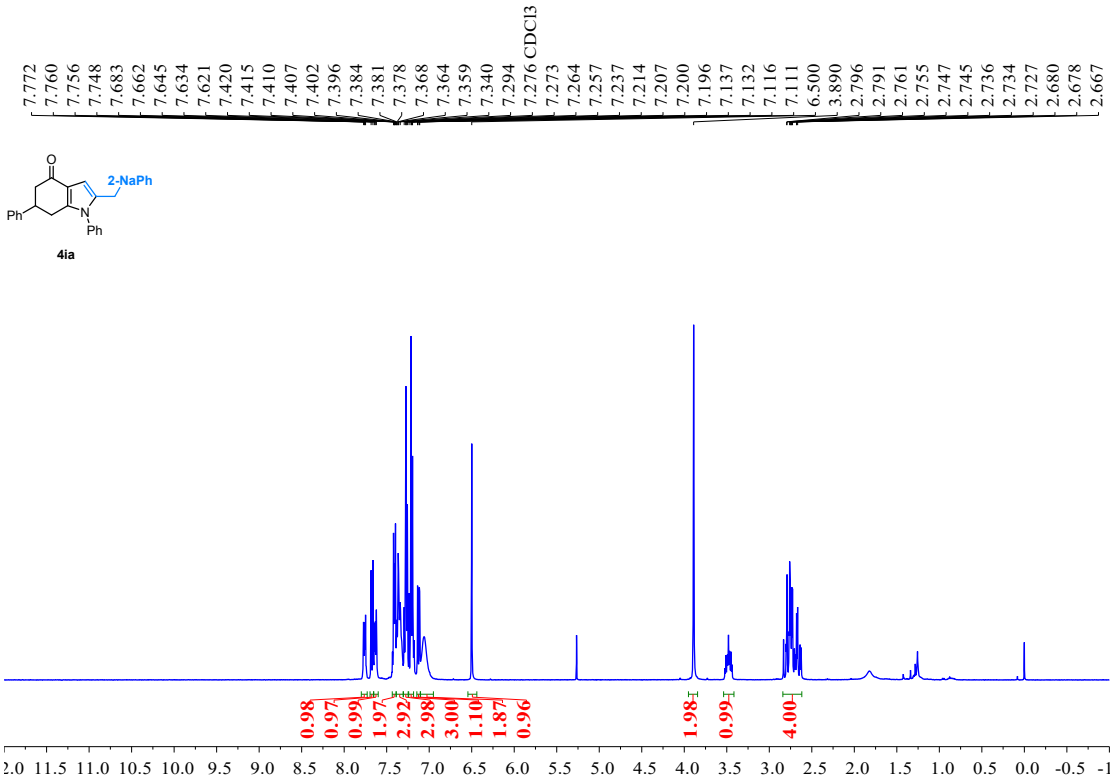
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Ph
N
Ph
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0.99
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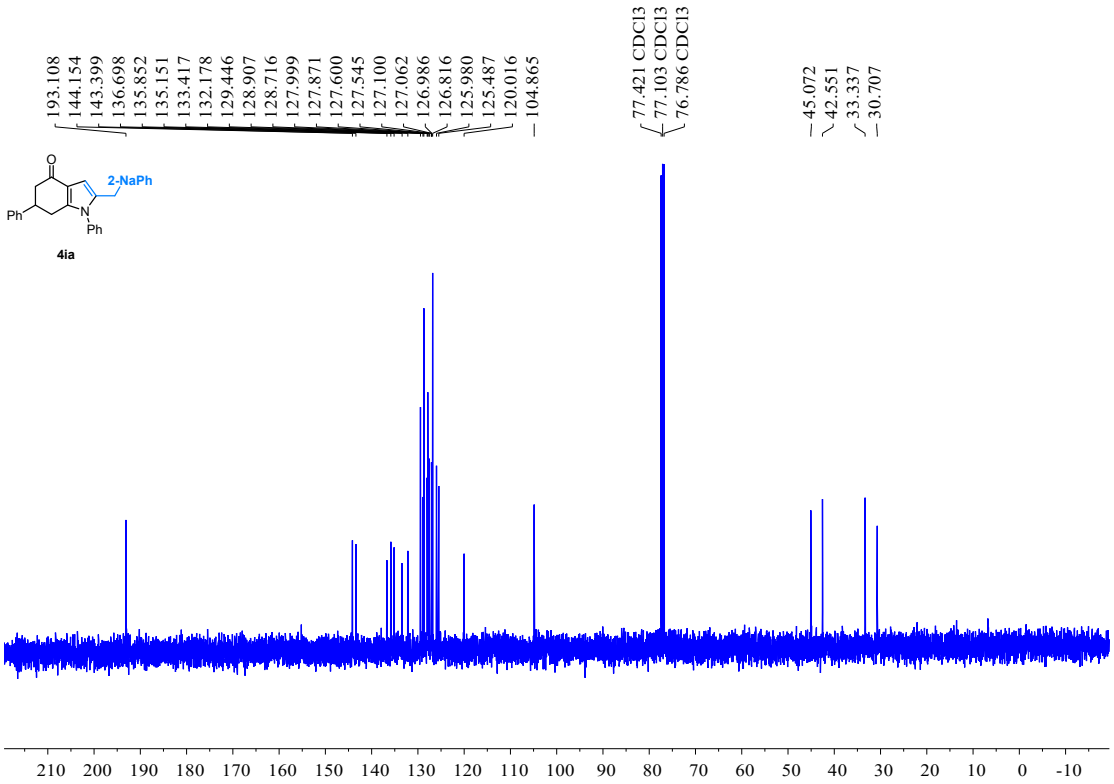
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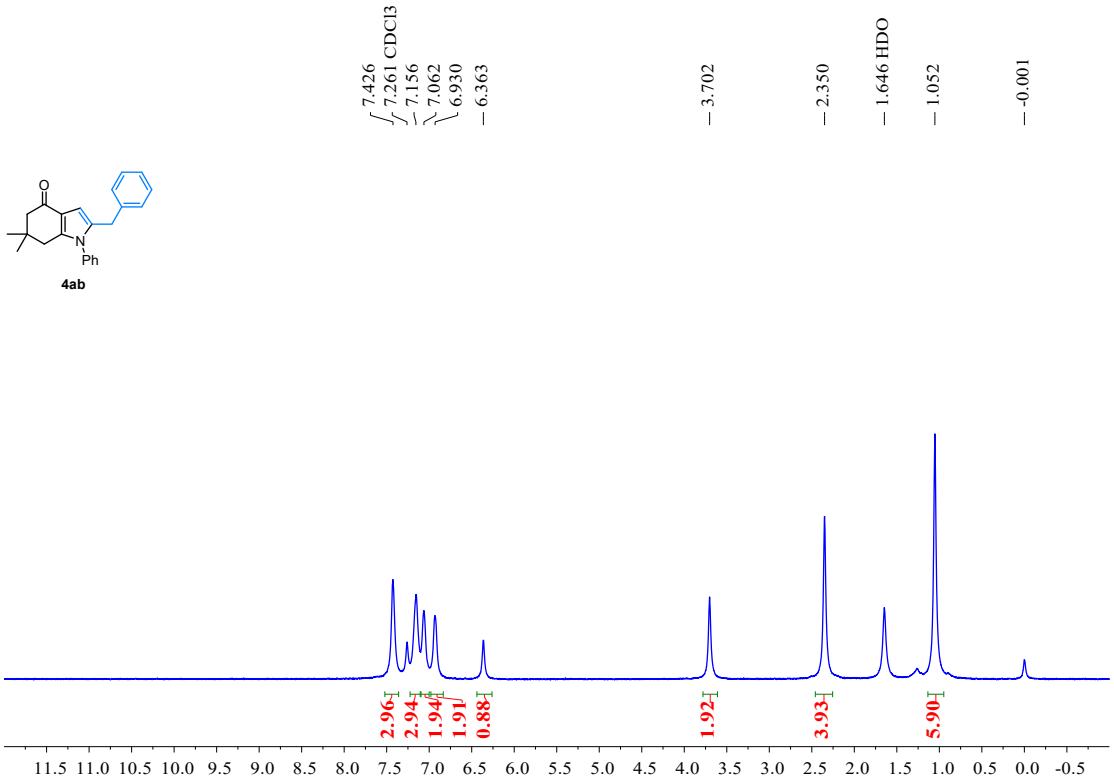
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2.94
1.94
1.91
0.88
1.92
3.93
5.90
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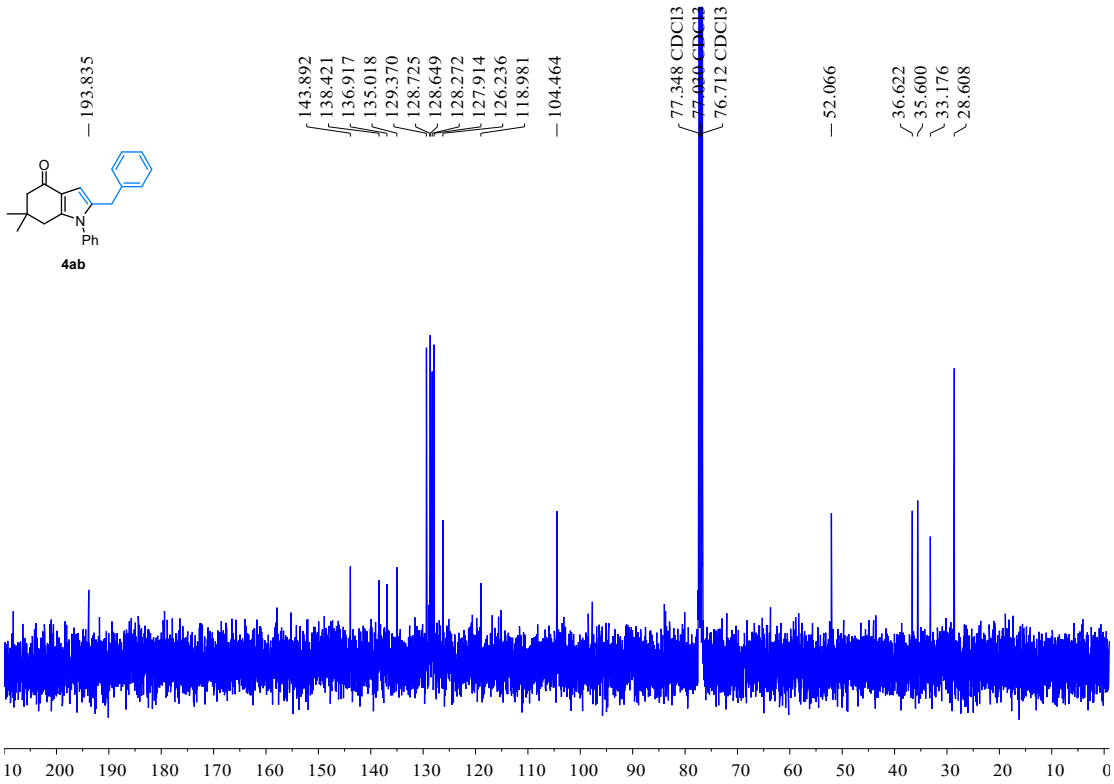
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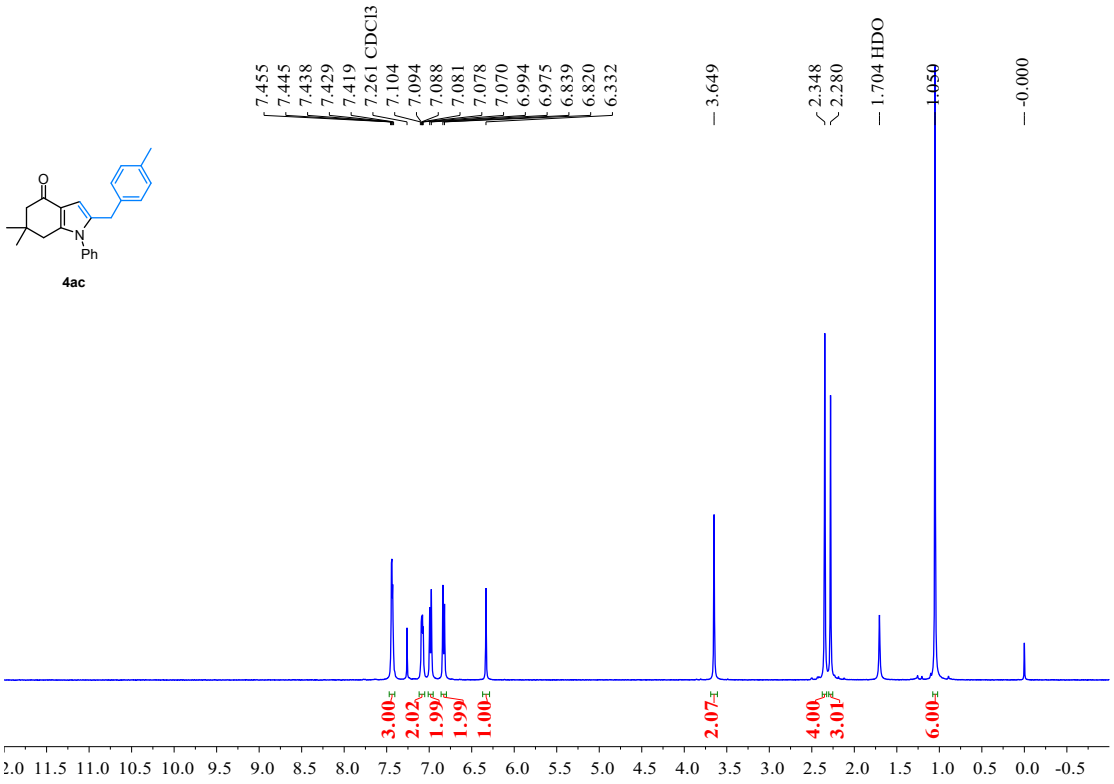
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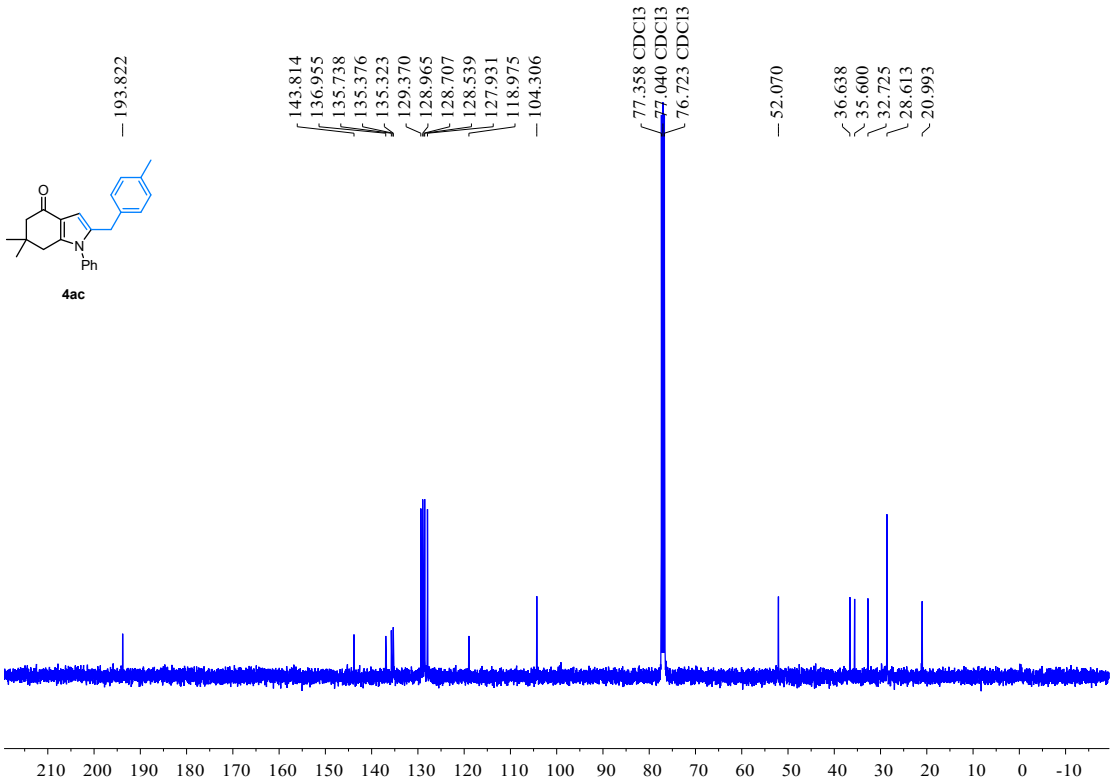
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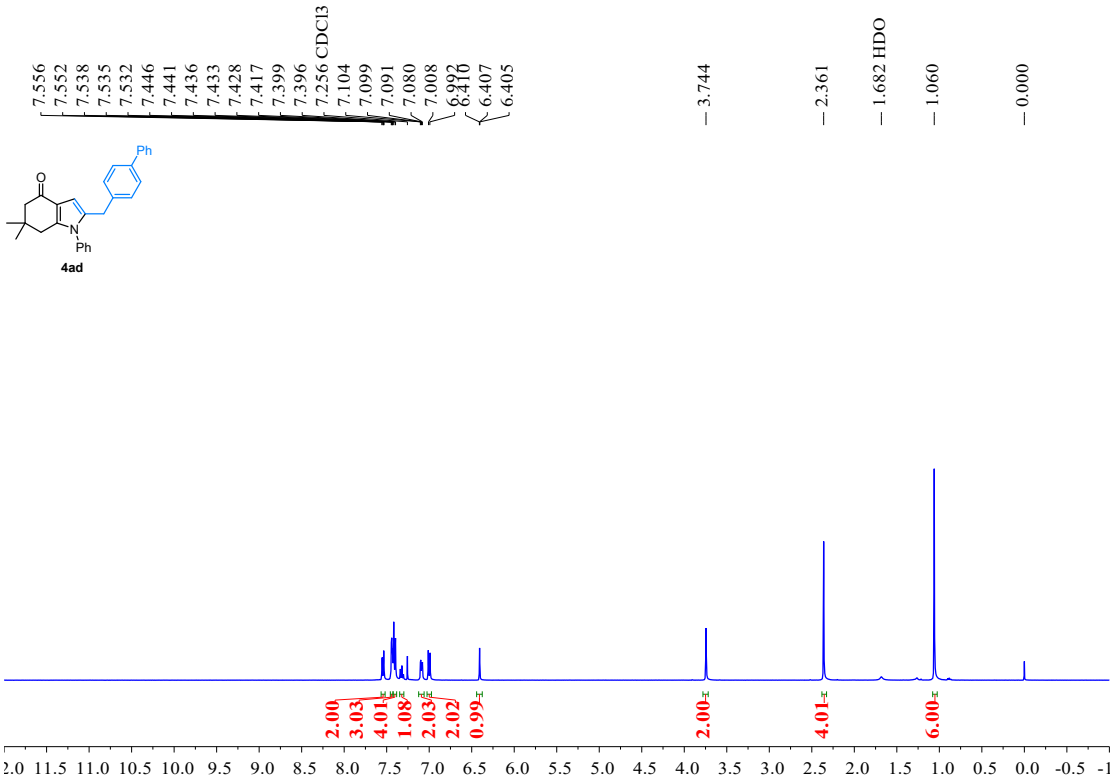
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2.02
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4.01
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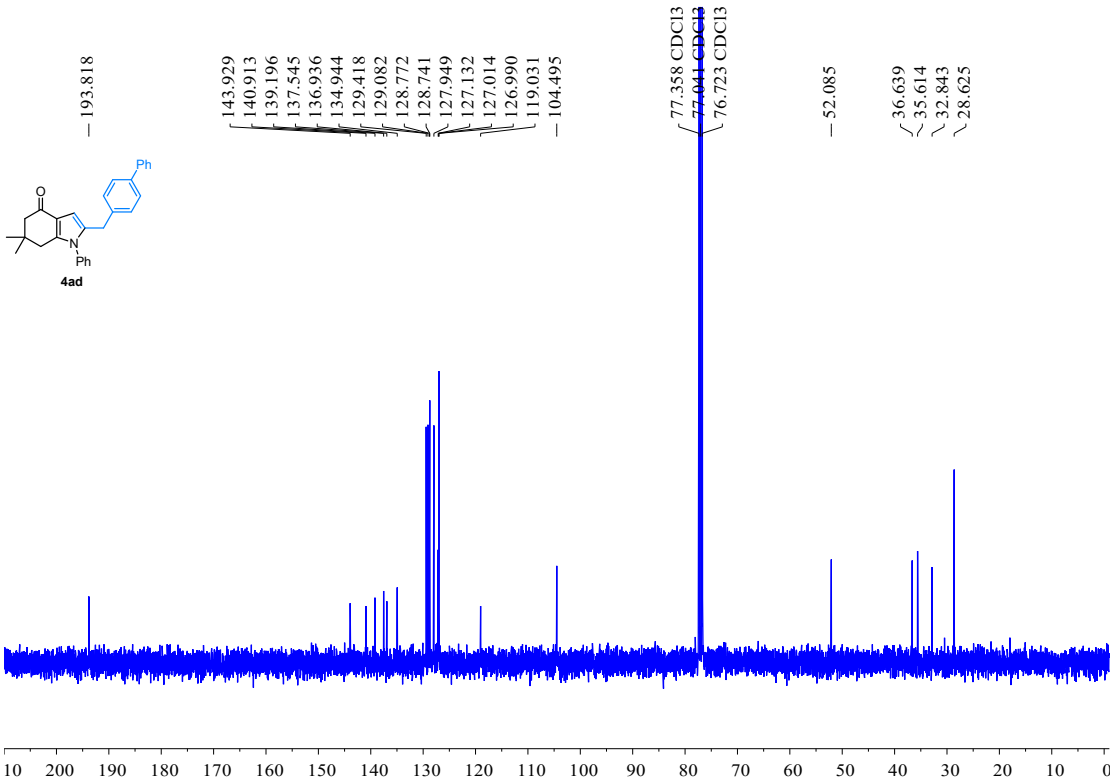
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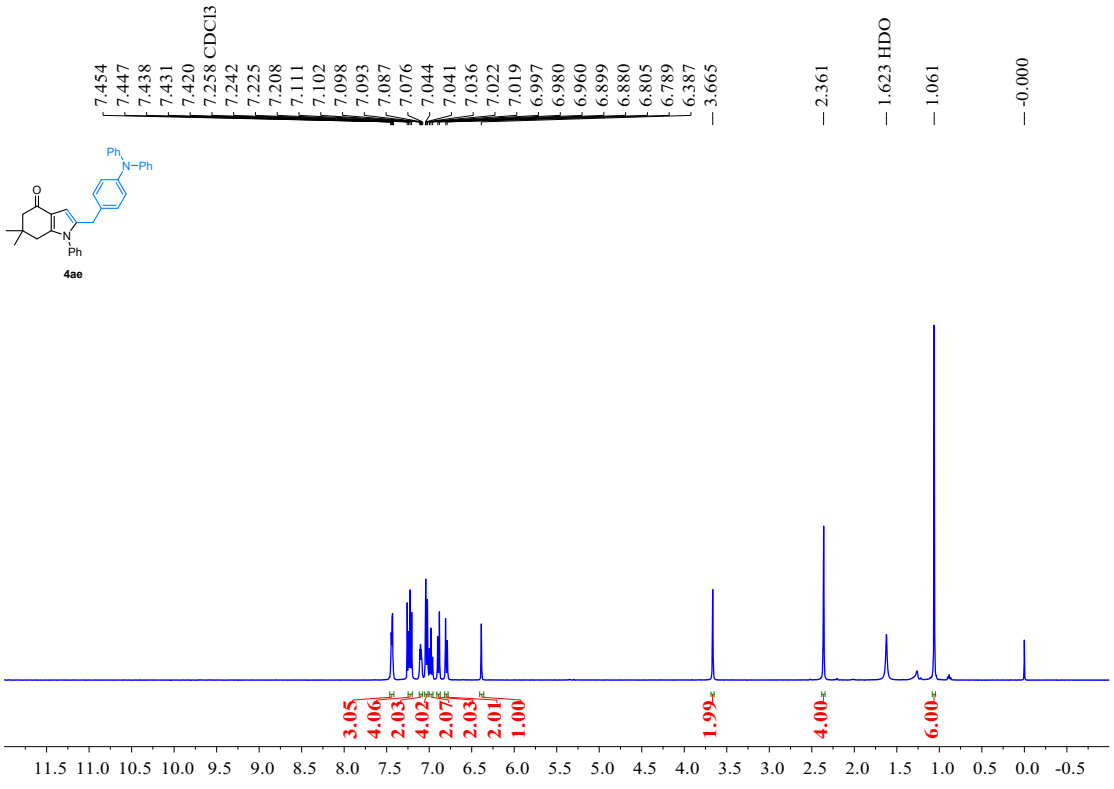
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N–Ph
O
N
Ph
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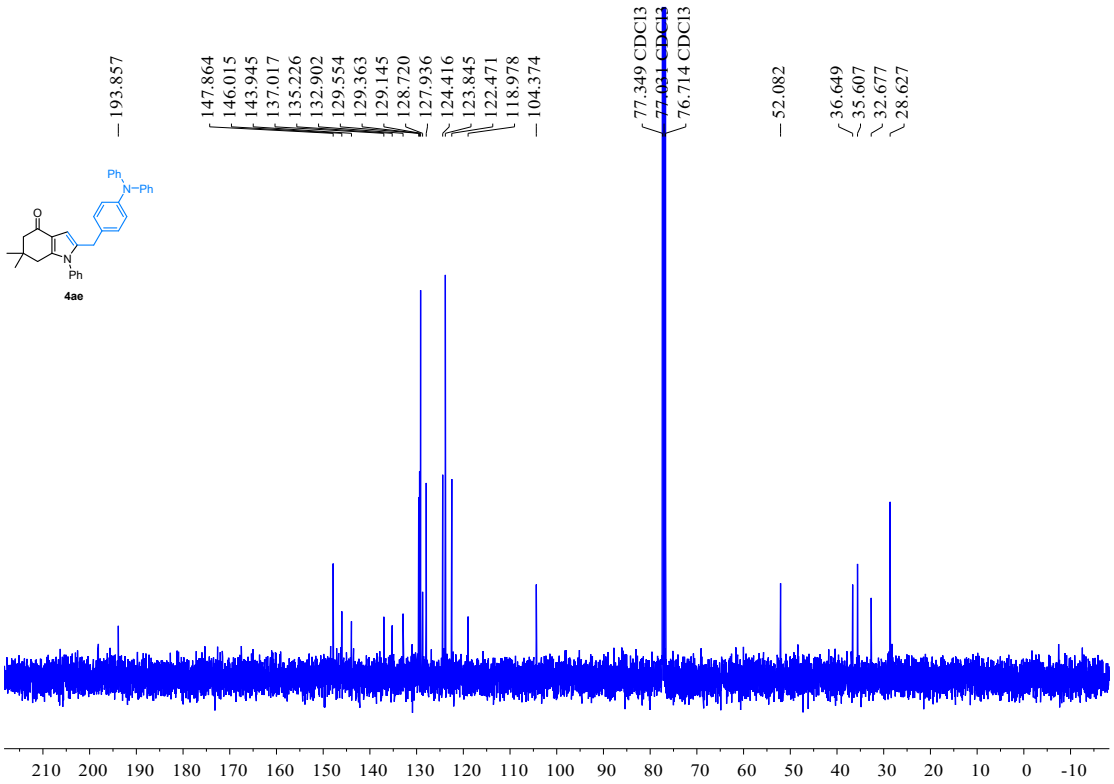
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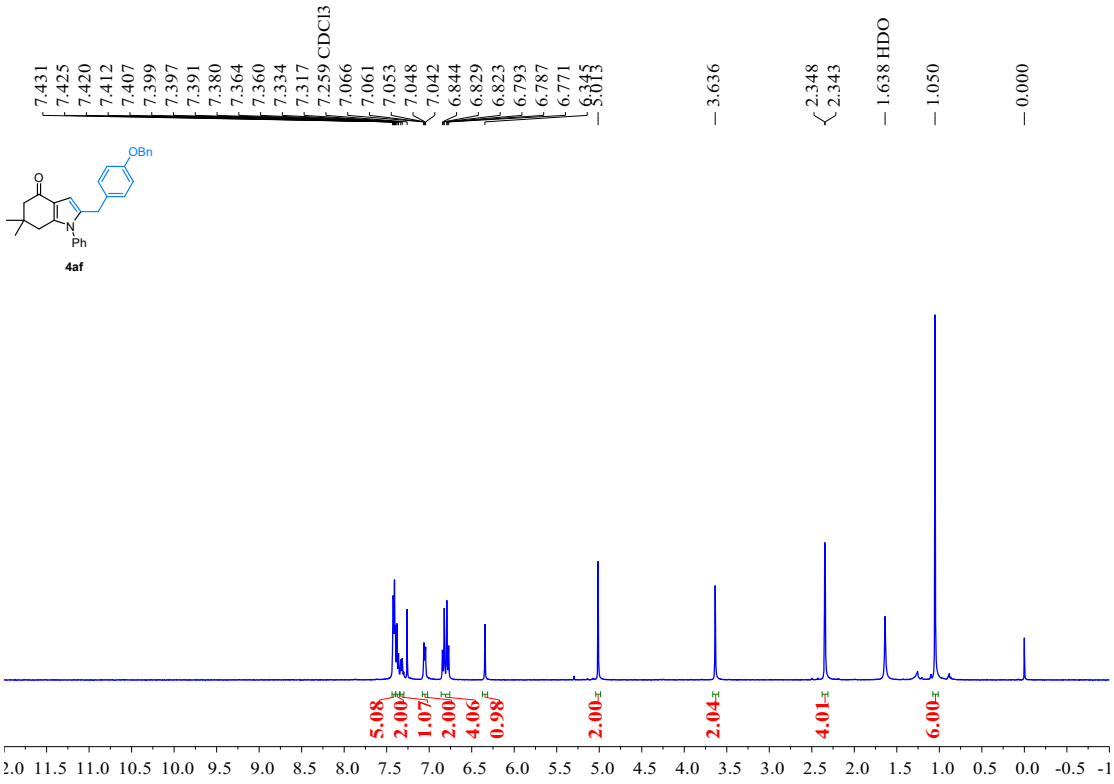
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OBn
O
N
Ph
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5.08
2.00
1.07
2.00
4.06
0.98
2.00
2.04
4.01
6.00
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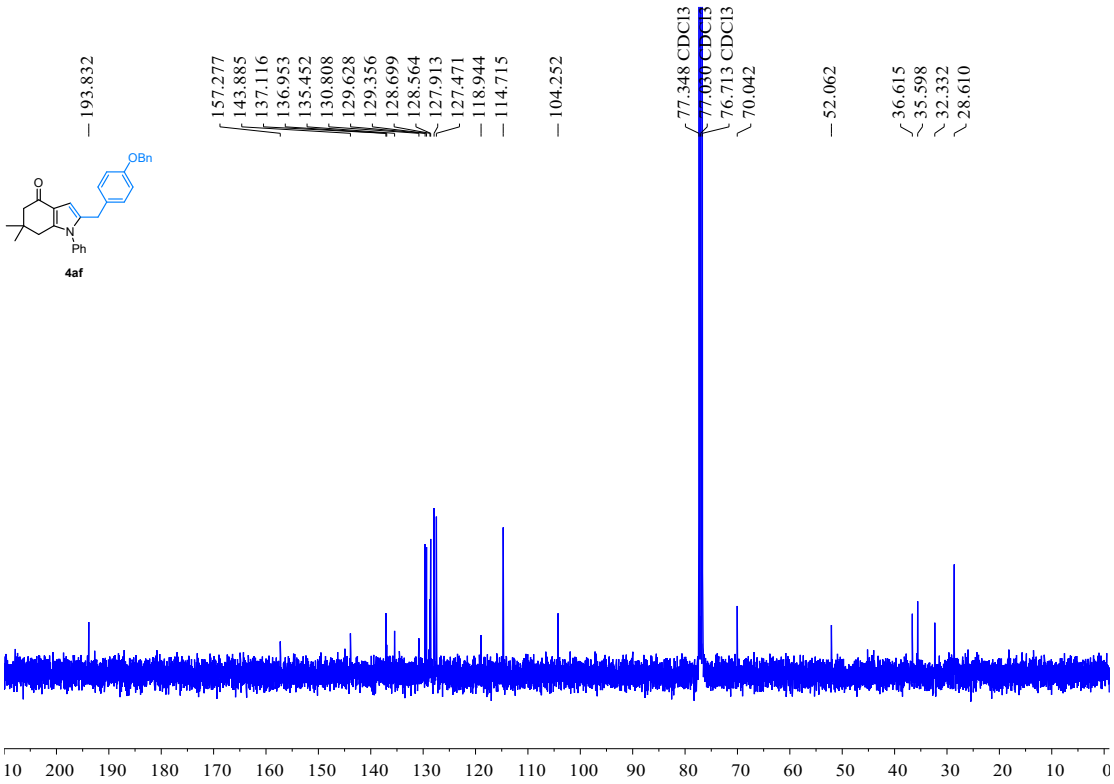
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Ph
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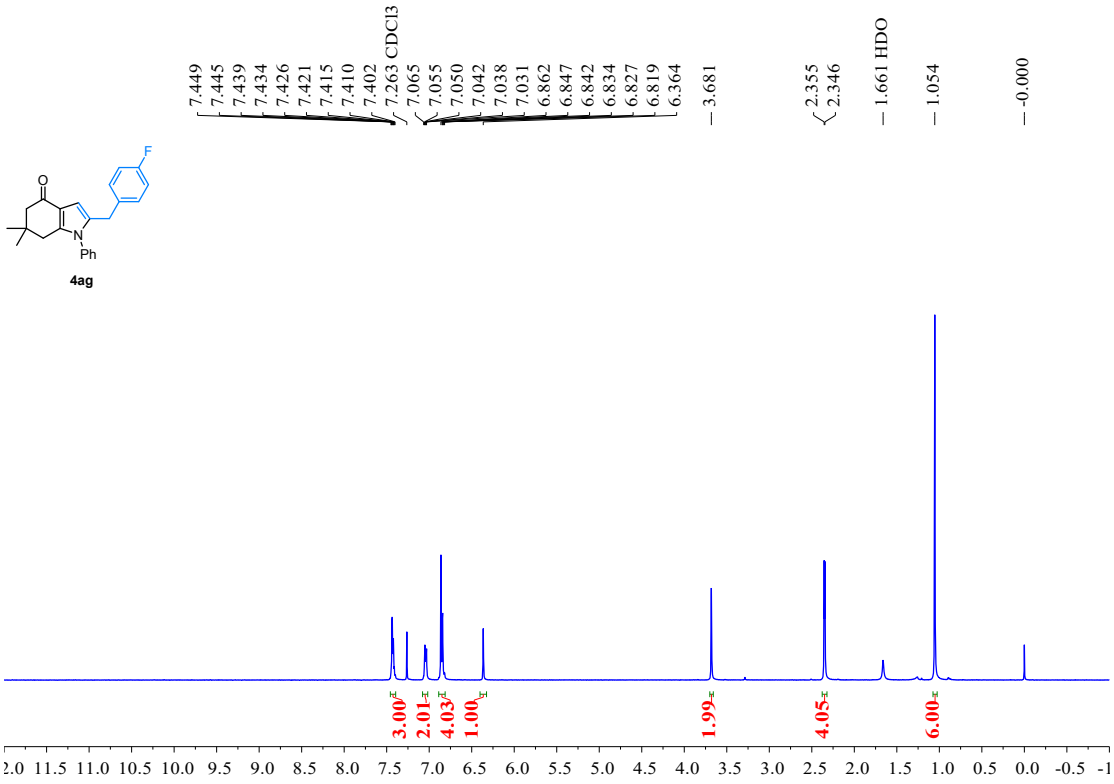
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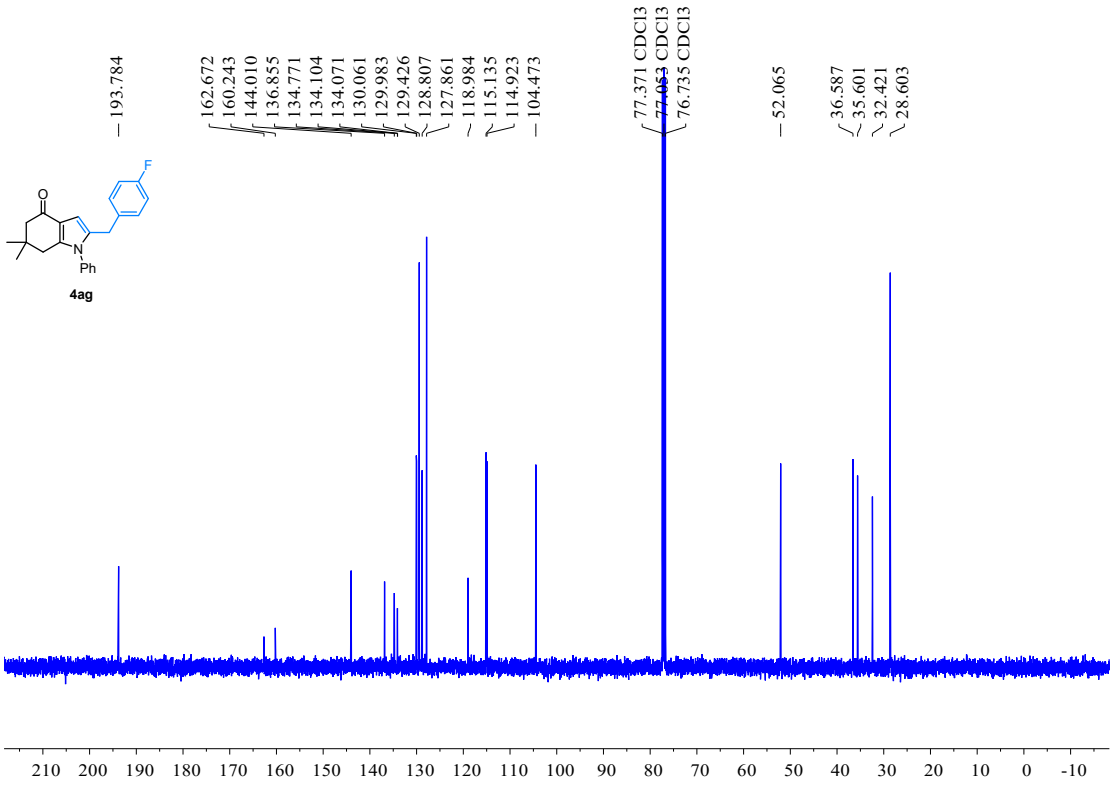
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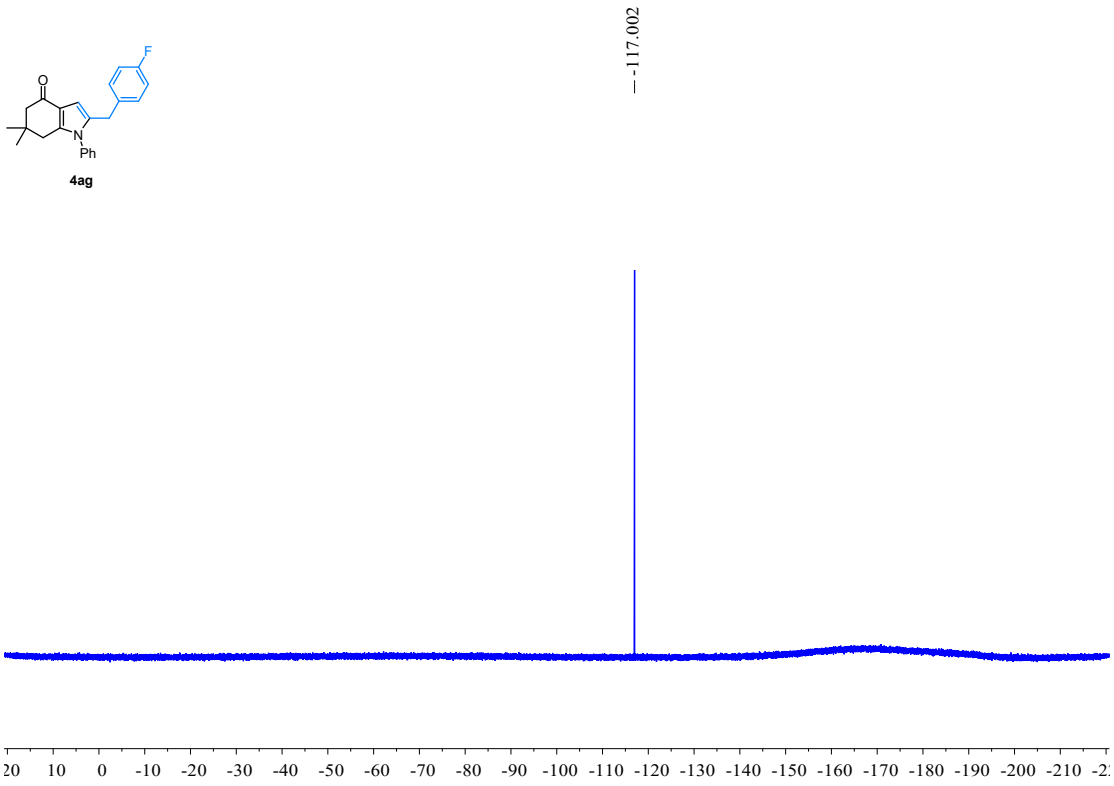
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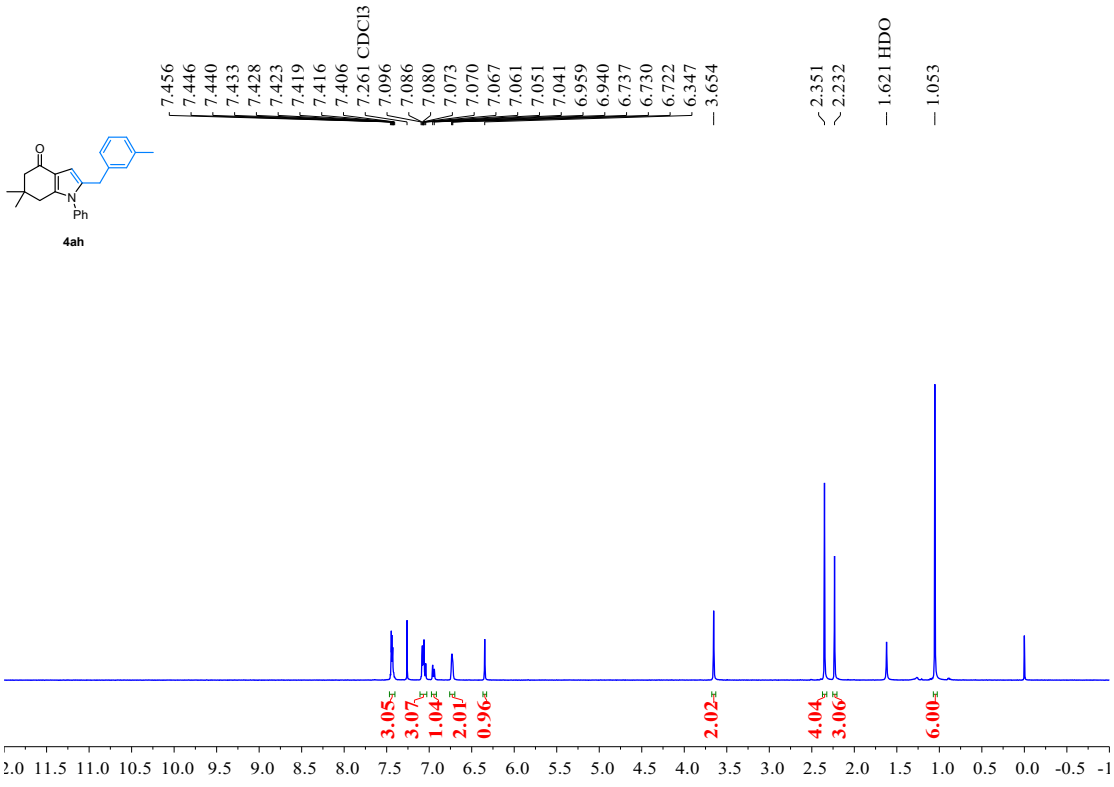
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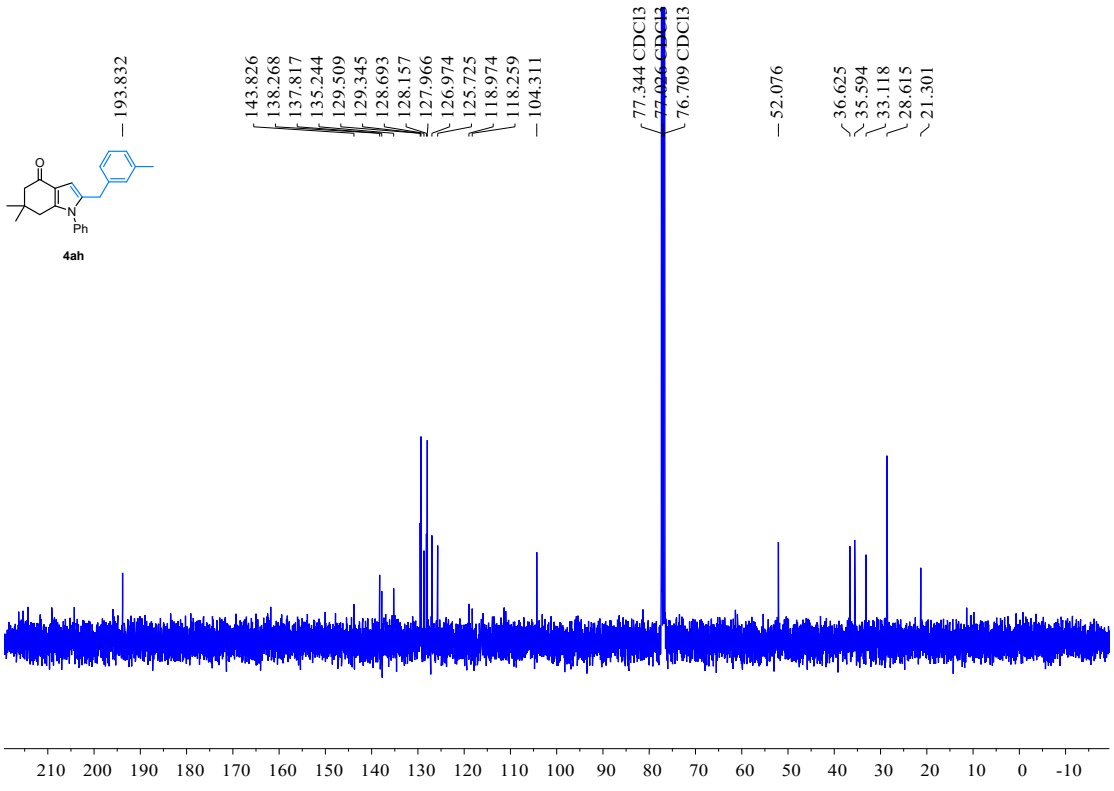
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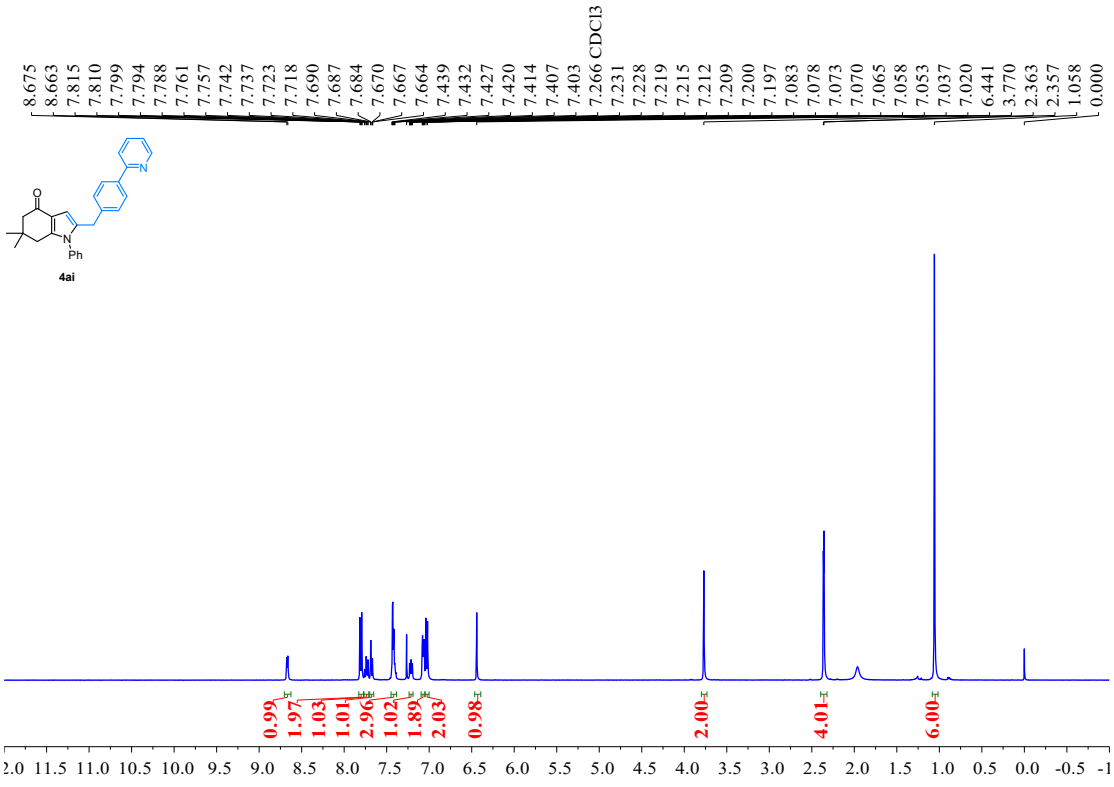
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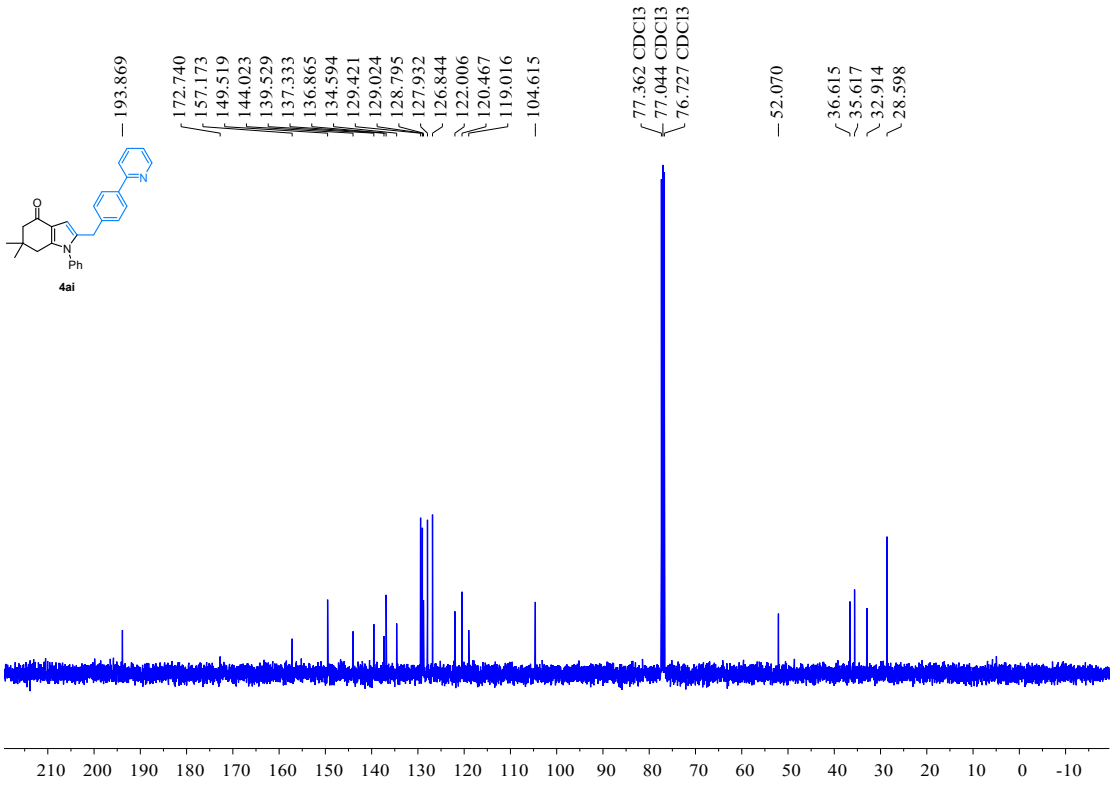
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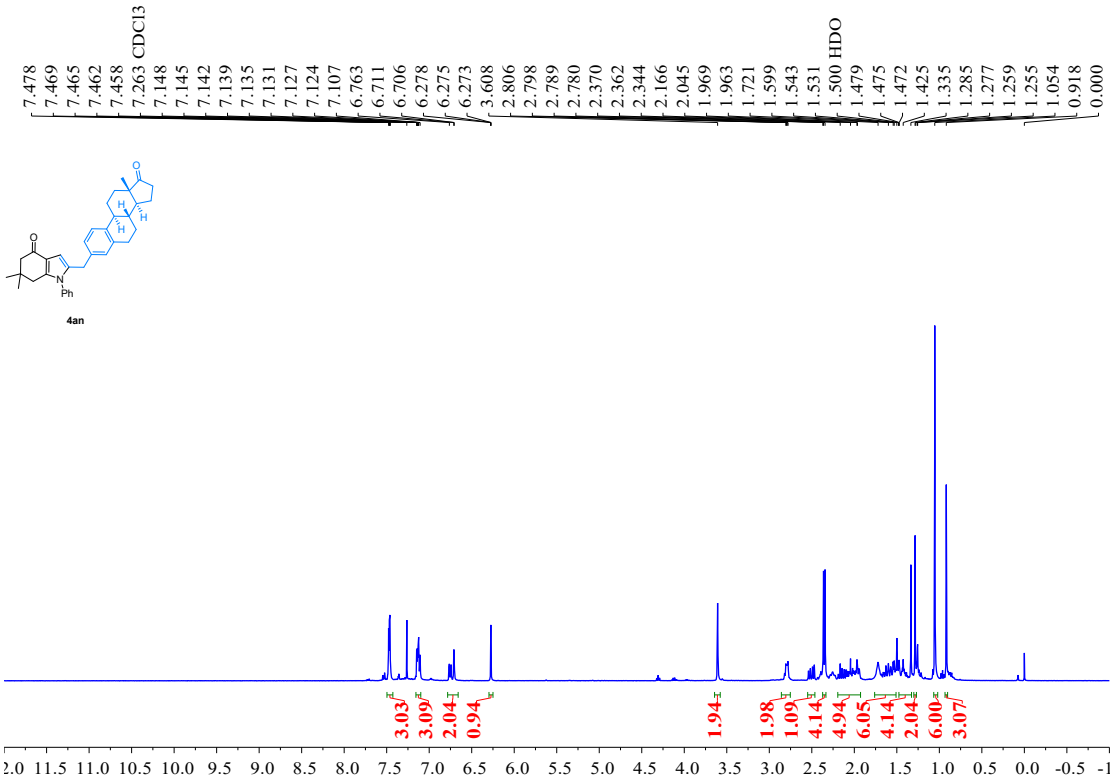
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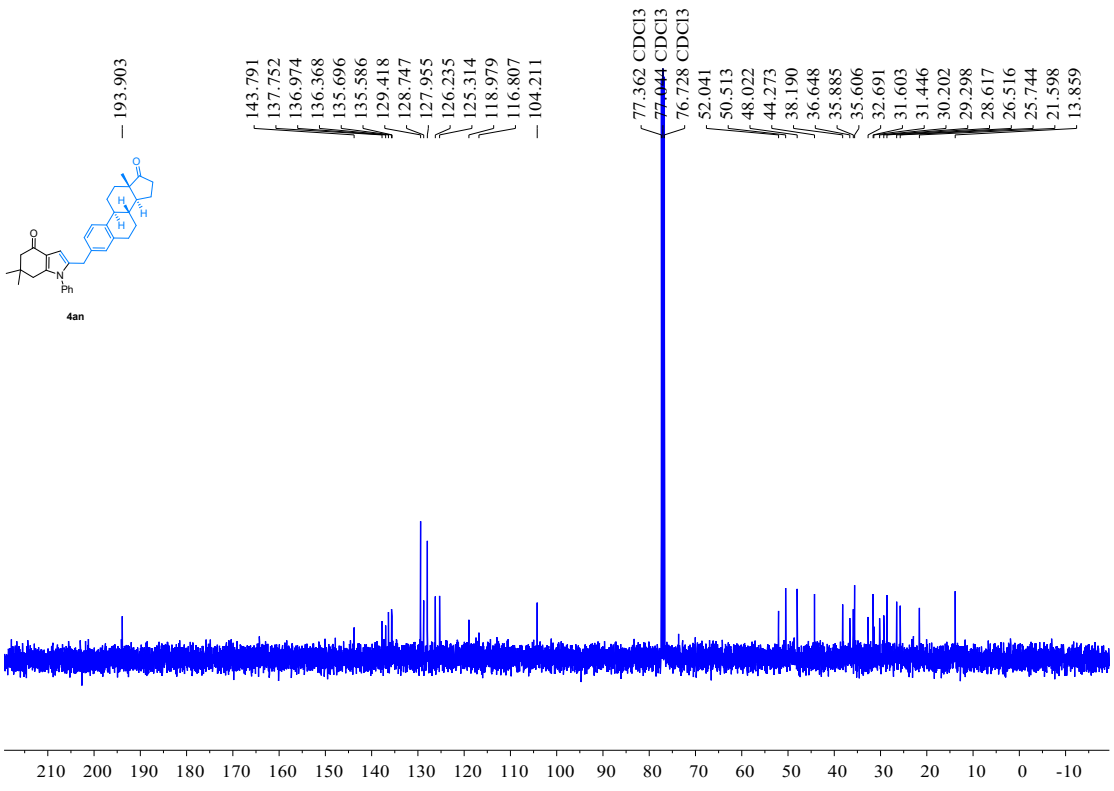
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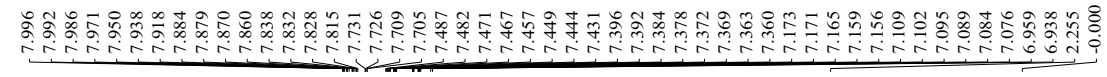
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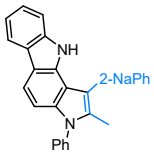
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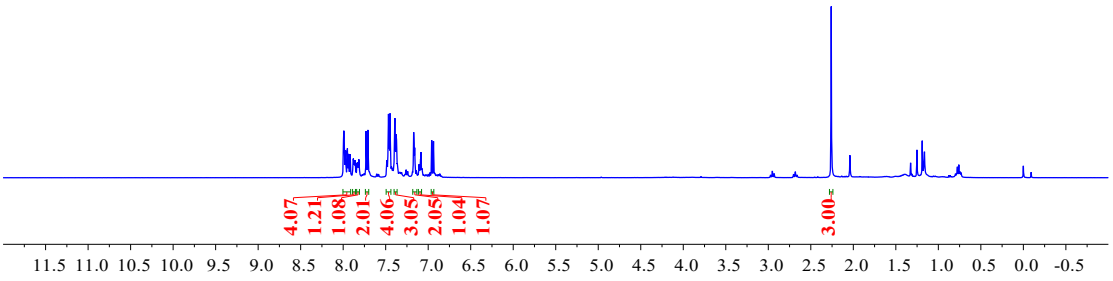
Ph

5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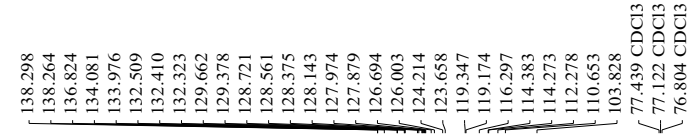
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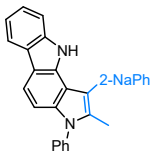
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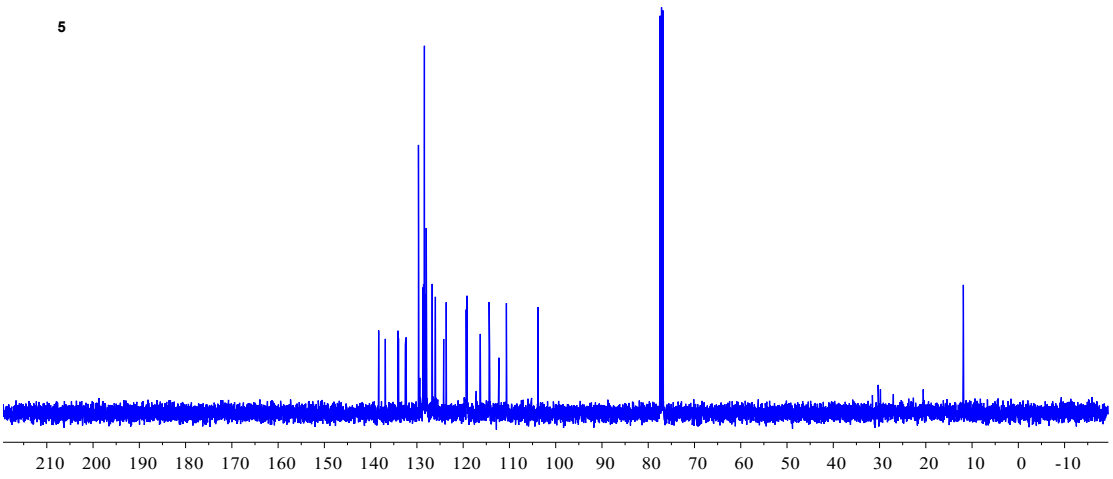
5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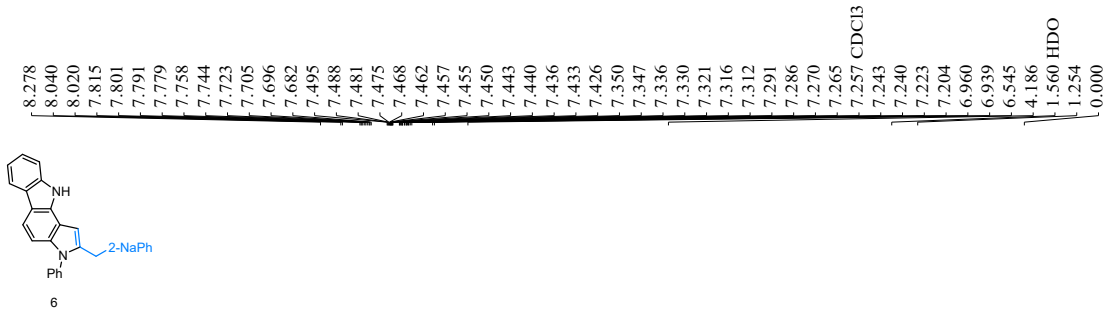
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7.336
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7.291
7.286
7.270
7.265
7.257 CDCl3
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7.240
7.223
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6.545
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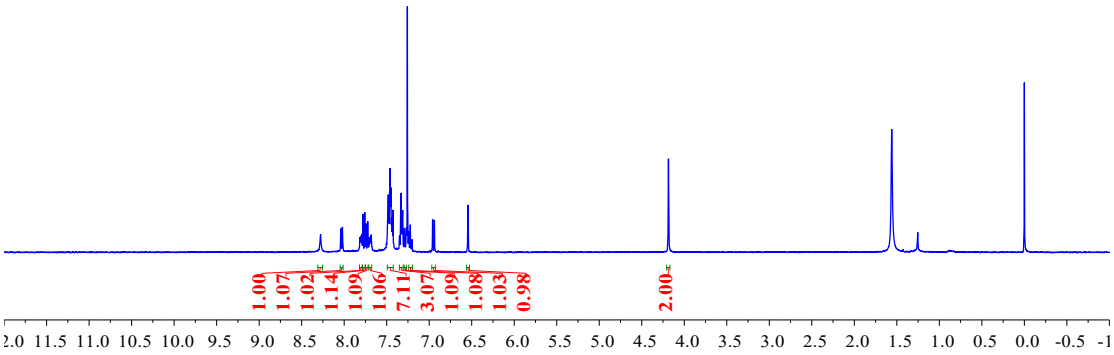
NH
N
Ph
2-NaPh
6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3.07
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1.08
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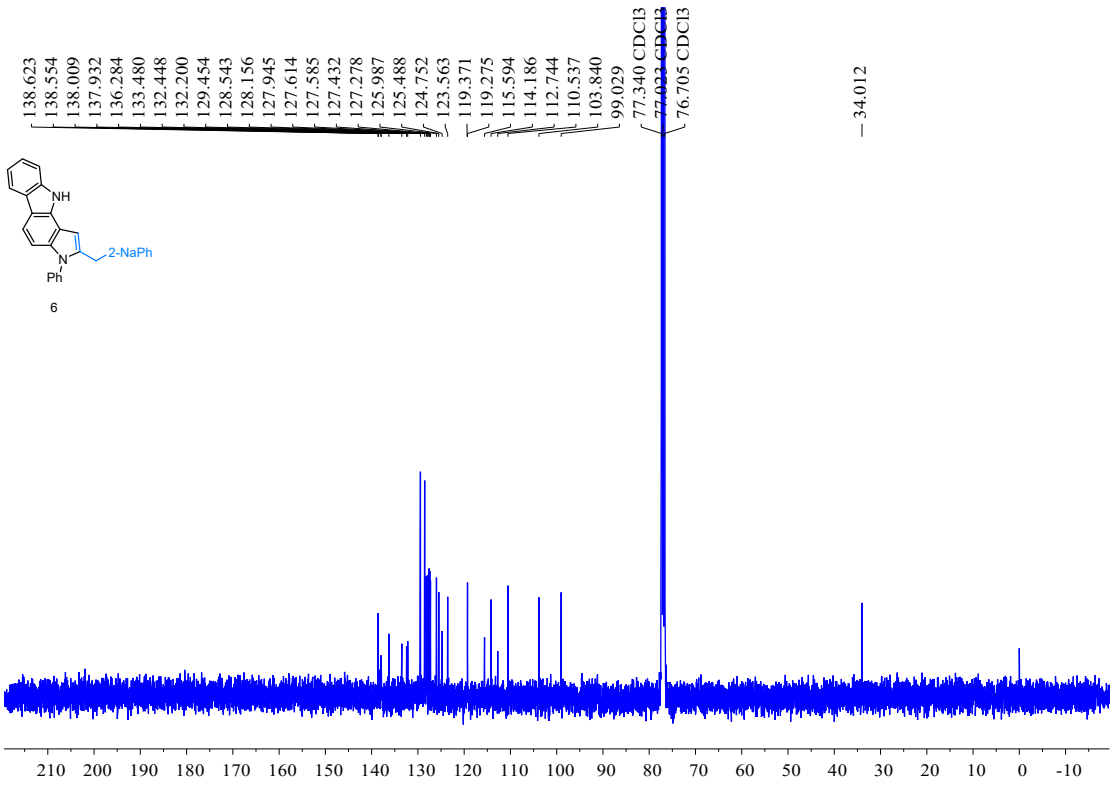
0.98
2.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1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77.023 CDCl3
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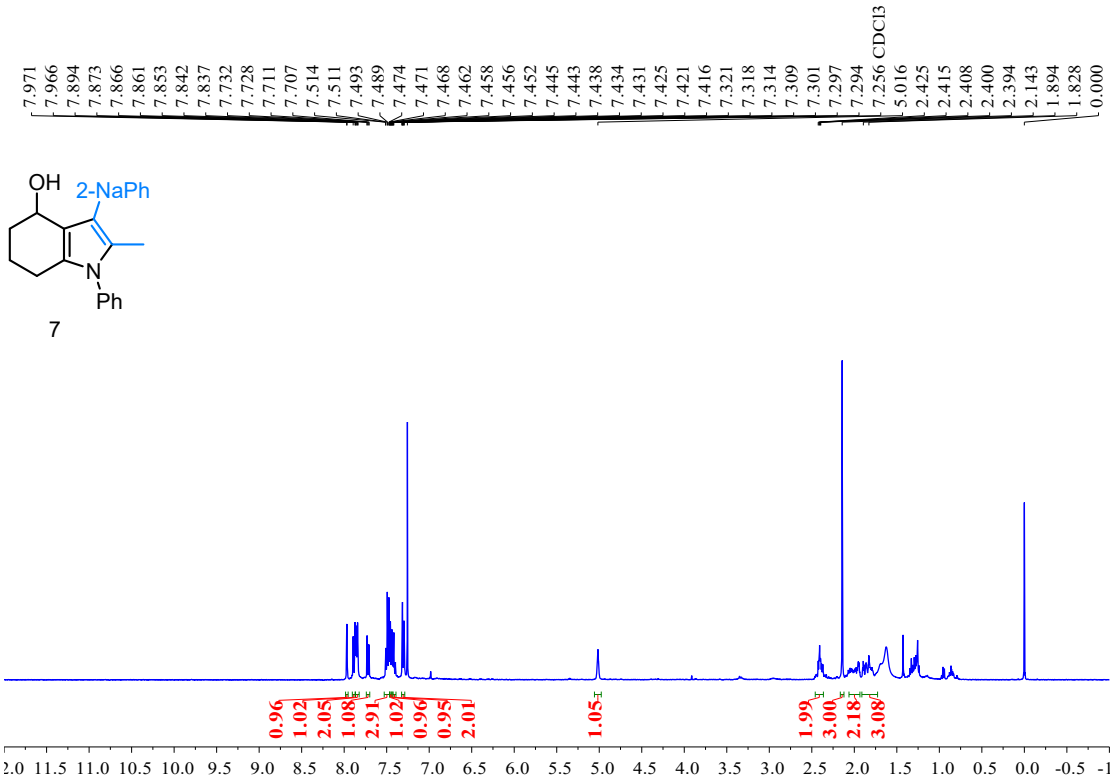
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7.511
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7.474
7.471
7.468
7.462
7.458
7.456
7.452
7.445
7.443
7.438
7.434
7.431
7.425
7.421
7.416
7.321
7.318
7.314
7.309
7.301
7.297
7.294
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2.415
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2.394
2.143
1.894
1.828
0.000
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N
Ph
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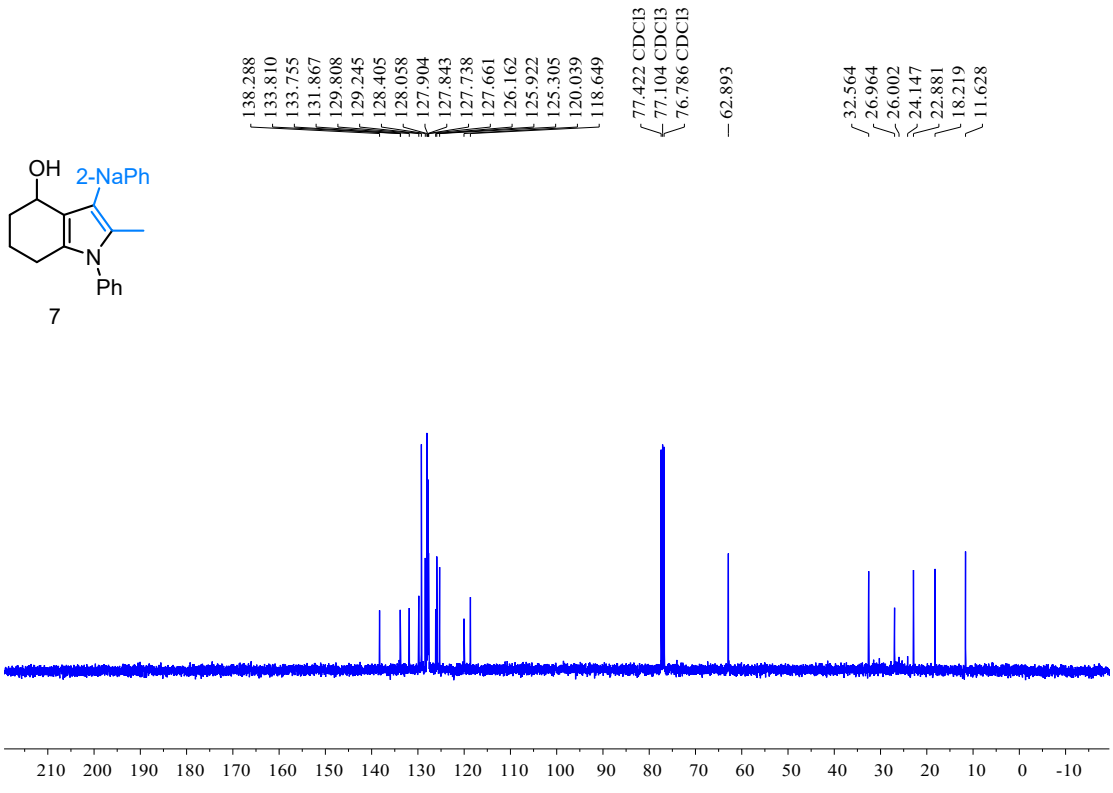
2.05
1.08
2.91
1.02
0.96
0.95
2.01
1.05
1.99
3.00
2.18
3.08
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1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127.661
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125.305
120.039
118.649
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77.104 CDCl3
76.786 CDCl3
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32.564
26.964
26.002
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N
Ph
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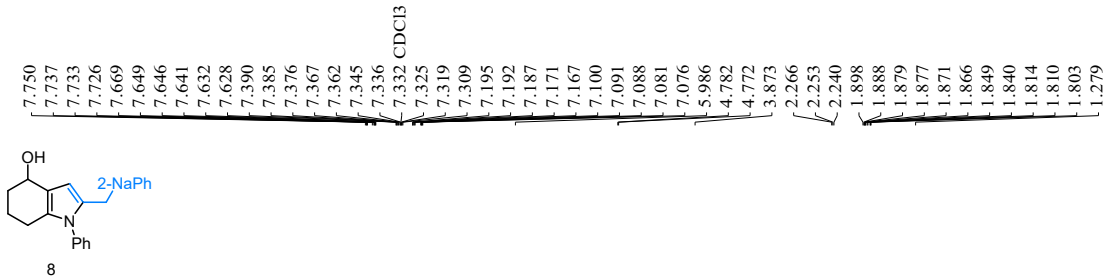
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7.367
7.362
7.345
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7.319
7.309
7.195
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7.171
7.167
7.100
7.091
7.088
7.081
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4.772
3.873
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1.888
1.879
1.877
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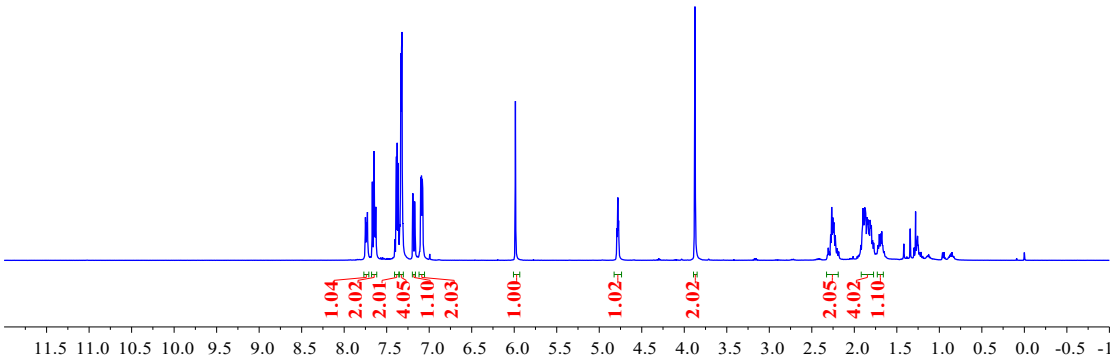
1.810
1.803
1.279

OH
2-NaPh
N
Ph

8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4.05
1.10
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1.00
1.02
2.02
2.05
4.02
1.10
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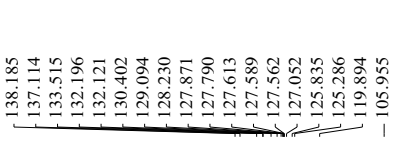
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127.562
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125.286
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105.955
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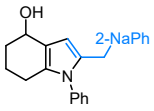
19.189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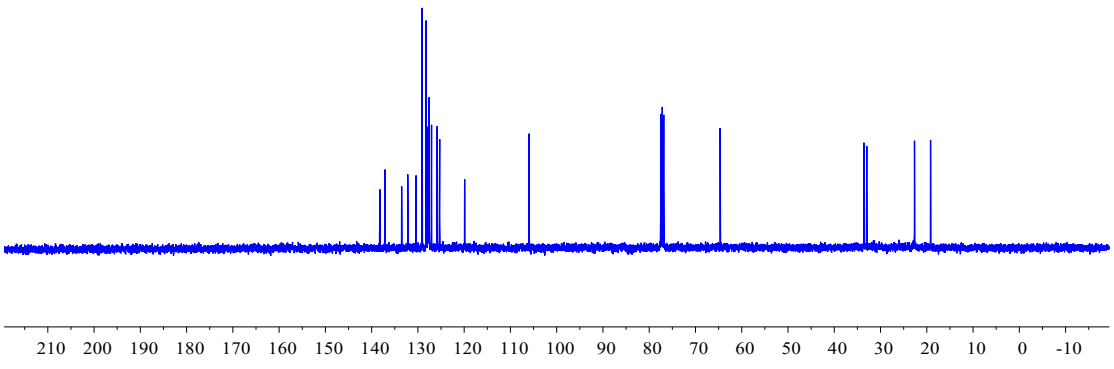
2-NaPh
N
Ph

8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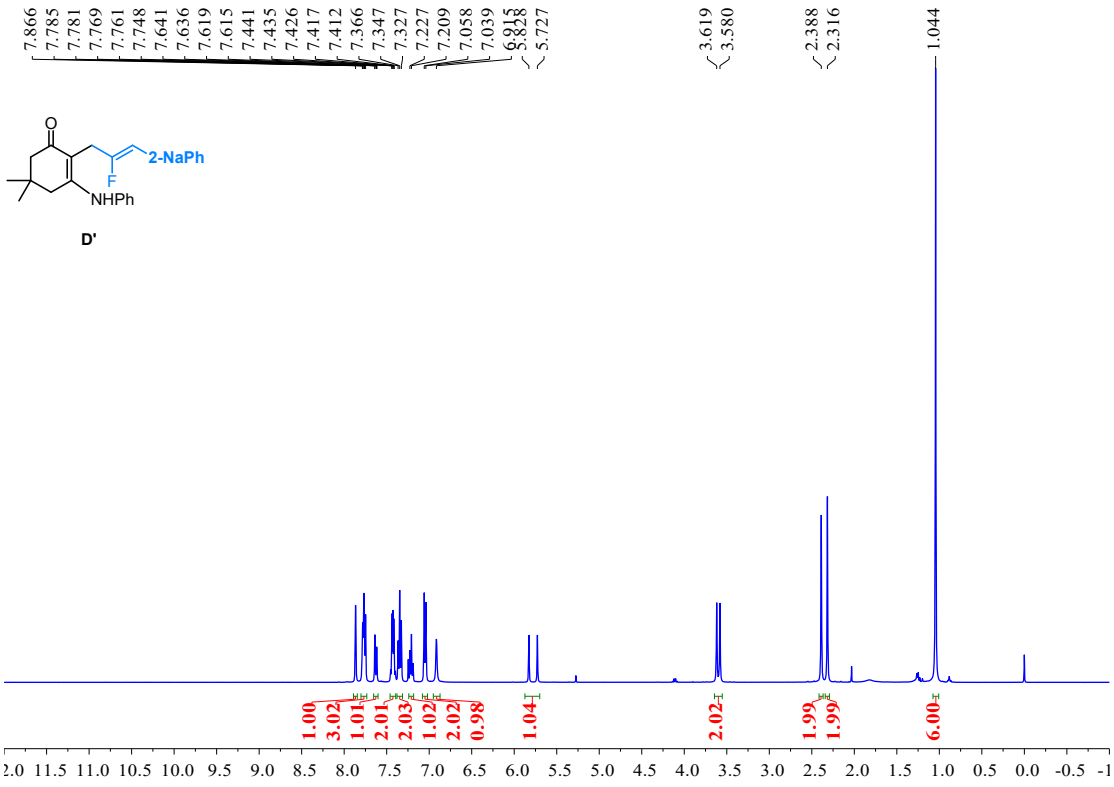
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7.327
7.227
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5.727
3.619
3.580
2.388
2.316
1.044
O
2-NaPh
F
NHPh
D'
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2.03
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1.04
2.02
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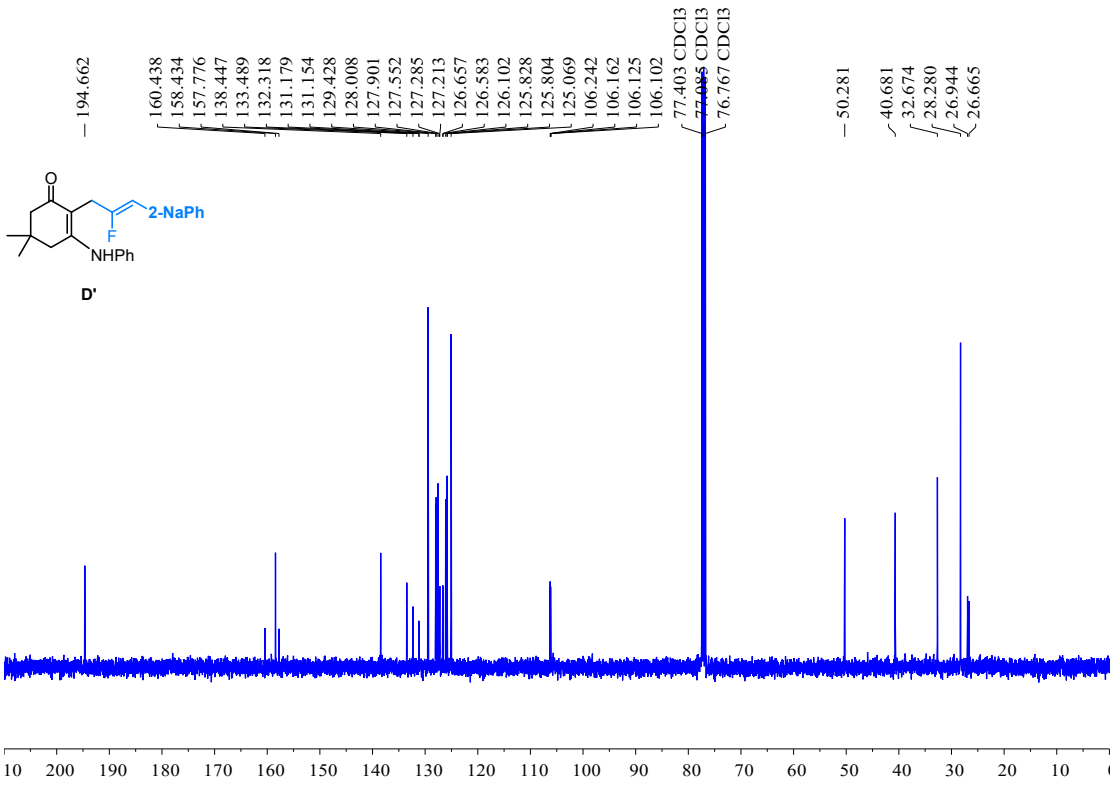
1.99
6.00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126.657
126.583
126.102
125.828
125.804
125.069
106.242
106.162
106.125
106.102
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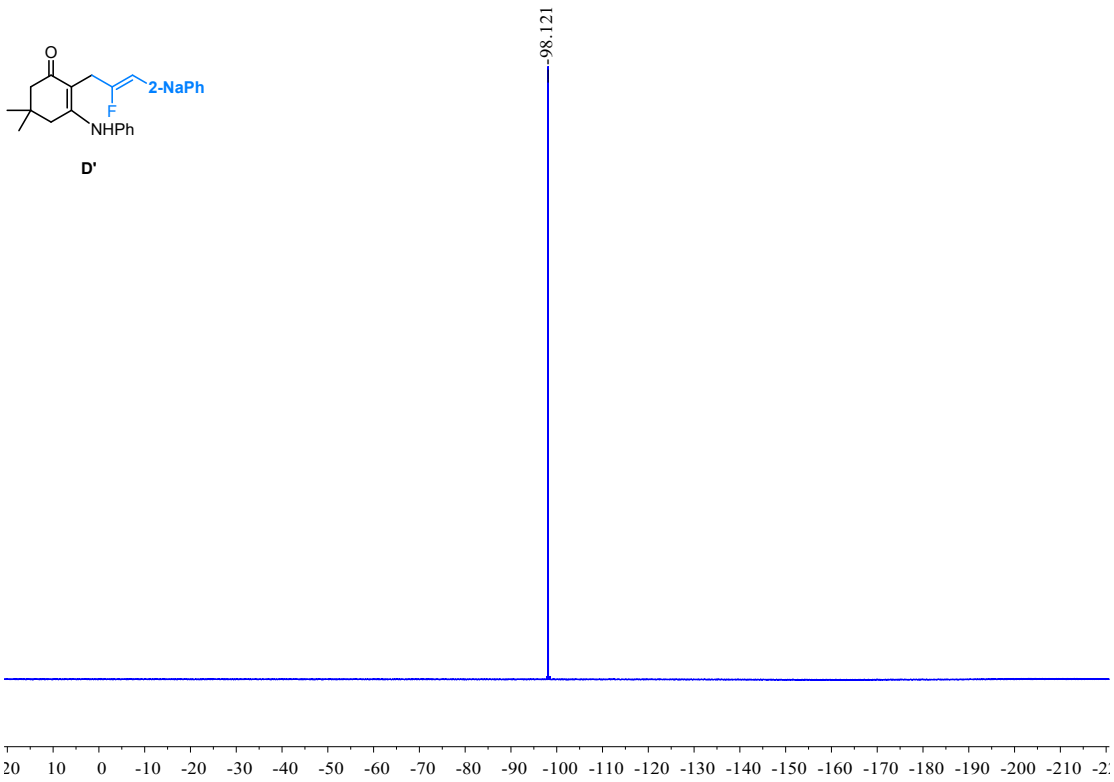
O
2-NaPh
F
NHPh
D'



9. X-Ray crystal structure of 3aa, 4aa

Table 2 Crystal data and structure refinement for 3aa (CCDC: 2303388)

Identification code	**3aa**
Empirical formula	$C_{27}H_{25}NO$
Formula weight	379.48
Temperature/K	296K
Crystal system	monoclinic
Space group	P 21/C
a/Å	17.256(10)
b/Å	10.823(6)
c/ Å	11.830(9)
α/°	90
β/°	103.45(2)
γ/ °	90
Volume/ Å^3	2149(2)
Z	4
ρ_{calc}g/cm^3	1.173
μ/mm^{-1}	0.070
F(000)	808.0
Crystal size/mm^3	0.4*0.35*0.1
Radiation	MoK\a(λ = 0.71073)

2Θ range for data collection/°	2.4272-22.9376
Index ranges	-20≤h≤20, -13≤k≤13, -12≤l≤14
Reflection collected	3928
Independent reflections	1761
Data/parameters	1761/267
Goodness-of-fit on F^2	0.928
Final R indexes [I>=2σ (I)]	$wR_2 = 0.2535$
Final R indexes [all data]	$R_1 = 0.0961$
Ellipsoid contour probability levels (%)	50

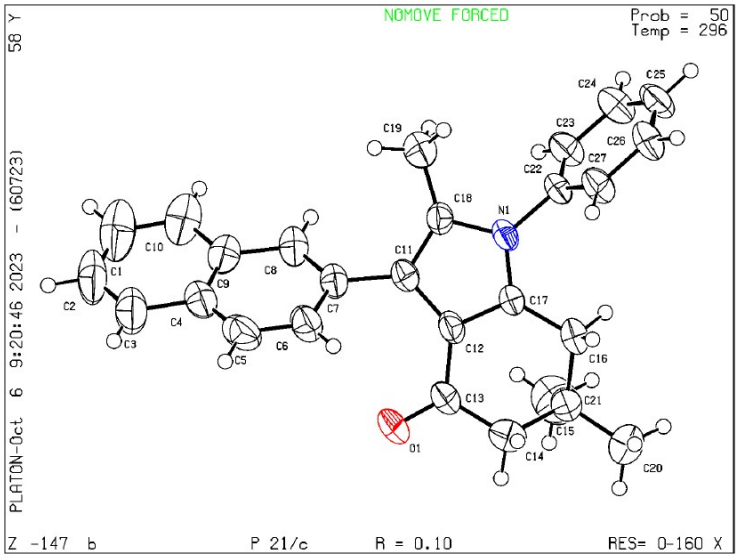


Table 1 Crystal data and structure refinement for 4aa (CCDC: 2303389)

Identification code	**4aa**
Empirical formula	$C_{27}H_{25}NO$
Formula weight	379.48
Temperature/K	296
Crystal system	monoclinic
Space group	P 1 21/C 1
a/Å	8.8172(5)
b/Å	11.7300(8)
c/ Å	20.8491(13)
α/°	90
β/°	100
γ/ °	90
Volume/ $Å^3$	2119.2(2)
Z	8
$\rho_{calc}g/cm^3$	1.189
μ/mm^{-1}	0.071
F(000)	808.0
Crystal size/mm^3	0.6×0.3×0.3
Radiation	MoK\a(λ = 0.71073)
2Θ range for data collection/°	2.35-27

Index ranges	-11≤h≤11, -15≤k≤15, -27≤l≤27
Reflection collected	9924
Independent reflections	4909
Data/parameters	4909/264
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	$wR_2 = 0.1437$
Final R indexes [all data]	$R_1 = 0.0555$
Ellipsoid contour probability levels (%)	50