Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

C(sp^3)-H Activation-Enabled Cross-Coupling of Two Aryl Halides: An Approach to 9,10-Dihydrophenanthrenes

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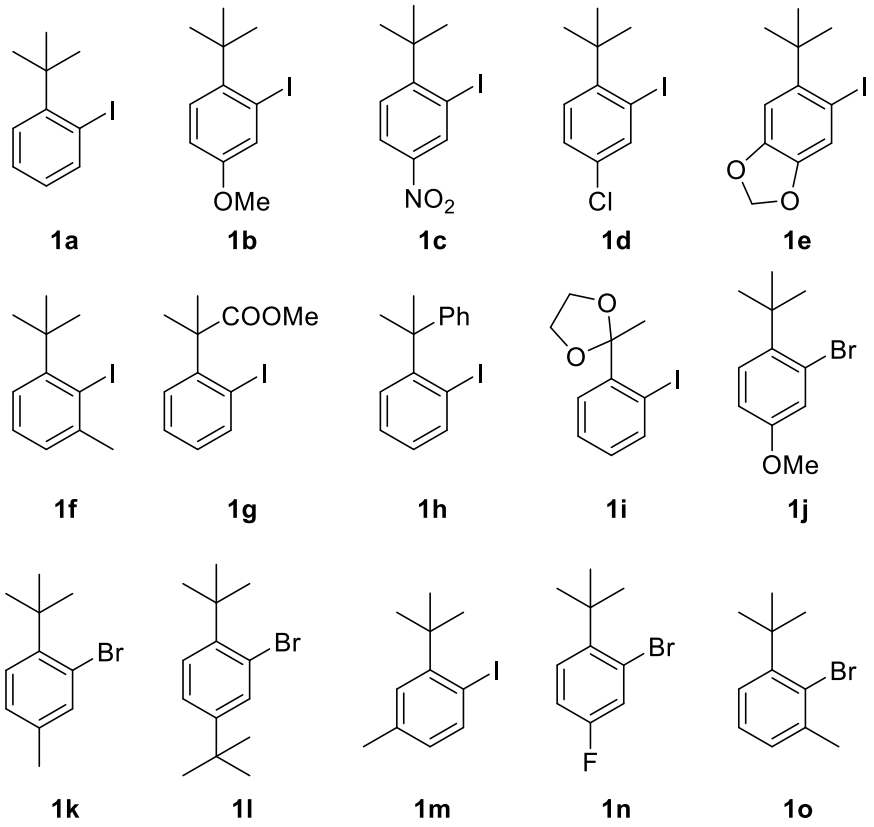
Contents

1. General Information

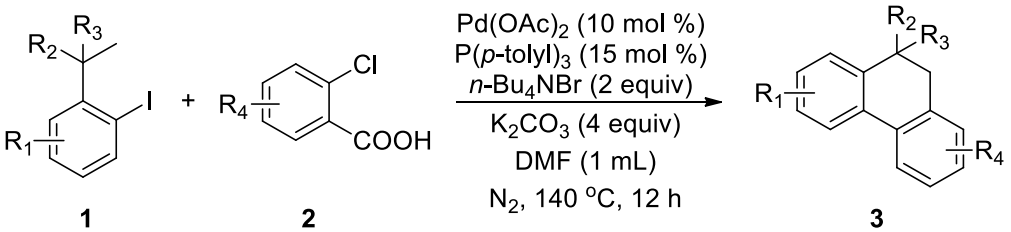
$Pd(OAc)_2$ was purchased from Strem Chemicals. All the solvents were purified by distillation prior to use. The substrates were synthesized according to reported procedures. Unless otherwise noted, the other commercial chemicals were used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker ARX400 instrument (400 MHz) or Bruker DRX-600 instrument (600 MHz). High resolution mass spectra were measured on Bruker micrOTOF II ESI-TOF mass spectrometer. GC-MS data were tested with ThermoFisher Trace1300-ISQ (EI). NMR spectra were recorded in $CDCl_3$. ^1H NMR spectra were referenced to residual $CHCl_3$ at 7.26 ppm, and ^{13}C NMR spectra were referenced to the central peak of $CDCl_3$ at 77.0 ppm. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

2. Synthesis of the Substrates



Substrate **1a**-**1o** were prepared by following the reported procedures.[1] All the 2-chlorobenzoic acids were commercially available.

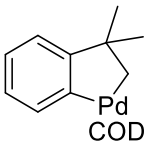
3. General Procedure for the Coupling Reaction



A 25 mL Schlenk-type tube (with a Teflon screw cap and a side arm) equipped with a magnetic

stir bar was charged with $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), P(*p*-tol)$_3$ (4.5 mg, 0.015 mmol), K_2CO_3 (55.2 mg, 0.4 mmol), *n*-Bu_4NCl (55.6 mg, 0.2 mmol), the corresponding aryl halide (0.1 mmol), the corresponding 2-chlorobenzoic acid (0.15 mmol), and DMF (1 mL). The reaction was frozen with liquid nitrogen and then the tube was evacuated and backfilled with nitrogen (10 times). The reaction was stirred at 140 °C for 12 h. Upon completion, the reaction mixture was cooled to room temperature, diluted with EtOAc (15 mL) and washed with brine (15 mL, 3 times). The organic phase was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by preparative silica gel TLC to afford the corresponding products.

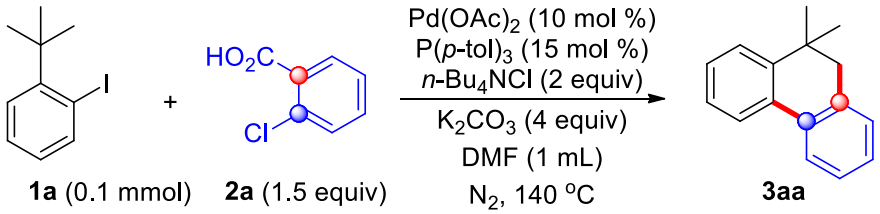
4. Synthesis of Palladacycle 1a-C



1a-C was prepared by following reported procedure.[2]

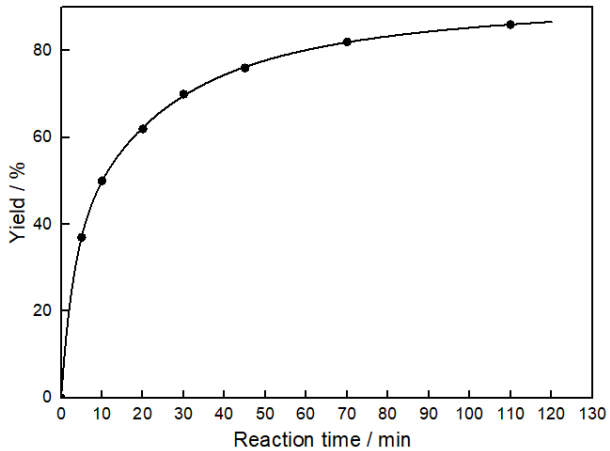
5. Time-Course of Yields

Seven reactions of **1a** and **2a** were carried out by following the general procedure of the coupling reaction. Each of the reactions was stopped at the times indicated in the following table. The reactions were worked up by following the general procedure and the yields were determined by ^{1}H NMR analysis of the crude reaction mixture using $CHCl_2CHCl_2$ as the internal standard.



1a (0.1 mmol) **2a** (1.5 equiv) **3aa**

Entry	1	2	3	4	5	6	7
Reaction time (minutes)	5	10	20	30	45	70	110
Yield (%)	37	50	62	70	76	82	86



6 Crystal Data and Structure Refinement for 3ad

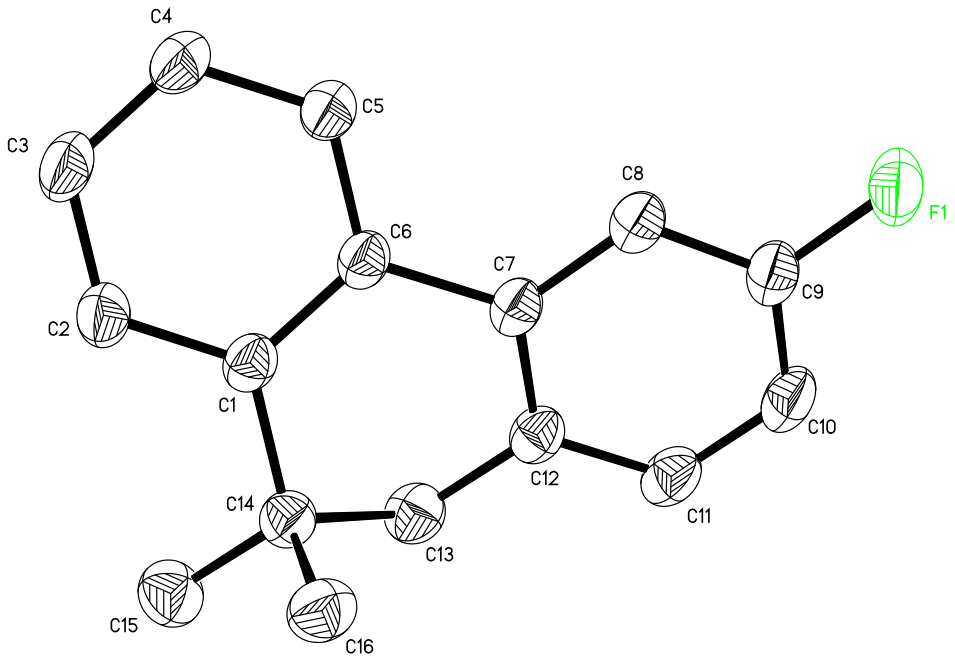


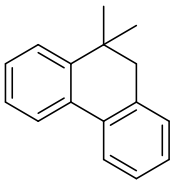
Table S1. Crystal data for 3ad

Identification code	200611a_a	
Empirical formula	C16 H15 F	
Formula weight	226.28	
Temperature	281(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 14.697(8) Å	α= 90°.
	b = 5.790(3) Å	β= 104.759(19)°.
	c = 14.578(8) Å	γ = 90°.
Volume	1199.5(11) $Å^3$	
Z	4	
Density (calculated)	1.253 Mg/m^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	480	
Crystal size	0.290 x 0.280 x 0.070 mm^3	
Theta range for data collection	2.867 to 25.334°.	
Index ranges	-17<=h<=17, -6<=k<=6, -17<=l<=17	

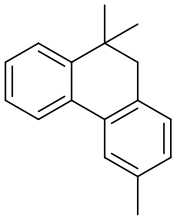
Reflections collected	13101
Independent reflections	2173 [R(int) = 0.0505]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2173 / 0 / 157
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0570, wR2 = 0.1493
R indices (all data)	R1 = 0.0756, wR2 = 0.1688
Extinction coefficient	0.026(5)
Largest diff. peak and hole	0.198 and -0.208 e.$Å^{-3}$

CCDC 2013468.

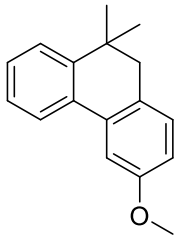
7 Characterization of the Products



9,9-dimethyl-9,10-dihydrophenanthrene (**3aa**): colorless oil (18.3 mg, 88%)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.42 (dd, J= 3.4, 5.7 Hz, 1H), 7.31-7.29 (m, 3H), 7.23 (dt, J= 1.0, 7.4 Hz, 1H), 7.20 (d, J= 7.3 Hz, 1H), 2.78 (s, 2H), 1.26 (s, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.42, 136.03, 134.18, 133.25, 128.65, 127.95, 127.43, 126.85, 126.55, 124.26, 124.09, 123.51, 44.05, 34.16, 27.93.
HRMS (ESI-TOF) *m/z*: calculated for $C_{16}H_{17}^+$: 209.1330 $(M + H)^+$, found: 209.1337.



3,9,9-trimethyl-9,10-dihydrophenanthrene (**3ab**): colorless oil (15.5 mg, 70%)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78-7.76 (m, 1H), 7.57 (s, 1H), 7.41-7.40 (m, 1H), 7.29-7.28 (m, 2H), 7.08 (d, J= 7.8 Hz, 1H), 7.05 (d, J= 7.8 Hz, 1H), 2.73 (s, 2H), 2.40 (s, 3H), 1.25 (s, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 145.53, 136.16, 133.97, 133.36, 133.03, 128.52, 128.16, 127.82, 126.49, 124.26, 124.25, 124.02, 43.66, 34.22, 27.96, 21.49.
MS (GC-MS) *m/z*: calculated for $C_{17}H_{18}$: 222.14, found: 222.14.

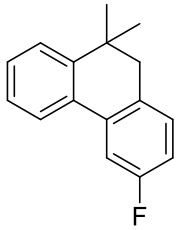


3-methoxy-9,9-dimethyl-9,10-dihydrophenanthrene (**3ac**): colorless oil (22.6 mg, 95%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75-7.73 (m, 1H), 7.42- 7.40 (m, 1H), 7.31-7.29 (m, 3H), 7.11 (d, J= 7.8 Hz, 1H), 6.79 (dt, J= 1.2, 8.4 Hz, 1H), 3.86 (s, 3H), 2.71 (s, 2H), 1.25 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.71, 145.65, 135.19, 133.23, 129.41, 128.40, 128.10, 126.53, 124.33, 124.11, 112.66, 109.40, 55.40, 43.20, 34.33, 27.96.

MS (GC-MS) *m/z*: calculated for $C_{17}H_{18}O$: 238.14, found: 238.13.

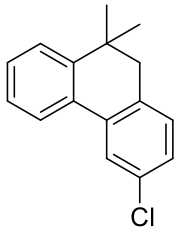


3-fluoro-9,9-dimethyl-9,10-dihydrophenanthrene (**3ad**): colorless solid (19.4 mg, 86%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70-7.68 (m, 1H), 7.45-7.41 (m, 2H), 7.34-7.29 (m, 2H), 7.14(dd, J= 6.0, 8.4 Hz, 1H), 6.92 (dt, J= 2.4, 8.4 Hz, 1H), 2.73 (s, 2H), 1.25 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.21 (d, J= 239.6 Hz), 145.45, 135.99 (d, J= 7.5 Hz), 132.42 (d, J= 1.8 Hz), 131.51 (d, J= 2.6 Hz), 129.83 (d, J= 7.8 Hz), 128.59, 126.68, 124.31 (d, J= 26.1 Hz), 113.93 (d, J= 21.3 Hz), 110.34 (d, J= 22.2 Hz), 43.22, 34.24, 27.90.

MS (GC-MS) *m/z*: calculated for $C_{16}H_{15}F$: 222.12, found: 222.12.

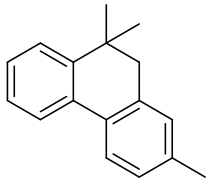


3-chloro-9,9-dimethyl-9,10-dihydrophenanthrene (**3ae**): brown solid (9.9 mg, 41%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72-7.71 (m, 2H), 7.43-7.41 (m, 1H), 7.34-7.29 (m, 2H), 7.19 (dd, J= 2.4, 7.8 Hz, 1H), 7.13 (d, J= 8.4 Hz, 1H), 2.73 (s, 2H), 1.25 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.44, 135.92, 132.49, 132.11, 129.90, 128.63, 127.20, 126.71, 124.39, 124.18, 123.64, 43.37, 34.15, 27.89.

MS (GC-MS) *m/z*: calculated for $C_{16}H_{15}Cl$: 242.09, found: 242.09.

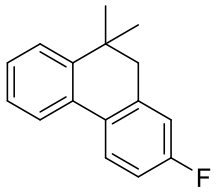


2,9,9-trimethyl-9,10-dihydrophenanthrene (**3af**): brown solid (15.5 mg, 70%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75-7.74 (m ,1H), 7.65 (d, J= 7.8 Hz, 1H), 7.41-7.39 (m, 1H), 7.30-7.27 (m, 2H), 7.11 (d, J= 7.8 Hz, 1H), 7.01 (s, 1H), 2.74 (s, 2H), 2.36 (s, 3H), 1.25 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.11, 137.21, 135.92, 133.33, 131.44, 129.38, 127.56, 126.49, 124.21, 123.78, 123.42, 44.06, 34.19, 27.96, 21.23.

MS (GC-MS) *m/z*: calculated for $C_{17}H_{18}$: 222.14, found: 222.14.

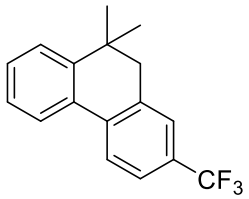


2-fluoro-9,9-dimethyl-9,10-dihydrophenanthrene (**3ag**): colorless oil (17.6 mg, 78%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71-7.69 (m, 2H), 7.41-7.40 (m, 1H), 7.30-7.27 (m, 2H), 6.98 (dt, J= 3.0, 9.0 Hz, 1H), 6.91 (dd, J= 3.0, 9.0 Hz, 1H), 2.75 (s, 2H), 1.25 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.29 (d, J= 244.5 Hz), 144.81, 138.42 (d, J= 7.7 Hz), 132.53, 130.36 (d, J= 3.2 Hz), 127.85, 126.67, 125.20 (d, J= 8.3 Hz), 124.33, 123.86, 115.36 (d, J= 21.0 Hz), 113.61 (d, J= 21.3 Hz), 44.09, 34.16, 27.84.

MS (GC-MS) *m/z*: calculated for $C_{16}H_{15}F$: 222.12, found: 222.11.

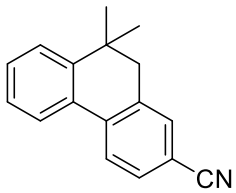


9,9-dimethyl-2-(trifluoromethyl)-9,10-dihydrophenanthrene (**3ah**): colorless oil (11.9 mg, 43%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, J= 8.4 Hz, 1H), 7.79 (dd, J= 1.2, 7.8 Hz, 1H), 7.55 (d, J= 7.8 Hz, 1H), 7.45-7.44 (m, 2H), 7.38-7.32 (m, 2H), 2.83 (s, 2H), 1.27 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.83, 137.65, 137.64, 136.57, 131.93, 129.09, 126.78, 125.38 (q, J= 3.8 Hz), 124.58, 124.47, 124.37 (q, J= 270.3 Hz), 123.77 (q, J= 3.8 Hz), 123.71, 43.80, 34.09, 27.90.

MS (GC-MS) *m/z*: calculated for $C_{17}H_{15}F_3$: 276.11, found: 276.11.

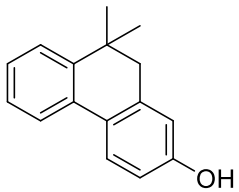


9,9-dimethyl-9,10-dihydrophenanthrene-2-carbonitrile (**3ai**): yellow oil (8.4 mg, 36%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, J= 0.6 Hz, 1H), 7.73 (dd, J= 1.2, 7.2 Hz, 1H), 7.51 (dd, J= 1.2, 7.2 Hz, 1H), 7.45-7.44 (m, 1H), 7.39-7.7.33 (m, 2H), 7.30 (d, J= 7.8 Hz, 1H), 2.83 (s, 2H), 1.26 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.37, 141.46, 135.53, 131.14, 130.73, 129.49, 129.29, 127.14, 127.00, 124.52, 124.26, 119.33, 110.82, 44.08, 34.03, 27.88.

HRMS (ESI-TOF) *m/z*: calculated for $C_{17}H_{16}N^+$: 234.1282 $(M + H)^+$, found: 234.1290.

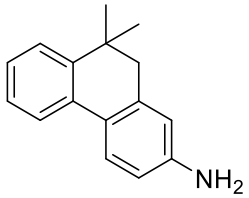


9,9-dimethyl-9,10-dihydrophenanthren-2-ol (**3aj**): colorless oil (11.2 mg, 50%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (dd, J= 1.2, 7.2 Hz, 1H), 7.63 (d, J= 8.4 Hz, 1H), 7.39 (dd, J= 1.2, 7.2 Hz, 1H), 7.28-7.23 (m, 2H), 6.77 (dd, J= 3.0, 8.4 Hz, 1H), 6.68 (d, J= 3.0 Hz, 1H), 4.92 (s, 1H), 2.71 (s, 2H), 1.25 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.05, 144.47, 138.02, 133.12, 127.33, 127.11, 126.54, 125.03, 124.21, 123.38, 115.42, 113.70, 44.21, 34.19, 27.89.

HRMS (ESI-TOF) *m/z*: calculated for $C_{16}H_{17}O^+$: 225.1279 $(M + H)^+$, found: 225.1273.

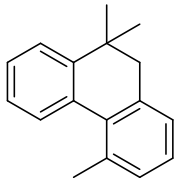


9,9-dimethyl-9,10-dihydrophenanthren-2-amine (**3ak**): yellow oil (14.9 mg, 67%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, J= 7.8 Hz, 1H), 7.55 (d, J= 7.8 Hz, 1H), 7.37 (d, J= 7.8 Hz, 1H), 7.24 (t, J= 7.2 Hz, 1H), 7.20 (t, J= 7.2 Hz, 1H), 6.62 (dd, J= 3.0, 8.4 Hz, 1H), 6.52 (d, J= 1.8 Hz, 1H), 3.69 (s, 2H), 2.67 (s, 2H), 1.24 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.89, 144.19, 137.49, 133.61, 126.51, 126.45, 125.20, 124.76, 124.12, 122.97, 115.16, 113.58, 44.32, 34.21, 27.94.

HRMS (ESI-TOF) *m/z*: calculated for $C_{16}H_{18}N^+$: 224.1439 $(M + H)^+$, found: 224.1432.

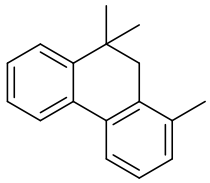


4,9,9-trimethyl-9,10-dihydrophenanthrene (**3al**): colorless oil (8.9 mg, 40%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68-7.66 (m, 1H), 7.42-7.41 (m, 1H), 7.29-7.27 (m, 2H), 7.18 (d, J= 7.2 Hz, 1H), 7.13 (t, J= 7.2 Hz, 1H), 7.06 (d, J= 7.2 Hz, 1H), 2.68 (s, 2H), 2.63 (s, 3H), 1.21 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.21, 137.87, 134.07, 134.06, 133.75, 130.60, 128.52, 127.12, 126.70, 126.24, 125.19, 123.67, 45.44, 34.15, 27.21, 23.18.

MS (GC-MS) *m/z*: calculated for $C_{17}H_{18}$: 222.14, found: 222.13.

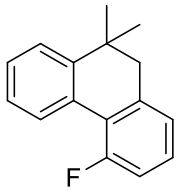


1,9,9-trimethyl-9,10-dihydrophenanthrene (**3am**): colorless oil (14.2 mg, 64%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76-7.75 (m, 1H), 7.63 (d, J= 7.8 Hz, 1H), 7.42-7.40 (m, 1H), 7.29-7.28 (m, 2H), 7.20 (t, J= 7.2 Hz, 1H), 7.12 (d, J= 7.8 Hz, 1H), 2.73 (s, 2H), 2.34 (s, 3H), 1.26 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.09, 135.66, 134.48, 134.15, 133.69, 129.30, 127.74, 126.49, 126.13, 124.46, 123.99, 121.54, 39.88, 33.93, 28.11, 19.81.

MS (GC-MS) *m/z*: calculated for $C_{17}H_{18}$: 222.14, found: 222.14.

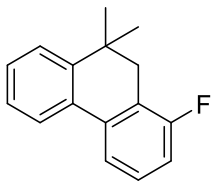


4-fluoro-9,9-dimethyl-9,10-dihydrophenanthrene (**3an**): colorless oil (14.7 mg, 65%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (dt, J= 1.2, 6.6 Hz, 1H), 7.44-7.42 (m, 1H), 7.32-7.28 (m, 2H), 7.19-7.15 (m, 1H), 7.04-6.99 (m, 2H), 2.75 (s, 2H), 1.25 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.15 (d, J= 248.9 Hz), 145.83, 139.38 (d, J= 3.5 Hz), 139.54 (d, J= 3.6 Hz), 128.38, 128.27, 128.16, 128.09, 126.29, 124.26 (d, J= 2.9 Hz), 123.93, 121.98 (d, J= 9.0 Hz), 114.85 (d, J= 24.3 Hz), 44.31, 34.19, 27.63.

MS (GC-MS) *m/z*: calculated for $C_{16}H_{15}F$: 222.12, found: 222.12.

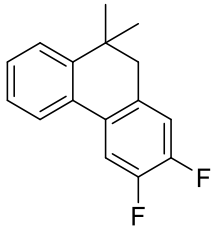


1-fluoro-9,9-dimethyl-9,10-dihydrophenanthrene (**3ao**): colorless oil (6.8 mg, 30%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (dd, J= 1.2, 7.2 Hz, 1H), 7.56 (d, J= 7.8 Hz, 1H), 7.43 (dd, J= 1.8, 7.8 Hz, 1H), 7.34-7.29 (m, 2H), 7.27-7.23 (m, 1H), 6.99 (t, J= 9.0 Hz, 1H), 2.80 (s, 2H), 1.28 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.64 (d, J= 240.9 Hz), 145.23, 136.56 (d, J= 5.1 Hz), 132.38 (d, J= 3.2 Hz), 128.47, 127.30 (d, J= 8.4 Hz), 126.59, 124.42, 124.36, 122.72 (d, J= 17.6 Hz), 119.11 (d, J= 3.0 Hz), 114.01 (d, J= 22.5 Hz), 34.98 (d, J= 2.9 Hz), 33.48, 28.04.

MS (GC-MS) *m/z*: calculated for $C_{16}H_{15}F$: 222.12, found: 222.12.

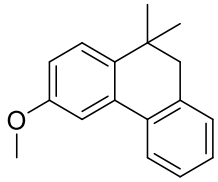


1-fluoro-9,9-dimethyl-9,10-dihydrophenanthrene (**3ap**): colorless oil (14.2 mg, 58%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62-7.61 (m, 1H), 7.53 (dd, J= 7.8, 11.4 Hz, 1H), 7.42-7.41 (m, 1H), 7.33-7.28 (m, 2H), 6.99 (dd, J= 8.4, 10.8 Hz, 1H), 2.71 (s, 2H), 1.25 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.27 (dd, J= 3.2, 203.6 Hz), 148.63 (d, J= 12.6 Hz), 144.87, 132.59 (dd, J= 3.6, 5.7 Hz), 131.65, 130.96 (dd, J= 3.9, 5.7 Hz), 128.45, 126.79, 124.43, 124.01, 117.18 (d, J= 16.8 Hz), 112.51 (d, J= 18.2 Hz), 43.18, 34.16, 27.80.

MS (GC-MS) *m/z*: calculated for $C_{16}H_{14}F_2$: 244.11, found: 244.11.

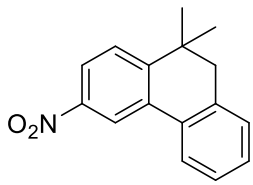


3-methoxy-10,10-dimethyl-9,10-dihydrophenanthrene (**3ba**): colorless oil (13.8 mg, 58%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, J= 7.2 Hz, 1H), 7.34-7.29 (m, 3H), 7.23 (t, J= 7.2 Hz, 1H), 7.19 (d, J= 7.2 Hz, 1H), 6.85 (dd, J= 3.0, 9.0 Hz, 1H), 3.86 (s, 3H), 2.76 (s, 2H), 1.23 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.30, 137.95, 136.44, 134.47, 134.07, 128.69, 127.57, 126.81, 125.34, 123.54, 113.02, 109.73, 55.37, 44.35, 33.67, 28.12.

HRMS (ESI-TOF) *m/z*: calculated for $C_{17}H_{19}O^+$: 239.1463 $(M + H)^+$, found: 239.1458.

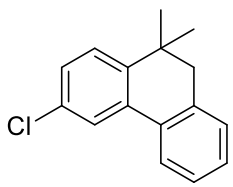


10,10-dimethyl-3-nitro-9,10-dihydrophenanthrene (**3ca**): brown oil (9.6 mg, 38%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, J= 8.6 Hz, 1H), 8.13 (dd, J= 2.4, 8.4 Hz, 1H), 7.84 (d, J= 7.8 Hz, 1H), 7.56 (d, J= 8.4 Hz, 1H), 7.38 (dt, J= 0.6, 7.2 Hz, 1H), 7.32 (dt, J= 1.2, 7.8 Hz), 7.24 (d, J= 7.2 Hz, 1H), 2.82 (s, 2H), 1.30 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.57, 135.85, 134.96, 132.22, 128.90, 128.85, 127.39, 125.45, 123.94, 122.48, 119.01, 43.27, 34.87, 27.60.

HRMS (ESI-TOF) *m/z*: calculated for $C_{16}H_{15}NO_2Na^+$: 276.1001 $(M + Na)^+$, found: 276.1008.

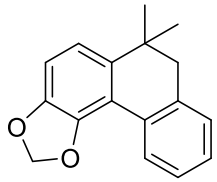


3-chloro-10,10-dimethyl-9,10-dihydrophenanthrene (**3da**): yellow oil (17.0 mg, 70%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, J= 2.4 Hz, 1H), 7.70 (d, J= 7.8 Hz, 1H), 7.34-7.30 (m, 2H), 7.27-7.23 (m, 2H), 7.20 (d, J= 7.2 Hz, 1H), 2.76 (s, 2H), 1.23 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.81, 136.15, 135.15, 133.05, 132.41, 128.77, 128.11, 127.61, 127.03, 125.86, 124.07, 123.62, 43.85, 34.00, 27.83.

MS (GC-MS) *m/z*: calculated for $C_{16}H_{15}Cl$: 242.09, found: 242.08.

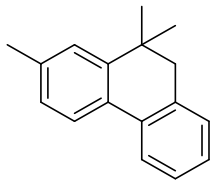


6,6-dimethyl-6,7-dihydrophenanthro[3,4-d][1,3]dioxole (**3ea**): colorless solid (8.3 mg, 33%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, J= 7.8 Hz, 1H), 7.29 (dt, J= 1.2, 7.8 Hz, 1H), 7.23 (dt, J= 1.2, 7.8 Hz, 1H), 7.19 (d, J= 7.2 Hz, 1H), 6.89 (d, J= 8.4 Hz, 1H), 6.75 (d, J= 7.8 Hz, 1H), 6.04 (s, 2H), 2.76 (s, 2H), 1.22 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 146.25, 144.47, 139.87, 136.18, 131.13, 128.12, 127.45, 126.78, 126.52, 117.05, 116.84, 107.17, 100.76, 44.53, 34.18, 28.35.

HRMS (ESI-TOF) *m/z*: calculated for $C_{16}H_{17}O_2^+$: 253.1228$(M + H)^+$, found: 253.1223.

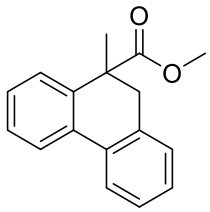


2,10,10-trimethyl-9,10-dihydrophenanthrene (**3fa**): colorless oil (15.1 mg, 68%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, J= 7.8 Hz, 1H), 7.67 (d, J= 7.8 Hz, 1H), 7.29 (t, J= 7.2 Hz, 1H), 7.22-7.17 (m, 3H), 7.11 (d, J= 8.4 Hz, 1H), 2.76 (s, 2H), 2.39 (s, 3H), 1.25 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.33, 137.65, 135.73, 134.24, 130.50, 128.57, 127.25, 127.01, 126.77, 124.98, 124.04, 123.19, 44.17, 34.09, 27.96, 21.54.

MS (GC-MS) *m/z*: calculated for $C_{17}H_{18}$: 222.14, found: 222.14.

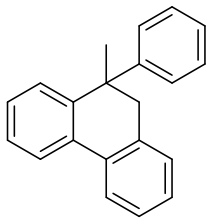


methyl 9-methyl-9,10-dihydrophenanthrene-9-carboxylate (**3ga**): colorless oil (18.6 mg, 74%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, J= 7.8 Hz, 1H), 7.73 (d, J= 7.8 Hz, 1H), 7.38-7.35 (m, 1H), 7.32-7.30 (m, 3H), 7.24-7.22 (m, 2H), 2.61 (s, 3H), 3.48 (d, J= 15.0 Hz, 1H), 2.84 (d, J= 15.0 Hz, 1H), 1.55 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.46, 139.11, 134.48, 133.53, 133.49, 128.47, 127.82, 127.74, 127.27, 126.00, 124.16, 123.73, 52.35, 46.96, 39.97, 23.67.

HRMS (ESI-TOF) *m/z*: calculated for $C_{17}H_{17}O_2^+$: 253.1228$(M + H)^+$, found: 253.1223.

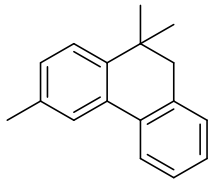


9-methyl-9-phenyl-9,10-dihydrophenanthrene (**3ha**): white solid (8.6 mg, 32%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, J= 7.2 Hz, 1H), 7.71 (d, J= 7.8 Hz, 1H), 7.34 (dt, J= 1.2, 7.8 Hz, 1H), 7.28-7.10 (m, 10H), 3.44 (d, J= 15.0 Hz, 1H), 2.99 (d, J= 15.0 Hz, 1H), 1.66 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.62, 144.14, 135.51, 134.13, 134.08, 128.37, 127.89, 127.71, 127.55, 127.18, 127.16, 1286.98, 126.93, 125.89, 124.09, 123.51, 44.45, 42.86, 27.58.

HRMS (ESI-TOF) *m/z*: calculated for $C_{21}H_{18}Na^+$: 293.1307 $(M + Na)^+$, found: 293.1319.

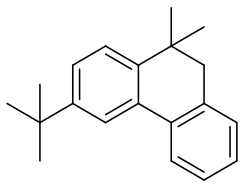


3,10,10-trimethyl-9,10-dihydrophenanthrene (**3ka**): colorless oil (12.4 mg, 56%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J= 7.8 Hz, 1H), 7.60 (s, 1H), 7.32-7.28 (m, 2H), 7.22 (t, J= 7.8 Hz, 1H), 7.18 (d, J= 7.2 Hz, 1H), 7.12 (d, J= 7.8 Hz, 1H), 2.76 (s, 2H), 2.40 (s, 3H), 1.24 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.59, 136.18, 135.93, 134.22, 133.11, 128.66, 128.64, 127.32, 126.78, 124.80, 124.22, 123.46, 44.23, 33.86, 28.01, 21.25.

MS (GC-MS) *m/z*: calculated for $C_{17}H_{18}$: 222.14, found: 222.14.

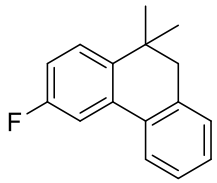


3-(tert-butyl)-10,10-dimethyl-9,10-dihydrophenanthrene (**3la**): colorless oil (21.4 mg, 81%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, J= 1.2 Hz, 1H), 7.78 (d, J= 7.8 Hz, 1H), 7.35- 7.30 (m, 3H), 7.22 (t, J= 7.2 Hz, 1H), 7.19 (d, J= 7.2 Hz, 1H), 2.76 (s, 2H), 1.38 (s, 9H), 1.25 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.09, 142.50, 136.24, 134.65, 132.72, 128.67, 127.24, 126.77, 124.97, 123.93, 123.41, 121.06, 44.22, 34.58, 33.82, 31.47, 27.97.

HRMS (ESI-TOF) *m/z*: calculated for $C_{20}H_{24}Na^+$: 287.1776 $(M + Na)^+$, found: 287.1766.



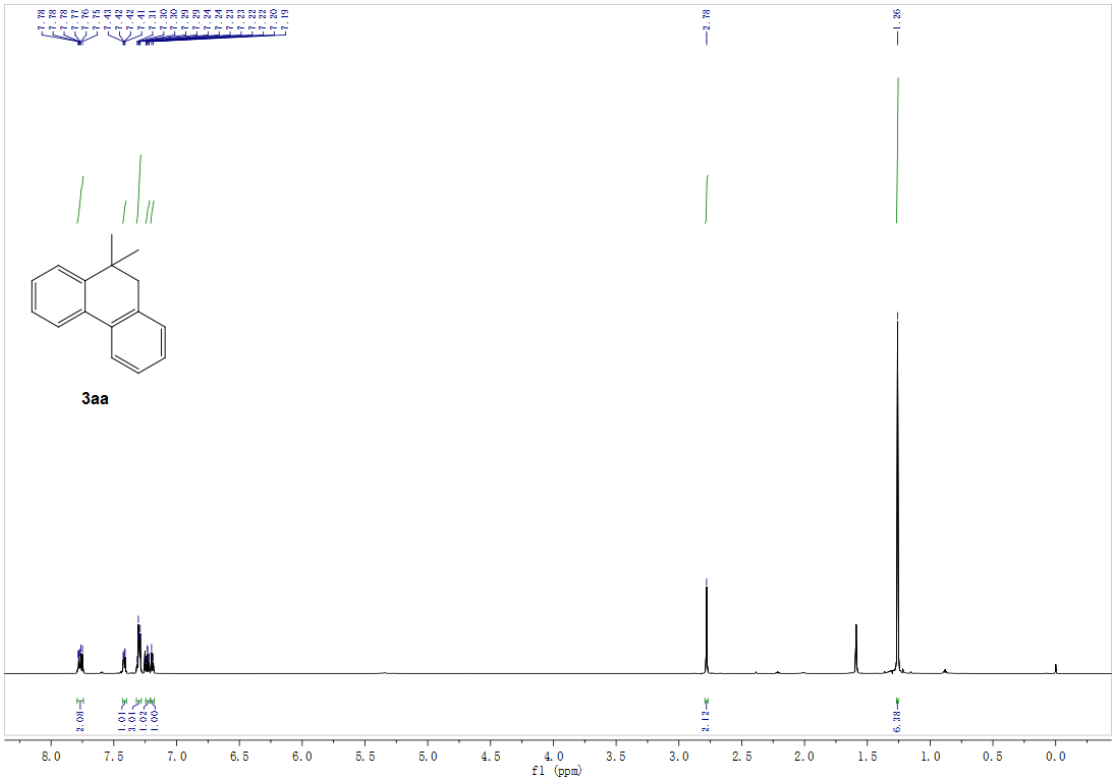
3-fluoro-10,10-dimethyl-9,10-dihydrophenanthrene (**3na**): colorless oil (19.9 mg, 88%)

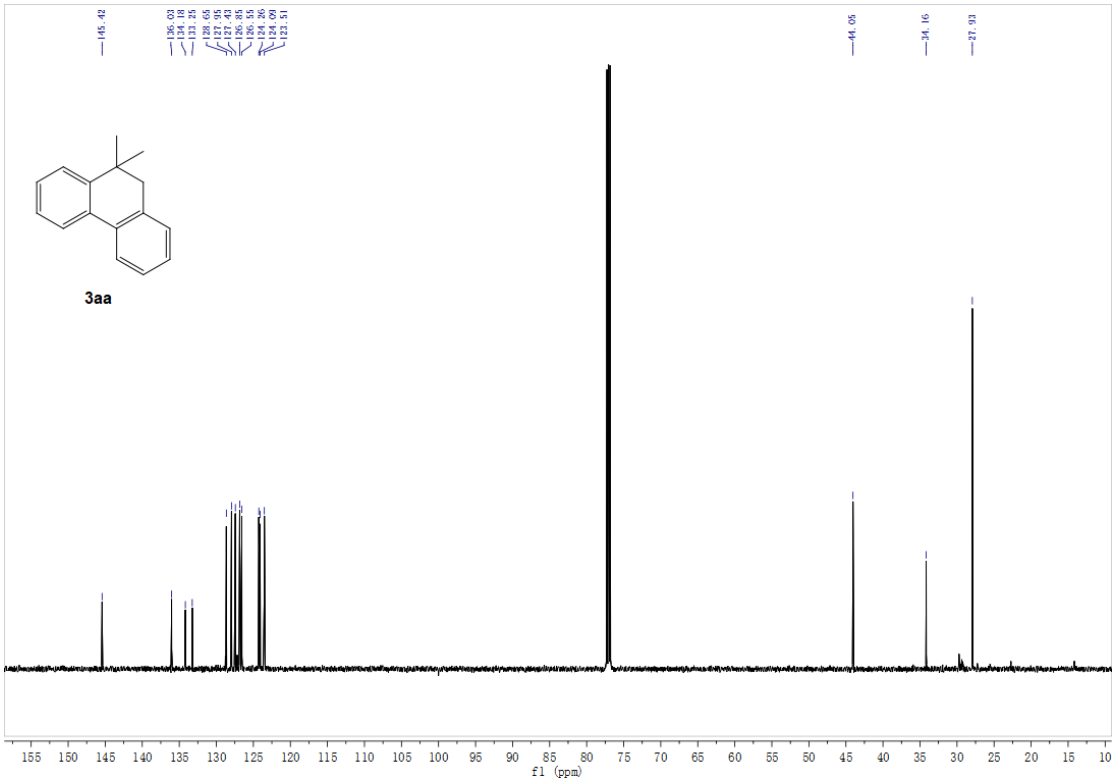
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, J= 7.8 Hz, 1H), 7.44 (dd, J= 2.4, 10.2 Hz, 1H), 7.35 (dd, J= 5.4, 8.4 Hz, 1H), 7.31 (t, J= 7.2 Hz, 1H), 7.26 (dt, J= 1.2, 7.8 Hz, 1H), 7.20 (d, J= 7.2 Hz, 1H), 6.96 (dt, J= 2.4, 10.8 Hz, 1H), 2.77 (s, 2H), 1.24 (s, 6H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 161.88 (d, J= 241.4 Hz), 141.07 (d, J= 2.9 Hz), 136.26, 135.35 (d, J= 7.5 Hz), 128.75, 128.06, 126.99, 125.90 (d, J= 8.0 Hz), 123.65, 114.24 (d, J= 20.9 Hz), 110.68 (d, J= 22.1 Hz), 44.05, 33.92, 28.03.
MS (GC-MS) *m/z*: calculated for $C_{16}H_{15}F$: 222.12, found: 222.11.

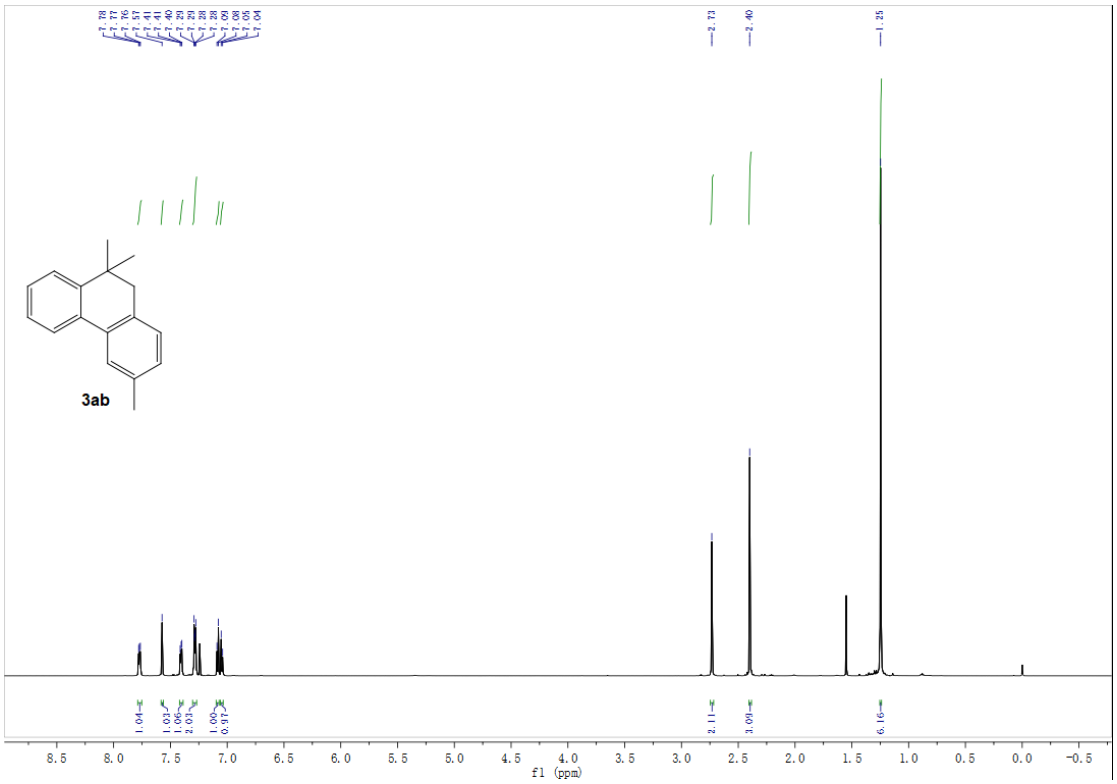
8 References

[1] Z. Wu, D. Ma, B. Zhou, X.-M. Ji, X.-T. Ma, X.-L. Wang and Y.-H. Zhang, *Angew. Chem. Int. Ed*., 2017, **129**, 12456.
[2] F. Qu, J. R. Khusnutdinova, N. P. Rath and L. M. Mirica, *Chem. Commun.*, 2014, **50**, 3036.

9 NMR Spectra



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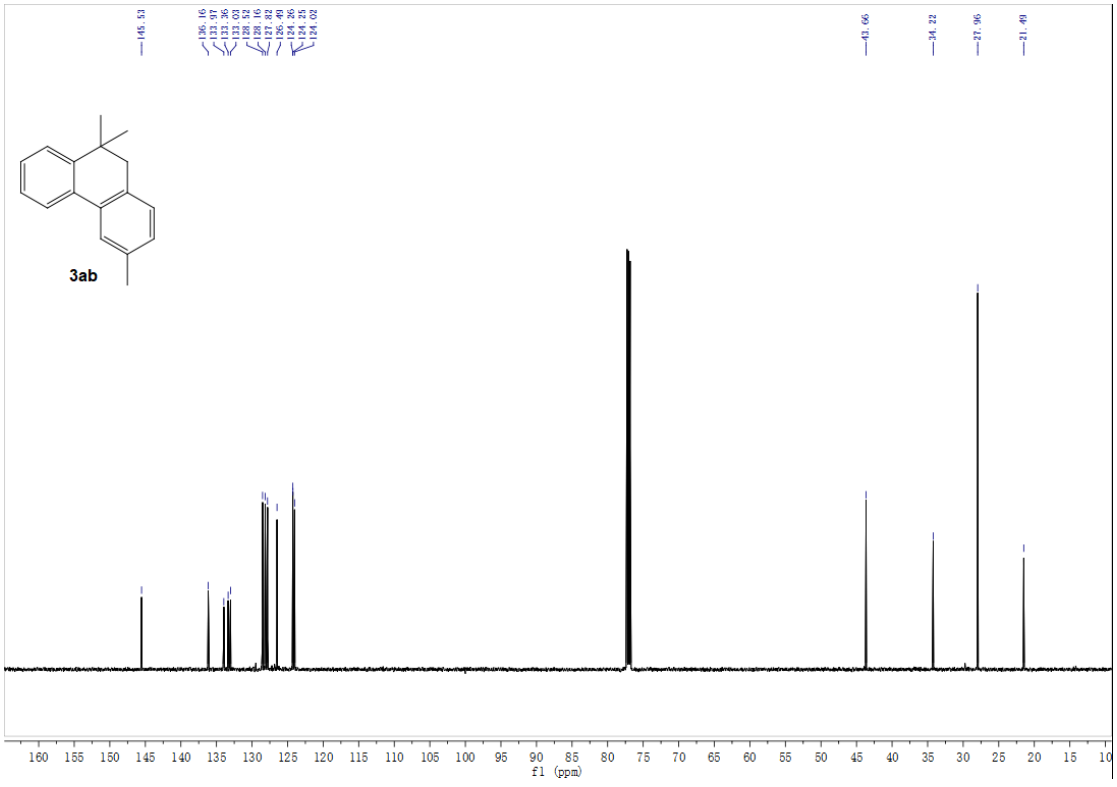
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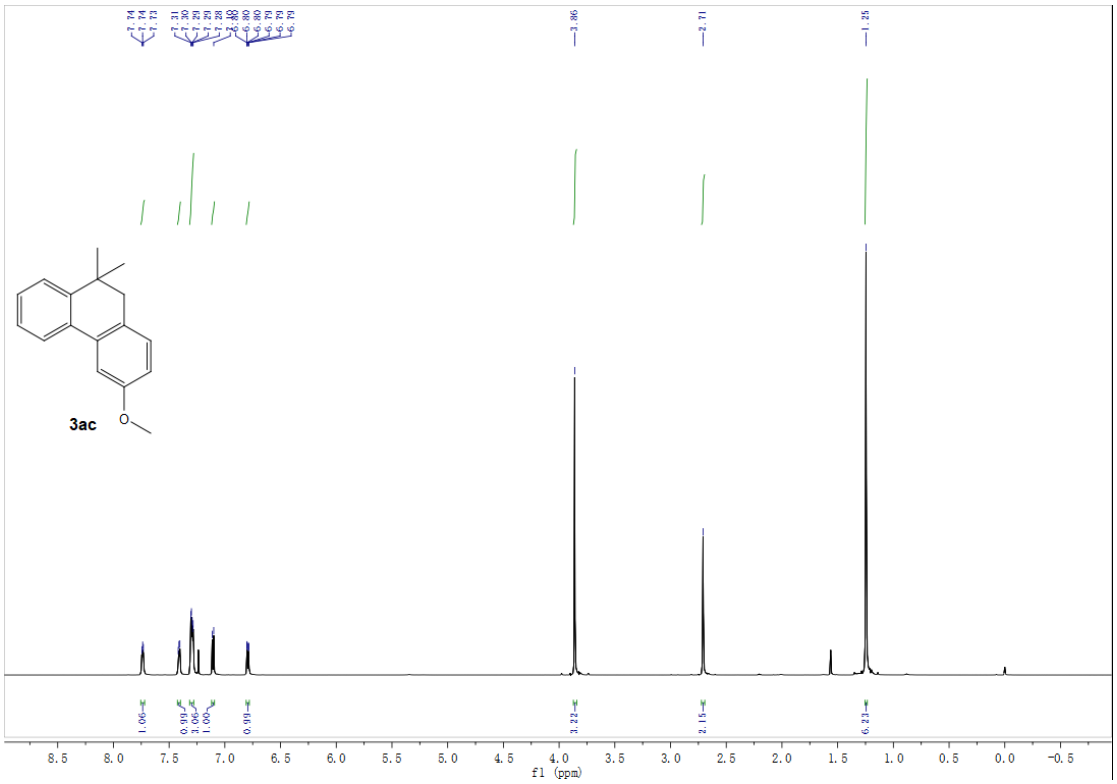
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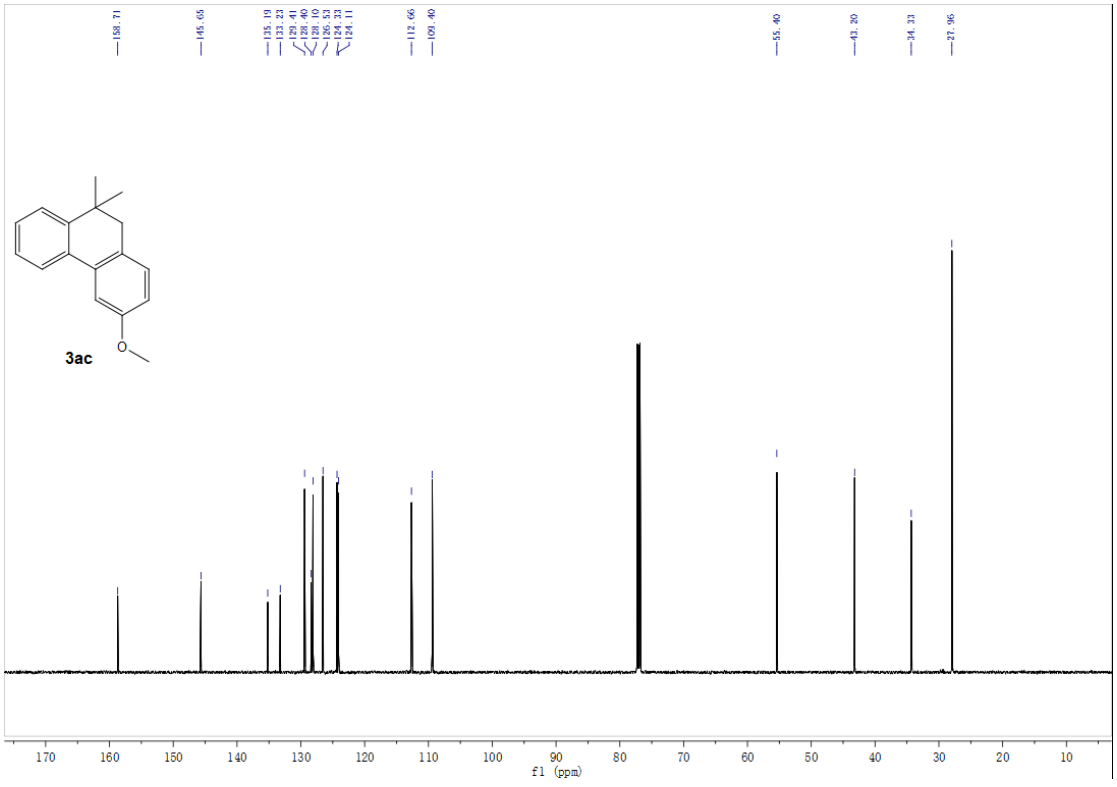
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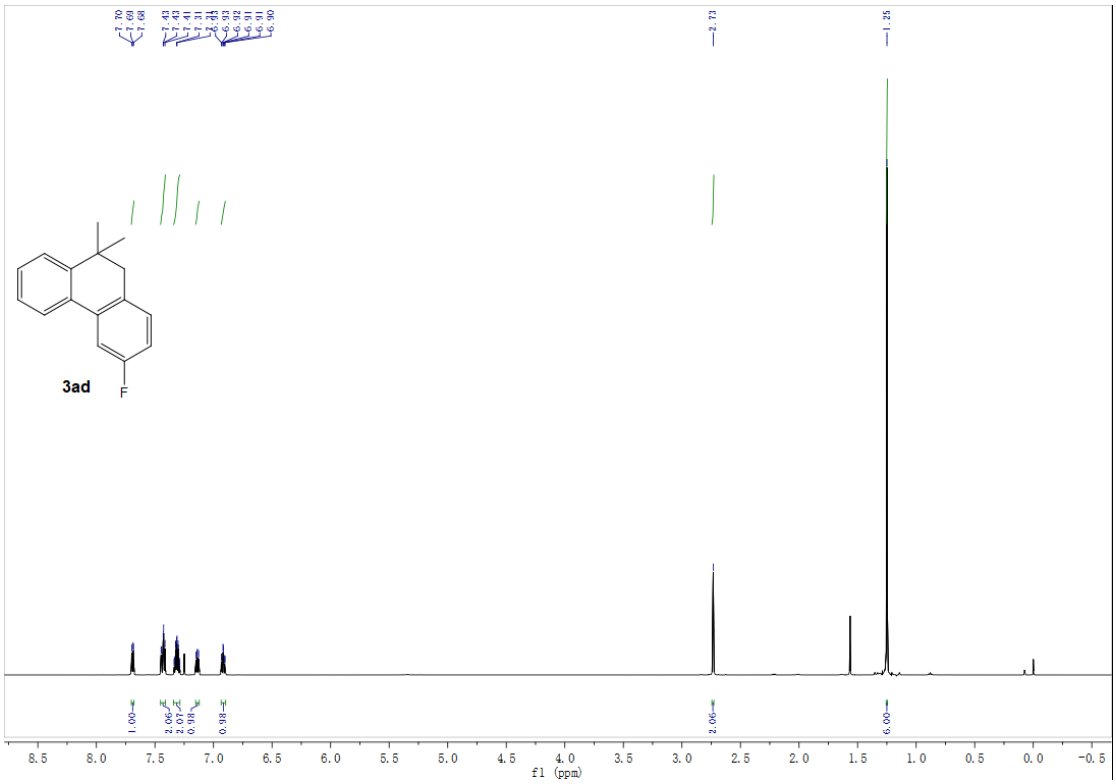
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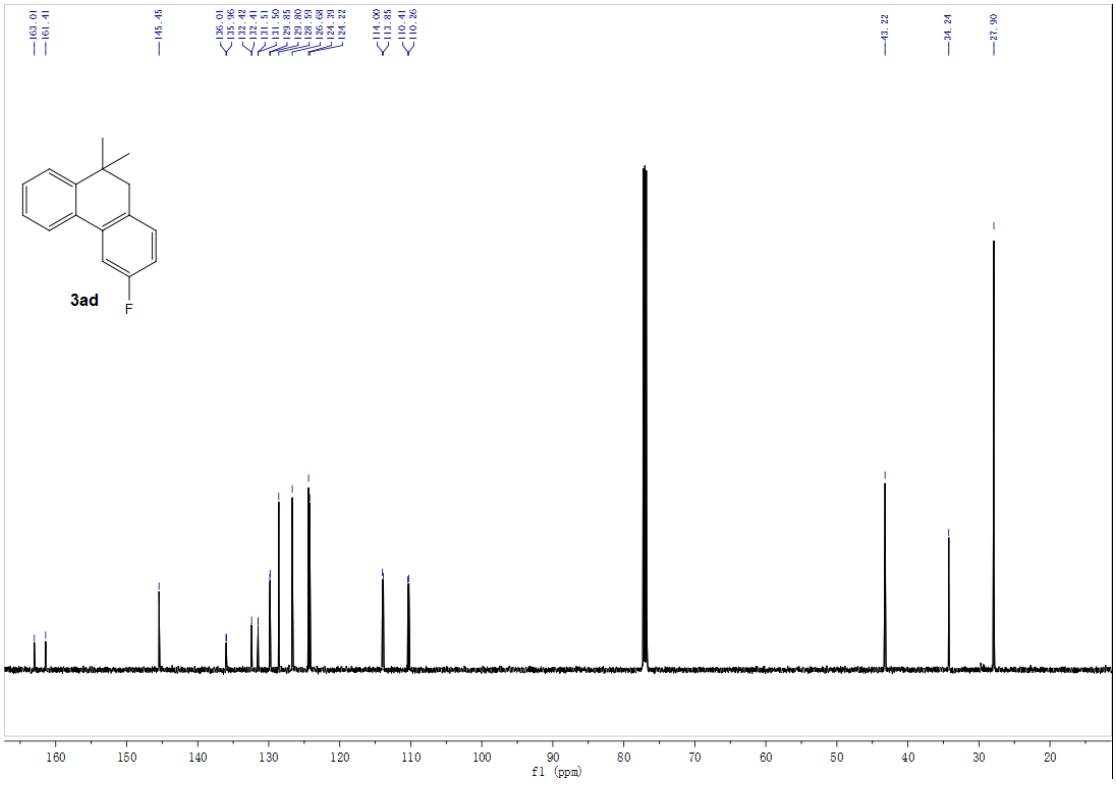
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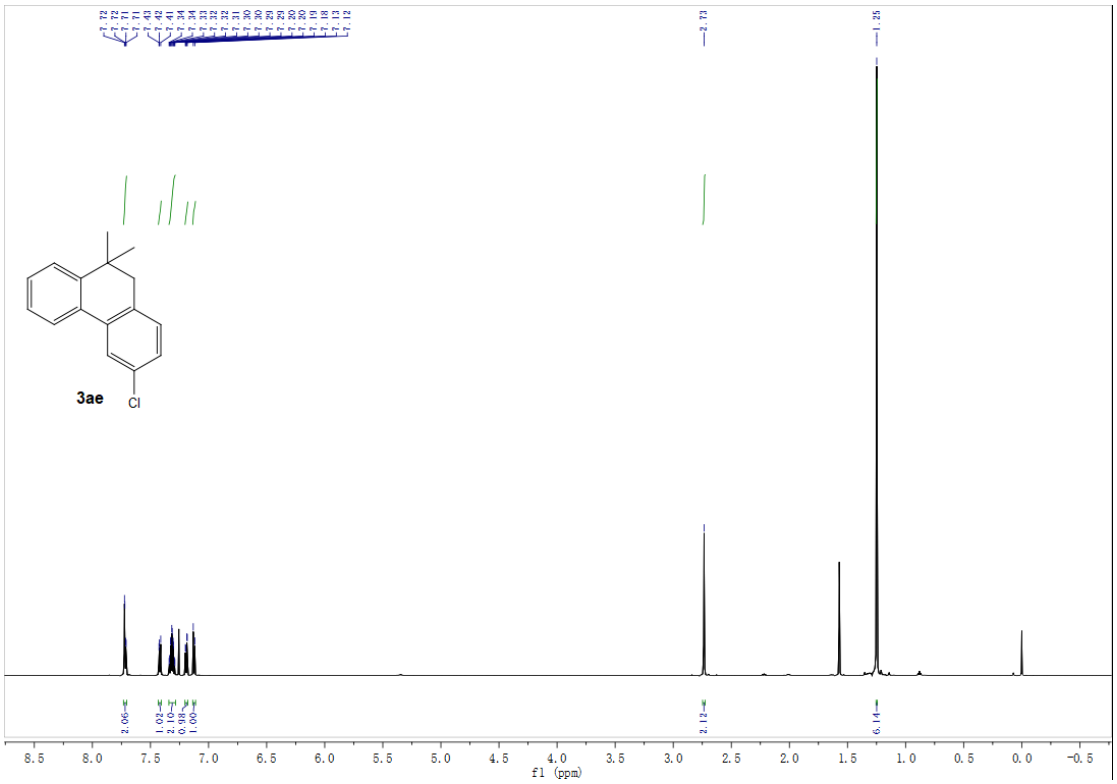
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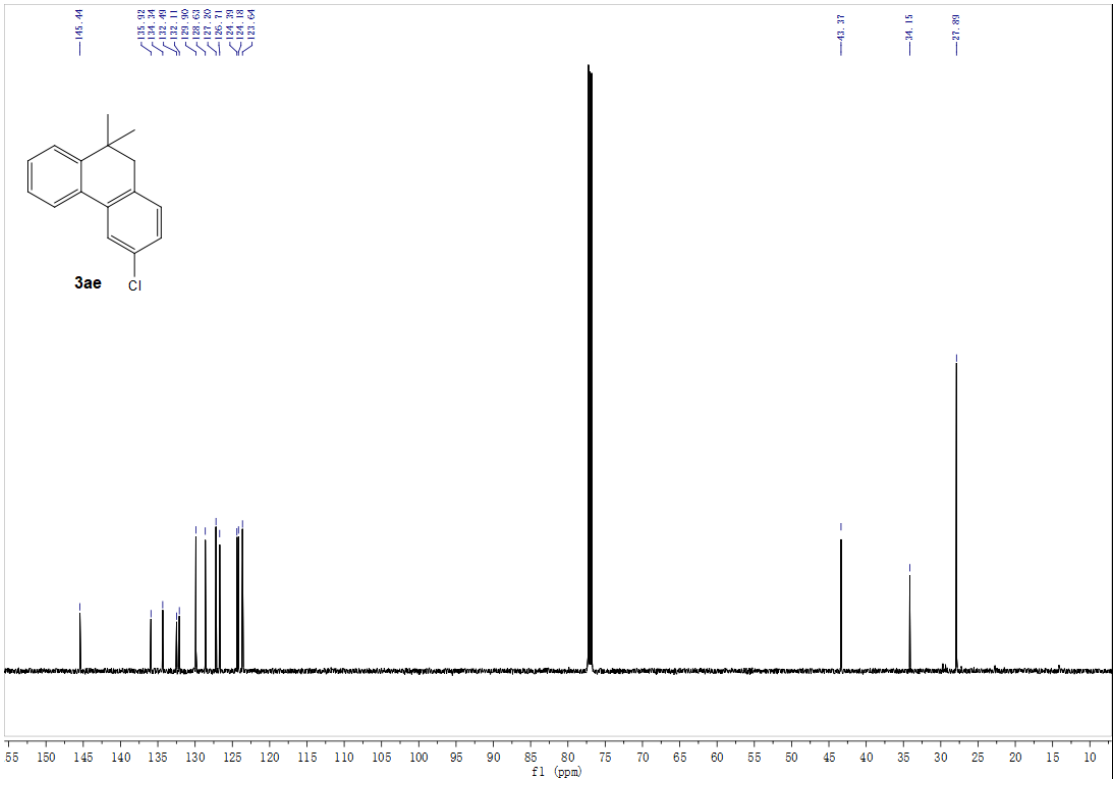
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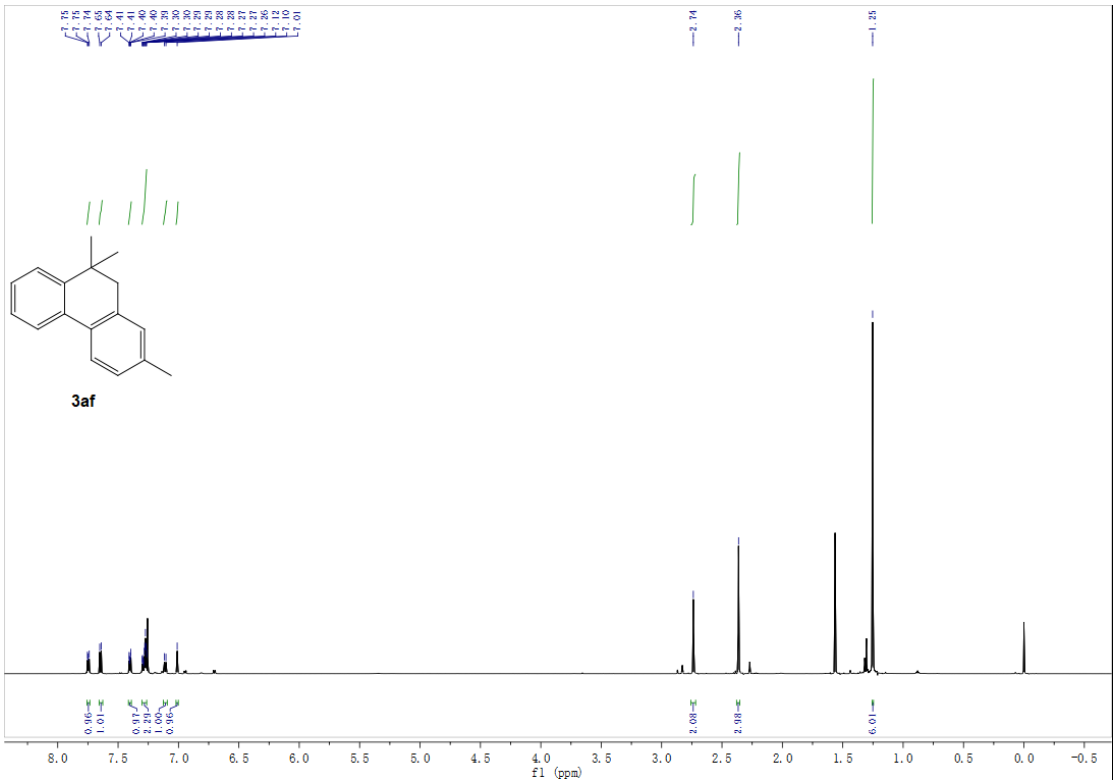
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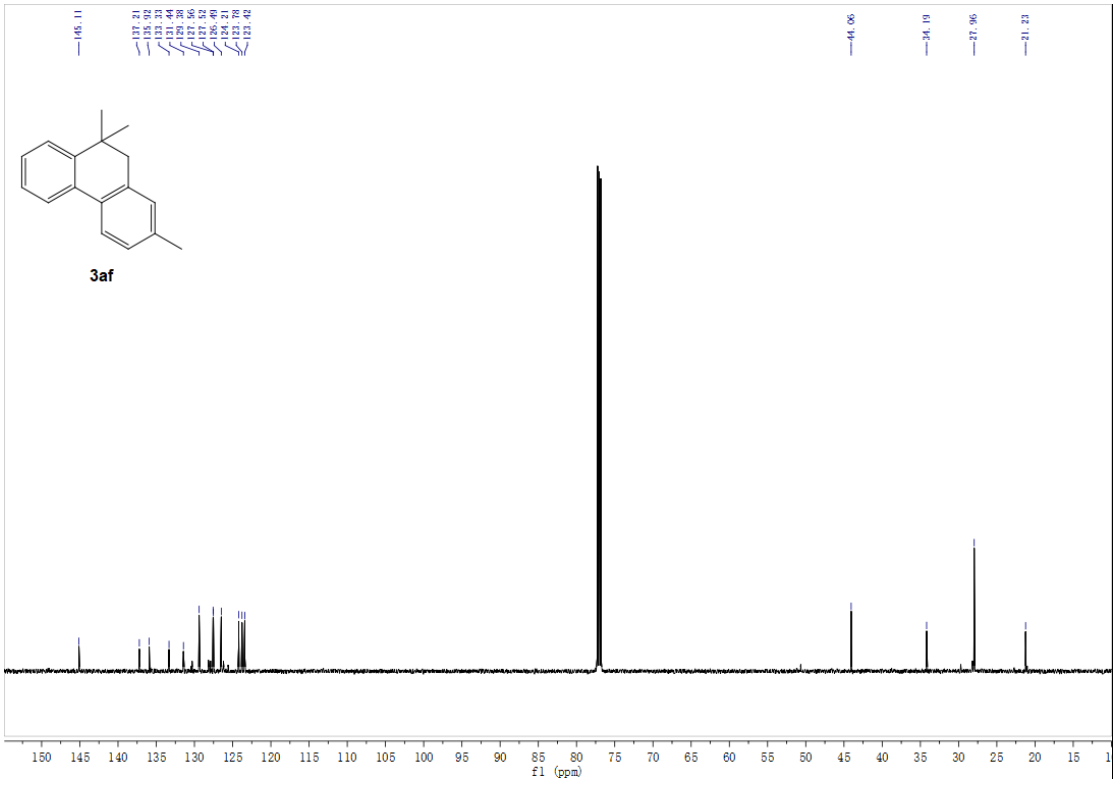
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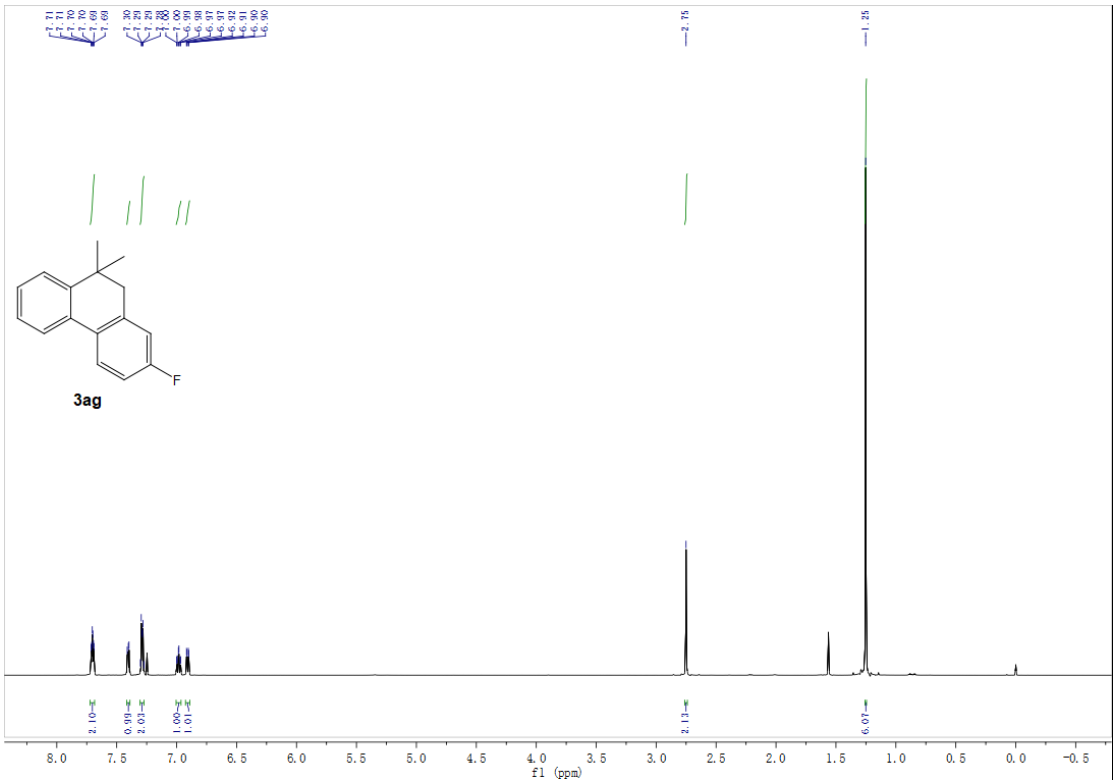
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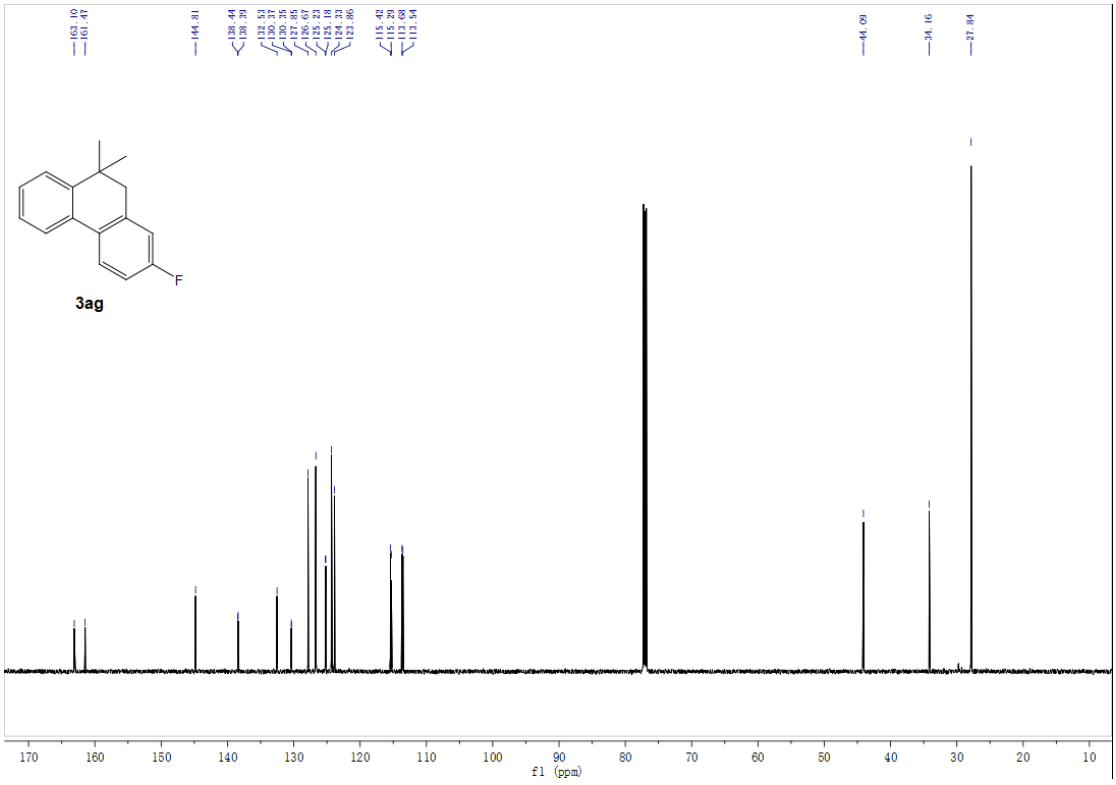
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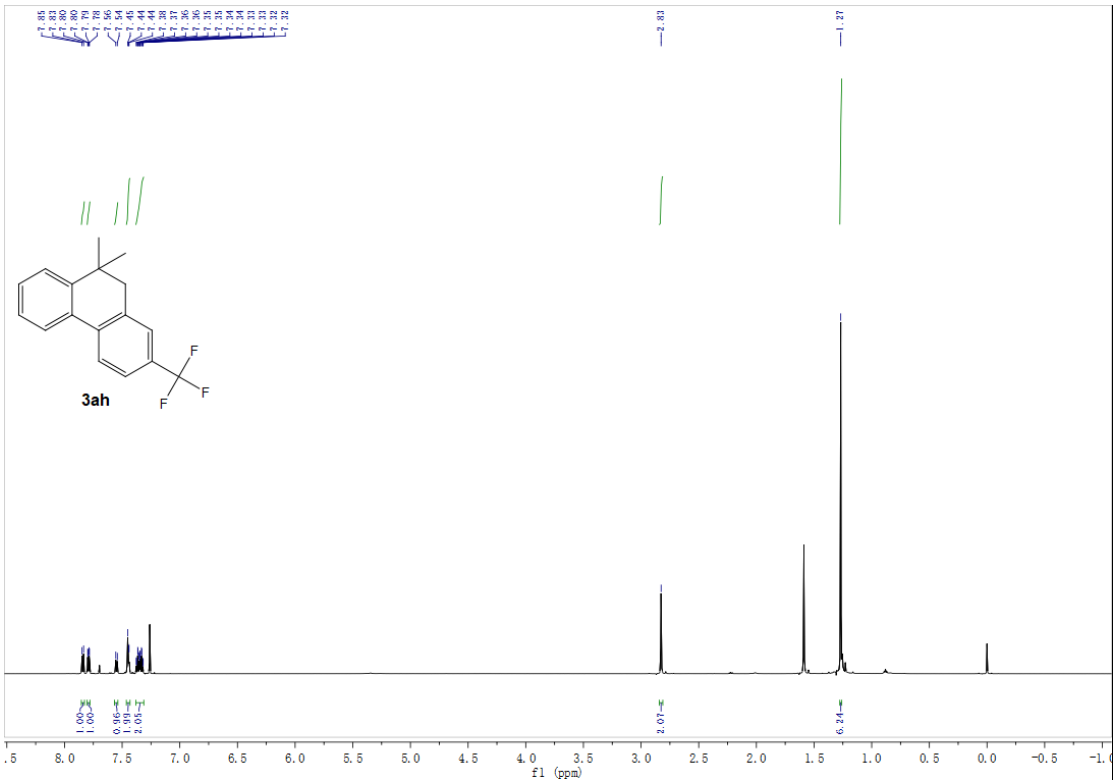
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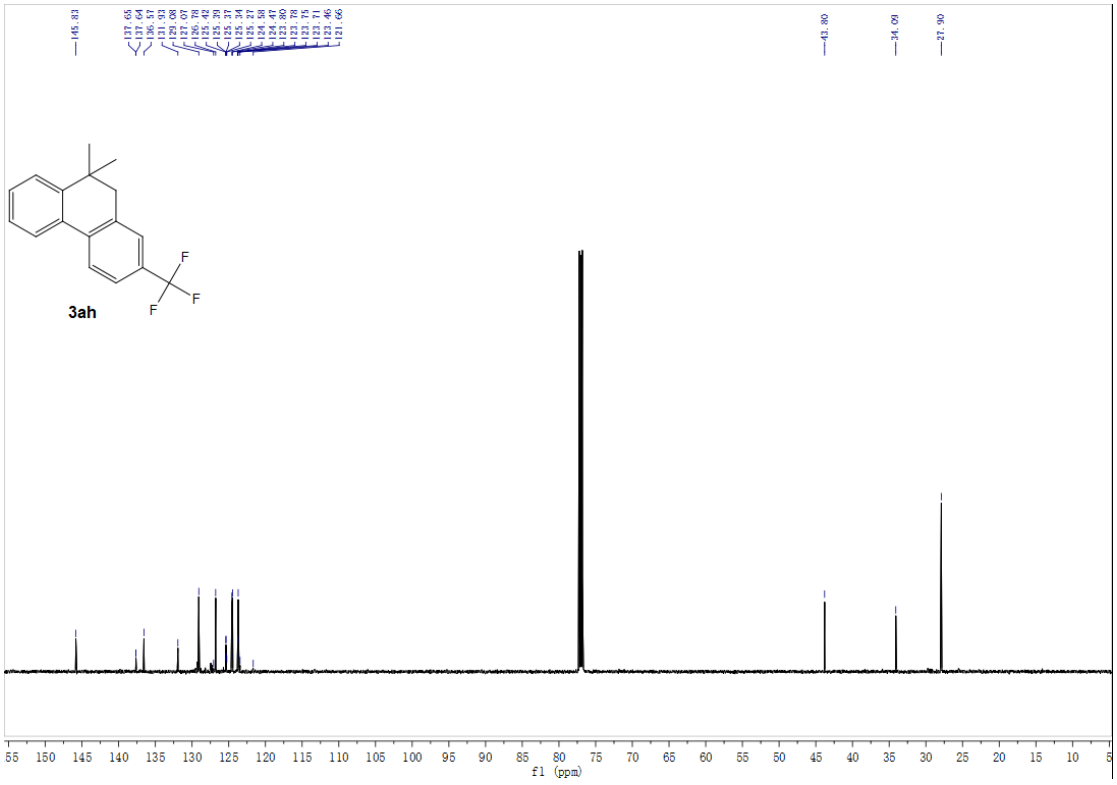
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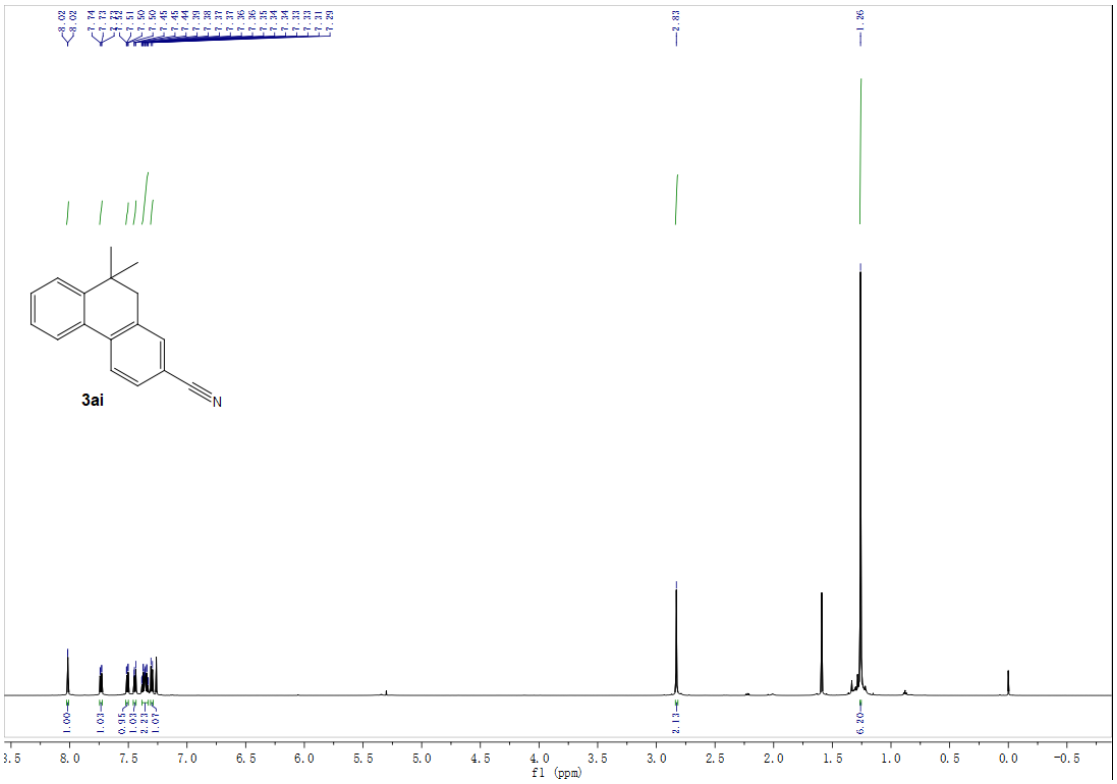
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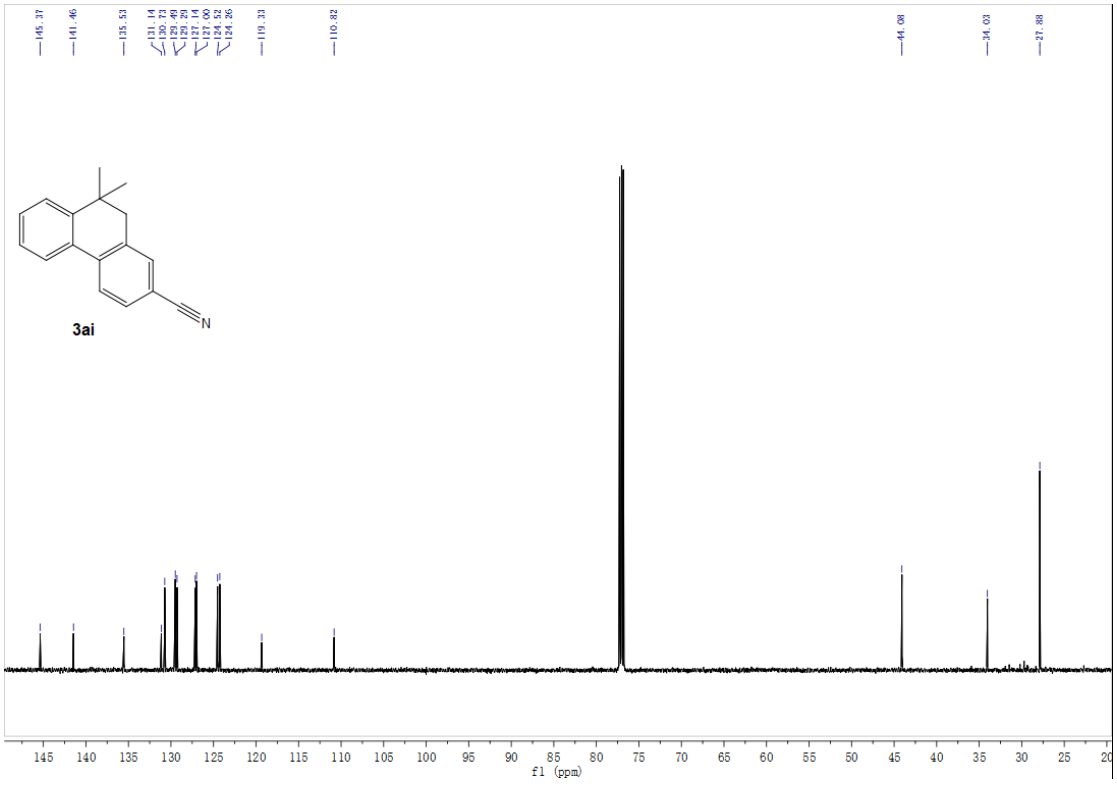
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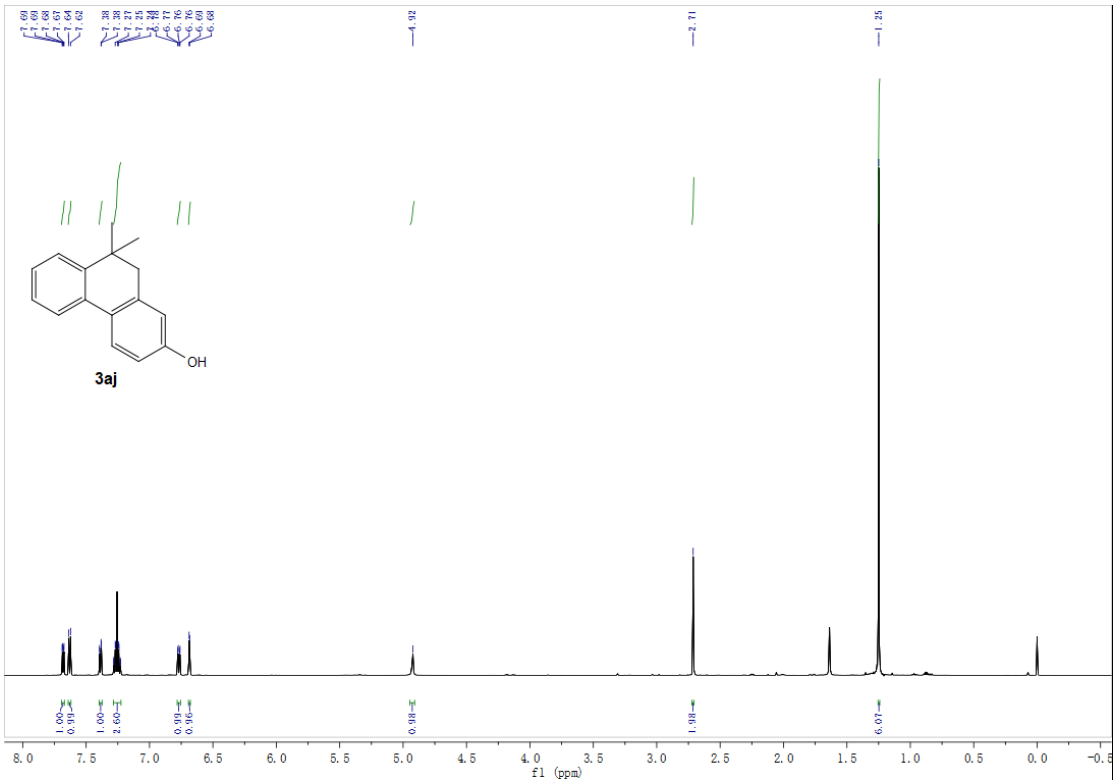
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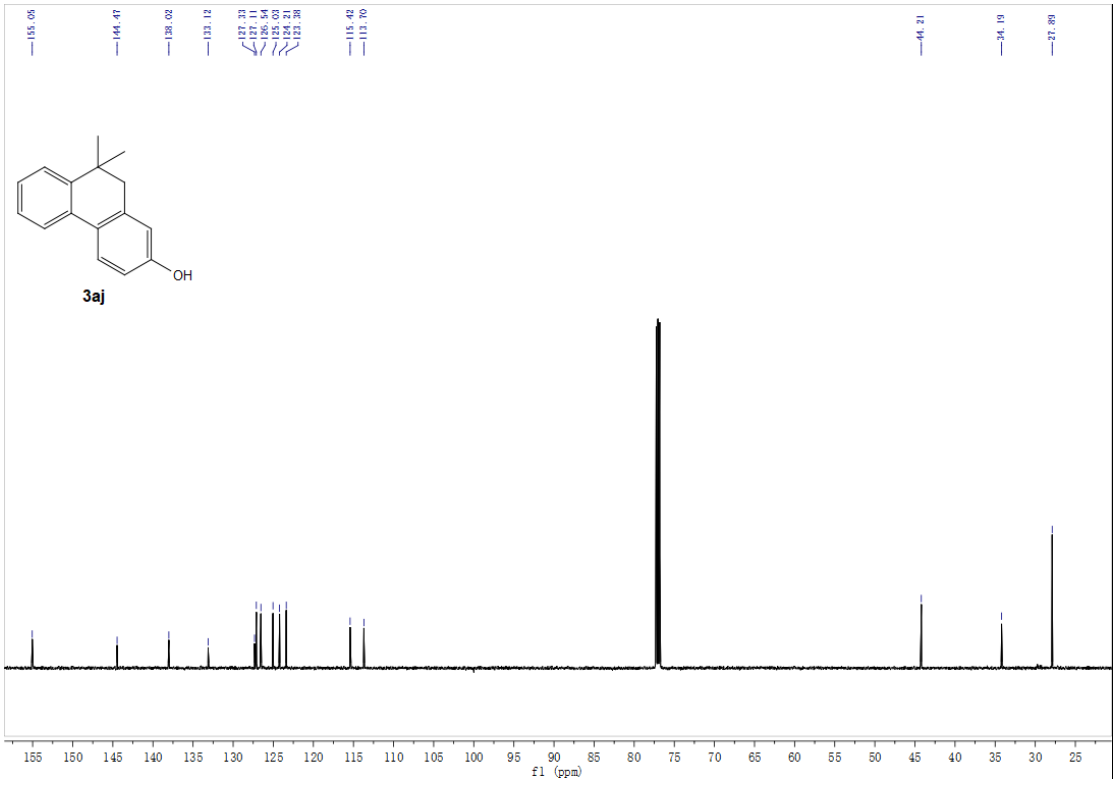
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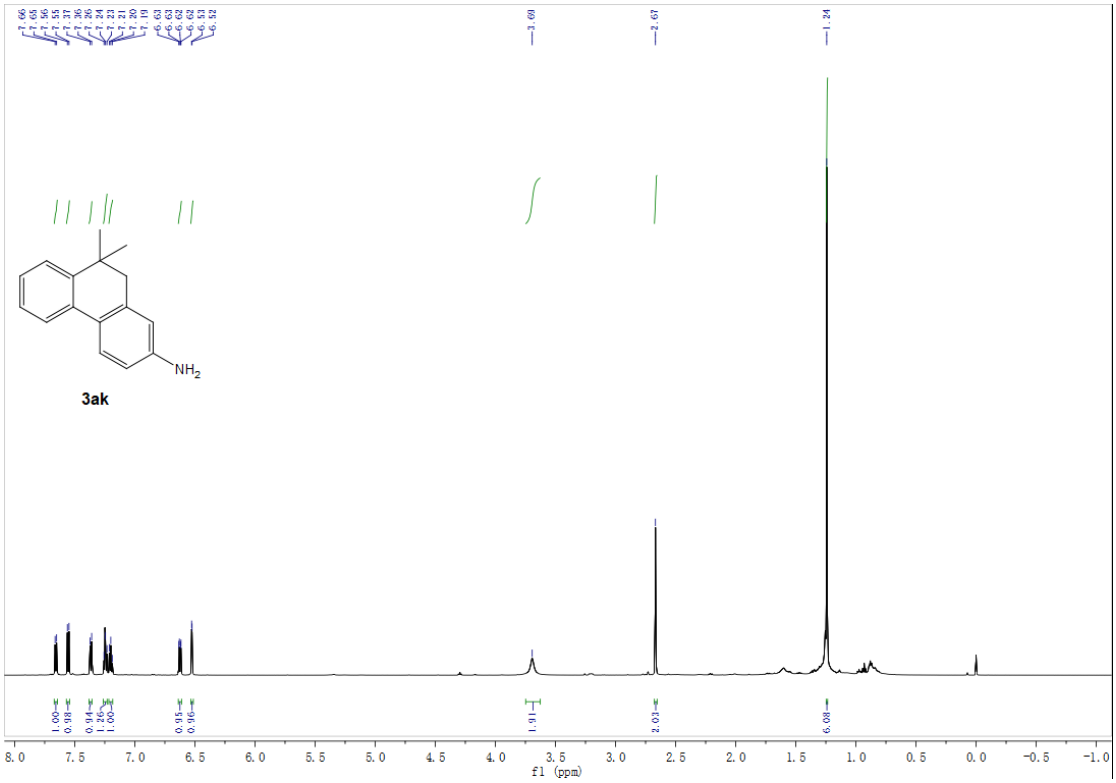
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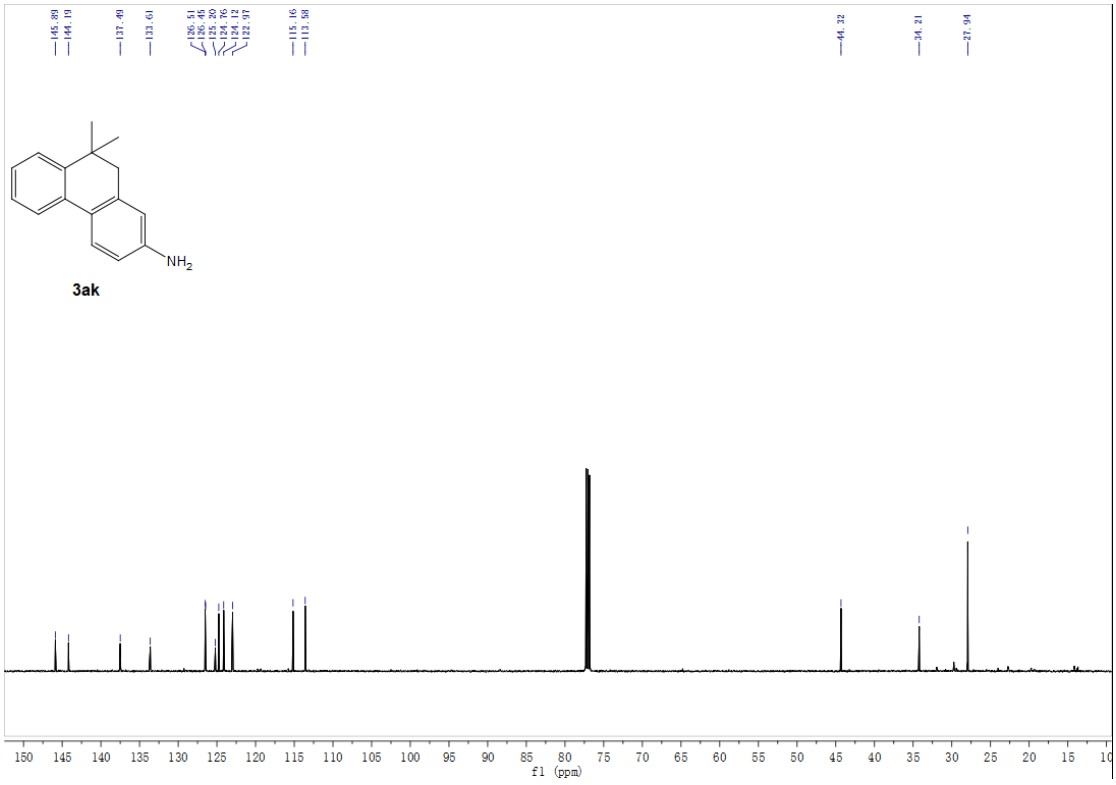
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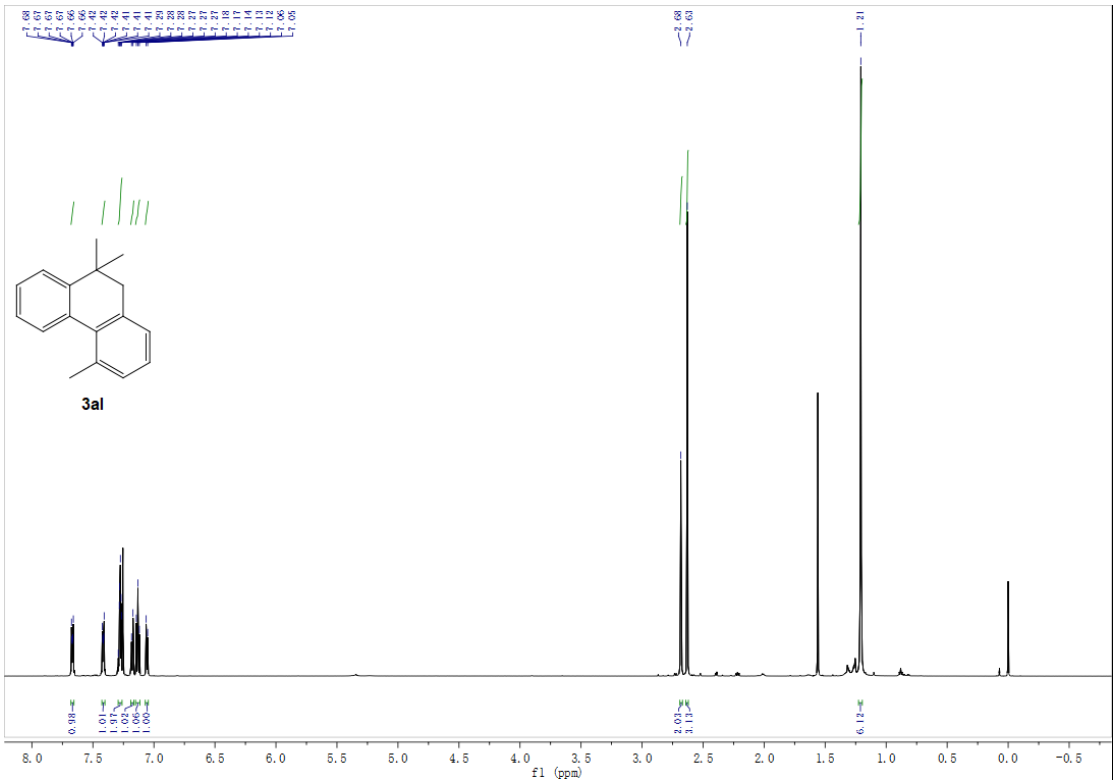
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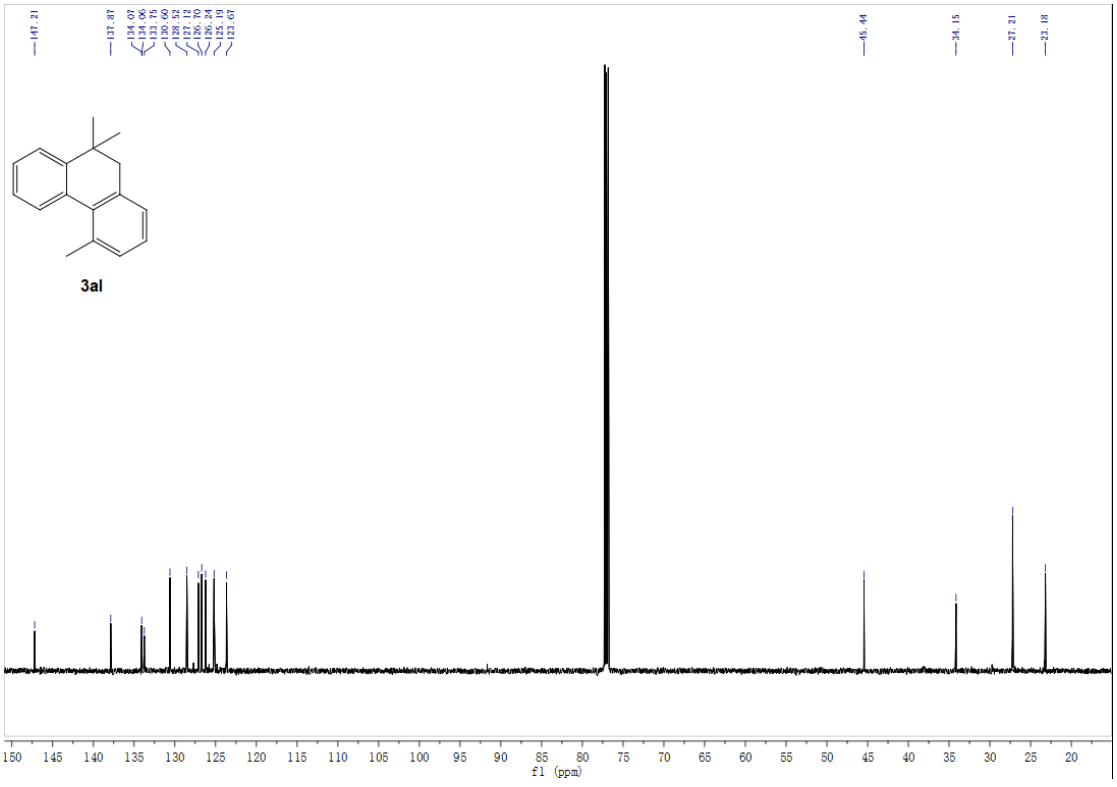
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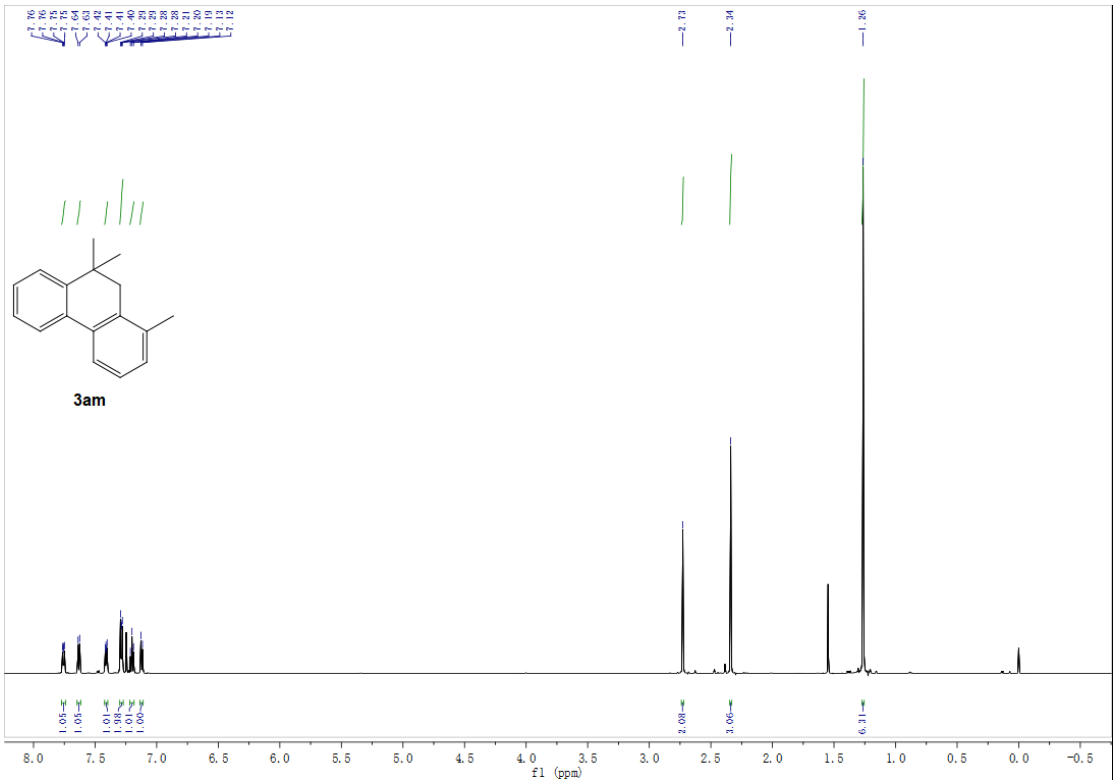
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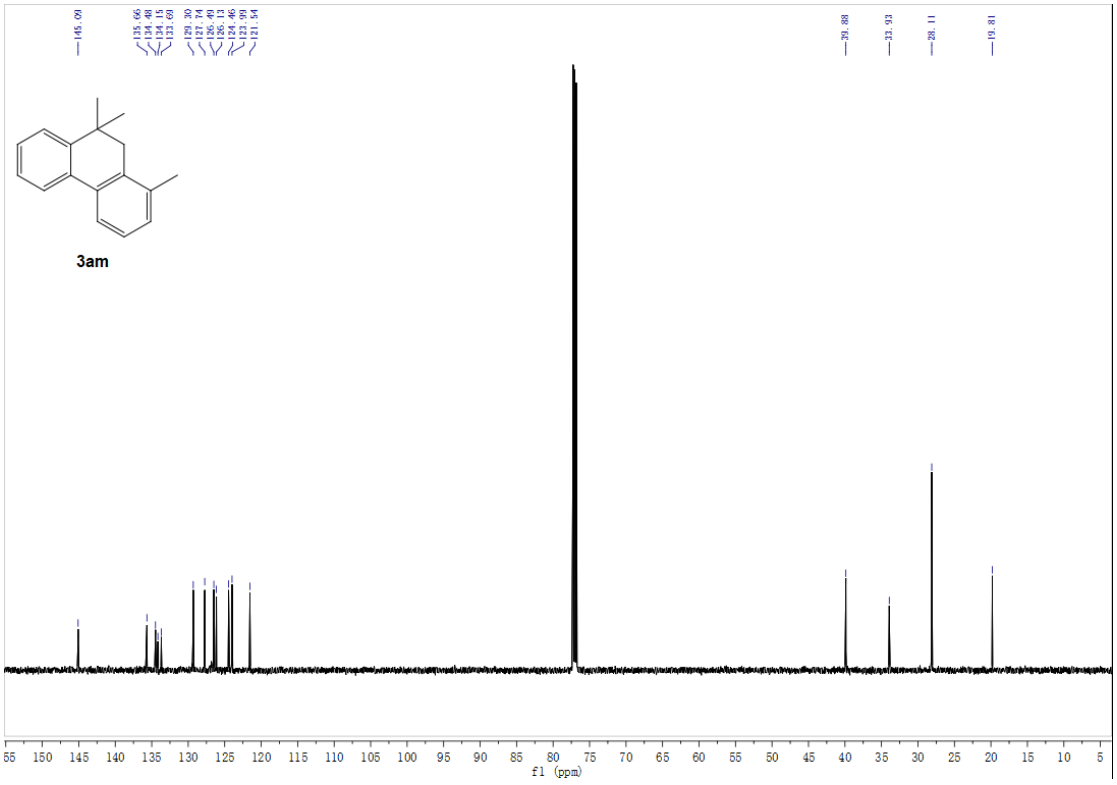
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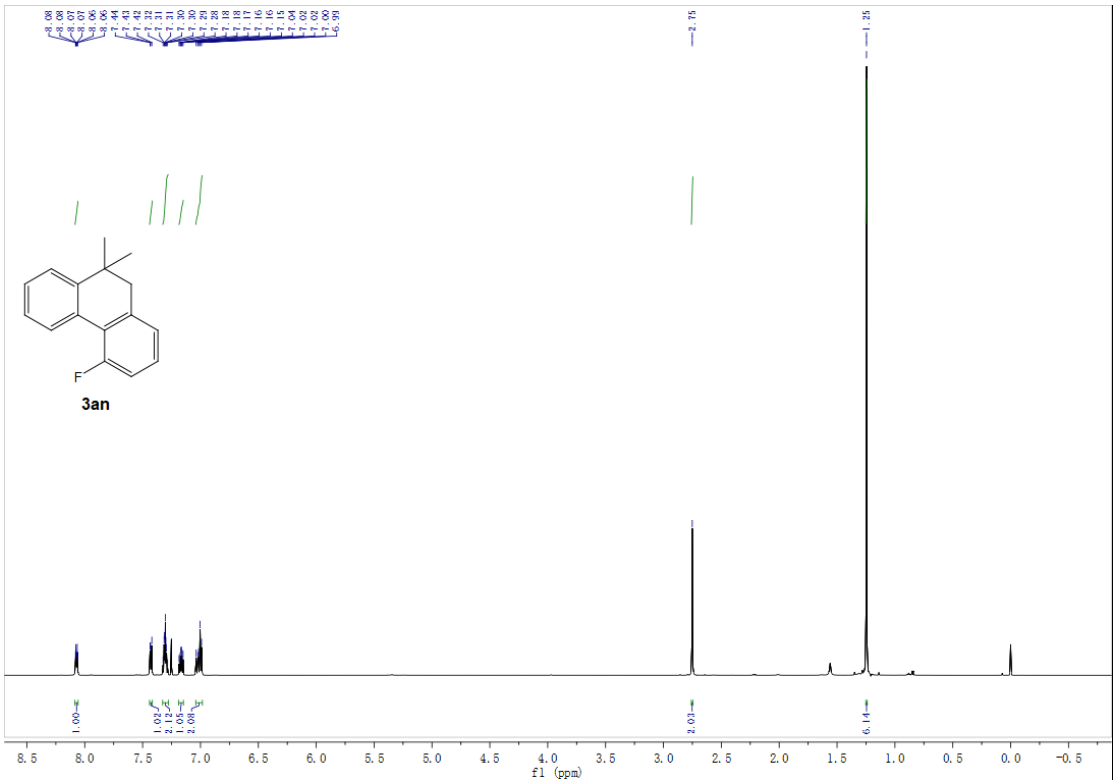
F
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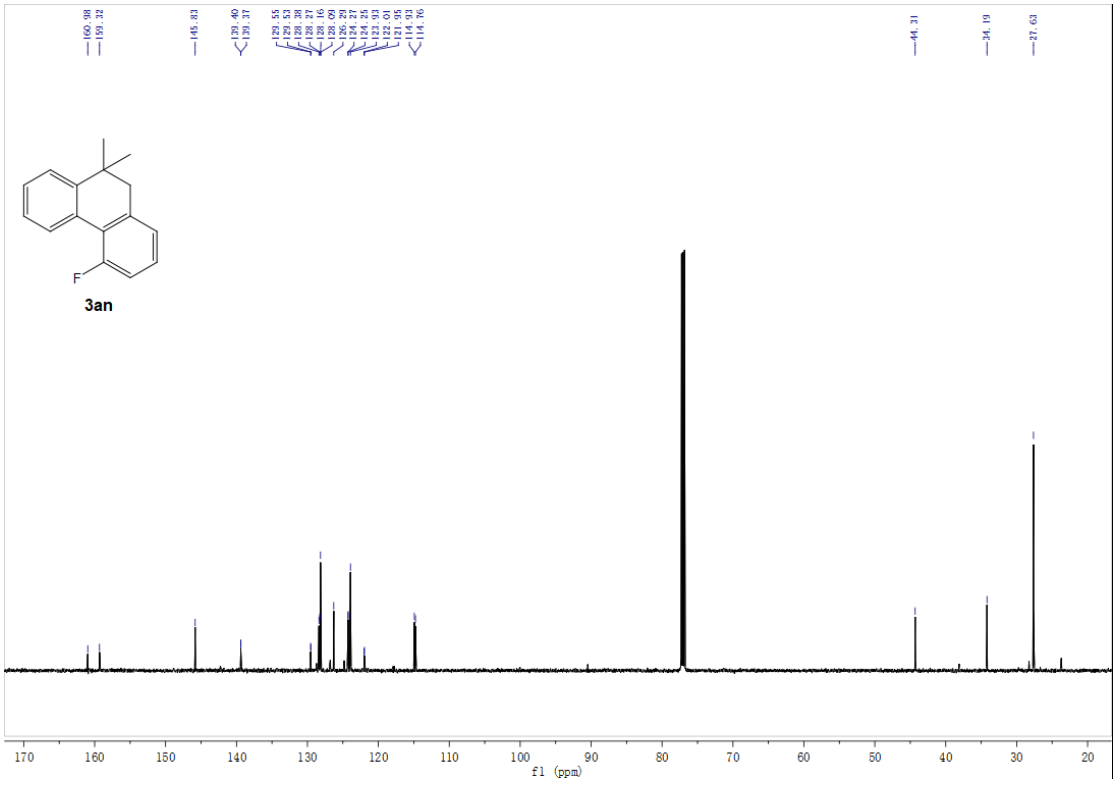
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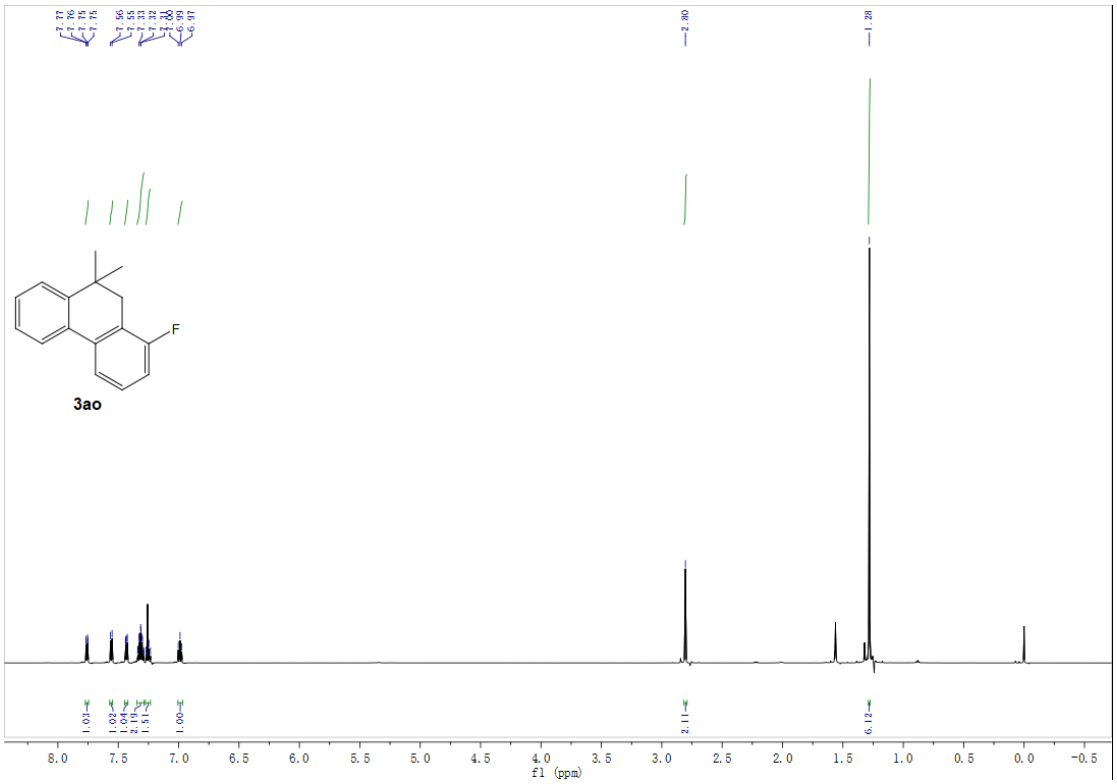
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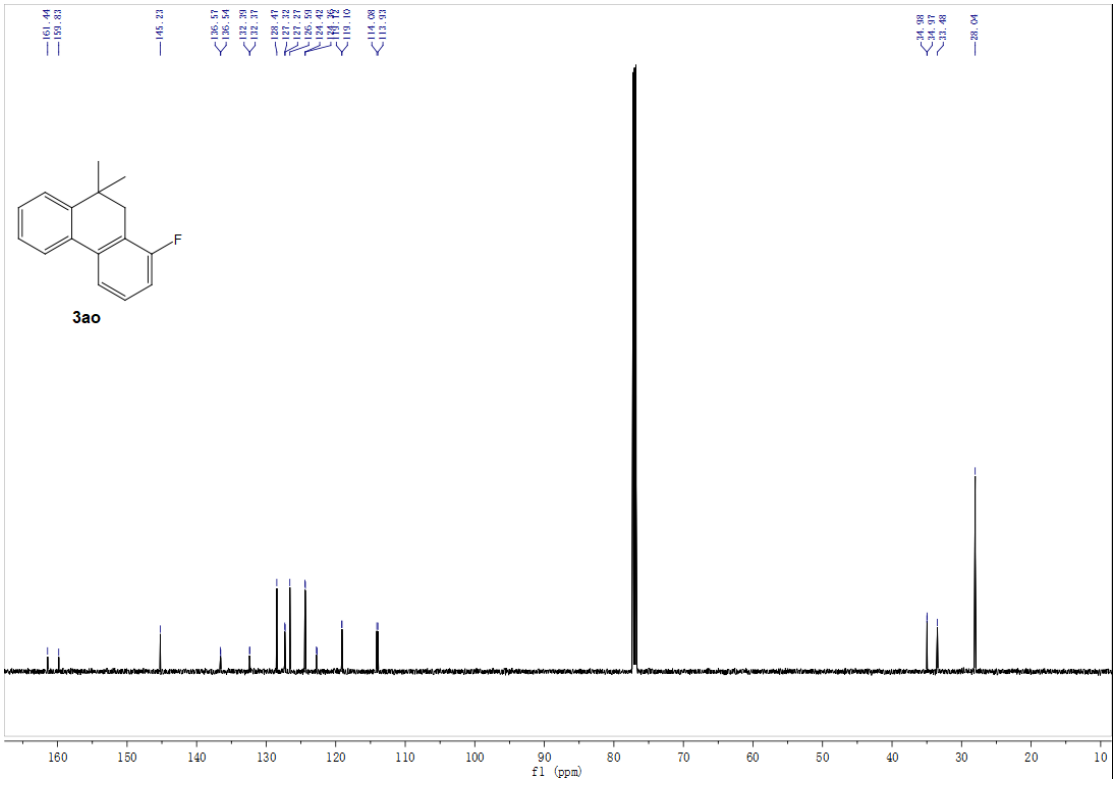
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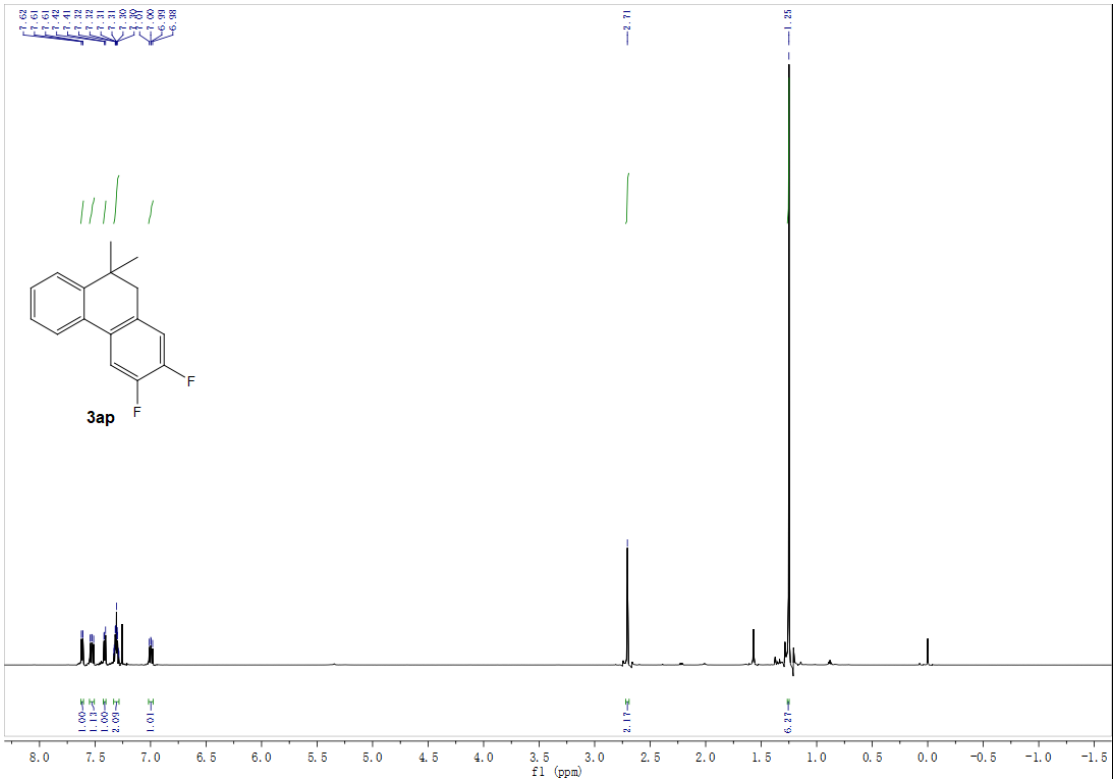
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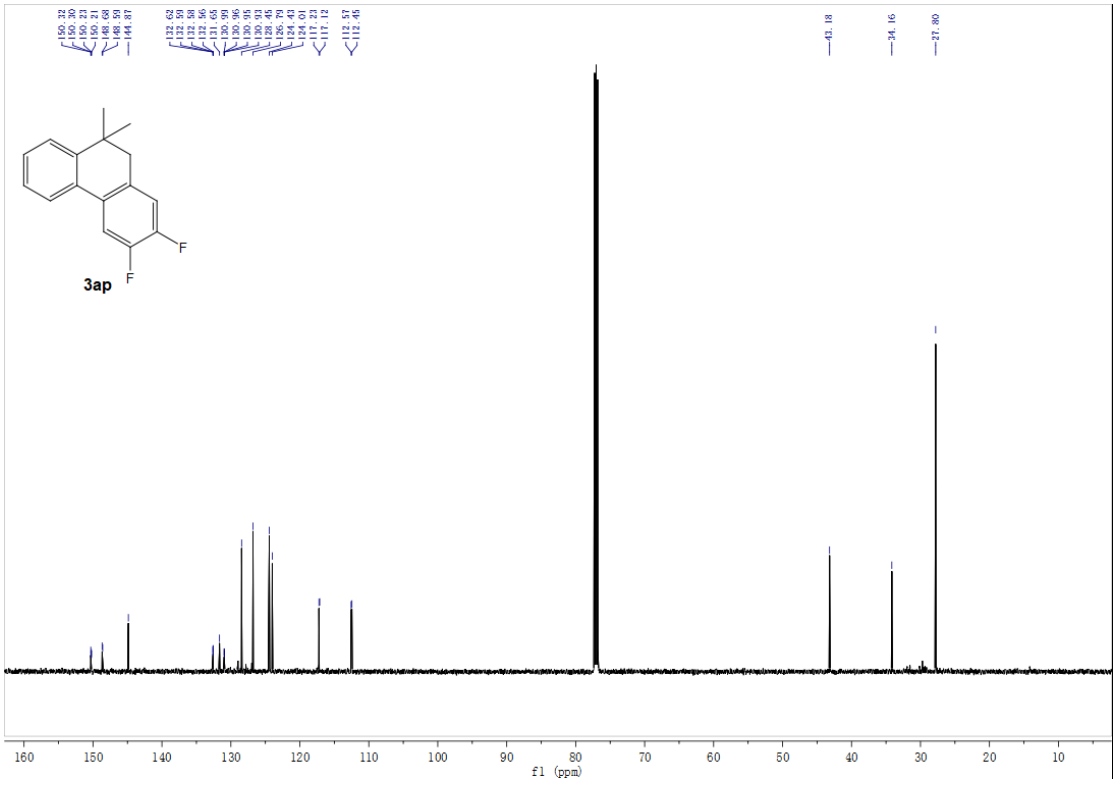
F
F
f1 (ppm)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F
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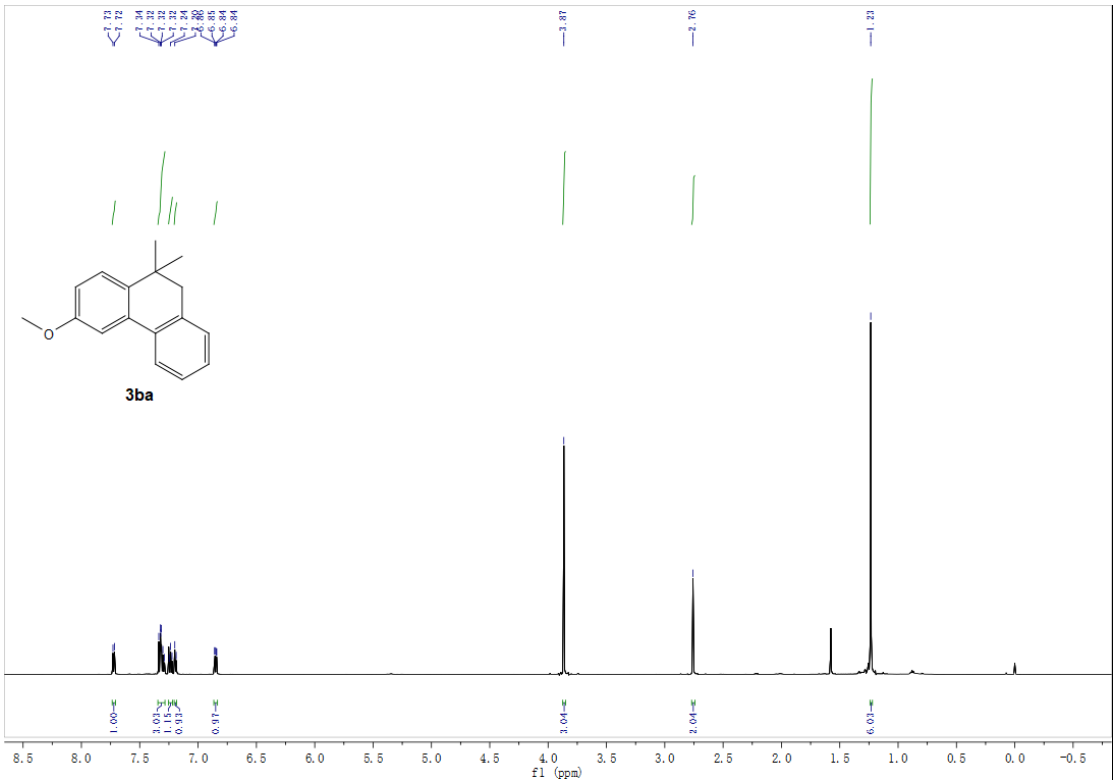
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7.23
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6.85
6.84
6.84
3.87
2.76
1.23
O
3ba
1.00
3.03
1.15
0.93
0.97
3.04
2.04
6.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
1.5
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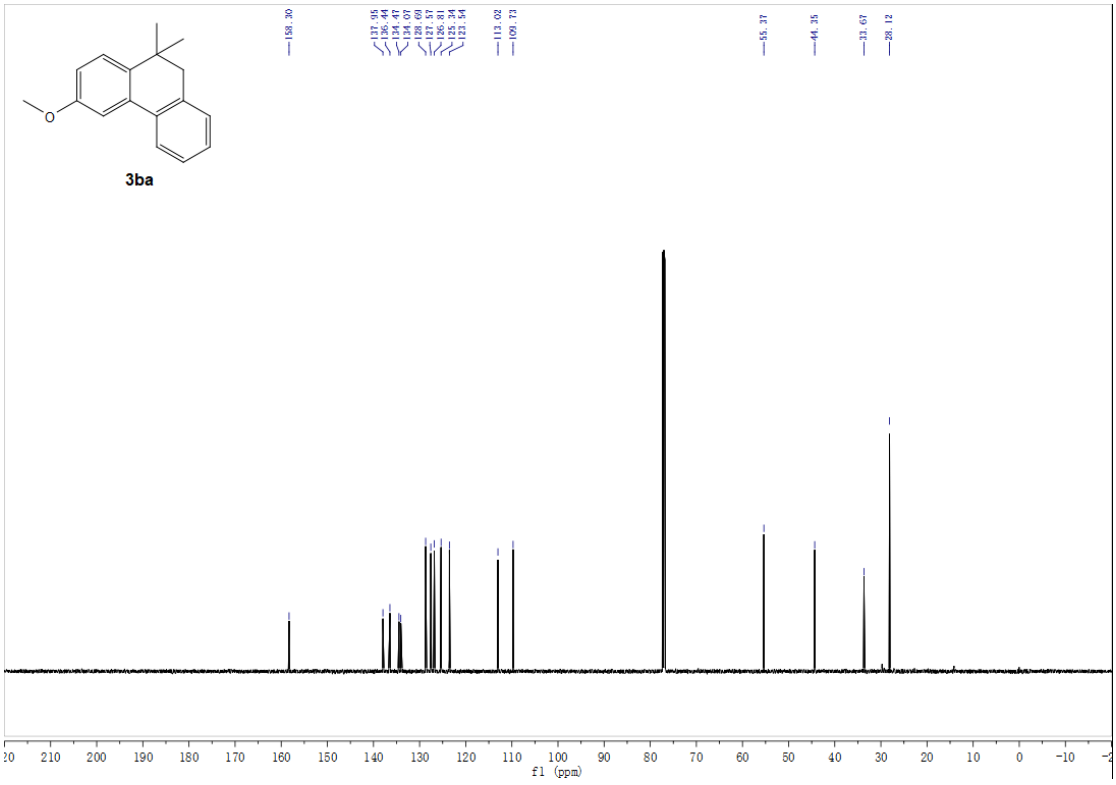
-0.5
f1 (ppm)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123.94
113.02
109.73
55.37
44.35
33.67
28.12
O
3ba
210
200
190
180
170
160
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140
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120
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100
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80
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40
30
20
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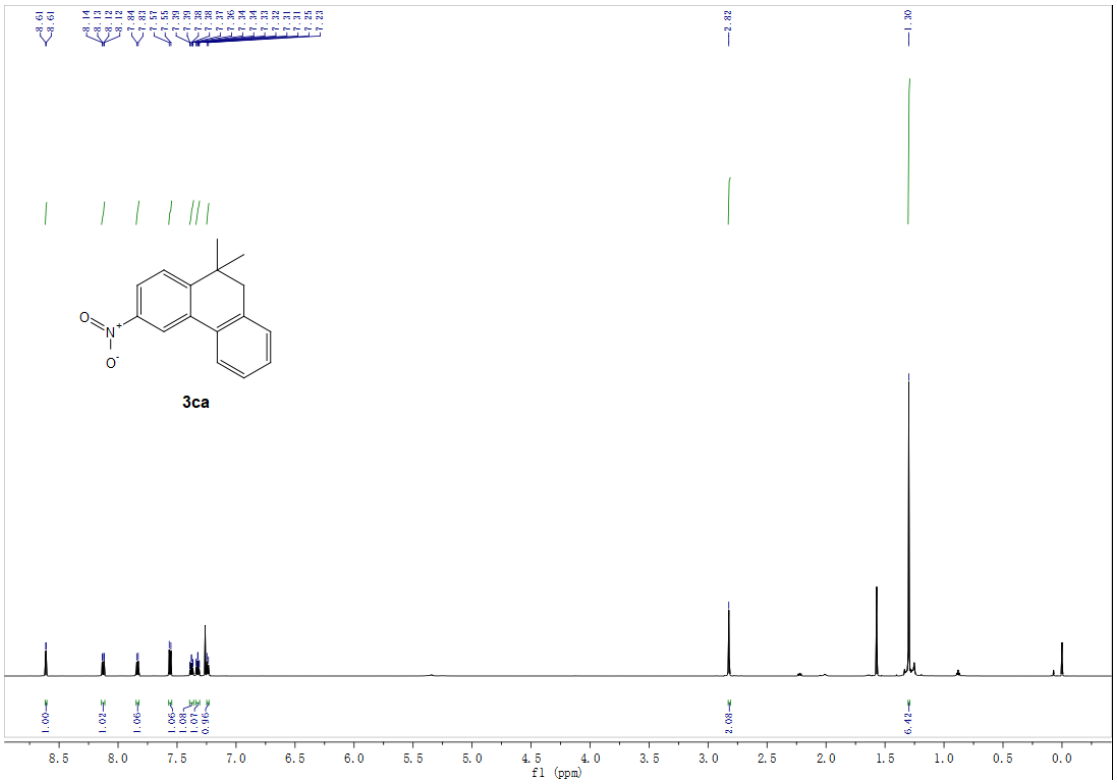
0
-10
f1 (ppm)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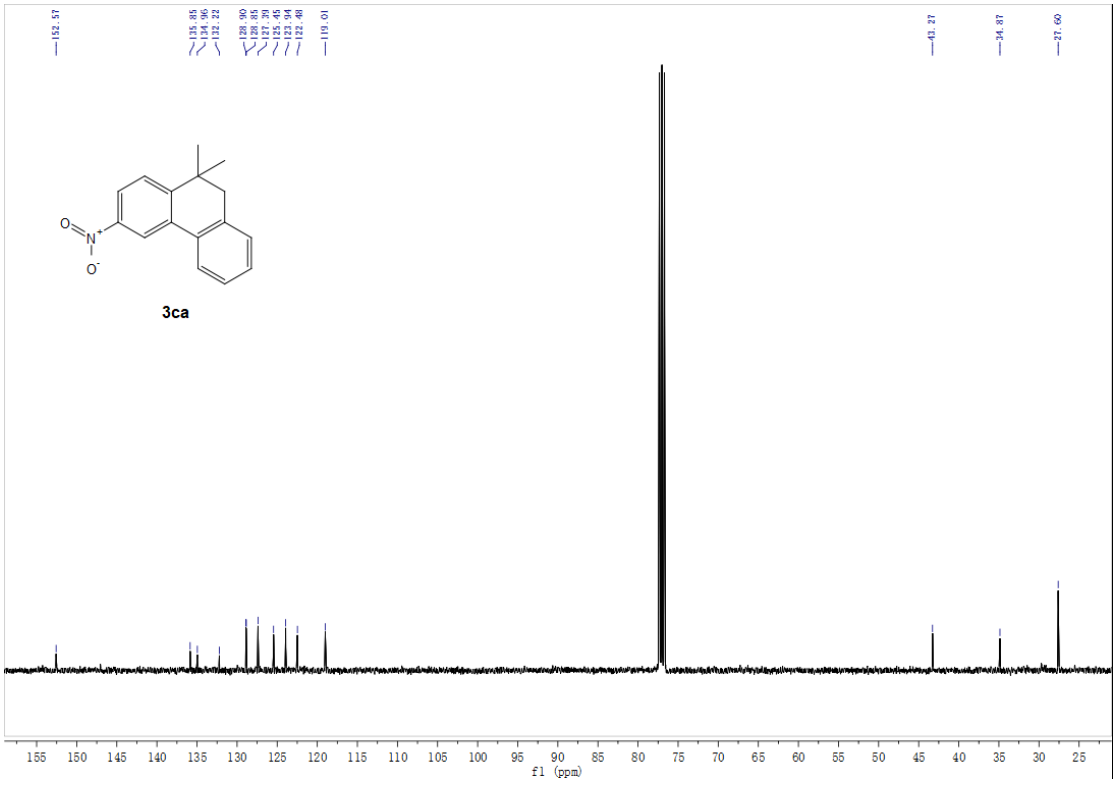
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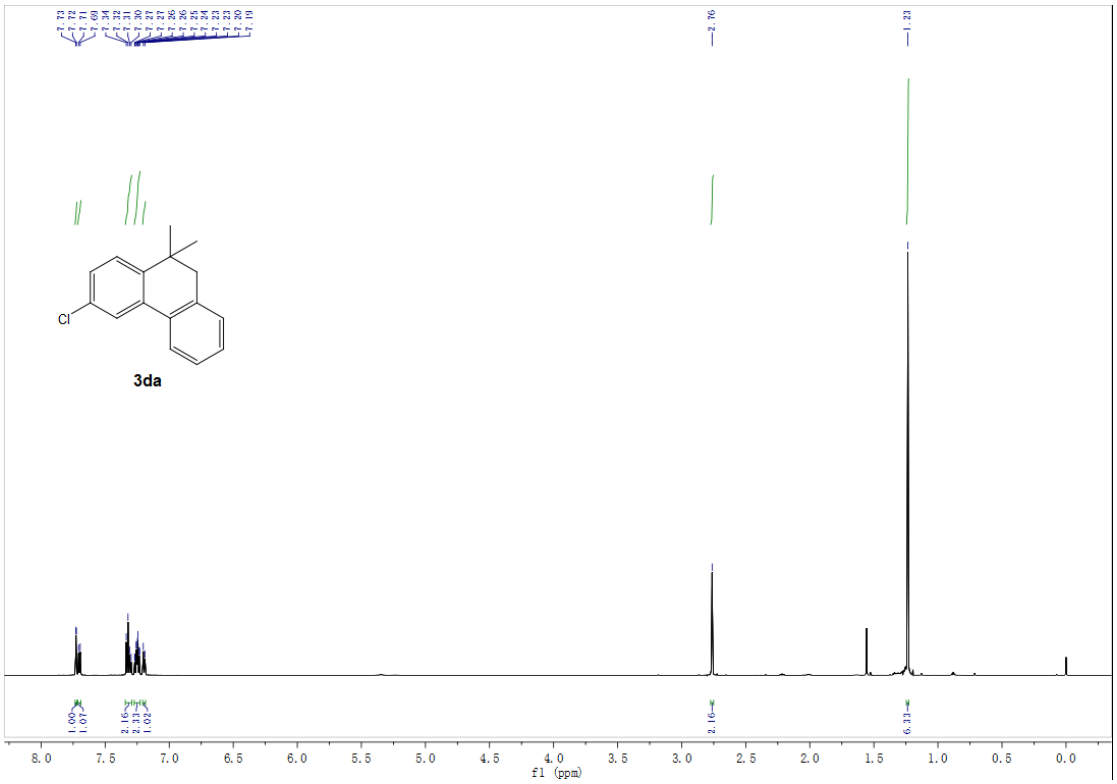
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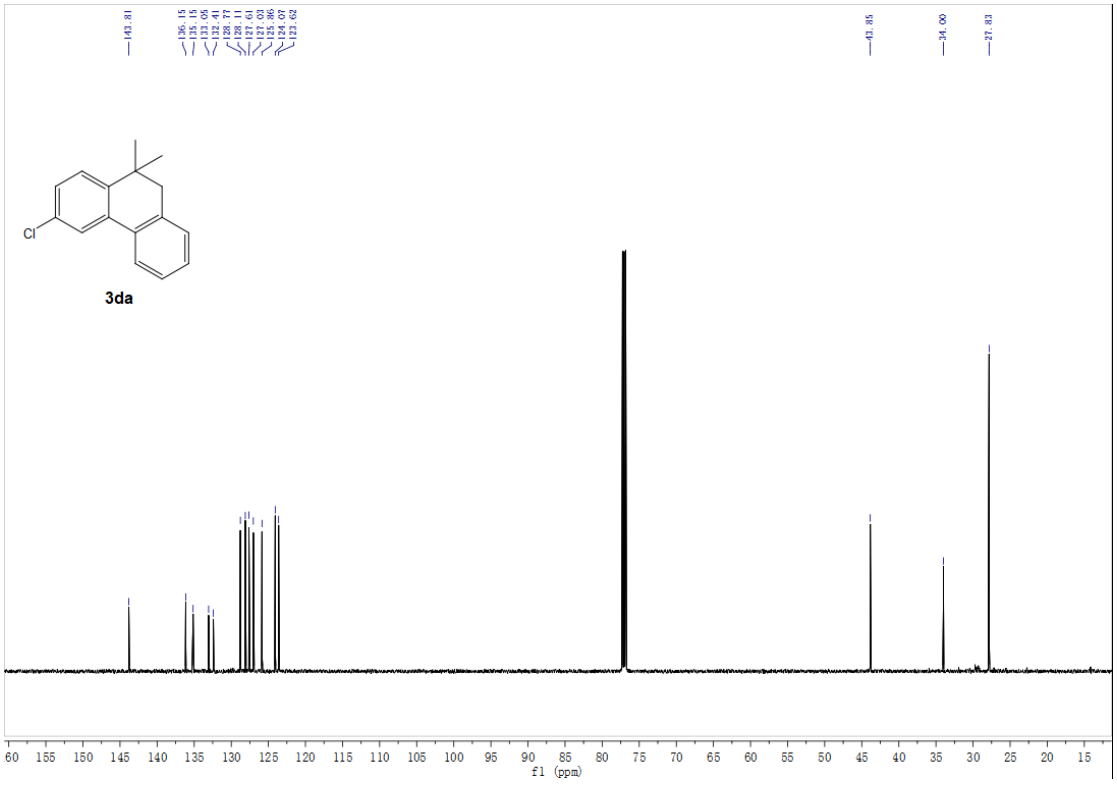
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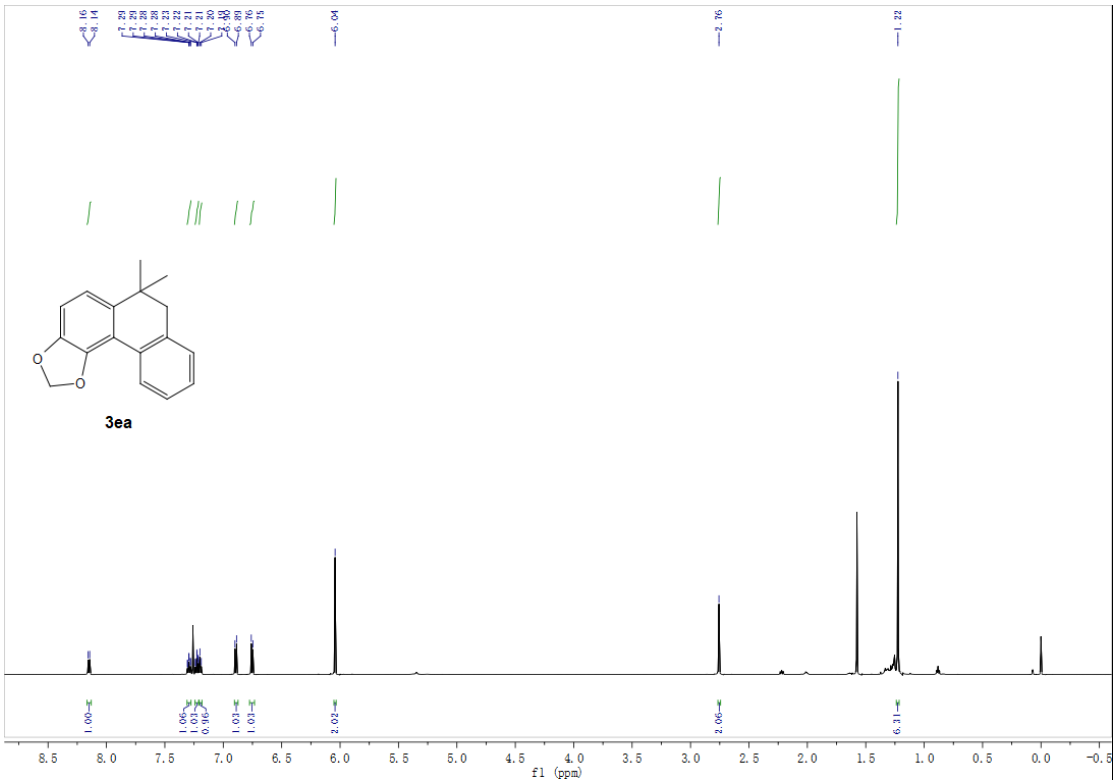
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7.21
7.20
7.19
6.76
6.75
6.04
2.76
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3ea
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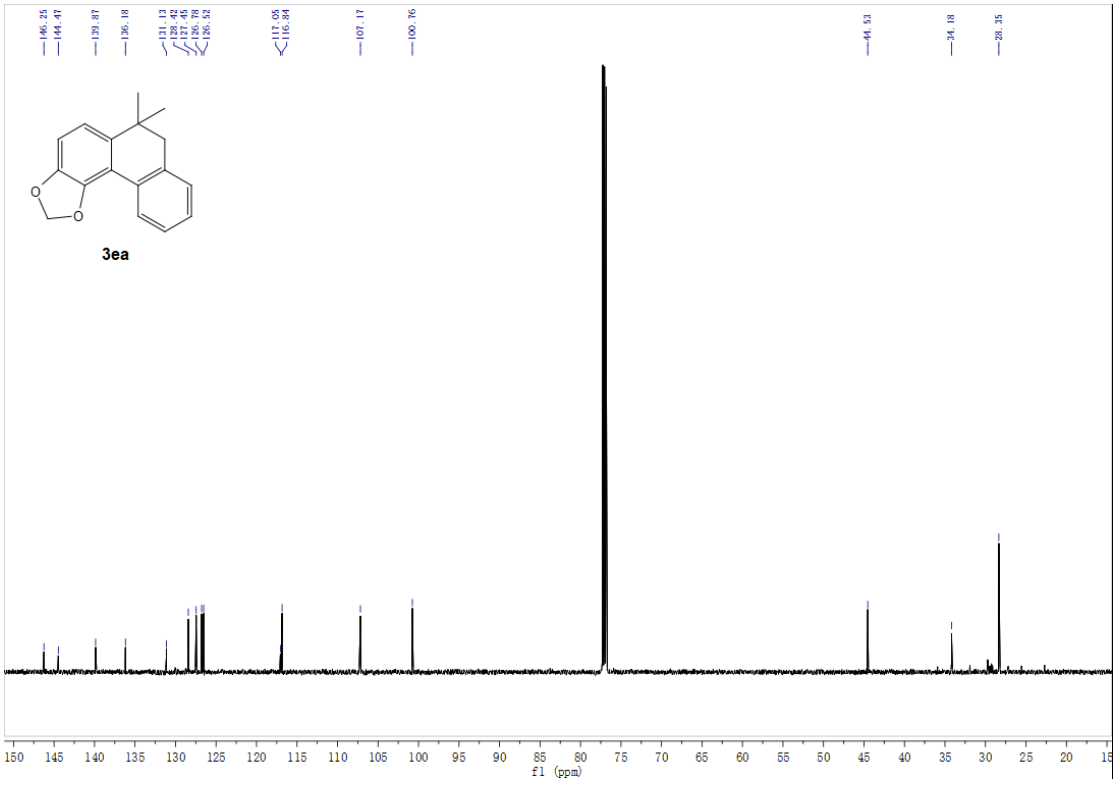
0.96
1.03
1.03
2.03
2.06
6.31
f1 (ppm)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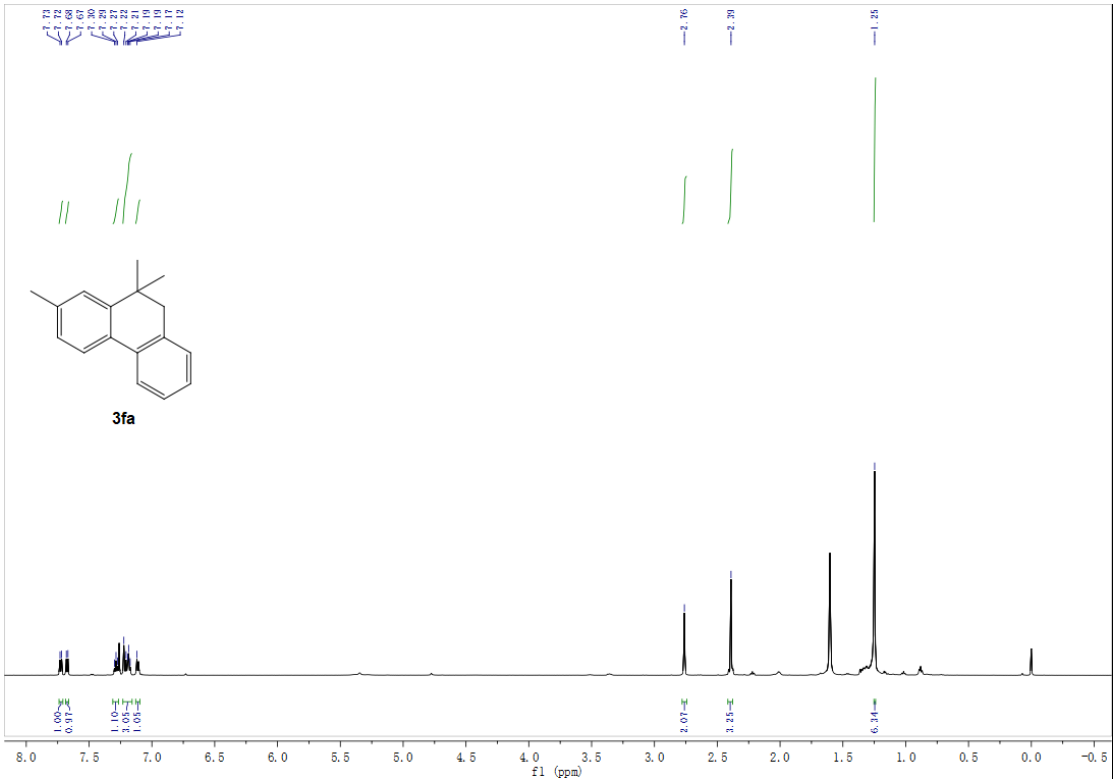
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2.76
2.39
1.25
3fa
1.00
0.97
1.10
3.05
1.05
2.07
3.25
6.34
8.0
7.5
7.0
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6.0
5.5
5.0
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2.0
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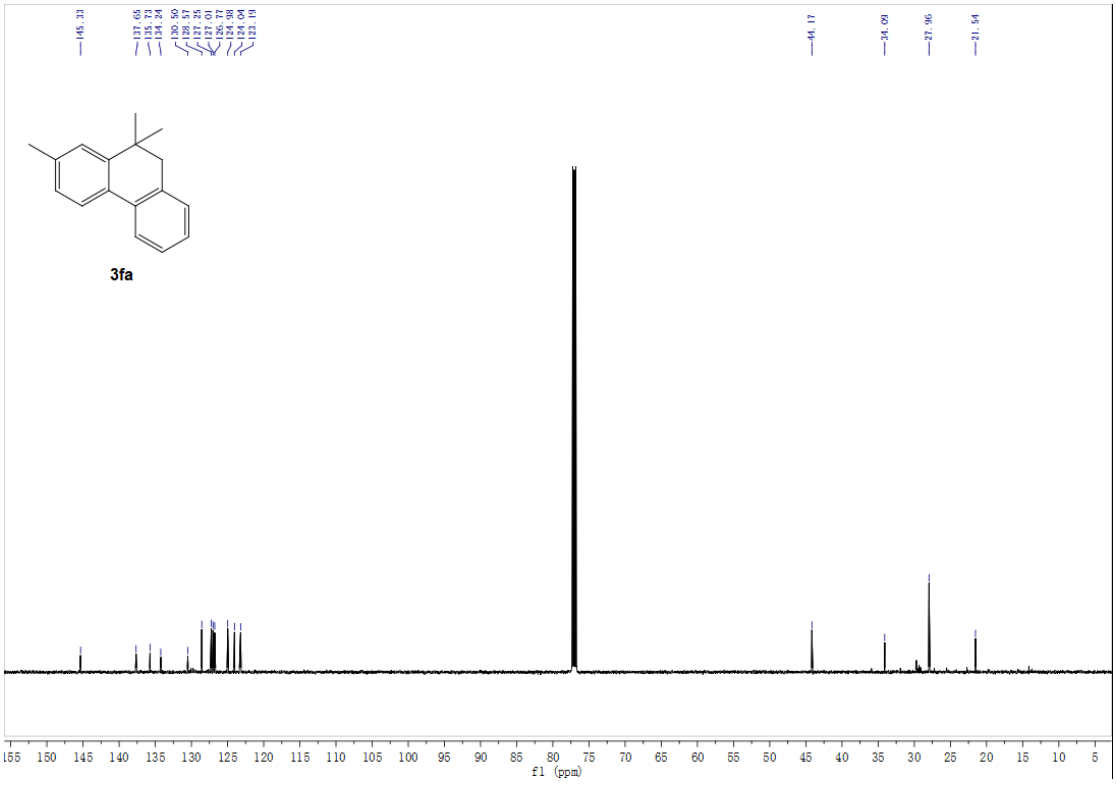
-0.5
f1 (ppm)


145.33
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123.10
44.17
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27.96
21.54
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100
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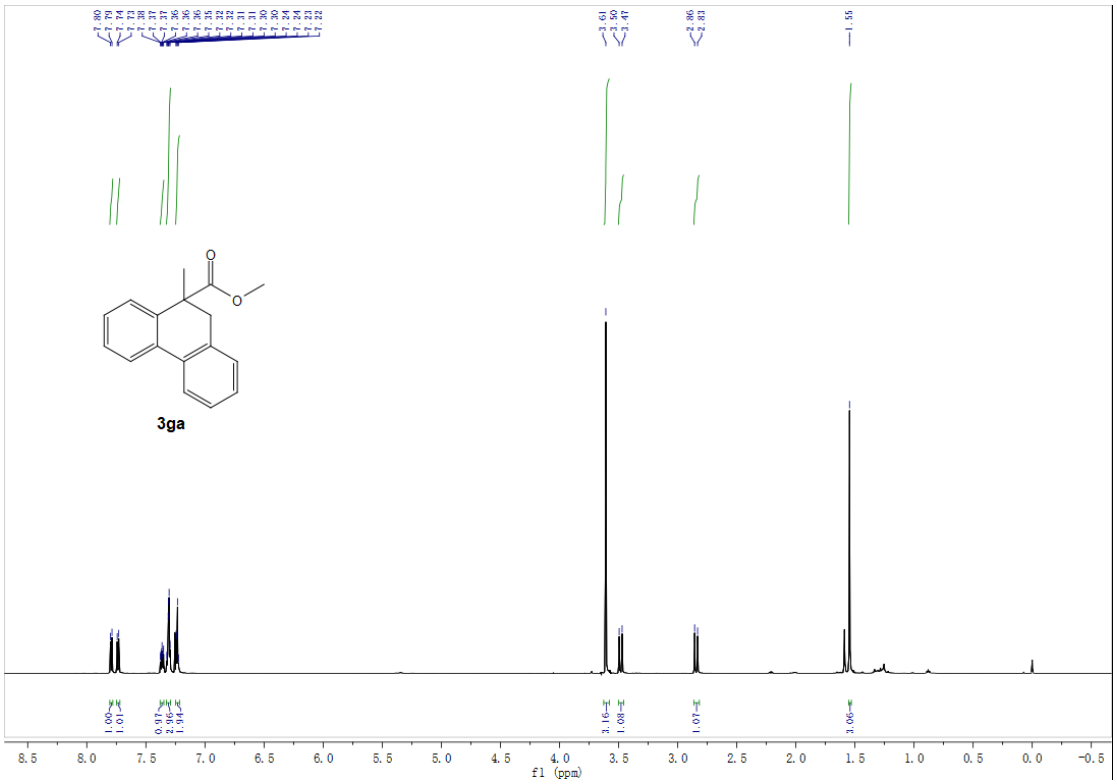
f1 (ppm)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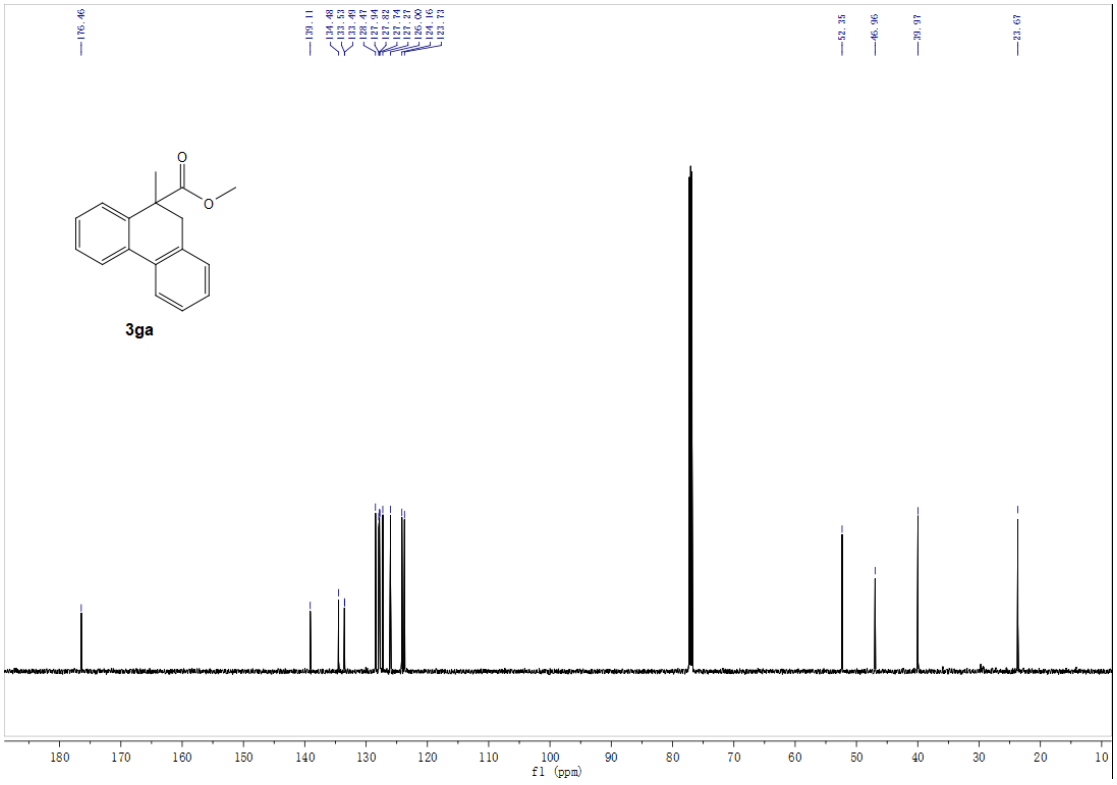
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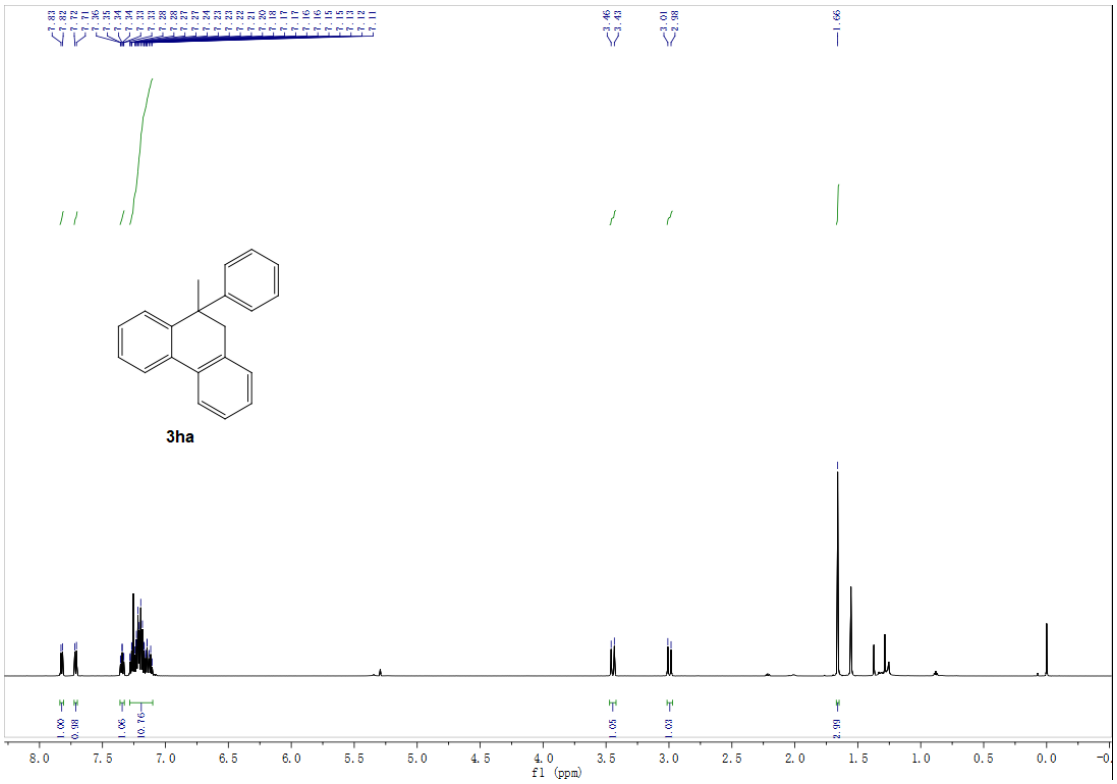
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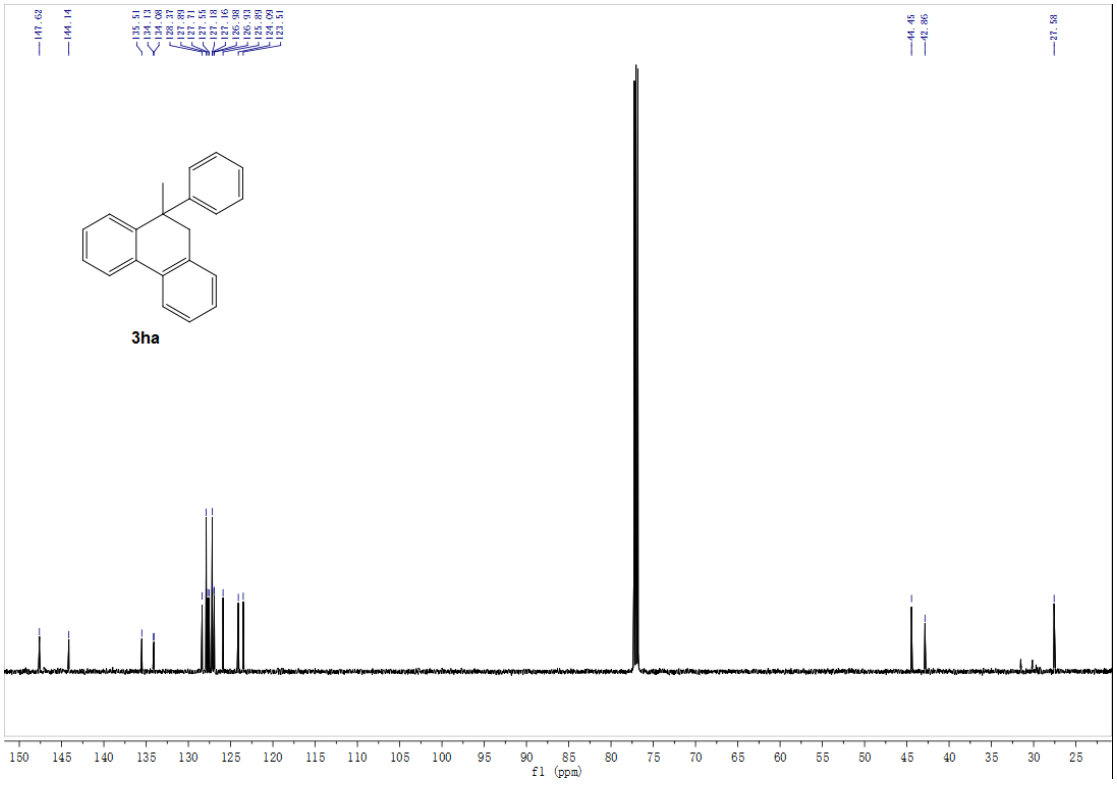
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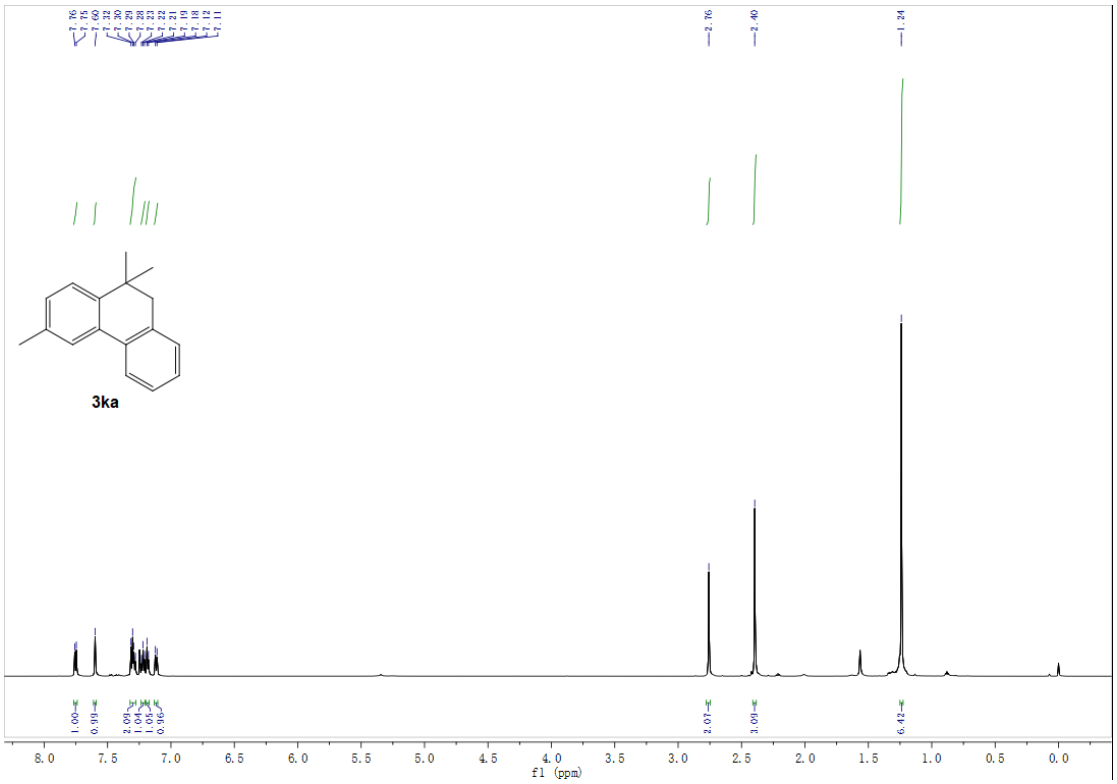
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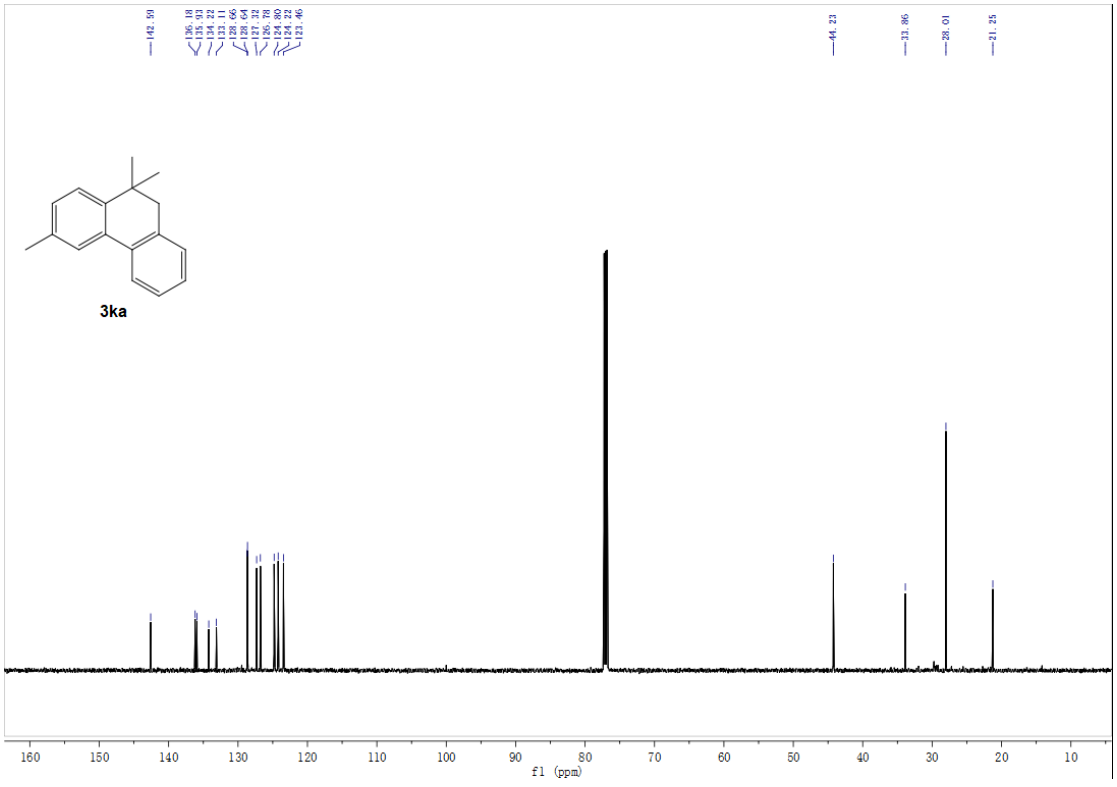
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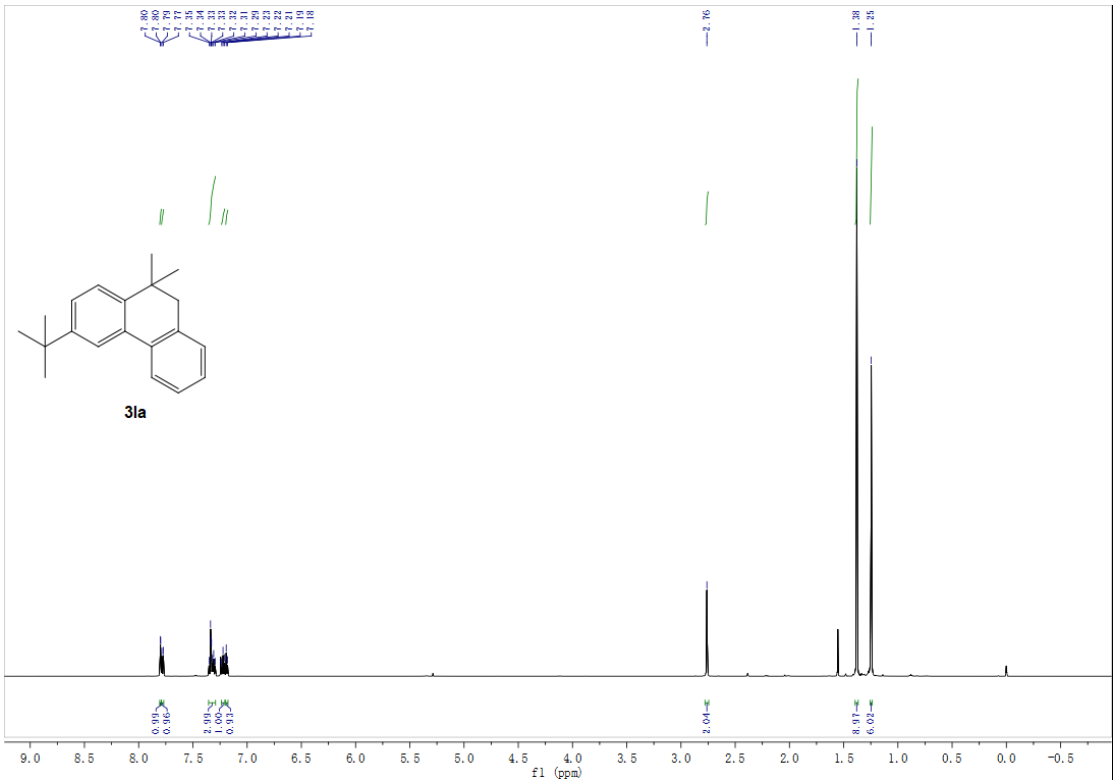
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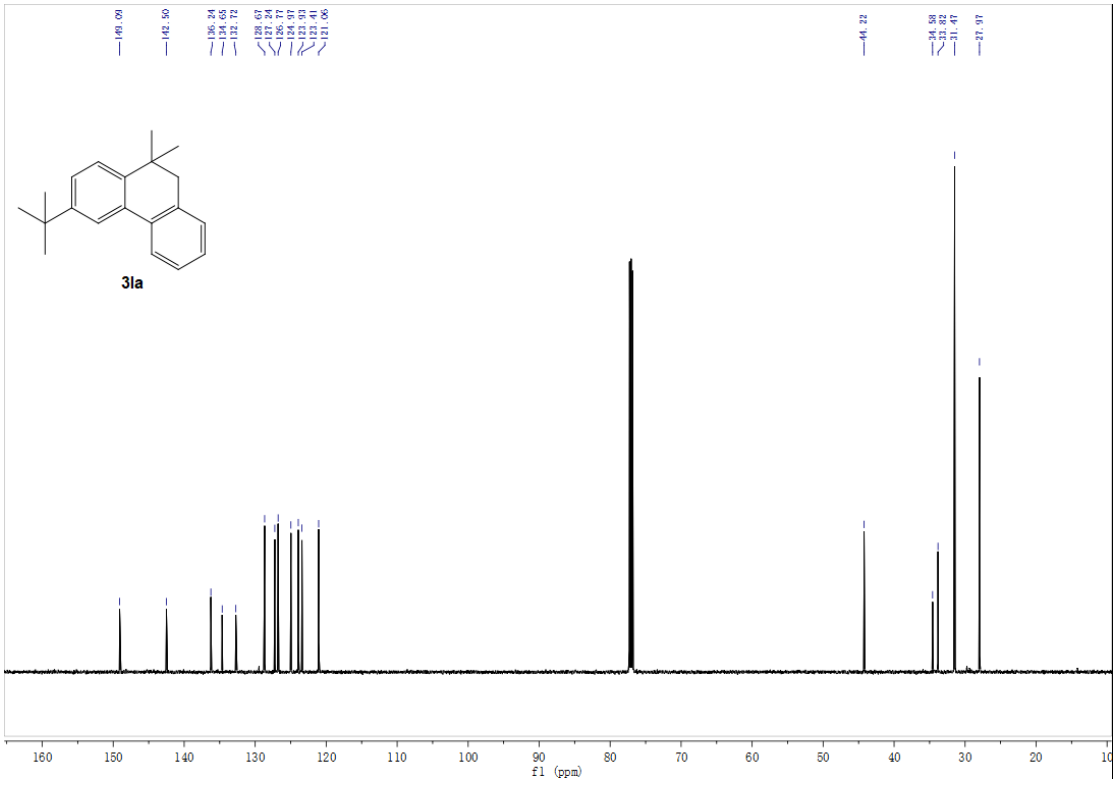
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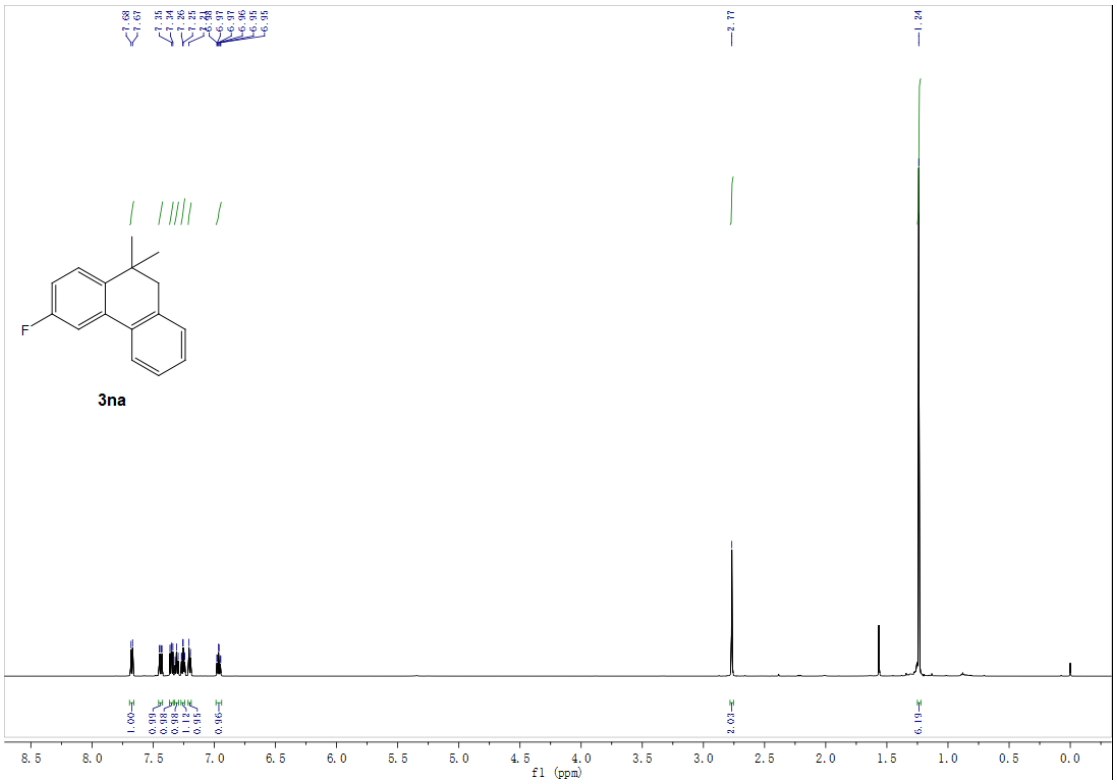
F
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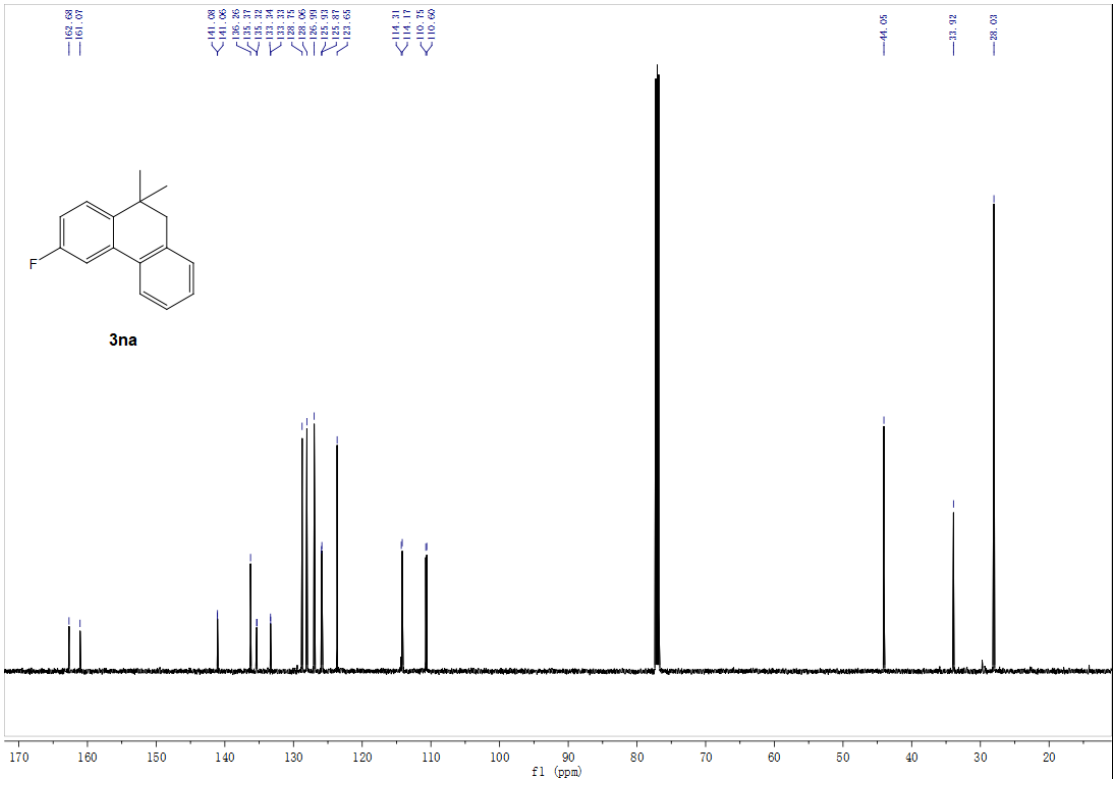
F
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f1 (ppm)