Supporting Information for

Photocatalytic iminyl radical-mediated C-C bond cleavage/ addition/cyclization cascade for synthesis of 1,2,3,4-tetrahydrophenanthrenes

Peng-Zi Wang,[a] Xiao-Ye Yu,[a] Chan-Yun Li,[a] Bin-Qing He,[a] Jia-Rong Chen,[a,*] and Wen-Jing Xiao[a,b*]

[a] Key Laboratory of Pesticide & Chemical Biology, Ministry of Education; College of Chemistry, Central China Normal University, 152 Luoyu Road, Wuhan, Hubei 430079, China.

[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, 345 Lingling Road, Shanghai 200032, China.

E-mail: chenjiarong@mail.ccnu.edu.cn; wxiao@mail.ccnu.edu.cn

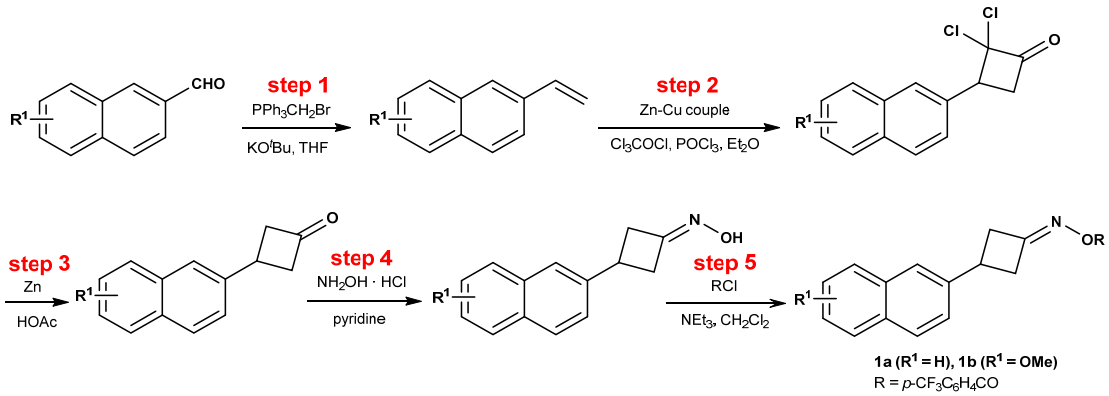
Table of Contents

1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400 or 600 MHz spectrophotometers. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 100 or 150 MHz with complete proton decoupling spectrophotometers. The high resolution mass spectra (HRMS) were measured on a Shimadzu LCMS-IT-TOF mass spectrometer or DIONEX UltiMate 3000 & Bruker Compact TOF or DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer by ESI. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

2. Preparation of Cyclobutanone Oxime Esters

2.1 Preparation of Cyclobutanone Oxime Esters 1a, 1b



To a 250 mL three-necked flask under argon were added aldehyde derivative (20.0 mmol, 1.0 equiv), potassium *tert*-butoxide (40.0 mmol, 2.0 equiv), and tetrahydrofuran (0.5 M), stirring for 30 min at 0 ℃. Then, methyltriphenylphosphonium bromide (30 mmol, 1.5 equiv) was added to the mixture. After stirring for 3 h, saturated ammonium chloride solution (30 mL) was added to the above solution, and the mixture was diluted with diethyl ether. The organic layer was washed with brine (30 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was subjected to column chromatography on SiO_2 with PE-EtOAc as an eluent to give vinylnaphthalene.

To a 250 mL three-necked flask under argon were added alkene derivative (1.0 equiv), zinc-copper couple (3.0 equiv), and anhydrous ether (0.5 M). To this was added a solution of trichloroacetyl chloride (2.0 equiv) and phosphorus oxychloride (1.1 equiv) in ether (0.5 M) over 1 h through an addition funnel. The suspension was stirred overnight at reflux. The resulting mixture was filtered through a pad of Celite and was washed with ether (80 mL). The organic solution was successively washed with water (30 mL), a saturated aqueous solution of $NaHCO_3$ (30 mL) and brine (30 mL), and dried over Na_2SO_4. Then the solution was filtered, concentrated and used in the next step without further purification.

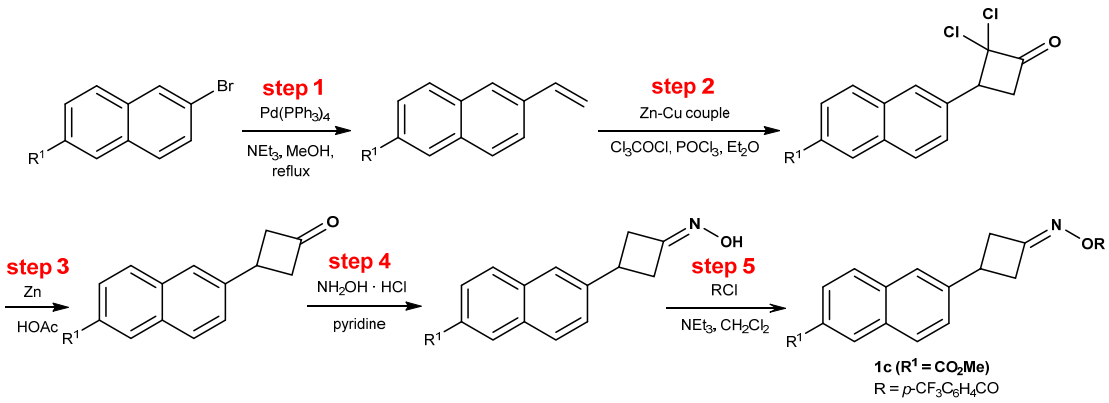
A mixture of 2,2-dichlorocyclobutanones (1.0 equiv) and zinc dust (4.0 equiv) in acetic acid (10 mL) was stirred at room temperature for 2 h and then heated at 80 °C for 5 h. The resulting mixture was allowed to cool to room temperature, then, the solution was diluted with water (30 mL) and extracted with ether (3*20 mL). The organic phase was washed successively with a saturated solution of aqueous $NaHCO_3$ (3*30 mL), water (30 mL) and brine (30 mL),

then dried over Na_2SO_4 and concentrated in vacuum. The crude material was then purified by flash chromatography with a mixture of petroleum ether and ethyl acetate to afford various cyclobutanones.

To a stirred solution of cyclobutanones (1.0 equiv) in pyridine (0.5 M) was added hydroxylamine hydrochloride (2.0 equiv) at rt. After stirring for 2 h, pyridine was removed under reduced pressure. The residue was diluted with water and extracted with EtOAc. The aqueous layer was extracted with EtOAc and the combined organicextracts were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to give the crude material, which were used in the next step without further purification.

To a mixture of cyclobutanone oxime (1.0 equiv), triethylamine (2.0 equiv) and DCM (0.5 M) in a 30-mL two-necked flask was added *p*-CF_3 benzoyl chloride (1.5 equiv) at 0 °C. After 6 h, water was added to the above solution, and the mixture was diluted with diethyl ether. The organic layer was washed with water and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was subjected to column chromatography on silica gel with PE-EtOAc as an eluent to give cyclobutanone oxime esters.[1]

2.2 Preparation of Cyclobutanone Oxime Esters 1c



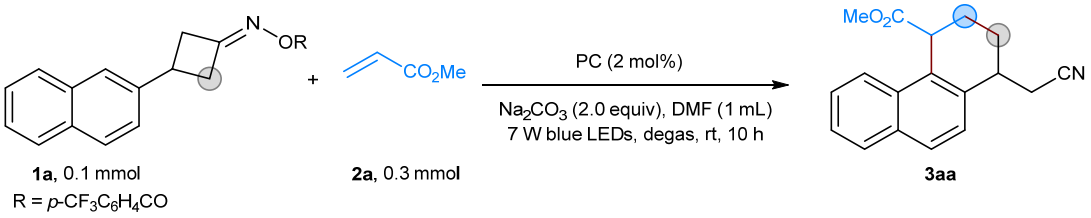
To a 250 mL three-necked flask under argon were added bromide (20.0 mmol, 1.0 equiv), tetrakis(triphenylphosphine)palladium (0.4 mmol, 2 mol%), triethylamine (40.0 mmol, 2.0 equiv) and ethanol (0.5 M). The suspension was stirred overnight at reflux. After that, water was added to the above solution, and the mixture was diluted with diethyl ether. The organic layer was washed with brine (30 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was subjected to column chromatography on silica gel with PE-EtOAc as an eluent to give vinylnaphthalene.

The following steps are same as the mentioned above.

3. Detailed Optimization of Reaction Conditions and Control Experiments

3.1 Optimization of Reaction Conditions

Table S1. Screening of Photocatalysts

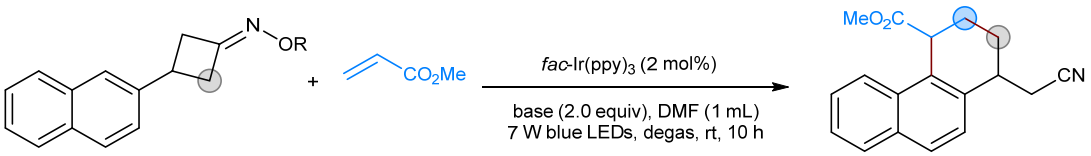


Entry[a]	Photocatalyst	dr[c]	Yield[b] [%]
1	***fac-Ir(ppy)$_3$***	***2:1***	***28***
2	Ir-(2,4-diFppy)$_3$	-	No reaction
3	Ir-(4-Fppy)$_3$	-	No reaction
4	Ir-(4-Fppy)$_2$(dtppy)PF$_6$	-	No reaction
5	Ir-(Fppy)$_2$bpy	-	No reaction
6	Ir-(ppy)$_2$(dtbbpy)PF$_6$	-	No reaction

[a] Unless otherwise noted, reactions were carried out with **1a** (38.34 mg, 0.10 mmol), **2a** (26.01 mg, 0.30 mmol), PC (2 mol%) and Na_2CO_3 (21.2 mg, 2.0 equiv) in DMF (1.0 mL) at rt under 7 W blue LEDs. [b] Determined by isolated yield. [c] Determined by ^{1}H NMR analysis after flash chromatography.

As shown in Table *S1*, among all the photocatalysts tested, *fac*-Ir(ppy)$_3$ gave the best results in terms of yield (28% yield, 2:1 dr), and was thus selected for further optimization studies.

Table S2. Screening of Bases



1a, 0.1 mmol
R = *p*-$CF_3C_6H_4CO$

2a, 0.3 mmol

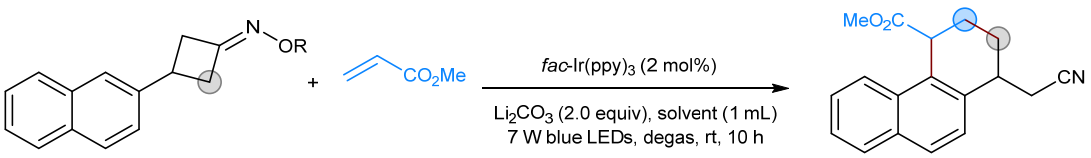
3aa

Entry[a]	Base	dr[c]	Yield[b] [%]
1	K_2CO_3	2:1	32
2	NaOAc	2:1	54
3	Cs_2CO_3	2:1	41
4	***Li_2CO_3***	***2:1***	***66***
5	Na_2CO_3	2:1	28
6	DABCO	2:1	20
7	DBU	2:1	19

[a] Unless otherwise noted, reactions were carried out with **1a** (38.34 mg, 0.10 mmol), **2a** (26.01 mg, 0.30 mmol), *fac*-Ir(ppy)$_3$ (2 mol%) and base (2.0 equiv) in DMF (1.0 mL) at rt under 7W blue LEDs. [b] Isolated yield. [c] Determined by ^{1}H NMR analysis after flash chromatography.

As shown in Table *S2*, among the bases tested, Li_2CO_3 gave the best results (66% yield, 2:1 dr), and was thus selected for further studies.

Table *S3*. Screening of Solvents



1a, 0.1 mmol
R = *p*-$CF_3C_6H_4CO$

2a, 0.3 mmol

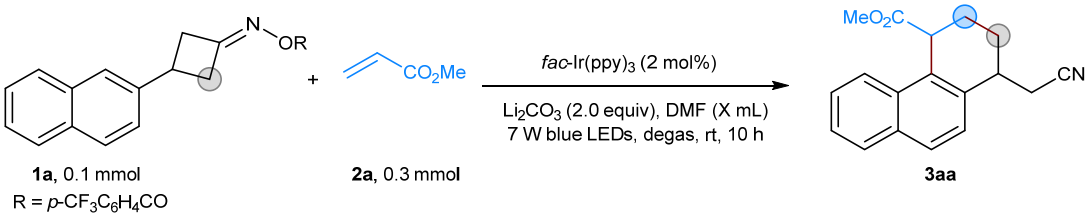
3aa

Entry[a]	Solvent	dr[c]	Yield[b] [%]
1	CH_3CN	2:1	41
2	CH_2Cl_2	2:1	43
3	DCE	2:1	39
4	toluene	2:1	36
5	$CF_3CH_2C_6H_5$	2:1	No reaction
6	DMSO	2:1	63 (45[d])
7	DMA	2:1	70 (55[d])
8	acetone	2:1	Not the desired point
9	CH_3OH	2:1	48
10	DCE	2:1	46
11	***DMF***	***2:1***	***85 (66[b])***

[a] Unless otherwise noted, reactions were carried out with **1a** (38.34 mg, 0.10 mmol), **2a** (26.01 mg, 0.30 mmol), *fac*-Ir(ppy)$_3$ (2 mol%) and Li_2CO_3 (14.78 mg, 2.0 equiv) in solvent (1.0 mL) at rt under 7 W blue LEDs.[b] NMR yield. [c] Determined by ^{1}H NMR analysis. [d] Isolated yield.

As show in Table *S3*, among all the solvents tested, DMF gave the best results in terms of yield (66% yield, 2:1 dr), and was thus selected for further optimization studies.

Table S4. Screening of Concentration



1a, 0.1 mmol
R = *p*-$CF_3C_6H_4CO$

2a, 0.3 mmol

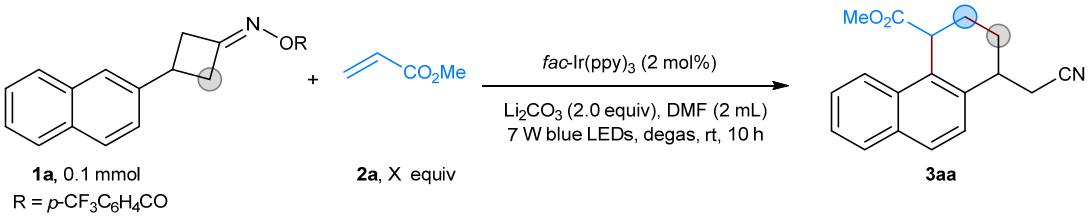
3aa

Entry[a]	Concentration	dr[c]	Yield[b] [%]
1	***0.05***	***2:1***	***80***
2	0.1	2:1	66
3	0.2	2:1	62
4	0.4	2:1	52

[a] Unless otherwise noted, reactions were carried out with **1a** (38.34 mg, 0.10 mmol), **2a** (26.01 mg, 0.30 mmol), *fac*-Ir(ppy)$_3$ (2 mol%) and Li_2CO_3 (2.0 equiv) in DMF (X mL) at rt under 7W blue LEDs. [b] Isolated yield. [c] Determined by ^{1}H NMR analysis after flash chromatography.

As shown in Table *S4*, among the concentration tested, 0.05 M gave the best result in terms of yield (80% yield, 2:1 dr) and the optimized reaction condition was confirmed.

Table S5. Screening of Substrate Ratios

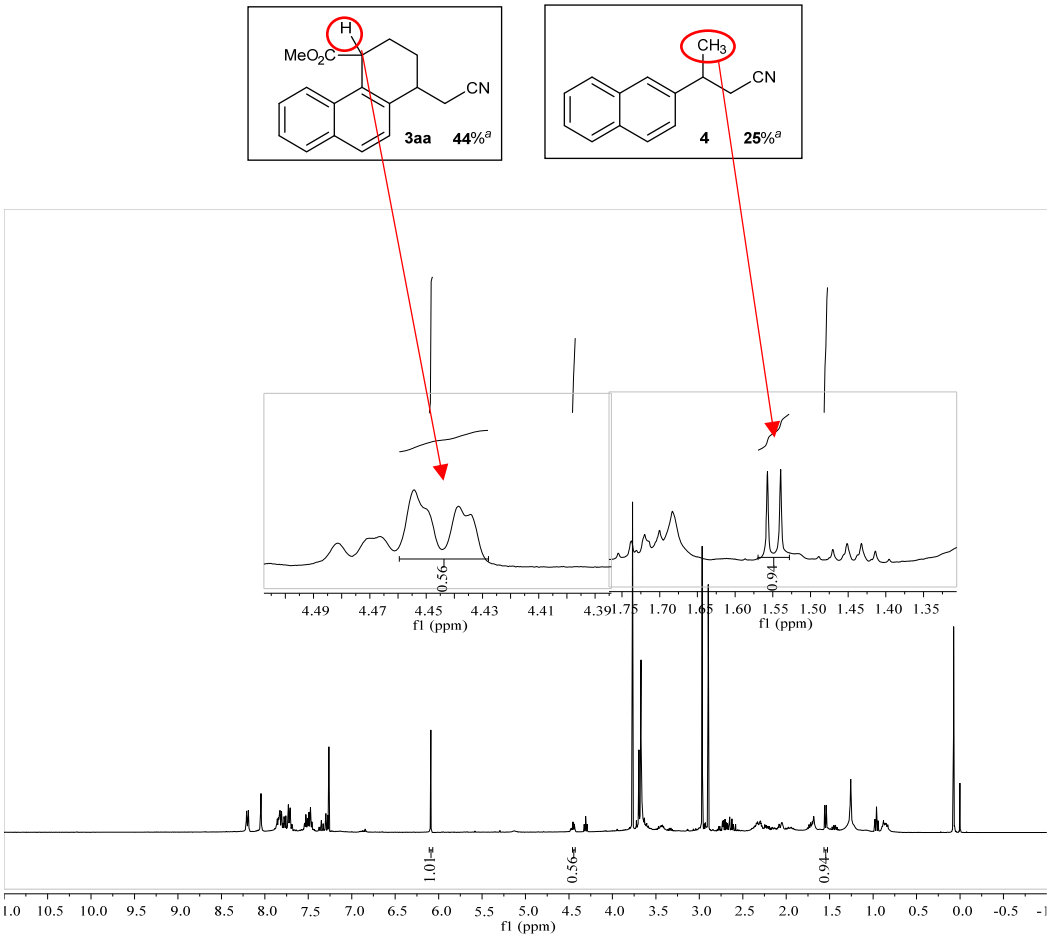


Entry[a]	Ratio of **2a** to **1a** (X)	dr[c]	Yield[b] [%]
1	***3.0***	***2:1***	***80***
2	1.5	2:1	65

[a] Unless otherwise noted, reactions were carried out with **1a** (38.34 mg, 0.10 mmol), **2a** (X equiv), *fac*-Ir(ppy)$_3$ (2 mol%) and Li_2CO_3 (2.0 equiv) in DMF (2 mL) at rt under 7 W blue LEDs. [b] Isolated yield. [c] Determined by ^{1}H NMR analysis after flash chromatography.

As shown in Table *S5*, among the ratio tested, 3.0 equiv of **2a** gave the best result in terms of yield (80% yield, 2:1 dr) and the optimized reaction condition was confirmed.

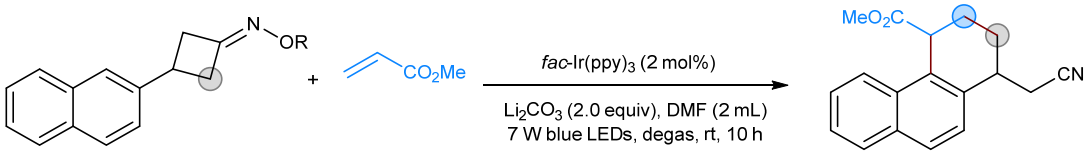
Detection of sideproduct 4 in the reaction mixture



[a] Reaction conditions: **1a** (38.34 mg, 0.10 mmol), **2a** (12.97 mg, 0.15 mmol), *fac*-Ir(ppy)$_3$ (2 mol%) and Na_2CO_3 (2.0 equiv) in DMF (1.0 mL) at rt under 7 W blue LEDs. Determined by ^{1}H NMR mixed spectra analysis.

3.2 Control Experiments for Synthesis of 3aa

Table *S6.* Control Experiments



1a, 0.1 mmol
R = *p*-$CF_3C_6H_4CO$

2a, 0.3 mmol

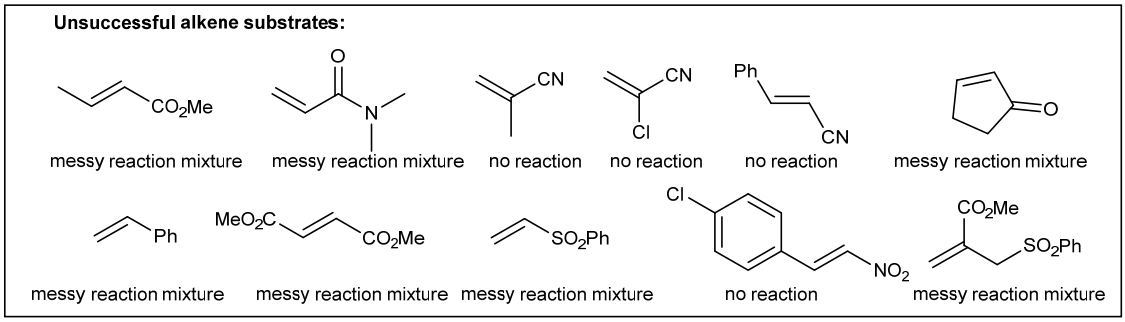
3aa

Entry[a]	*hv*	Photocatalyst	Base	Yield[b] (%)
1[c]	-	+	+	No reaction
2[d]	+	-	+	No reaction
4[e]	+	+	-	49
5	+	+	+	80

[a] Unless otherwise noted, reactions were carried out with **1a** (38.34 mg, 0.10 mmol), **2a** (26.01 mg, 0.30 mmol), *fac*-$Ir(ppy)_3$ (2 mol%) and Li_2CO_3 (2.0 equiv) in DMF (2 mL) at rt under 7 W blue LED. [b] Isolated yield. [c] Without visible light irradiation. [d] Without photocatalyst. [e] Without base.

The results of Table S6 reveal that synthesis of **3aa** is indeed a photocatalytic process.

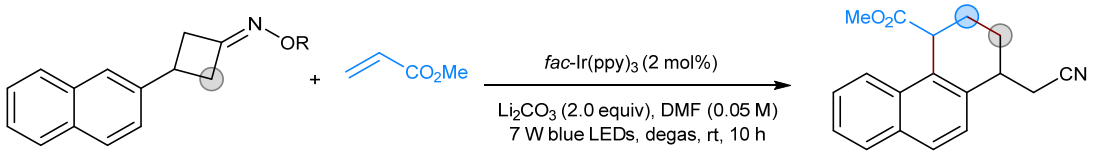
3.3 Unsuccessful Alkene Substrates



As shown above, we have also reacted a series of other 1,1-disubstituted, 1,2-disubstituted alkene substrates with **2a** under the standard conditions. Unfortunately, these unsuccessful substrates resulted in no conversion or messy reaction mixture. Further optimization of catalytic system to address these limitations is ongoing.

4. General Procedure and Spectral Data of Products

4.1 General Procedure for Synthesis of 3



1a, 0.2 mmol
R = *p*-$CF_3C_6H_4CO$

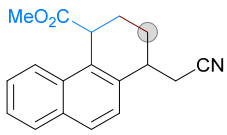
2a, 0.6 mmol

3aa

1a (76.67 mg, 0.2 mmol), **2a** (52.02 mg, 0.6 mmol), *fac*-Ir(ppy)$_3$ (2 mol%) and Li_2CO_3 (2.0 equiv) were dissolved in DMF (4 mL). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times). After that, the solution was stirred at a distance of ~5 cm from a 7W blue LEDs (450-460 nm) at room temperature about 10 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethylacetate 5:1) directly to give the desired product **3aa** in 80% yield as a colorless oil.

4.2 Spectral Data of Products

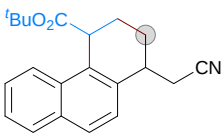
methyl 1-(cyanomethyl)-1,2,3,4-tetrahydrophenanthrene-4-carboxylate 3aa



3aa

43.58 mg, 78% yield (2:1 dr); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 – 7.74 (m, 5H, major+minor), 7.53 – 7.44 (m, 3H, major+minor), 7.31 (d, *J* = 8.6 Hz, 1H, minor), 7.26 (d, *J* = 8.5 Hz, 1H, major), 4.46 (d, *J* = 4.3 Hz, 1H, major), 4.43 (d, *J* = 6.4 Hz, 1H, minor), 3.68 (s, 2H, minor), 3.66 (s, 3H, major), 3.43 – 3.36 (m, 2H, major+minor), 2.95 – 2.03 (m, 6H, major+minor). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm, major+minor) 175.1, 174.7, 134.6, 132.7, 132.5, 132.4, 132.4, 129.8, 128.9, 128.5, 127.0, 126.9, 125.8, 125.8, 125.5, 122.9, 122.8, 118.8, 118.6, 52.4, 52.4, 41.8, 41.0, 35.2, 24.6, 23.0, 22.0. IR (in KBr): 2930, 2250, 1720, 1375, 1312, 1125 cm^{-1}. HRMS (EI): m/z [M + Na]$^+$ calcd for $C_{18}H_{17}NNaO_2$: 302.1151, found: 302.1153.

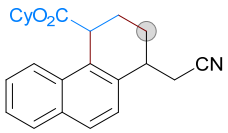
tert-butyl 1-(cyanomethyl)-1,2,3,4-tetrahydrophenanthrene-4-carboxylate 3ab



3ab

56.57 mg, 88% yield (2:1 dr); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 – 7.67 (m, 6H, major+minor), 7.54 – 7.42 (m, 4H, major+minor), 7.31 (d, *J* = 8.6 Hz, 1H, minor), 7.26 (d, *J* = 7.9 Hz, 1H, major), 4.34 (d, *J* = 5.4 Hz, 1H, minor), 4.30 (d, *J* = 6.8 Hz, 1H, major), 3.43 – 3.34 (m, 2H, major+minor), 2.97 – 1.97 (m, 7H, major+minor), 1.40 (s, 5H, minor), 1.39 (s, 9H, major). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm, major+minor) 174.0, 173.4, 134.6, 134.5, 132.7, 128.7, 128.6, 128.1, 128.1, 126.8, 126.6, 126.0, 125.7, 125.6, 125.4, 123.1, 123.0, 118.9, 118.7, 81.2, 81.1, 45.5, 42.8, 41.9, 35.6, 35.2, 34.6, 29.7, 28.0, 28.0, 27.9, 25.5, 25.0, 24.7, 24.5, 22.8, 21.9. IR (in KBr): 2875, 2250, 1730, 1375, 1130, 880 cm^{-1}. HRMS (EI): m/z [M + Na]$^+$ calcd for $C_{21}H_{23}NNaO_2$: 344.1621, found: 344.1623.

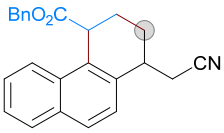
cyclohexyl 1-(cyanomethyl)-1,2,3,4-tetrahydrophenanthrene-4-carboxylate 3ac



3ac

45.00 mg, 70% yield (3:1 dr); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.90 – 7.68 (m, 4H, major+minor), 7.52 – 7.42 (m, 3H, major+minor), 7.33 (d, *J* = 8.5 Hz, 1H, minor), 7.27 (d, *J* = 8.4 Hz, 1H, major), 4.79 – 4.77 (m, 2H, major+minor), 4.42 (d, *J* = 5.8 Hz, 1H, minor), 4.39 (d, *J* = 6.4 Hz, 1H, major), 4.02 (s, 1H, major), 2.98 – 1.22 (m, 22H, major+minor). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm, major+minor) 174.1, 173.5, 134.6, 132.7, 132.5, 132.4, 130.0, 129.3, 128.7, 128.6, 128.2, 128.2, 127.3, 127.3, 126.8, 126.7, 126.1, 125.7, 125.6, 125.4, 123.0, 123.0, 118.8, 118.6, 73.2, 73.0, 42.1, 41.3, 35.6, 35.2, 31.4, 31.4, 31.2, 31.2, 25.5, 25.2, 25.2, 25.1, 24.7, 24.5, 23.5, 23.4, 23.2, 22.9, 22.7, 22.0. IR (in KBr): 2935, 1720, 1380, 1135 cm^{-1}. HRMS (EI): m/z [M + Na]$^{+}$ calcd for $C_{23}H_{25}NNaO_2$: 370.1777, found: 370.1777.

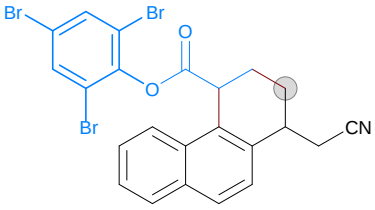
benzyl 1-(cyanomethyl)-1,2,3,4-tetrahydrophenanthrene-4-carboxylate 3ad



3ad

53.32 mg, 75% yield (3:1 dr); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81 – 7.67 (m, 4H, major+minor), 7.48 – 7.41 (m, 3H, major+minor), 7.34 – 7.21 (m, 8H, major+minor), 5.18 (t, *J* = 10.2 Hz, 1H, minor), 5.10 (t, *J* = 12.2 Hz, 2H, major), 4.48 (d, *J* = 4.6 Hz, 1H, minor), 4.45 (d, *J* = 6.2 Hz, 1H, major), 3.42 – 3.38 (m, 2H, major+minor), 2.93 – 1.90 (m, 6H, major+minor). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm, major+minor) 174.3, 173.9, 135.7, 135.6, 134.7, 134.7, 132.7, 132.4, 132.3, 129.6, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.2, 128.1, 127.3, 127.3, 126.9, 126.9, 126.8, 126.2, 126.1, 125.7, 125.7, 125.5, 122.9, 122.8, 118.6, 66.8, 66.7, 41.7, 41.0, 35.4, 35.1, 25.4, 25.0, 24.7, 24.5, 22.9, 21.8. IR (in KBr): 2900, 1740, 1375, 1140, 750 cm^{-1}. HRMS (EI): m/z [M + Na]$^{+}$ calcd for $C_{24}H_{21}NNaO_2$: 378.1464, found: 378.1460.

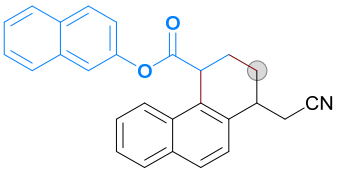
2,4,6-tribromophenyl 1-(cyanomethyl)-1,2,3,4-tetrahydrophenanthrene-4 carboxylate 3ae



3ae

77.47 mg, 67% yield (1:1 dr); whitle solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.21 (d, *J* = 8.4 Hz, 1H, minor), 8.17 (d, *J* = 8.4 Hz, 1H, major), 7.84 – 7.47 (m, 12H, major+minor), 7.37 (d, *J* = 8.6 Hz, 1H, minor), 7.30 (d, *J* = 8.5 Hz, 1H, major), 4.87 – 4.81 (m, 2H, major+minor), 3.50 – 3.43 (m, 2H, major+minor), 3.03 – 2.12 (m, 12H, major+minor). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm, major+minor) 170.0, 169.6, 145.3, 135.1, 135.1, 135.0, 135.0, 134.9, 132.8, 132.4, 132.2, 132.1, 128.9, 128.9, 128.7, 128.6, 128.5, 127.6, 127.4, 126.9, 126.9, 126.9, 126.0, 126.0, 125.3, 123.6, 123.6, 120.0, 119.9, 118.7, 118.6, 41.1, 40.7, 35.4, 35.0, 25.5, 25.3, 25.1, 24.7, 23.0, 21.5. IR (in KBr): 3125, 1750, 1375, 1065 cm^{-1}. HRMS (EI): m/z [M + Na]$^{+}$ calcd for $C_{23}H_{16}Br_3NNaO_2$: 597.8623, found: 597.8633.

naphthalen-2-yl 1-(cyanomethyl)-1,2,3,4-tetrahydrophenanthrene-4-carboxylate 3af

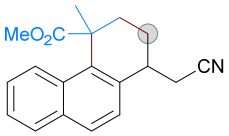


3af

56.37 mg, 72% yield (2:1 dr); whitle solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.13 (d, *J* = 3.5 Hz, 1H, minor), 8.11 (d, *J* = 3.5 Hz, 1H, major), 7.88 – 7.73 (m, 7H, major+minor), 7.66 – 7.41 (m, 7H, major+minor), 7.38 (d, *J* = 8.6 Hz, 1H, minor), 7.33 (d, *J* = 8.5 Hz, 1H, major), 7.12 (dd, *J* = 8.9, 2.3 Hz, 1H, minor), 7.09 (dd, *J* = 8.9, 2.4 Hz, 1H, major), 4.75 (d, *J* = 5.2 Hz, 1H, minor), 4.72 (d, *J* = 6.5, 1H, major), 3.53 – 3.44 (m, 2H, major+minor), 3.02 – 2.13 (m, 9H, major+minor). ^{13}C NMR (100 MHz, CDCl3) δ (ppm, major+minor) 173.5, 173.0, 148.3, 135.0, 133.6, 133.6, 132.8, 132.6, 132.4, 131.4, 129.4, 129.4, 129.2, 128.9, 128.9, 128.7, 128.7, 128.4, 127.7, 127.6, 127.5, 127.2, 126.9, 126.6, 126.0, 125.9, 125.7, 125.7, 125.6, 122.8,

122.7, 120.7, 118.7, 118.6, 118.3, 118.2, 41.9, 41.2, 35.6, 35.1, 25.6, 25.2, 24.8, 24.5, 23.1, 22.1. HRMS (EI): m/z [M + Na]$^+$ calcd for $C_{27}H_{21}NNaO_2$: 414.1464, found: 414.1465.

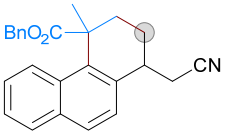
methyl 1-(cyanomethyl)-4-methyl-1,2,3,4-tetrahydrophenanthrene-4-carboxylate 3ag



3ag

46.94 mg, 80% yield; whitle solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81 – 7.73 (m, 3H), 7.47 – 7.41 (m, 2H), 7.30 (d, *J* = 8.6 Hz, 1H), 3.57 (s, 3H), 3.48 – 3.38 (m, 1H), 2.91 (dd, *J* = 16.9, 4.5 Hz, 1H), 2.75 (dd, *J* = 17.0, 8.5 Hz, 1H), 2.31 – 2.20 (m, 2H), 2.09 – 1.95 (m, 2H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.0, 135.7, 133.5, 133.2, 131.5, 129.1, 128.4, 126.4, 125.3, 125.2, 124.1, 118.3, 52.4, 45.8, 36.0, 35.4, 25.9, 24.5, 24.3. IR (in KBr): 3125, 2360, 1375, 1130, 750 cm^{-1}. HRMS (EI): m/z [M + Na]$^+$ calcd for $C_{19}H_{19}NNaO_2$: 316.1308, found: 316.1306.

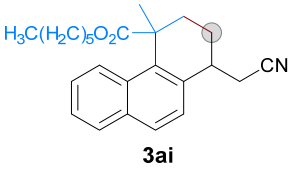
benzyl 1-(cyanomethyl)-4-methyl-1,2,3,4-tetrahydrophenanthrene-4-carboxylate 3ah



3ah

56.90 mg, 77% yield; whitle solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79 (d, *J* = 8.1 Hz, 1H), 7.71 (dd, *J* = 14.1, 8.6 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.16 (m, 6H), 6.94 (d, *J* = 6.9 Hz, 2H), 5.09 (d, *J* = 12.3 Hz, 1H), 4.98 (d, *J* = 12.3 Hz, 1H), 3.45 – 3.38 (m, 1H), 2.88 (dd, *J* = 17.0, 4.3 Hz, 2H), 2.73 (dd, *J* = 17.0, 8.5 Hz, 2H), 2.28 – 2.19 (m, 2H), 2.08 – 1.92 (m, 2H), 1.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 178.1, 135.7, 135.6, 133.5, 133.2, 131.5, 129.0, 128.3, 128.3, 128.0, 128.0, 126.3, 125.3, 125.2, 124.3, 118.3, 66.8, 45.9, 36.0, 35.4, 25.8, 24.5, 24.3. IR (in KBr): 3375, 2360, 1685, 1380, 1200 cm^{-1}. HRMS (EI): m/z [M + Na]$^+$ calcd for $C_{25}H_{23}NNaO_2$: 392.1621, found: 392.1620.

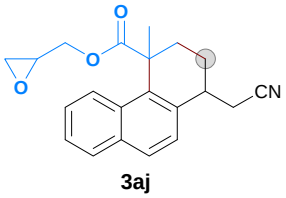
hexyl 1-(cyanomethyl)-4-methyl-1,2,3,4-tetrahydrophenanthrene-4-carboxylate 3ai



3ai

51.62 mg, 71% yield (3:1 dr); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.85 – 7.67 (m, 5H, major+minor), 7.49 – 7.35 (m, 3H, major+minor), 7.22 (d, *J* = 8.5 Hz, 1H, major+minor), 4.11 – 3.96 (m, 2H, major+minor), 3.48 – 3.42 (m, 1H, minor), 3.40 – 3.30 (m, 1H, major), 2.87 – 2.61 (m, 3H, minor), 2.32 – 1.96 (m, 4H, major+minor), 1.76 (s, 3H, major), 1.71 (s, 1H, minor), 1.56 – 0.74 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm, major+minor) 179.0, 134.9, 133.7, 133.6, 131.4, 129.2, 128.3, 127.0, 126.3, 125.3, 124.3, 118.6, 65.3, 46.2, 36.4, 32.2, 31.1, 28.2, 25.3, 24.8, 24.4, 22.4, 22.2, 13.9. IR (in KBr): 3125, 1690, 1375, 1125 cm^{-1}. HRMS (EI): m/z [M + Na]$^+$ calcd for $C_{24}H_{29}NNaO_2$: 386.2090, found: 386.2092.

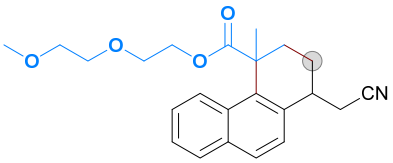
oxiran-2-ylmethyl 1-(cyanomethyl)-4-methyl-1,2,3,4-tetrahydrophenanthrene-4-carboxylate 3aj



3aj

37.57 mg, 56% yield (14:6:1 dr); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm, major+minor) 7.82 – 7.68 (m, 5H), 7.47 – 7.41 (m, 3H), 7.31 – 7.23 (m, 2H), 4.42 – 4.25 (m, 2H), 3.95 – 3.85 (m, 2H), 3.49 – 3.37 (m, 2H), 3.02 – 1.93 (m, 13H), 1.86 (s, 3H), 1.78 (s, 1H), 1.28 – 1.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm, major+minor) 178.2, 178.1, 135.4, 135.4, 133.6, 133.6, 133.2, 131.5, 131.5, 129.5, 129.3, 129.1, 128.4, 127.1, 126.3, 126.3, 125.3, 125.3, 124.2, 124.1, 124.0, 118.3, 118.2, 65.9, 65.8, 64.8, 49.0, 48.9, 45.9, 44.7, 44.6, 44.3, 36.0, 35.5, 25.7, 24.8, 24.5, 24.4, 24.3. IR (in KBr): 3125, 1690, 1375, 1125 cm^{-1}. HRMS (EI): m/z [M + Na]$^+$ calcd for $C_{21}H_{21}NNaO_3$: 358.1414, found: 358.1414.

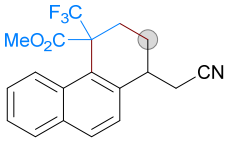
2-(2-methoxyethoxy)ethyl 1-(cyanomethyl)-4-methyl-1,2,3,4 tetrahydrophenanthrene-4-carboxylate 3ak



3ak

46.54 mg, 61% yield (6:1 dr); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm, major+minor) 7.81 – 7.67 (m, 4H), 7.47 – 7.40 (m, 2H), 7.23 (d, *J* = 8.5 Hz, 1H), 4.34 – 4.28 (m, 1H), 4.11 – 4.05 (m, 1H), 3.60 – 3.36 (m, 4H), 3.29 (s, 3H), 3.27–3.22 (m, 3H), 2.84 – 2.69 (m, 2H), 2.38 – 2.14 (m, 3H), 1.97 (d, *J* = 13.1 Hz, 1H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm, major+minor) 178.8, 134.6, 133.9, 133.6, 131.4, 129.2, 128.3, 127.1, 126.3, 125.3, 124.3, 118.7, 71.7, 70.1, 68.7, 64.2, 46.2, 36.5, 32.2, 24.8, 24.2, 22.2. IR (in KBr): 2875, 2250, 1730, 1125, 870 cm^{-1}. HRMS (EI): m/z [M + Na]$^{+}$ calcd for $C_{23}H_{27}NNaO_4$: 382.2013, found: 382.2010.

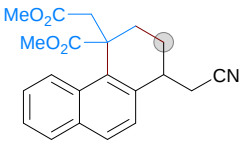
methyl 1-(cyanomethyl)-4-(trifluoromethyl)-1,2,3,4-tetrahydrophenanthrene-4-carboxylate 3al



3al

53.49 mg, 77% yield; colorless oil (2:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89 – 7.75 (m, 5H, major+minor), 7.52 – 7.45 (m, 3H, major+minor), 7.37 (d, *J* = 8.6 Hz, 1H, minor), 7.31 (d, *J* = 8.5 Hz, 1H, major), 3.72 (s, 3H, major), 3.68 (s, 2H, minor), 3.60 – 3.48 (m, 2H, major+minor), 2.97 – 1.87(m, 9H, major+minor). IR (in KBr): 3120, 2375, 1375, 1120 cm^{-1}. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm, major+minor) 172.3, 171.8, 137.4, 137.3, 133.6, 133.2, 131.9, 131.7, 130.8, 130.7, 129.1, 129.0, 127.1, 126.8, 126.7, 126.0, 125.8, 125.3, 124.8, 124.5, 118.3, 118.1, 54.7, 54.5, 54.3, 53.1, 53.0, 35.9, 35.8, 29.9, 27.1, 25.2, 24.5, 23.4, 21.8. IR (in KBr): 3125, 1750, 1375, 1140 cm^{-1}. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm, major+minor) -63.5, -64.3. HRMS (EI): m/z [M + H]$^{+}$ calcd for $C_{19}H_{17}NO_2F_3$: 370.1025, found: 370.1025.

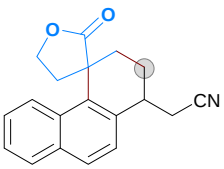
methyl 1-(cyanomethyl)-4-(2-methoxy-2-oxoethyl)-1,2,3,4-tetrahydrophenanthrene-4-carboxylate 3am



3am

50.60 mg, 72% yield (3:1 dr); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82 – 7.69 (m, 3H, major+minor), 7.49 – 7.42 (m, 2H, major+minor), 7.30 (d, *J* = 8.5 Hz, 1H, major+minor), 3.63 (s, 3H, major), 3.61 (s, 1H, minor), 3.50 – 3.39 (m, 2H, major+minor), 3.32 (s, 3H, major), 3.24 (s, 1H, minor), 3.07 – 2.77 (m, 4H, major+minor), 2.34 – 2.06 (m, 3H, major+minor). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm, major+minor) 177.7, 177.1, 171.3, 171.2, 136.1, 135.1, 133.5, 133.3, 132.4, 132.0, 131.3, 131.2, 129.5, 129.3, 129.1, 128.7, 126.9, 126.7, 126.6, 125.4, 125.3, 123.5, 123.2, 119.0, 118.5, 52.8, 52.8, 51.3, 48.6, 47.5, 41.4, 40.2, 36.5, 36.2, 30.5, 28.5, 24.6, 23.4, 23.1, 22.5. IR (in KBr): 2937, 2250, 1740, 1375, 1190 cm^{-1}. HRMS (EI): m/z [M + H]$^{+}$ calcd for $C_{21}H_{22}NO_4$: 352.1543, found: 352.1543.

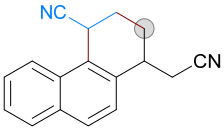
2-(2-oxo-2',3',4,5-tetrahydro-1'H,2H-spiro[furan-3,4'-phenanthren]-1'-yl)acetonitrile 3an



3an

15.73 mg, 27% yield; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82 (dd, *J* = 22.2, 8.1 Hz, 2H), 7.63 – 7.48 (m, 3H), 7.26 – 7.24 (m, 1H), 4.82 – 4.54 (m, 2H), 3.44 – 3.41 (m, 1H), 2.95 – 2.70 (m, 3H), 2.49 – 2.44 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 181.6, 136.2, 134.0, 130.8, 130.2, 129.8, 129.6, 127.0, 126.9, 125.7, 123.5, 118.5, 65.6, 46.7, 36.1, 35.6, 27.4, 24.4, 22.4. IR (in KBr): 2900, 2365, 1375, 1130, 750 cm^{-1}. HRMS (EI): m/z [M + H]$^{+}$ calcd for $C_{19}H_{18}NO_2$: 292.1332, found: 292.1335.

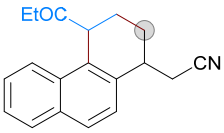
1-(cyanomethyl)-1,2,3,4-tetrahydrophenanthrene-4-carbonitrile 3ao



3ao

41.87 mg, 85% yield (2:1 dr); whitle solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06– 8.01 (m, 2H, major+minor), 7.88 – 7.83 (m, 3H, major+minor), 7.68 – 7.55 (m, 2H, major+minor), 7.38 (d, *J* = 8.7 Hz, 1H, minor), 7.29 (d, *J* = 8.6 Hz, 1H, major), 4.57 – 4.53 (m, 2H, major+minor), 3.49 – 3.43 (m, 2H, major+minor), 3.06 – 2.08 (m, 10H, major+minor). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm, major+minor) 134.4, 134.2, 132.9, 132.4, 131.2, 131.0, 129.7, 129.0, 128.8, 127.8, 127.8, 126.8, 126.5, 126.5, 125.9, 124.9, 124.7, 122.4, 122.3, 120.6, 120.5, 118.3, 118.0, 35.2, 34.4, 27.2, 26.7, 26.1, 25.7, 24.7, 24.5, 23.4, 21.9. IR (in KBr): 3125, 2875, 2250, 1625, 1375, 875 cm^{-1}. HRMS (EI): m/z [M + Na]$^+$ calcd for $C_{17}H_{14}N_2Na$: 269.1049, found: 269.1050.

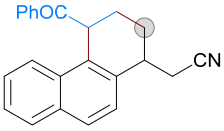
2-(4-propionyl-1,2,3,4-tetrahydrophenanthren-1-yl)acetonitrile 3ap



3ap

38.83 mg, 70% yield (10:1 dr); whitle solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm, major+minor) 7.83 – 7.75 (m, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.32 (dd, *J* = 18.9, 8.6 Hz, 1H), 4.49 – 4.47(m, 1H), 3.41 – 3.39 (m, 1H), 2.95 – 2.48 (m, 4H), 2.26 – 1.97 (m, 4H), 1.03 (q, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm, major+minor) 213.0, 212.2, 135.0, 134.9, 132.8, 132.6, 132.2, 132.2, 130.6, 129.9, 128.9, 128.8, 128.2, 127.0, 126.6, 125.7, 125.7, 125.6, 122.8, 122.7, 118.7, 118.6, 49.2, 48.2, 35.6, 35.2, 34.4, 34.1, 25.5, 24.7, 24.6, 24.5, 23.2, 21.7, 8.0, 7.9. IR (in KBr): 3130, 2375, 1630, 1375 cm^{-1}. HRMS (EI): m/z [M + Na]$^+$ calcd for $C_{19}H_{19}NNaO$: 300.1359, found: 300.1359.

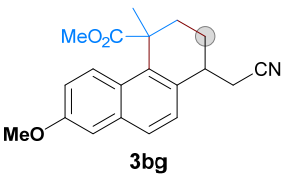
2-(4-propionyl-1,2,3,4-tetrahydrophenanthren-1-yl)acetonitrile 3aq



3aq

44.91 mg, 69% yield; whitle solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm,) 8.19 (d, *J* = 7.3 Hz, 2H), 7.74 (m, 3H), 7.61 – 7.53 (m, 3H), 7.43 – 7.32 (m, 3H), 5.48 (d, *J* = 6.5 Hz, 1H), 3.49 – 3.45 (m, 1H), 2.95 – 2.64 (m, 2H), 2.44 – 1.99 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.8, 135.6, 135.2, 133.5, 132.9, 131.9, 130.2, 129.1, 128.9, 128.6, 128.2, 126.9, 126.8, 125.6, 122.8, 118.8, 42.3, 35.1, 24.6, 22.3, 21.5. IR (in KBr): 3130, 1630, 1375, 1190 cm^{-1}. HRMS (EI): m/z [M + Na]$^+$ calcd for $C_{23}H_{19}NNaO$: 348.1359, found: 348.1360.

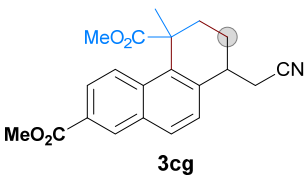
methyl 1-(cyanomethyl)-7-methoxy-4-methyl-1,2,3,4-tetrahydrophenanthrene-4-carboxylate 3bg



3bg

52.39 mg, 81% yield (2:1 dr); whitle solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm, major) 7.65 (dd, *J* = 9.4, 3.0 Hz, 2H), 7.27 – 7.25 (m, 1H), 7.12 – 7.09 (m, 2H), 3.90 (s, 3H), 3.57 (s, 3H), 3.45 – 3.38 (m, 1H), 2.92 – 2.71 (m, 2H), 2.27 – 1.98 (m, 4H), 1.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm, major) 179.1, 156.9, 135.7, 134.7, 131.3, 127.3, 126.8, 125.8, 125.6, 118.6, 118.4, 107.2, 55.2, 52.4, 45.8, 35.9, 35.4, 26.0, 24.5, 24.4. IR (in KBr): 2930, 1720, 1625, 1375, 1250 cm^{-1}. HRMS (EI): m/z [M + Na]$^+$ calcd for $C_{20}H_{21}NNaO_3$: 346.1414, found: 346.1414.

dimethyl 8-(cyanomethyl)-5-methyl-5,6,7,8-tetrahydrophenanthrene-2,5-dicarboxylate 3cg



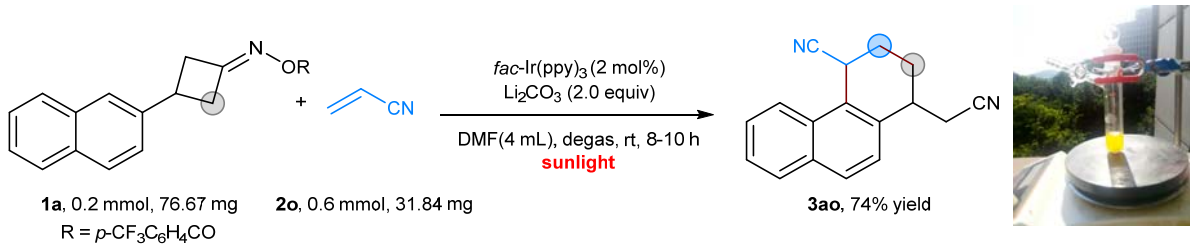
3cg

56.22 mg, 80% yield (3:1 dr); whitle solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm, major) 8.54 (s, 1H), 8.03 – 8.00 (m, 1H), 7.86 – 7.81 (m, 2H), 7.39 – 7.25 (m, 1H), 3.97 (s, 3H), 3.57 (s, 3H), 3.49 – 3.42 (m, 1H), 2.95 – 2.76 (m, 2H), 2.54 – 2.00 (m, 4H), 1.83 (s, 3H), 1.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm, major) 178.6, 166.9, 166.9, 136.1,

136.0, 134.7, 133.9, 133.7, 133.5, 132.5, 132.1, 131.9, 129.5, 129.1, 128.6, 126.8, 126.4, 126.1, 125.7, 125.7, 124.4, 123.7, 118.1, 117.7, 52.6, 52.5, 52.2, 52.2, 47.2, 45.8, 42.7, 37.0, 36.2, 35.3, 27.5, 25.8, 25.3, 24.4, 24.2, 24.0. IR (in KBr): 2950, 2260, 1740, 1250, 750 cm^{-1}. HRMS (EI): m/z $[M + Na]^+$ calcd for $C_{21}H_{21}NNaO_4$: 373.1363, found: 373.1363.

5. Preparative Utility of the Methodology

5.1. Sun-Light Driven Reaction



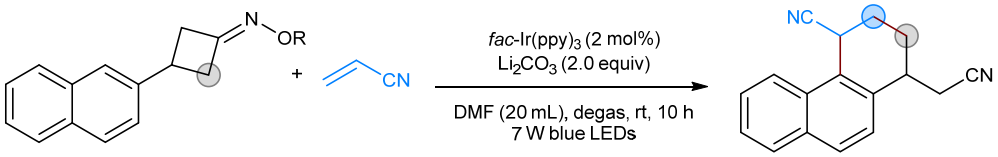
1a, 0.2 mmol, 76.67 mg
R = *p*-$CF_3C_6H_4CO$

2o, 0.6 mmol, 31.84 mg

3ao, 74% yield

1a (76.67 mg, 0.2 mmol), **2o** (31.84 mg, 0.6 mmol), *fac*-Ir(ppy)$_3$ (2 mol%) and Li_2CO_3 (2.0 equiv) were dissolved in DMF 4 mL). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times). After that, the solution was stirring under sun light for 8 h until the reaction was completed, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethylacetate 5:1) directly to give the desired product **3ao** in 74% yield as white soild.

5.2. 1.0 mmol Reaction



1a, 1.0 mmol, 383.37 mg
R = *p*-$CF_3C_6H_4CO$

2o, 3.0 mmol, 159.18 mg

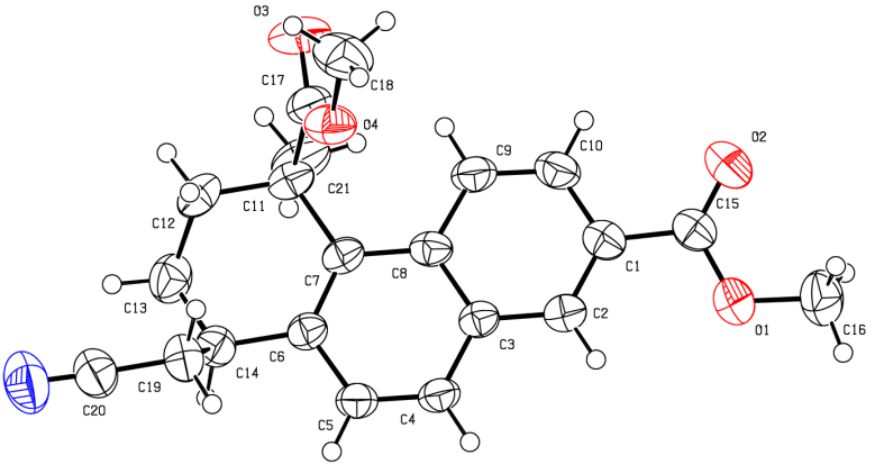
3ao, 80% yield

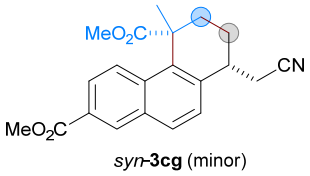
1a (383.37 mg, 1 mmol), **2o** (159.18 mg, 3 mmol), *fac*-Ir(ppy)$_3$ (2 mol%) and Li_2CO_3 (2.0 equiv) were dissolved in DMF (20 mL). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times). After that, the solution was stirred at a distance of ~5 cm from a 7 W blue LEDs (450-460 nm) at room temperature about 10 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ ethylacetate 5:1) directly to give the desired product **3ao** in 80% yield as white soild.

Reference:

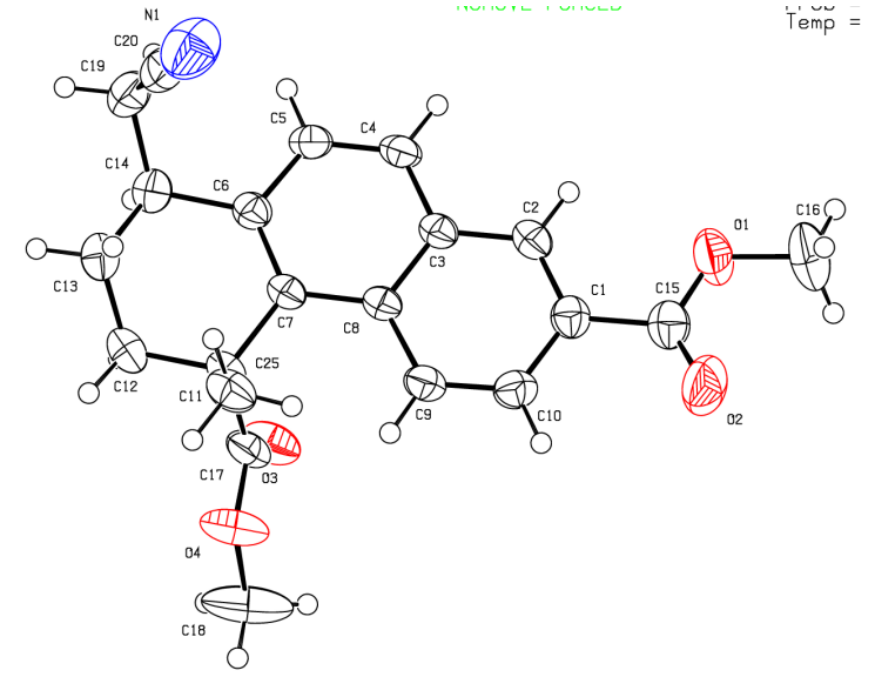
[1] a) J. Ramnauth, E. Lee-Ruff, *Can. J. Chem*. **2001**, ***79***, 114–120. b) Ṡ. M. Vesna, M. Zlatko, V. Hrvoj, *Chem. Soc.Perkin Trans. 2*, **2002**, 2154–2158. c) B.-L. Zhao, Z.-Z. Shi, *Angew. Chem. Int. Ed.* **2017**, *56*, 12727 – 12731. d) H.-B. Yang, N. Selander, *Chem. Eur. J.* **2017**, *23*, 1779 – 1783. e) L.–Y. Li, H.-G. Chen, M.-J. Mei, L. Zhou, *Chem. Commun*. **2017**, *53*, 11544-11547. f) Y.-R. Gu, X.-H. Duan, L. Yang, L.-N. Guo, *Org. Lett*. **2017**, *19*, 5908–5911. g) J. Wu, J.-Y. Zhang, P. Cao, S.-L. Xu, L.-N. Guo, *J. Org. Chem*. **2018**, *83*, 1046–1055. h) X.-Y. Yu. J.-R. Chen, P.-Z. Wang, M.-N. Yang, D. Liang, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2018**, *57*, 738 – 743.

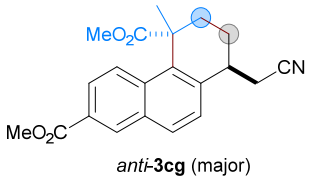
6. X-Ray Structures of 3ag and 3cg



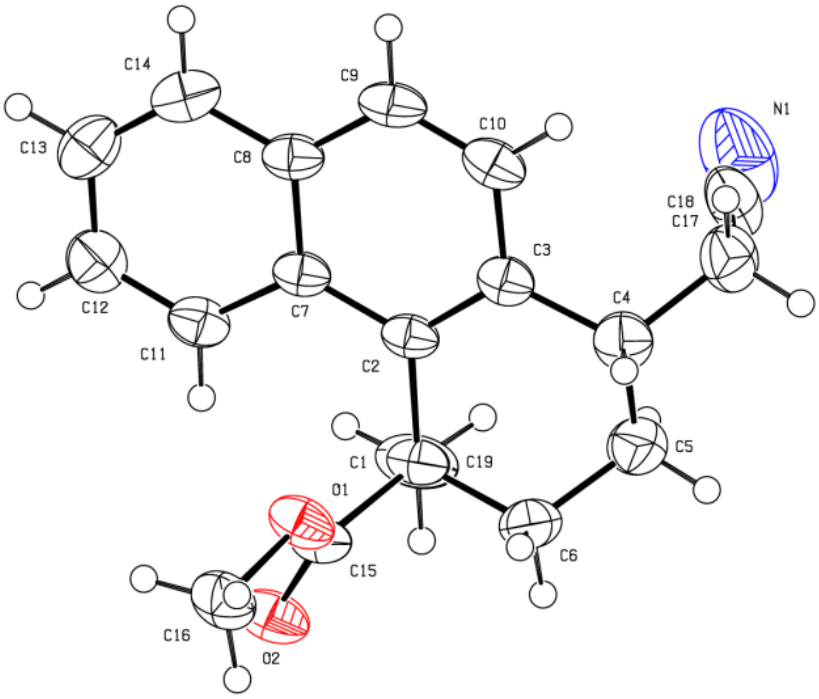


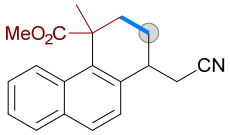
syn-**3cg** (minor)





anti-**3cg** (major)





3ag

7. Complete Reference for Gaussian 09

Density functional theory (DFT) calculations were performed for the varification of the mechanism. The DFT method em ployed in this work is ωB97xD which was cliamed to show excellent performance on both short range and long range int eraction [Chai, J. D.; Head-Gordon, M., Long-range corrected hybrid density functionals with damped atom-atom dispers ion corrections. Phys. Chem. Chem. Phys. 2008, 10 (44), 6615-6620.]. Frequency analysis was used to verify the nature of stationary points. Geometries were determined with 6-31+G(d) basis set while energies were determined by single poi nt calculations with 6-311+G(d,p) basis set upon optimized structures. All calculations were performed using the Gaussia n 09 package [Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G .; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloi no, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T .; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J .; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C .; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo , C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision D.01; Gaussian, Inc.: Wallin gford, CT, 2013.]

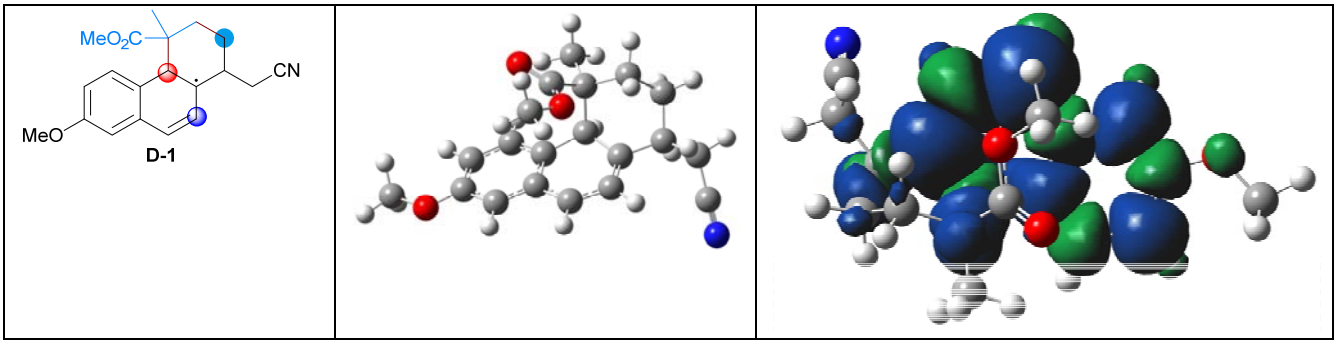
8. DFT Calculation on the Intermediates D-1 and D-2

input file of D1

%chk=D11.chk
%nprocshared=16
%mem=10GB

opt freq wb97xd/6-31+g(d)

D1 (Spin density map. Isovalue=0.0004)



0 2

C	-0.38880000	-7.46600000	0.10520000
C	0.44400000	-8.48210000	0.59690000
C	1.80940000	-8.23840000	0.78480000
C	2.34030000	-7.01460000	0.37260000
C	1.50600000	-5.99230000	-0.11190000
C	0.12320000	-6.19940000	-0.20530000
O	2.66350000	-9.18970000	1.36560000
C	2.17760000	-10.23950000	2.21920000
C	-0.80780000	-5.07350000	-0.69480000
C	1.35140000	-3.77680000	-1.23050000
C	2.08400000	-4.66290000	-0.54200000
C	-1.57210000	-4.29200000	0.42760000
C	-2.29790000	-3.02540000	-0.15500000
C	-2.42130000	-3.05550000	-1.70020000
C	-1.02020000	-3.11210000	-2.38810000
C	-0.42600000	-1.68870000	-2.60070000
C	0.72950000	-1.71150000	-3.49160000
N	1.63990000	-1.72450000	-4.20640000
C	-0.57320000	-3.85020000	1.48850000
C	-2.62530000	-5.25610000	1.06560000
O	-0.59760000	-4.31480000	2.61960000
O	0.31340000	-2.92270000	1.09880000
C	1.29030000	-2.56840000	2.09810000
H	-1.41220000	-7.69800000	-0.14300000
H	0.02050000	-9.45530000	0.81890000
H	3.40420000	-6.83910000	0.46820000
H	1.60950000	-10.99570000	1.65860000
H	1.55750000	-9.82400000	3.02760000
H	3.05020000	-10.73850000	2.66850000
H	-1.52190000	-5.57910000	-1.36190000
H	1.82920000	-2.83480000	-1.49230000

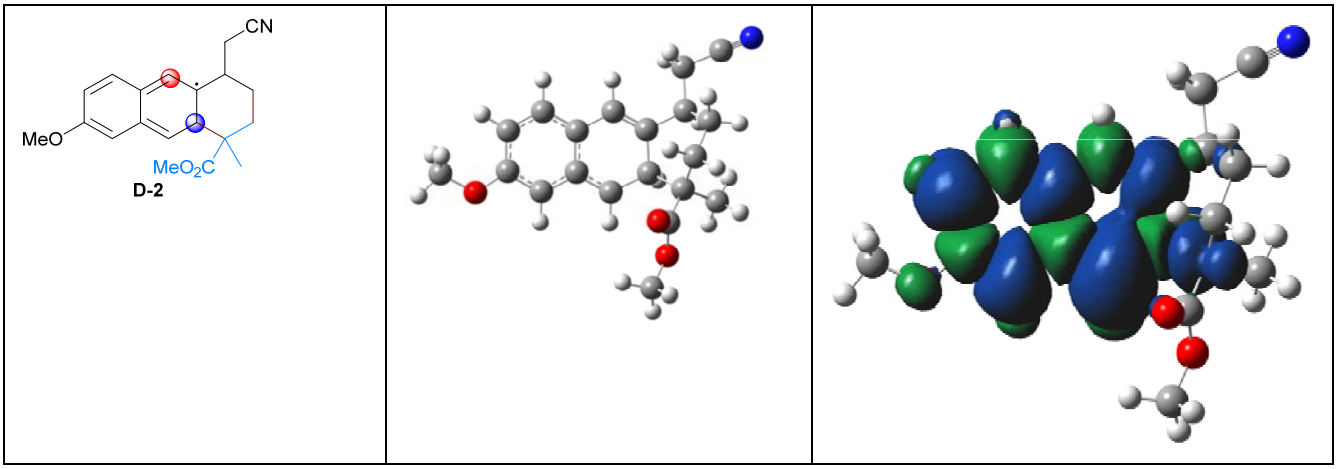
H	3.12040000	-4.42840000	-0.28580000
H	-1.77120000	-2.09450000	0.10560000
H	-3.31020000	-2.92510000	0.27070000
H	-2.97860000	-2.17060000	-2.04430000
H	-3.03810000	-3.92630000	-1.97670000
H	-1.17440000	-3.53130000	-3.39780000
H	-0.16000000	-1.22510000	-1.63860000
H	-1.14990000	-1.02940000	-3.10340000
H	-2.13520000	-6.09960000	1.57440000
H	-3.30690000	-5.66190000	0.29780000
H	-3.23820000	-4.73610000	1.81920000
H	0.81930000	-2.18780000	3.01690000
H	1.92130000	-1.76970000	1.68060000
H	1.93430000	-3.42820000	2.33470000
C	-0.07170000	-4.09230000	-1.63280000

--link1--
%nprocshared=16
%chk=D11.chk
%mem=10GB
sp wb97xd/6-311+g(d,p) geom=allcheck scrf=(smd,solvent=n,n-DiMethylFormamide)

Input file of D2

%chk=D22.chk
%nprocshared=16
%mem=10GB
opt freq wb97xd/6-31+g(d) scf=(conver=6,xqc) iop(5/85=30)

D2 (Spin density map. Isovalue=0.0004)



0 2

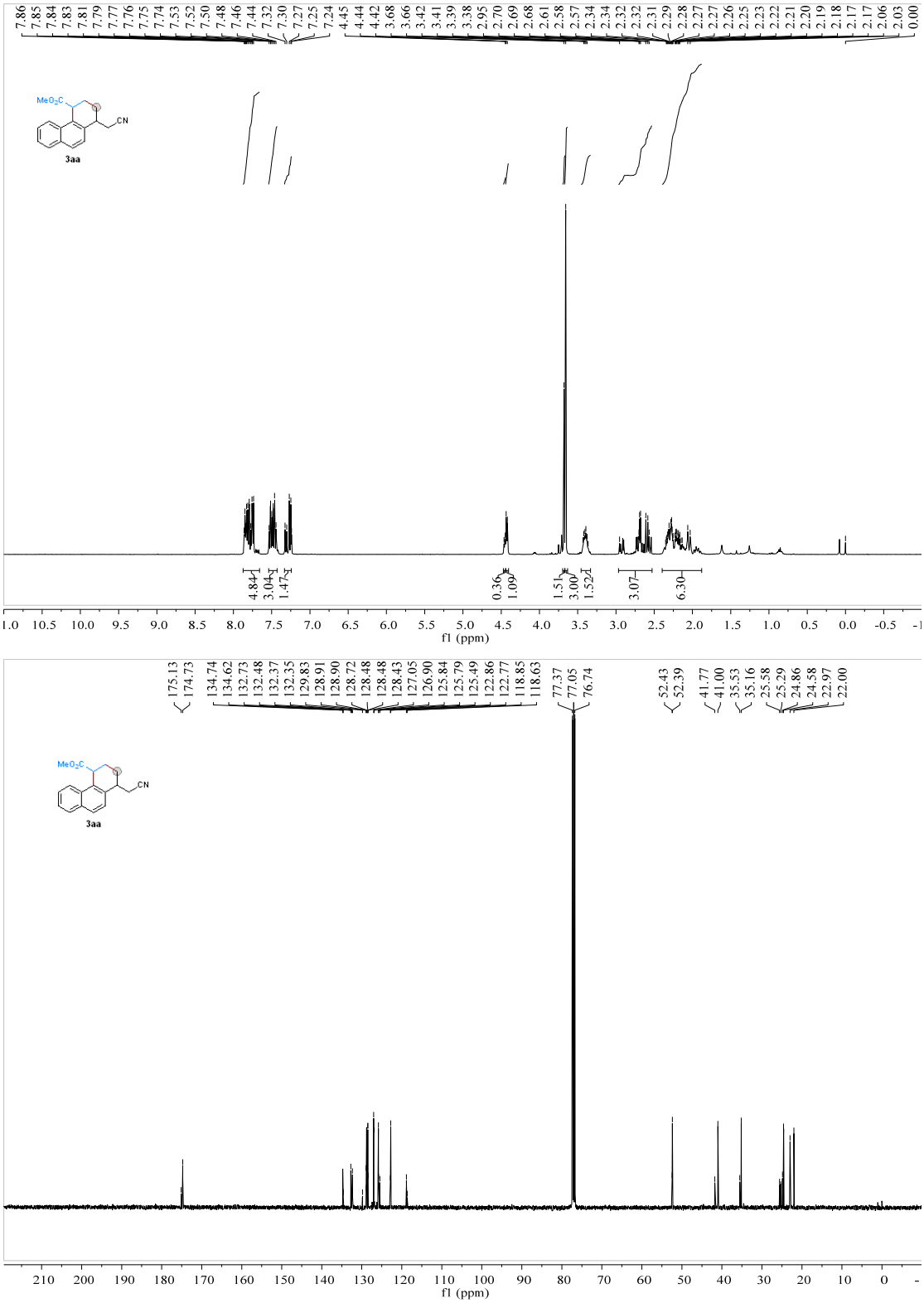
C	0.60380000	-1.74860000	2.03500000
C	0.13000000	-2.68500000	2.96110000
C	-0.91300000	-3.94940000	0.98870000
C	0.37560000	-3.51840000	0.21830000
C	-1.47860000	-5.30720000	0.52000000
C	-1.06360000	-4.10650000	-1.75510000
C	0.41760000	-3.90450000	-1.30960000
C	1.03940000	-2.83420000	-2.22790000
C	1.16640000	-5.26970000	-1.51840000
O	1.96040000	0.85270000	4.28320000
C	1.06900000	1.97120000	4.39790000
O	0.39400000	-1.79500000	-2.19230000
H	-0.74280000	-6.07990000	0.77810000
H	-1.61280000	-3.16850000	-1.57380000
H	-1.13010000	-4.30500000	-2.83590000
H	0.80870000	-6.06460000	-0.85760000
H	2.23980000	-5.18580000	-1.31070000
H	1.04480000	-5.63700000	-2.54760000
H	1.64530000	2.84040000	4.74790000
H	0.27330000	1.75790000	5.12760000
H	0.61700000	2.21640000	3.42480000
H	1.25450000	-3.99410000	0.68380000
C	-0.58050000	-3.96530000	2.50150000
H	-0.76260518	-4.76414309	3.18967689
C	0.51060000	-2.00560000	0.52650000
H	0.50320016	-1.19616490	-0.17325714
C	1.18370000	-0.55800000	2.47710000
H	1.49032922	0.13356136	1.72038248
C	1.35360000	-0.32180000	3.84390000
C	0.92120000	-1.27390000	4.77020000
H	1.04094743	-1.16178394	5.82755072
C	0.31210000	-2.45120000	4.32720000
H	-0.03747424	-3.21403764	4.99111007
C	-1.78670000	-5.26870000	-1.00650000
H	-2.84775840	-5.16965356	-1.10265026
H	-1.46981309	-6.17867102	-1.47172621
C	-2.74942259	-5.65473962	1.31738709
H	-2.47505487	-6.00954298	2.28884832
H	-3.35885737	-4.78078687	1.41585454
C	-3.53799861	-6.74946600	0.57487647
N	-4.12512930	-7.56453954	0.02204356
O	2.39581288	-2.48858187	-1.93533852
C	3.11409369	-2.29830129	-3.15712655
H	2.95756929	-1.30080410	-3.51124444

H	4.15835363	-2.45600311	-2.98522160
H	2.76381276	-2.99571895	-3.88911826

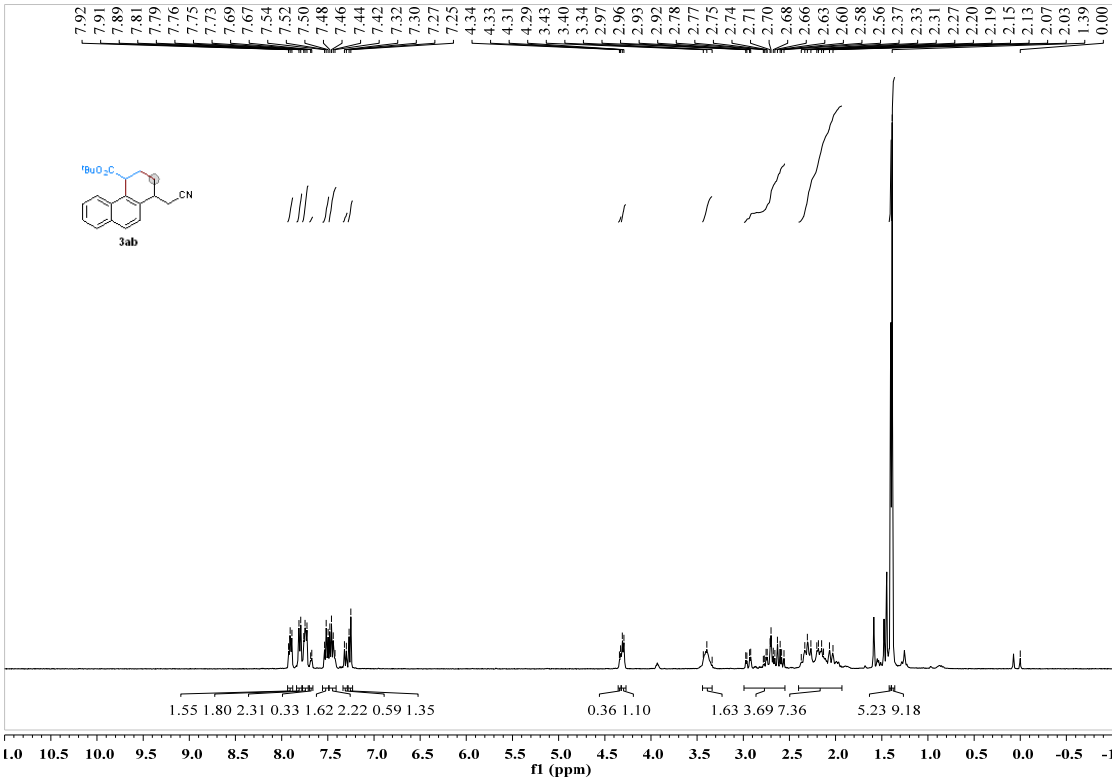
--link1--
%nprocshared=16
%chk=D22.chk
%mem=20GB
sp wb97xd/6-311+g(d,p) geom=allcheck scrf=(smd,solvent=n,n-DiMethylFormamide) scf=(conver=6,xqc) iop(5/85=30)

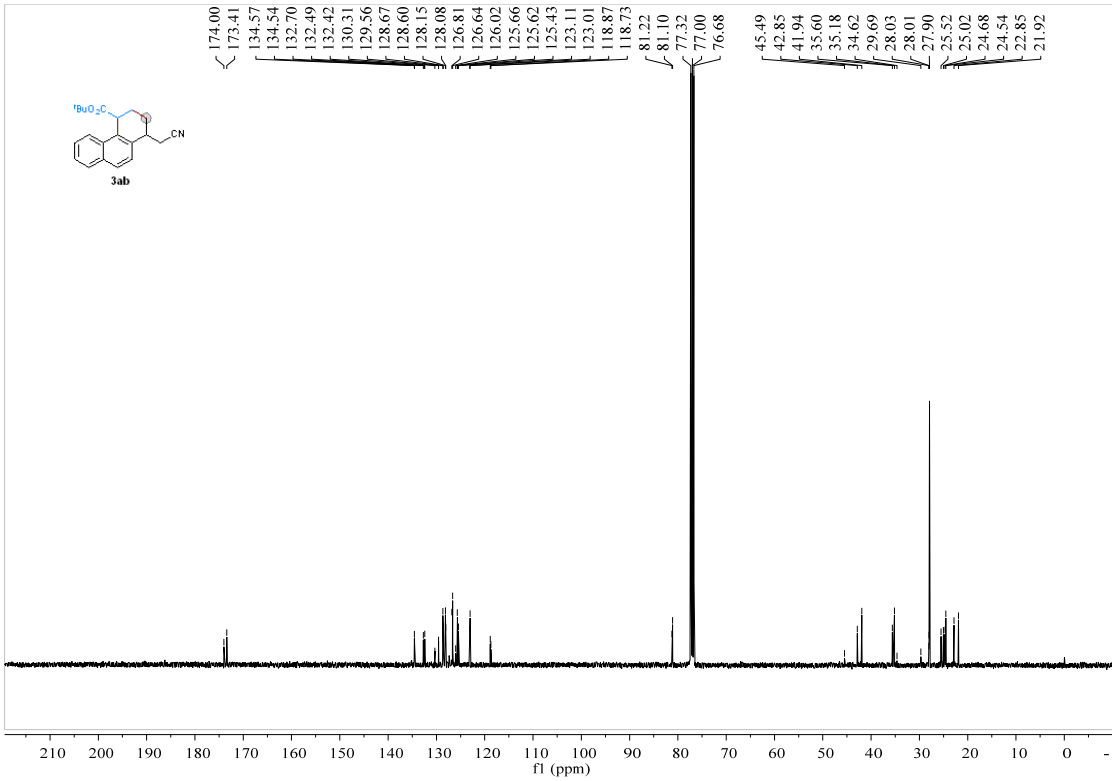
9. The Spectra of products

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3aa

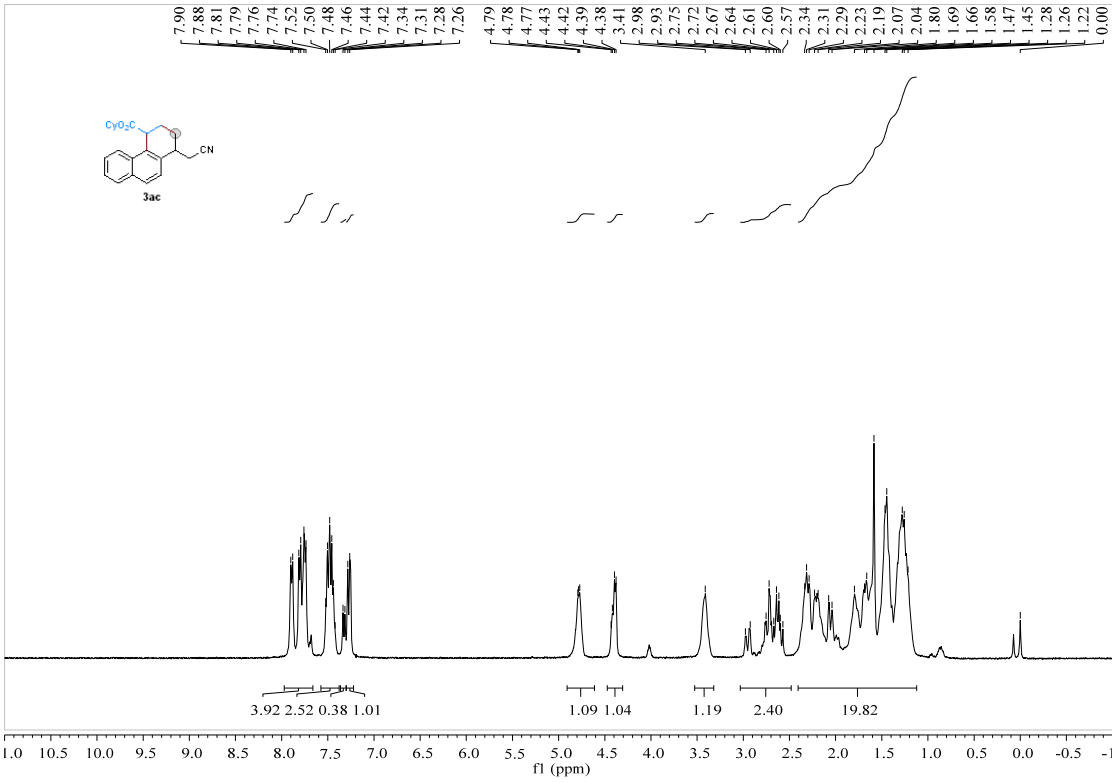


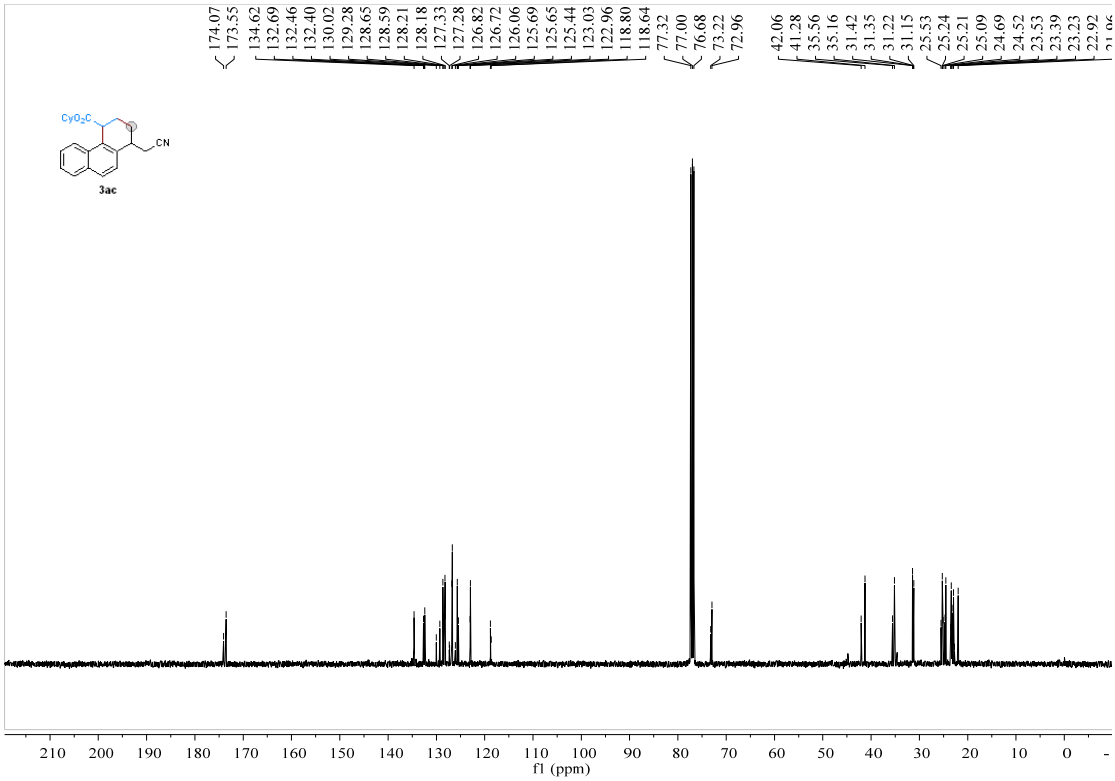
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ab



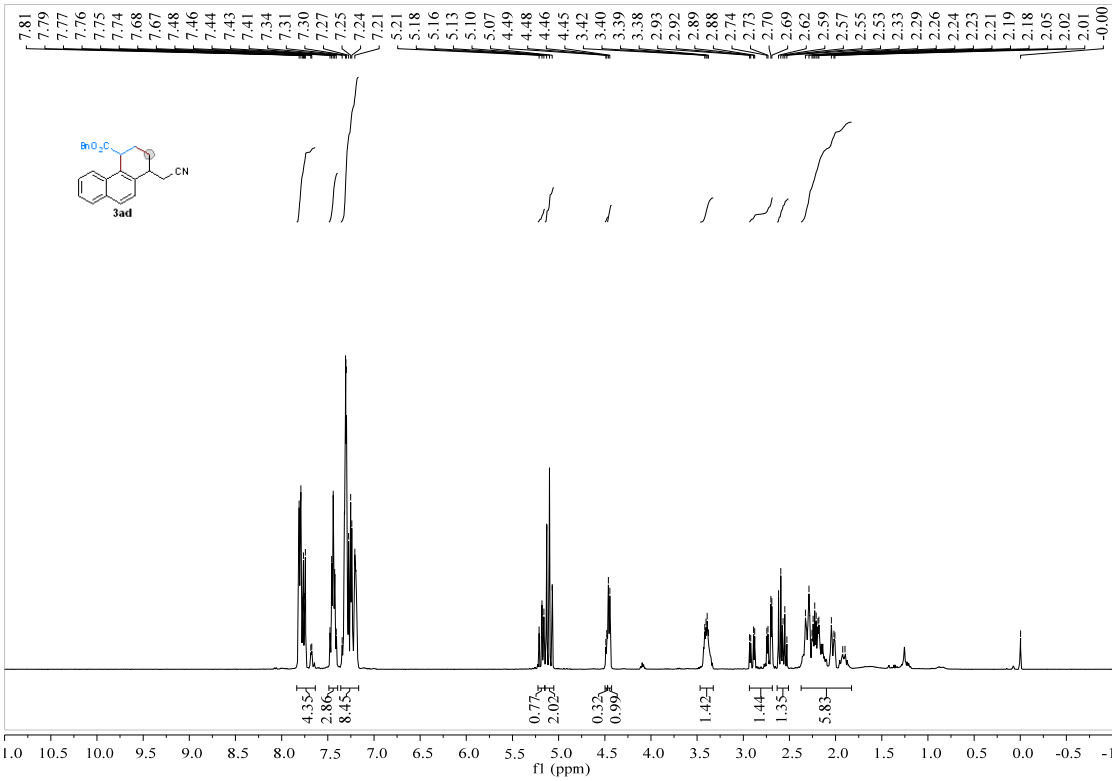


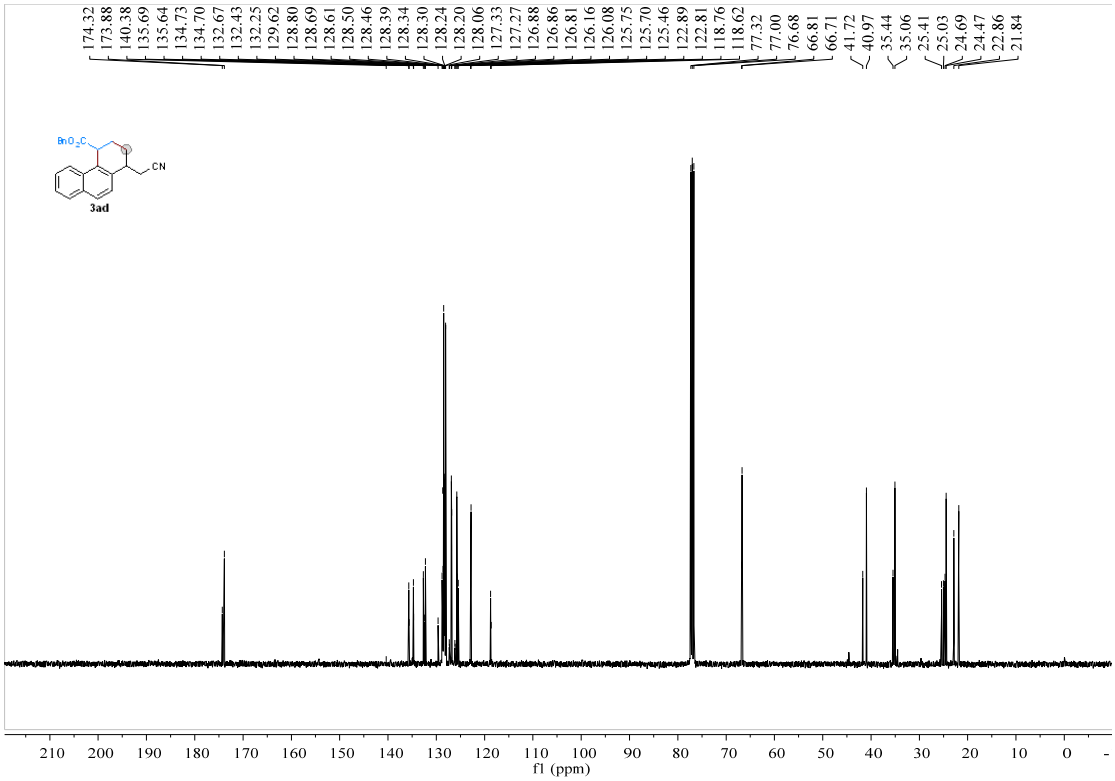
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ac



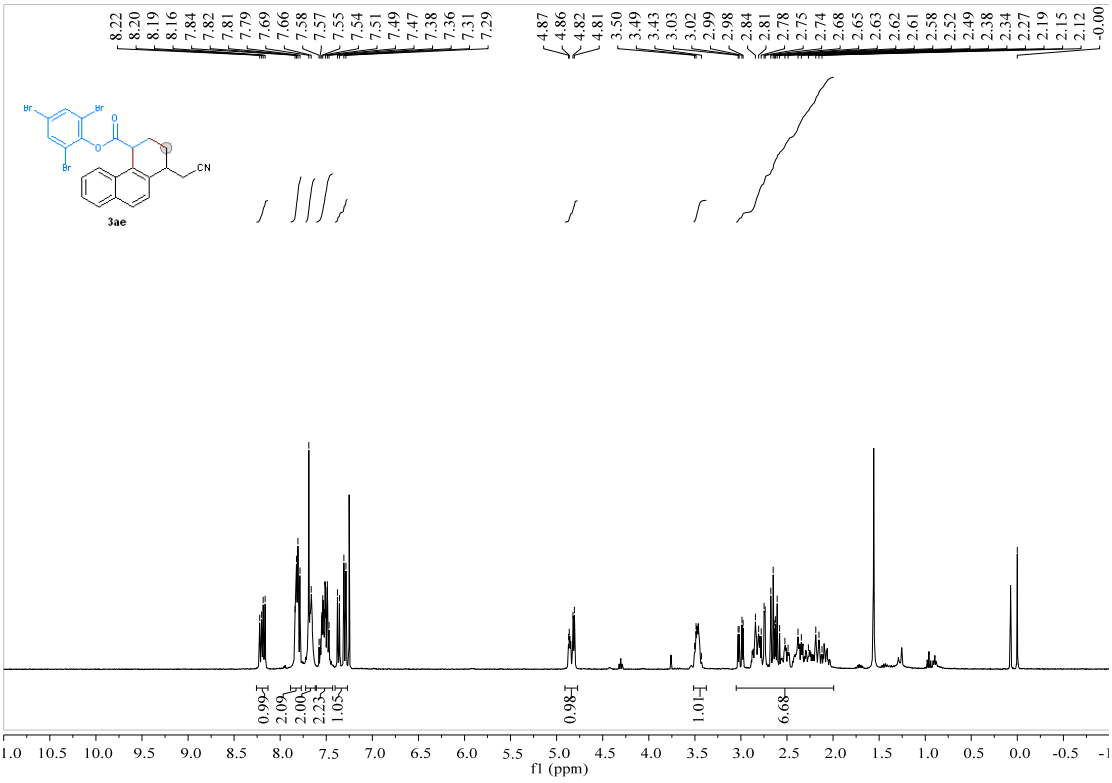


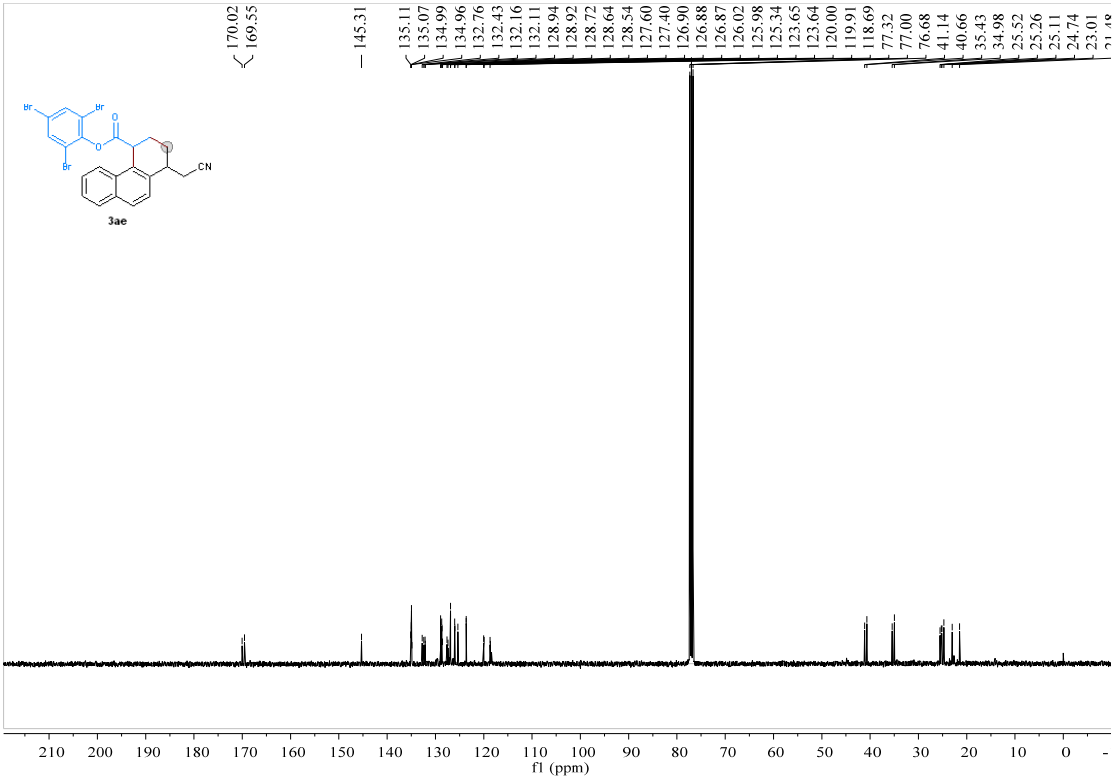
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ad



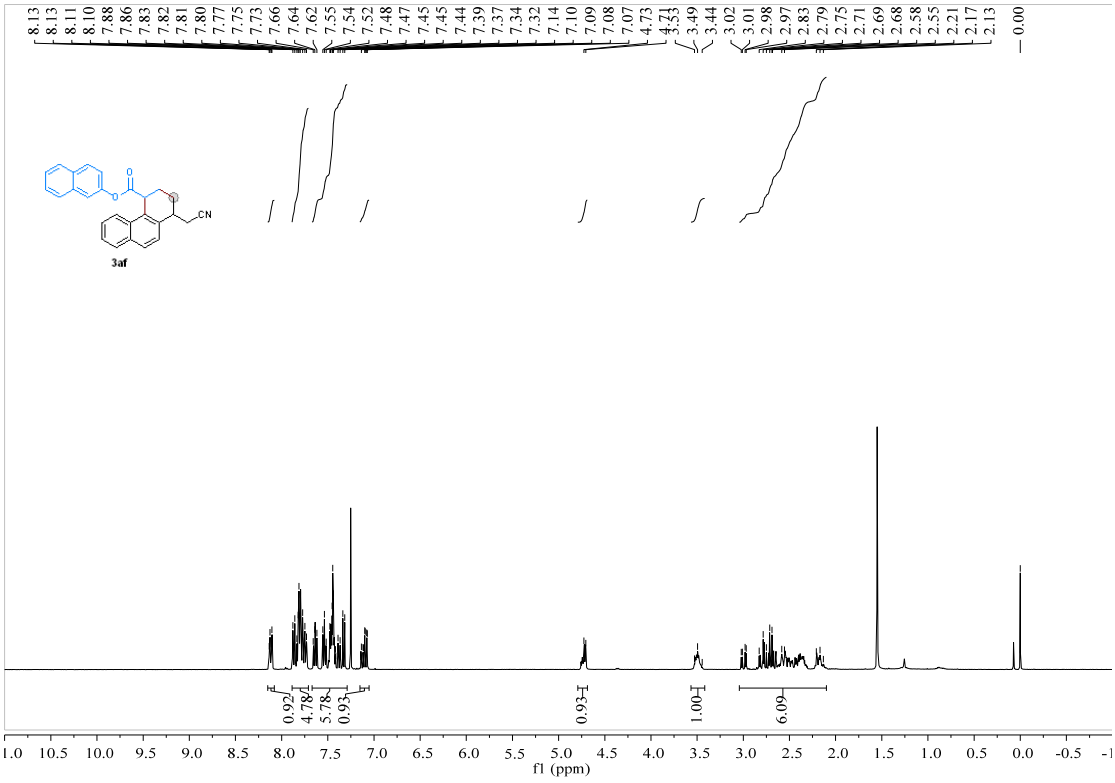


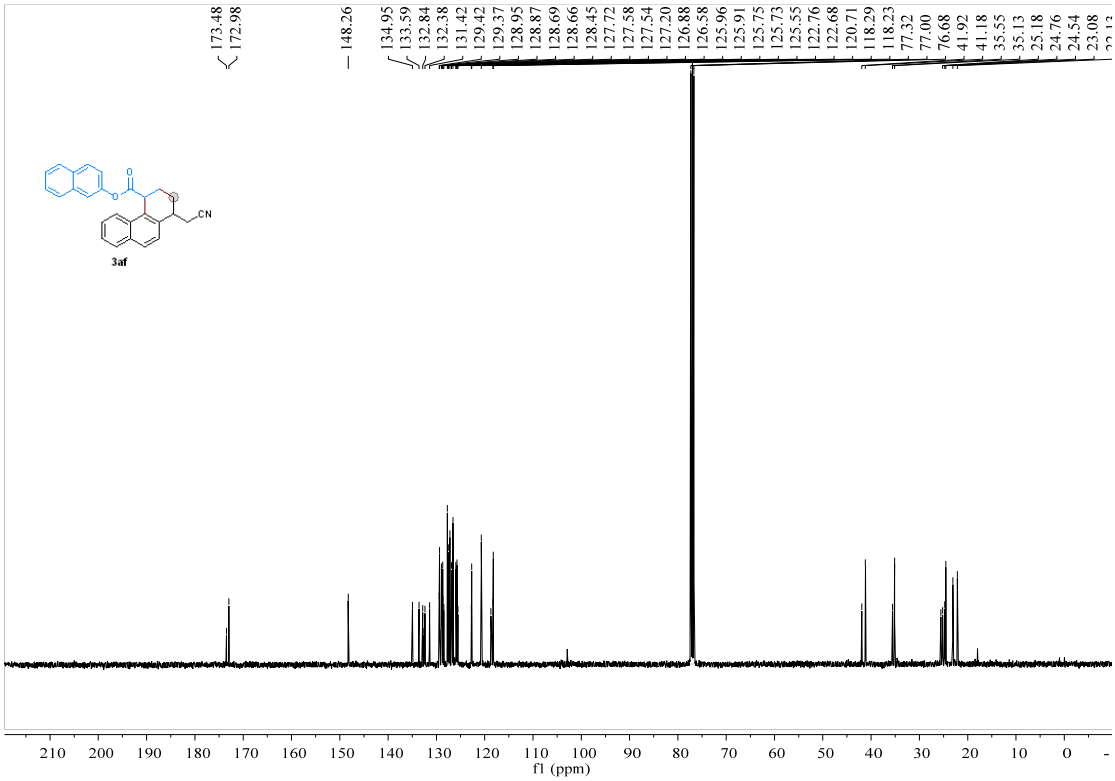
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ae



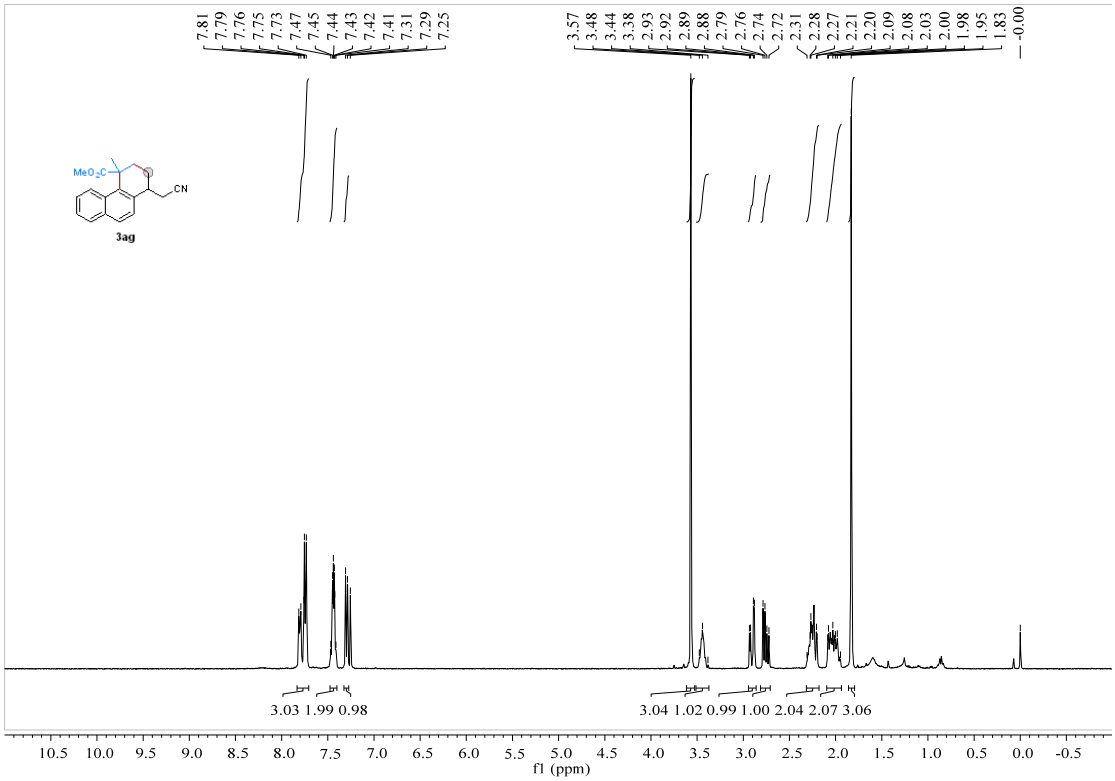


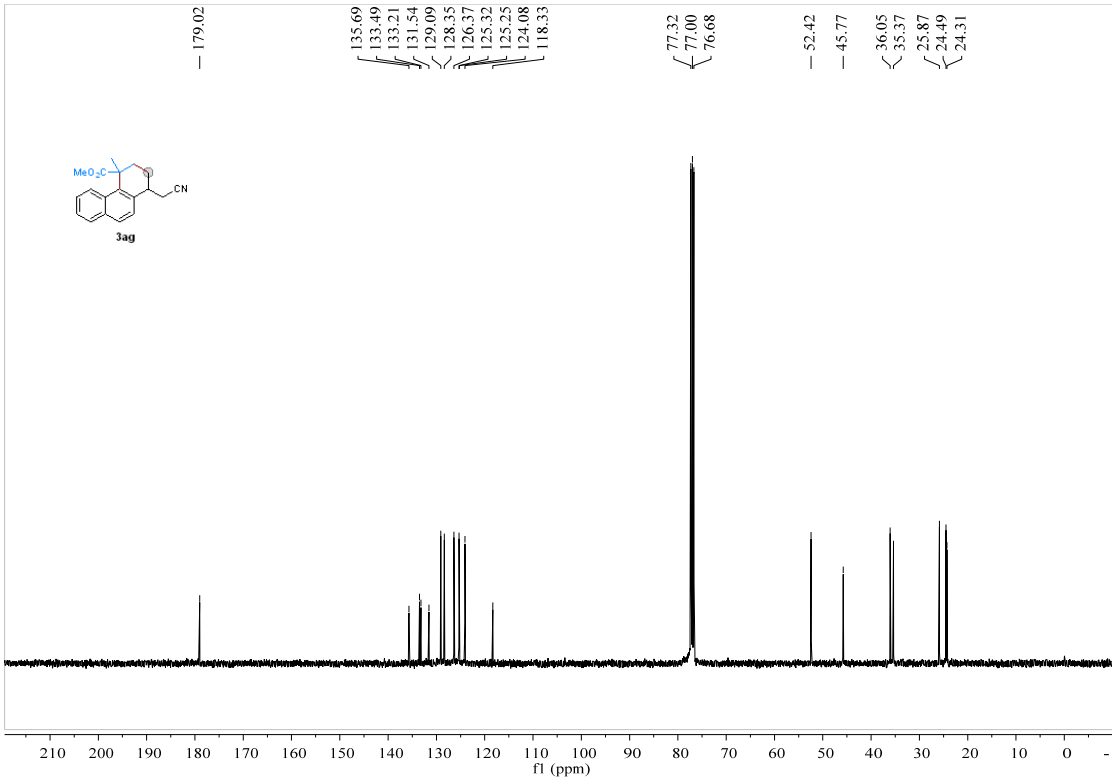
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3af



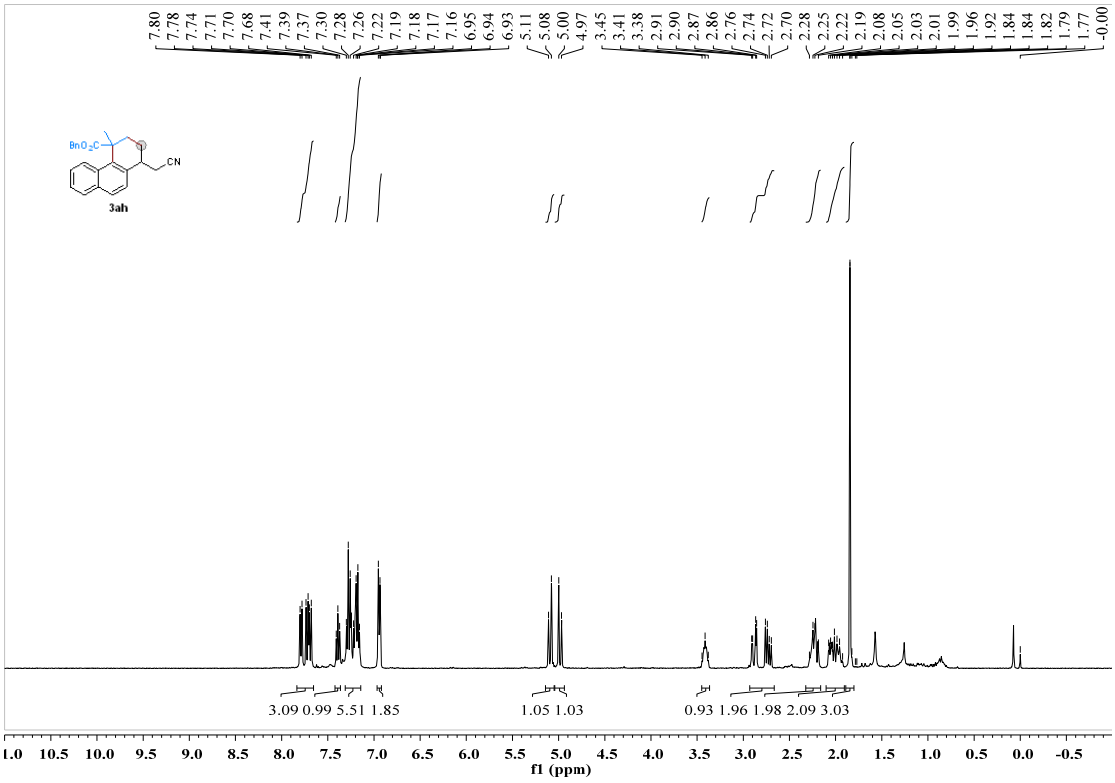


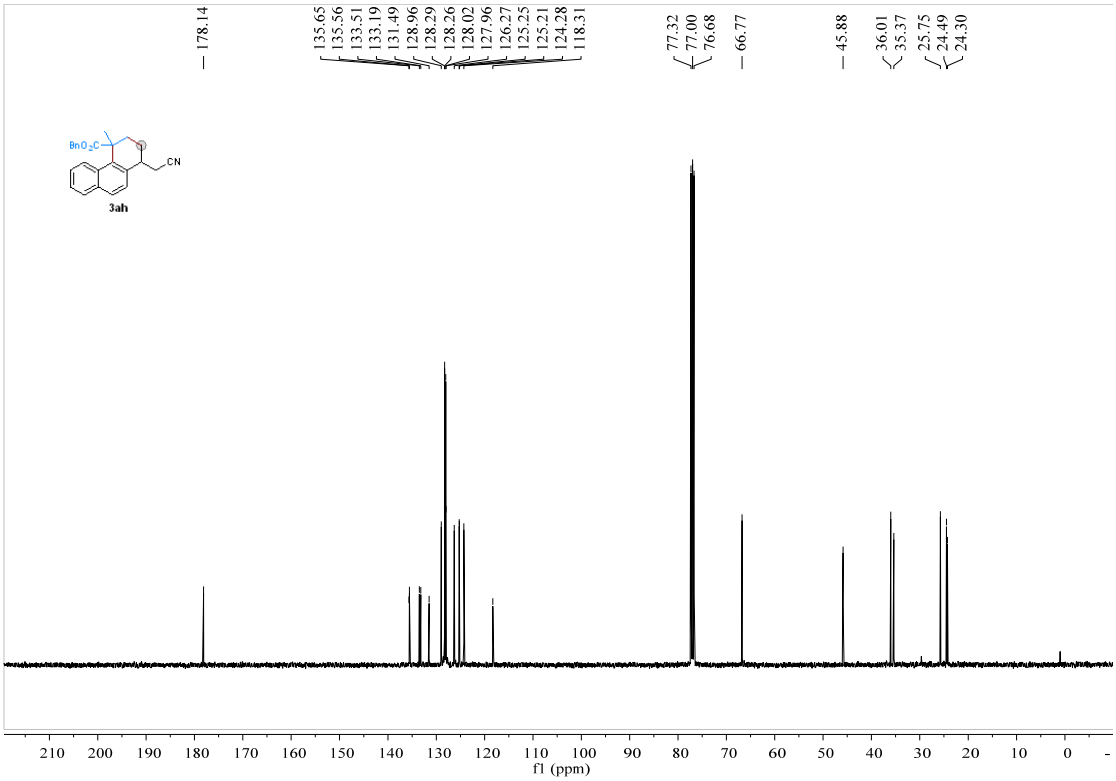
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ag



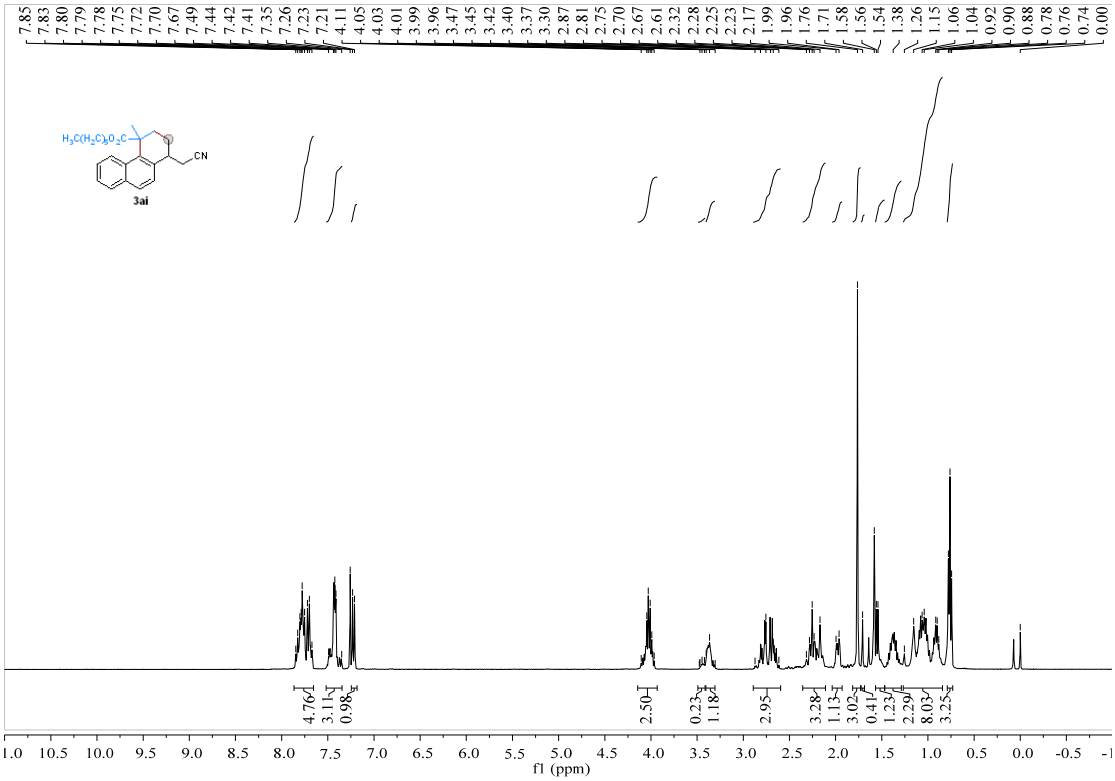


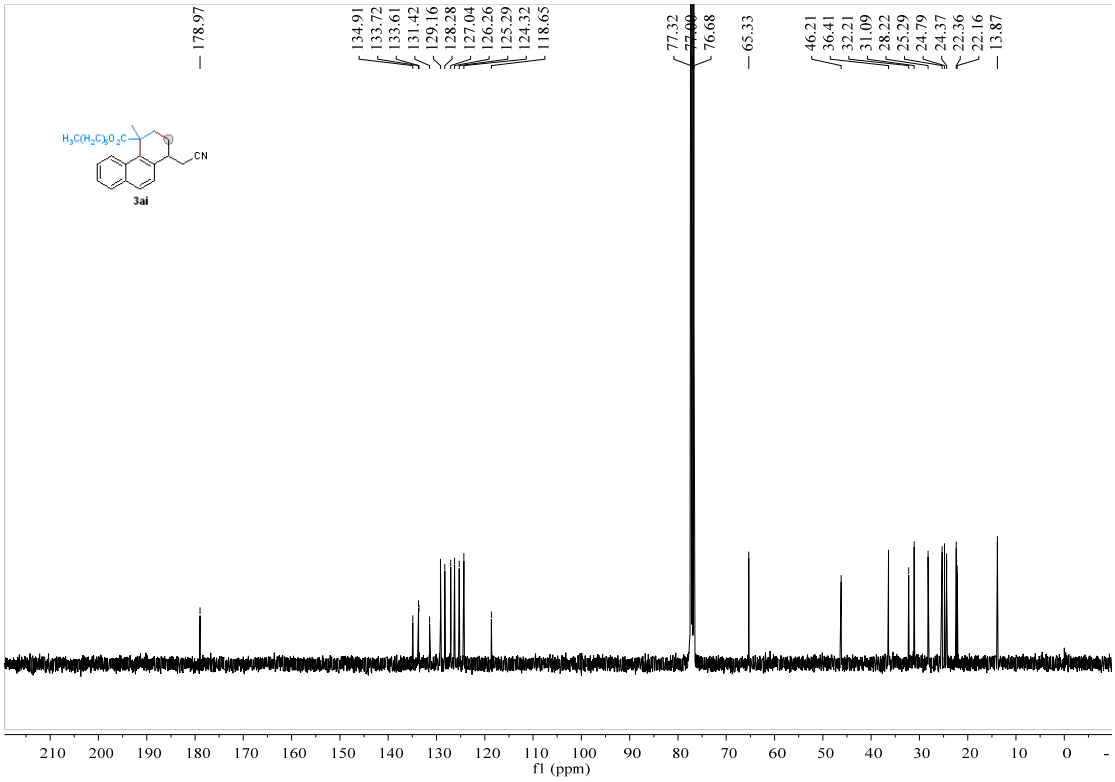
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ah



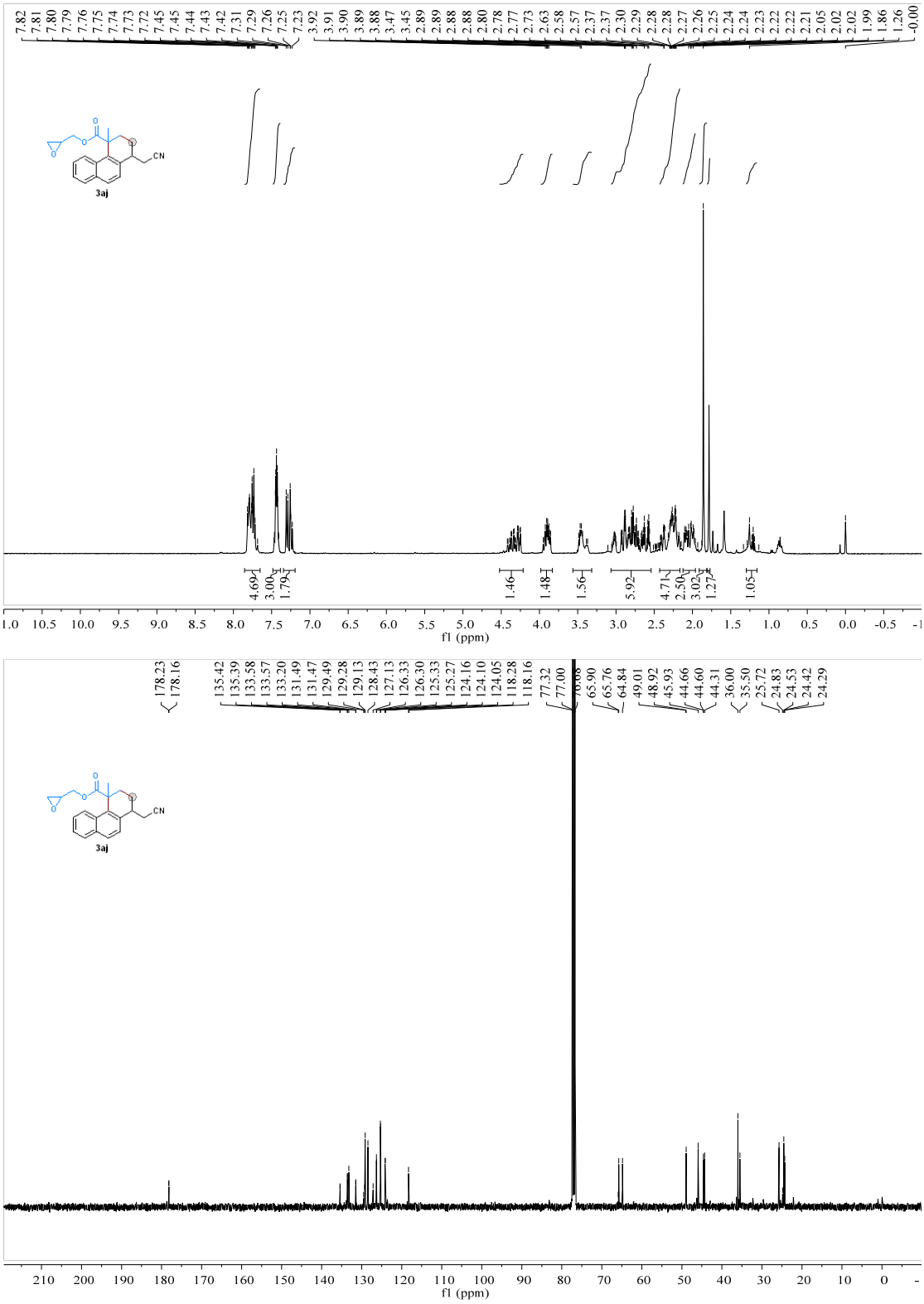


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ai

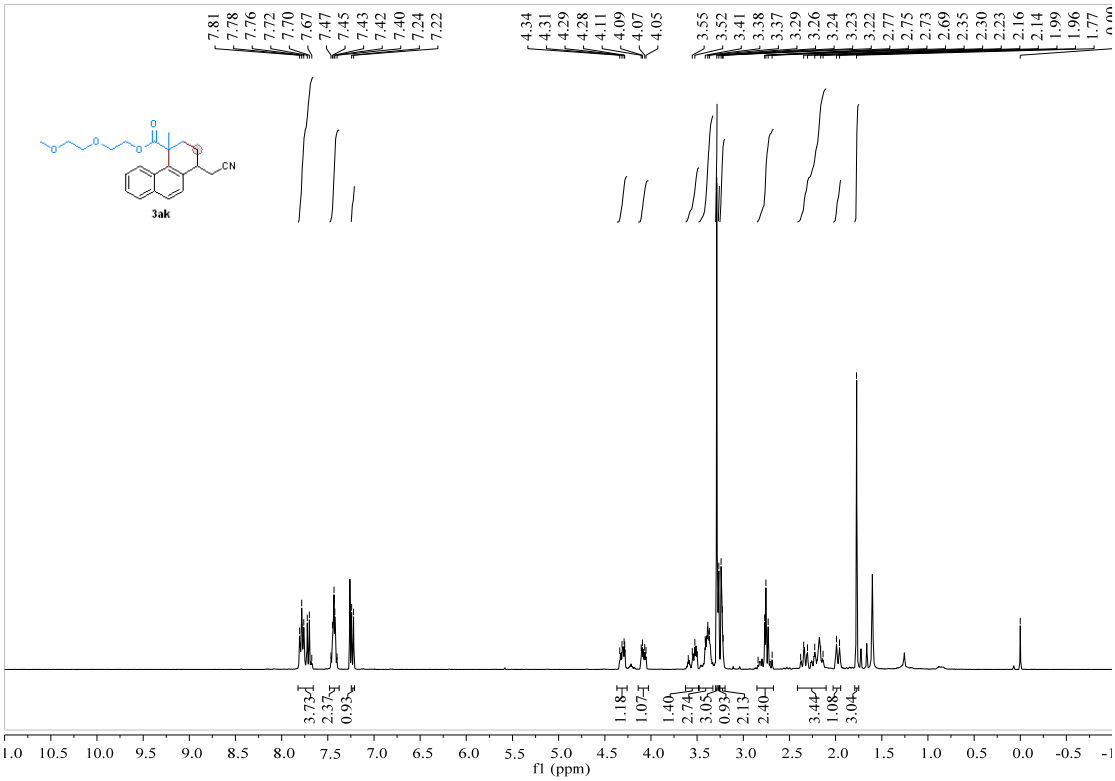


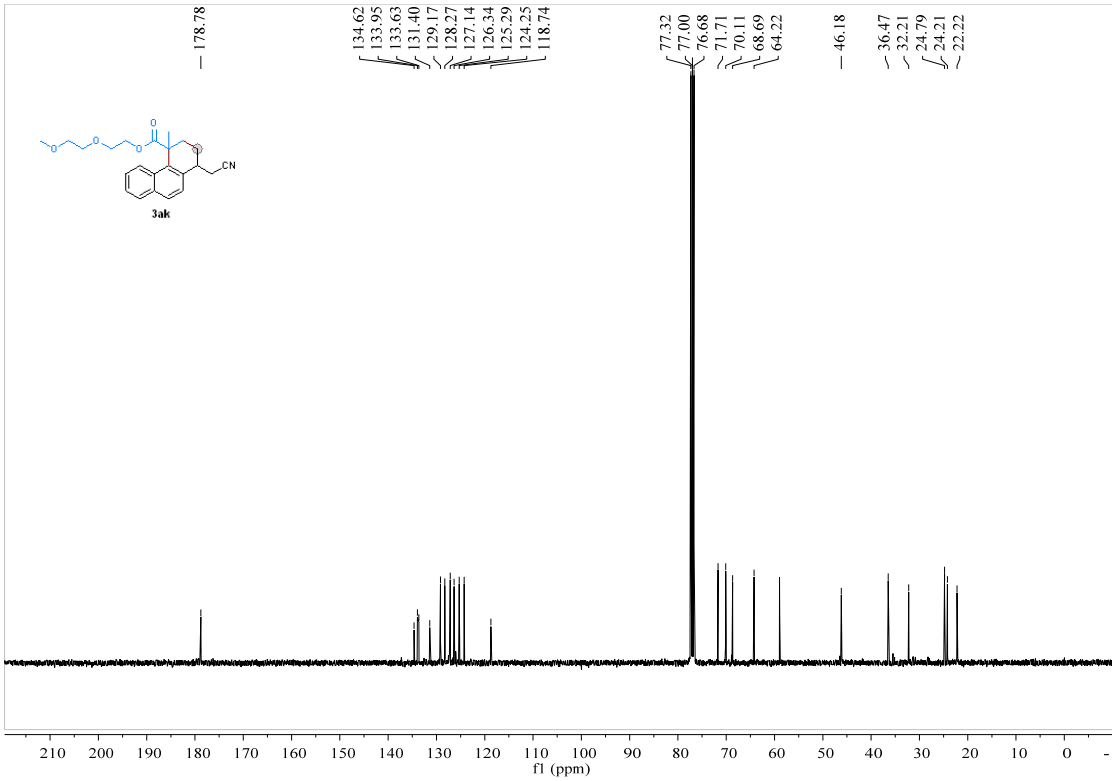


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3aj

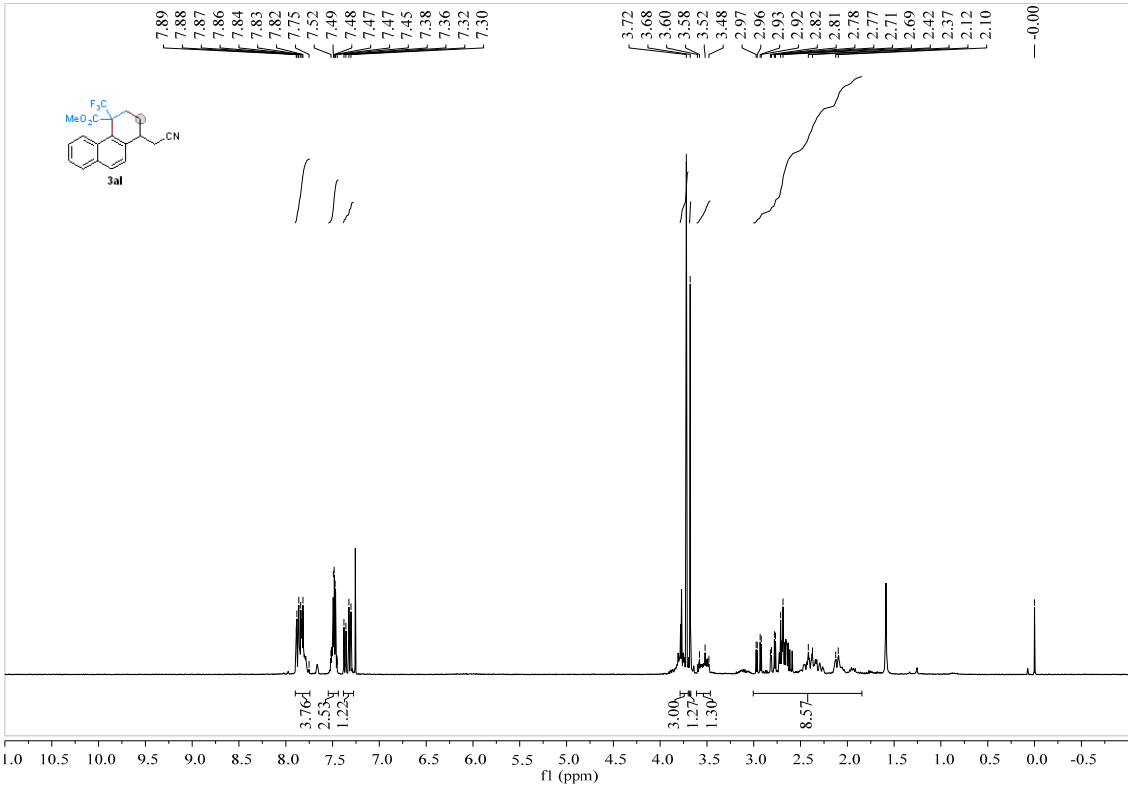


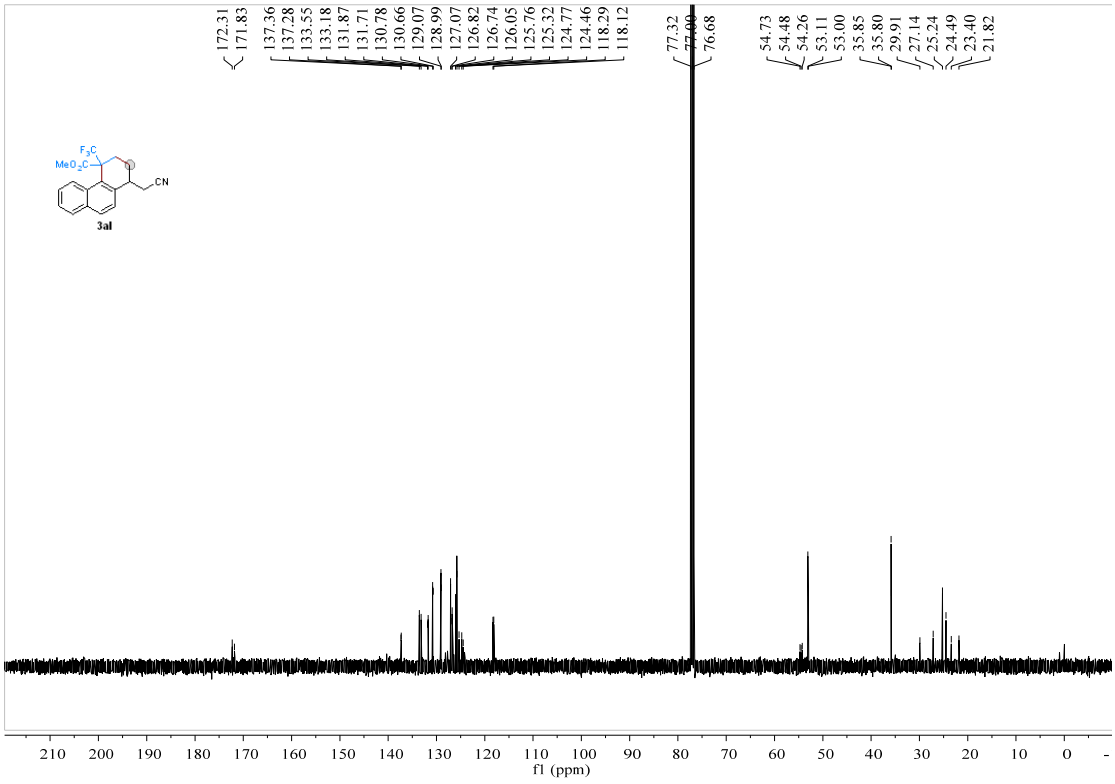
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ak

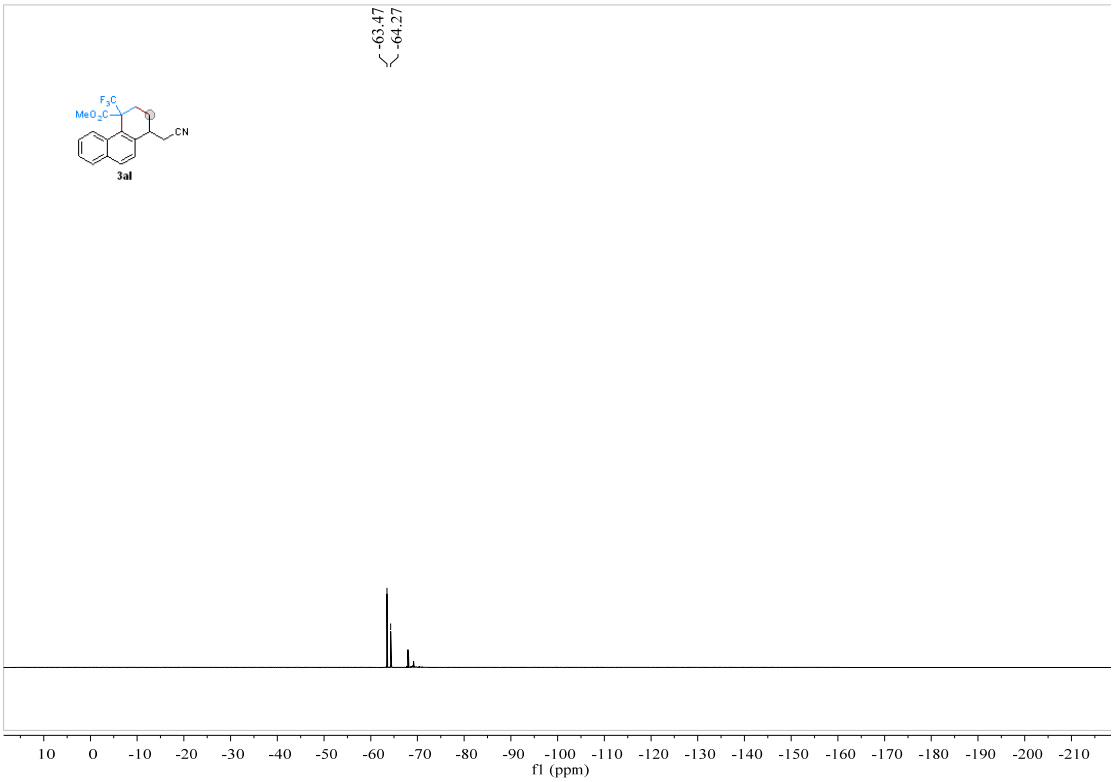




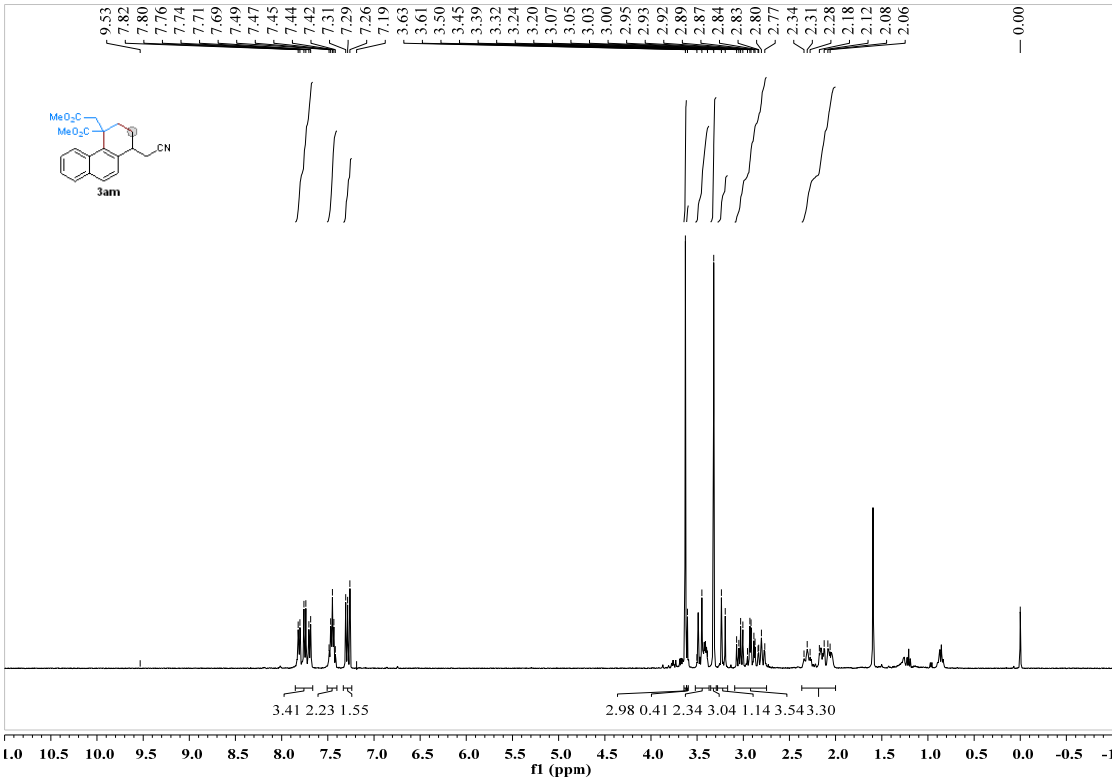
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3al

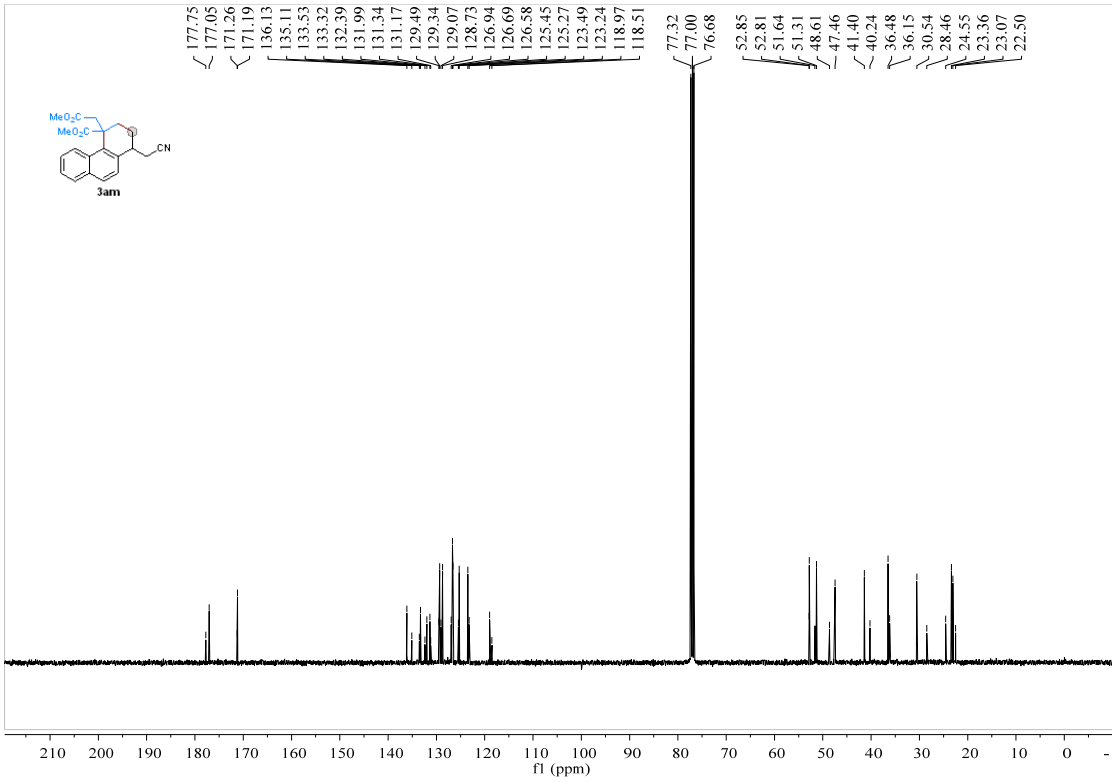




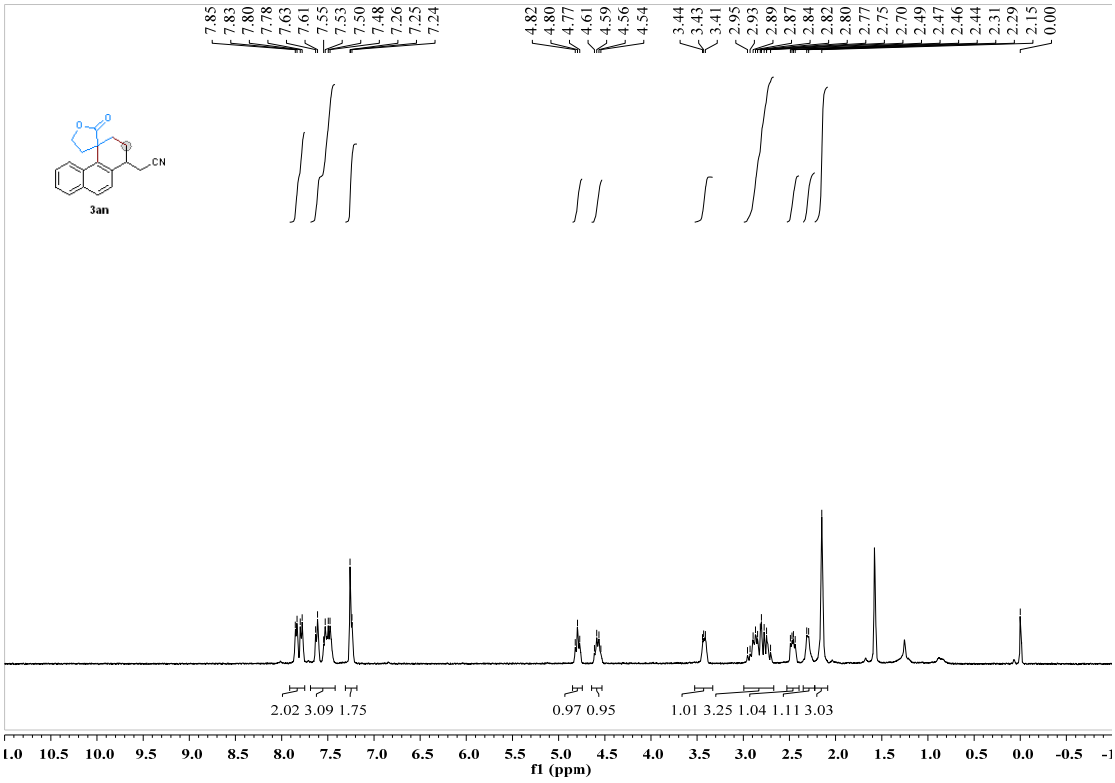

-63.47
-64.27
F3C
MeO2C
CN
3al
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

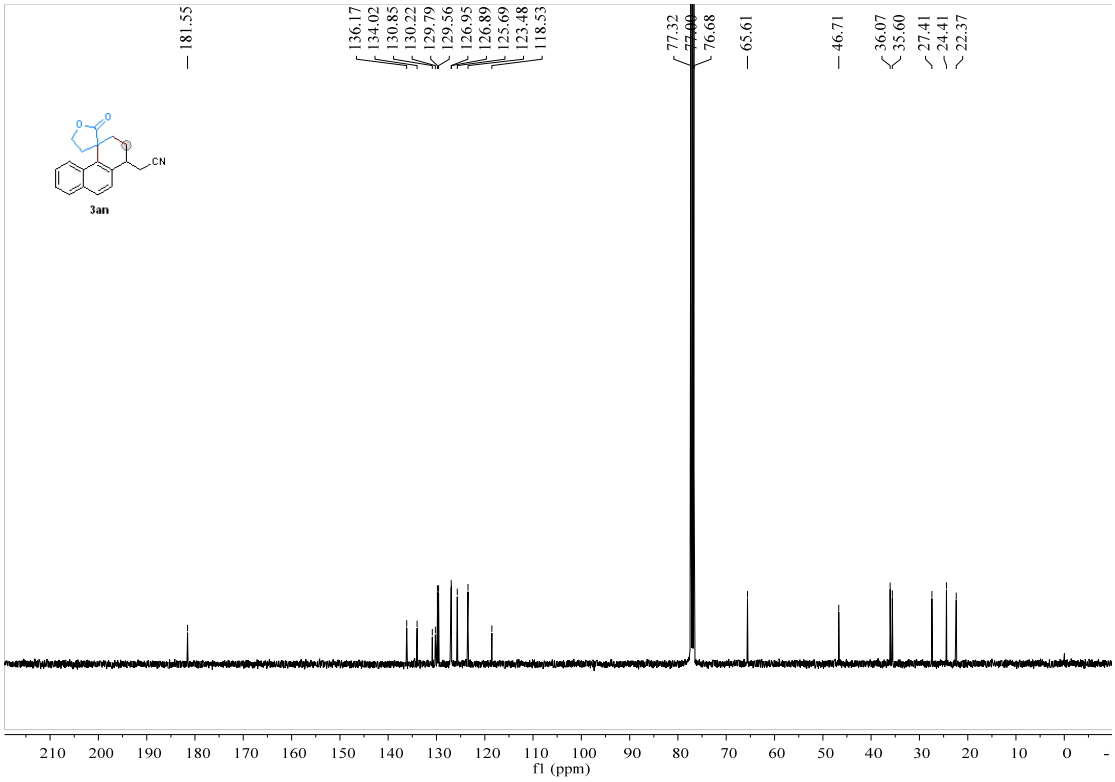
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3am



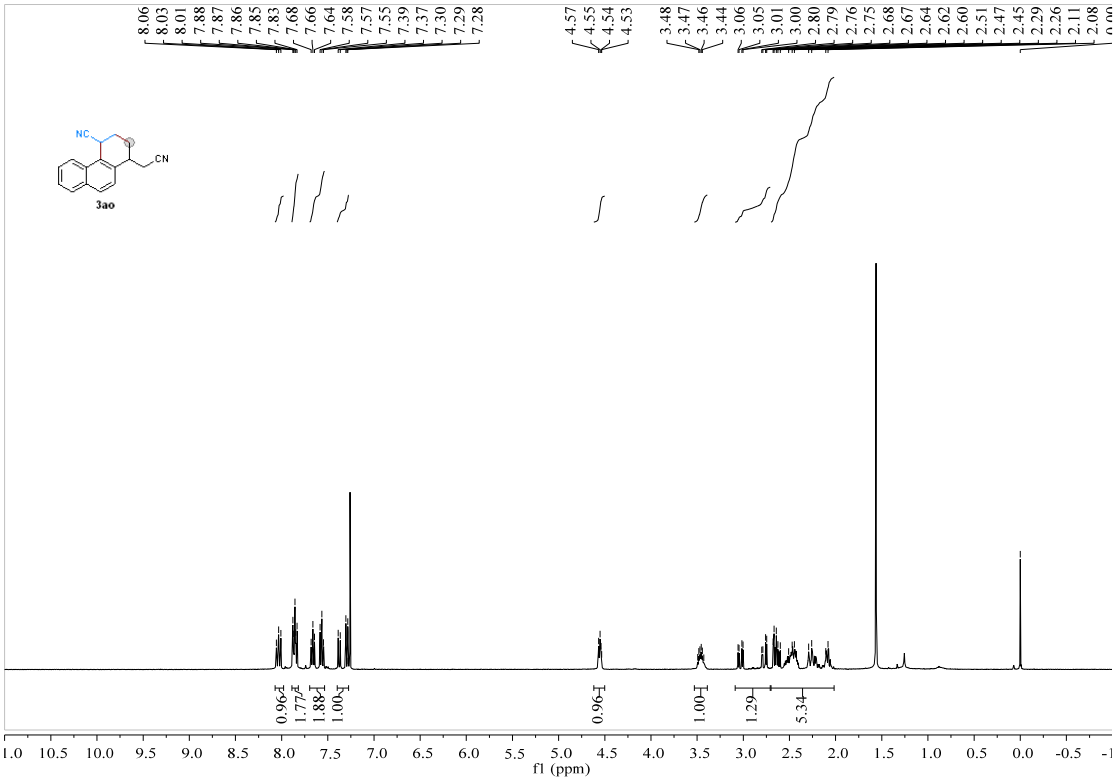


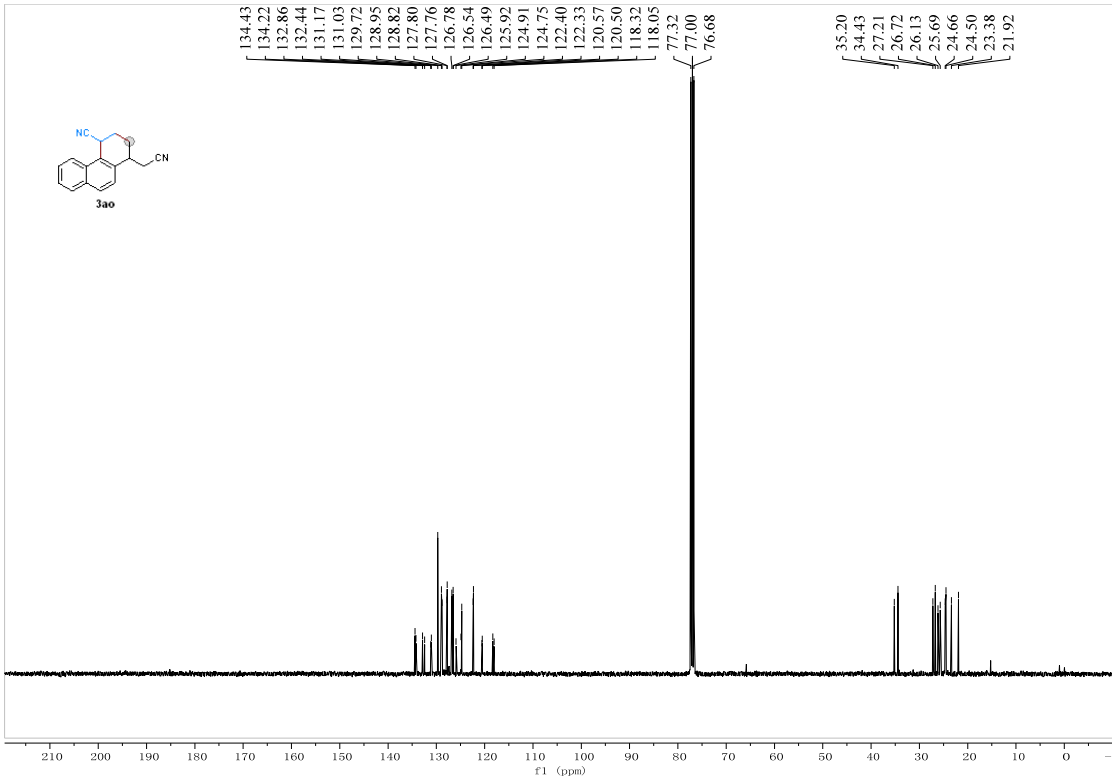
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3an



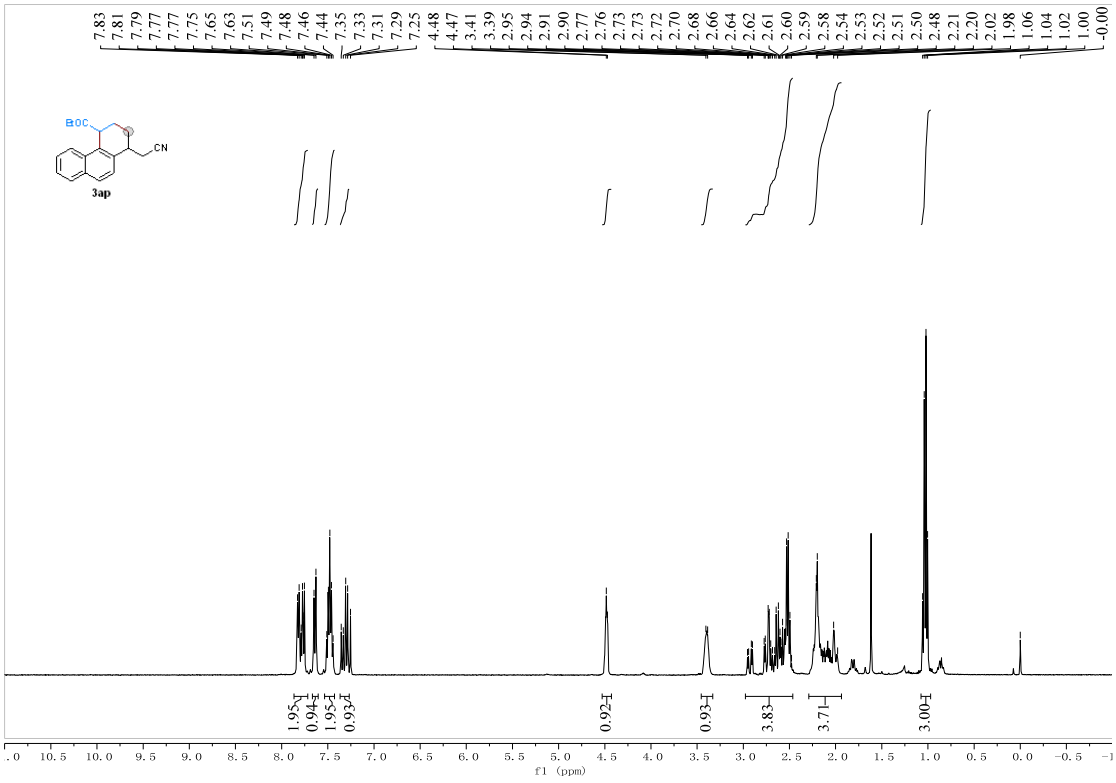


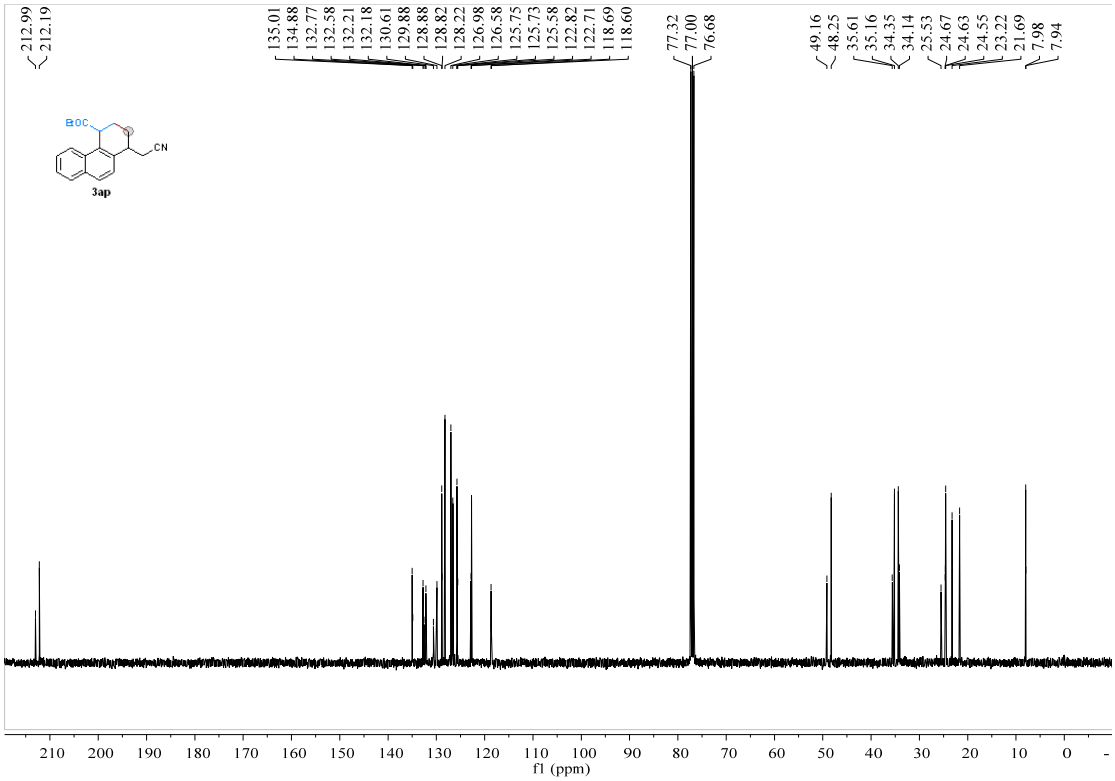
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ao



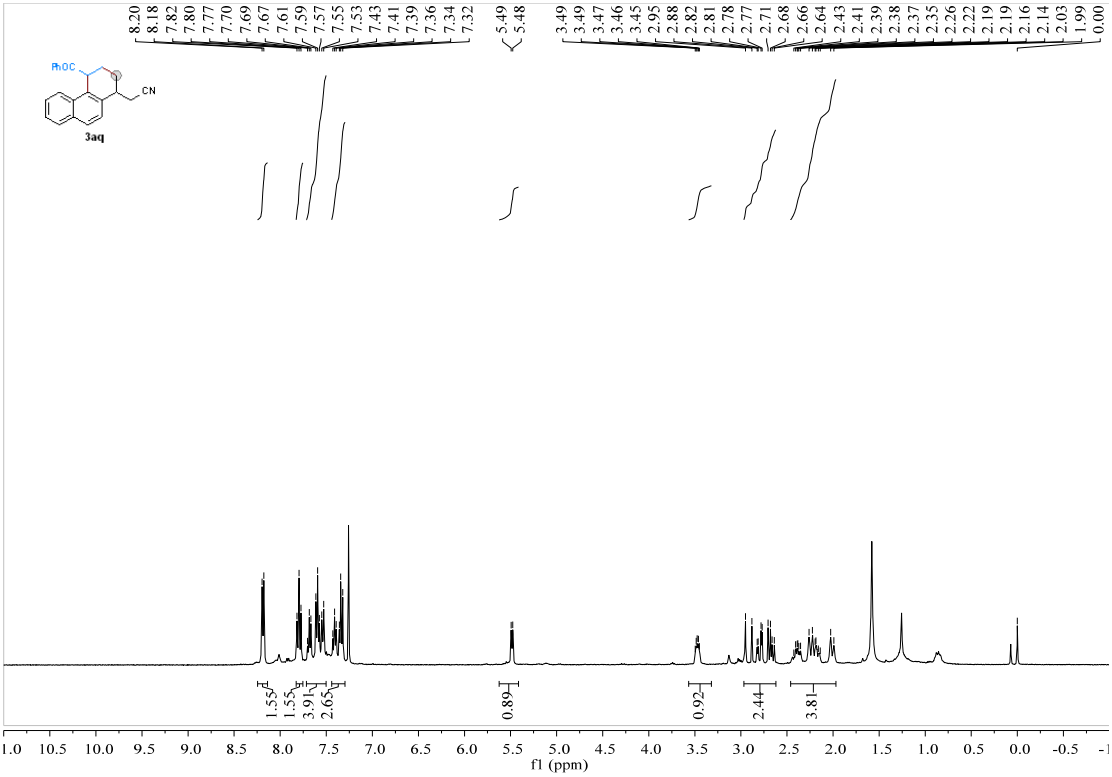


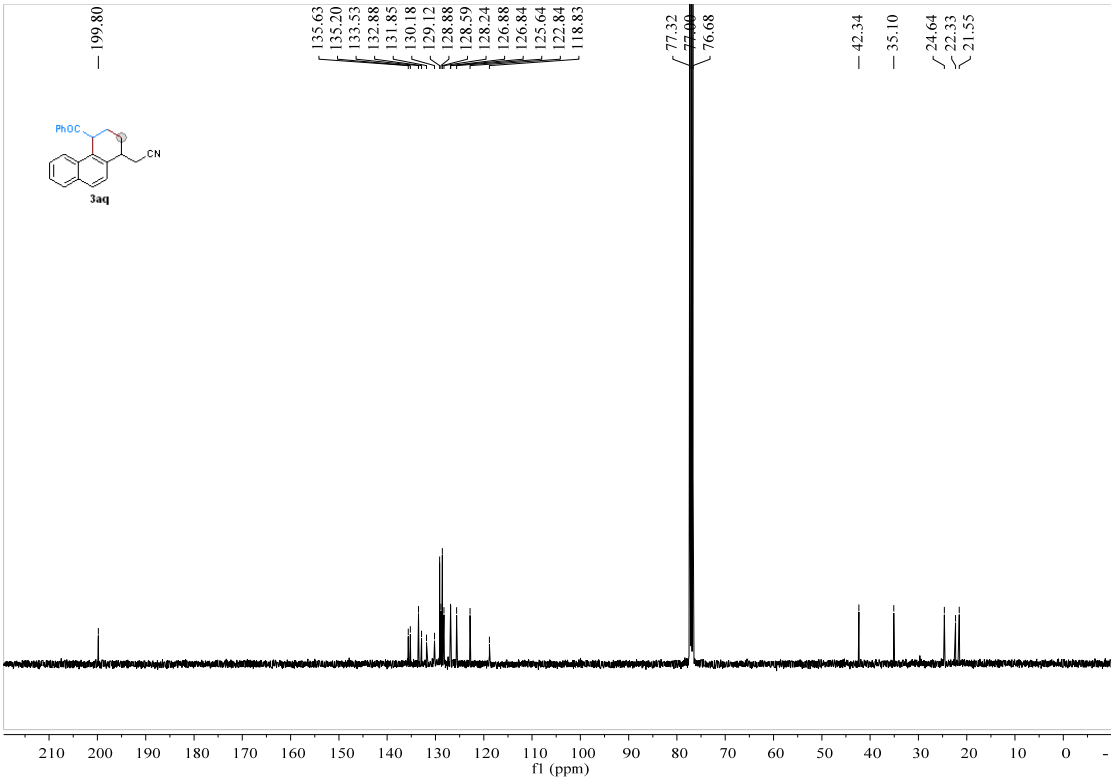
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ap



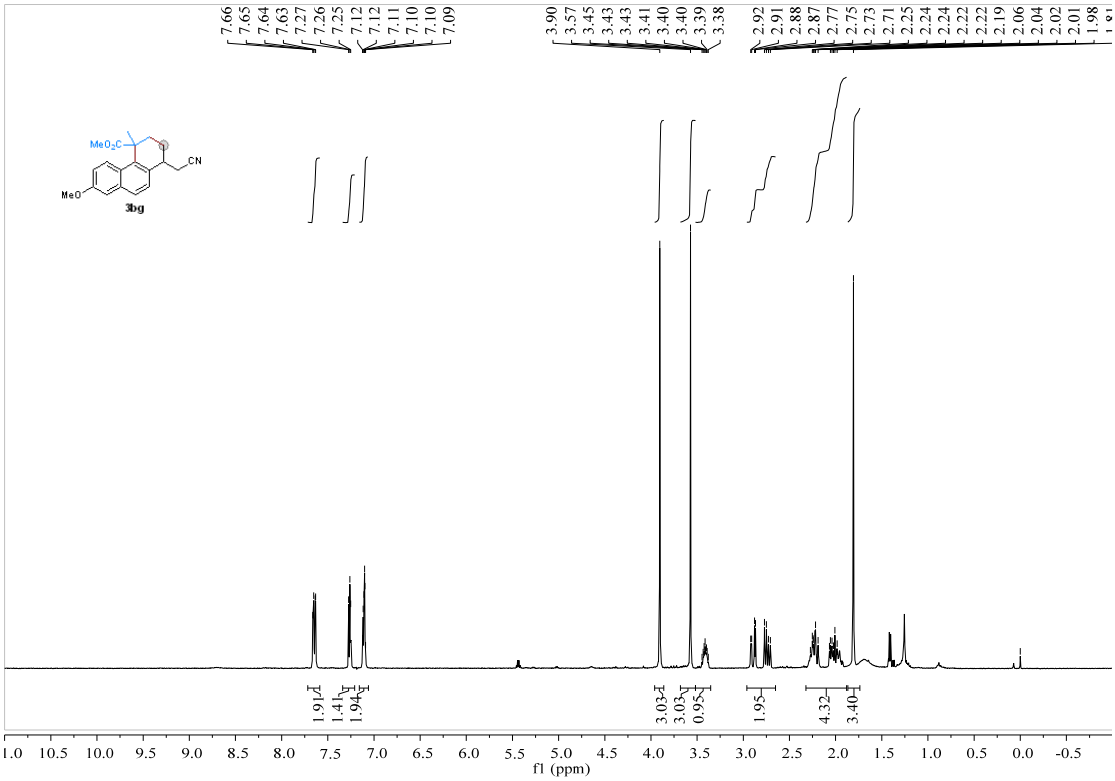


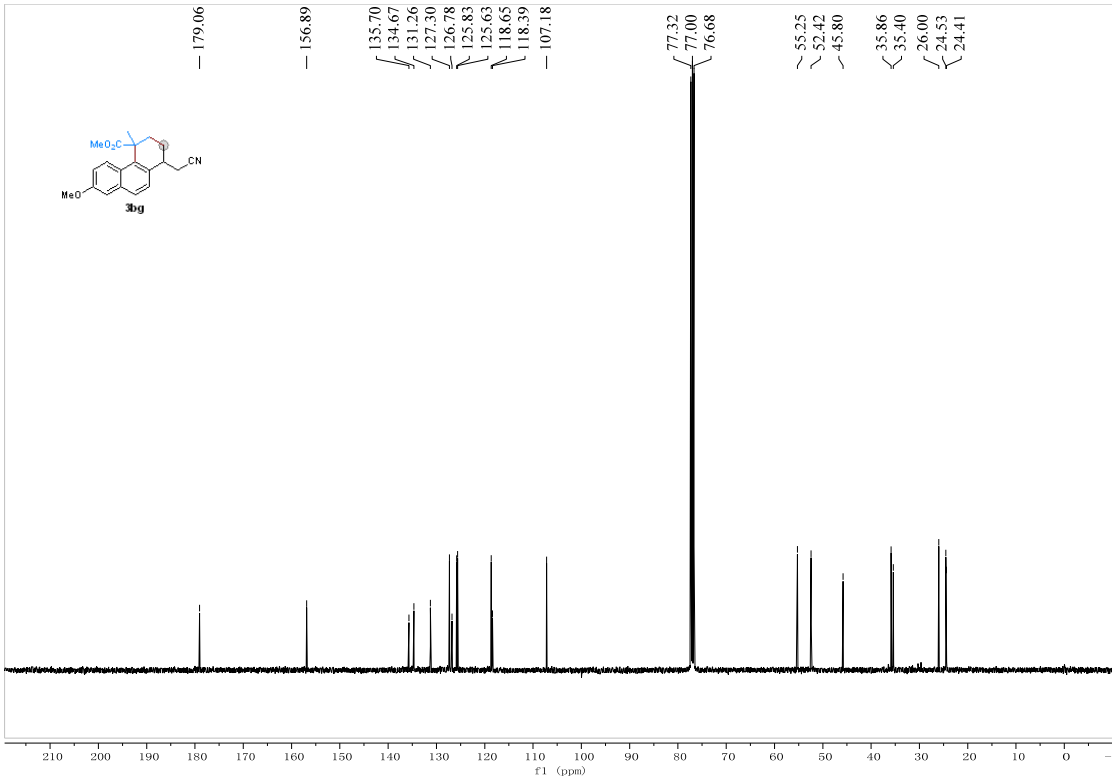
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3aq





^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3bg





^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3cg