Supporting Information

Palladium-catalyzed synthesis of spirooxindoles and [3,4]-fused oxindoles from alkene-tethered carbamoyl chlorides

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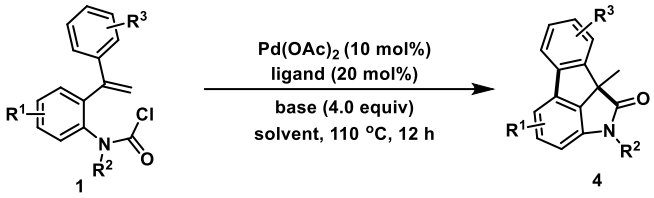
General information:

The ^{1}H NMR, ^{19}F NMR and ^{13}C NMR were recorded with Bruker 400 MHz spectrometer instruments in $CDCl_3$. The chemical shifts (δ) of ^{1}H NMR and ^{13}C NMR were measured in ppm, referenced to residual ^{1}H and ^{13}C signals of nondeuterated $CDCl_3$ (δ = 7.26 and 77.16) as internal standards. All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200~300 mesh). Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates and visualized by UV-light (254 nm). Melting points were obtained on a Yanaco-241 apparatus and are uncorrected. HRMS were recorded on VG ZAB-HS mass spectrometer with ESI resource.

Optimization of Reaction Conditions:[a, b]



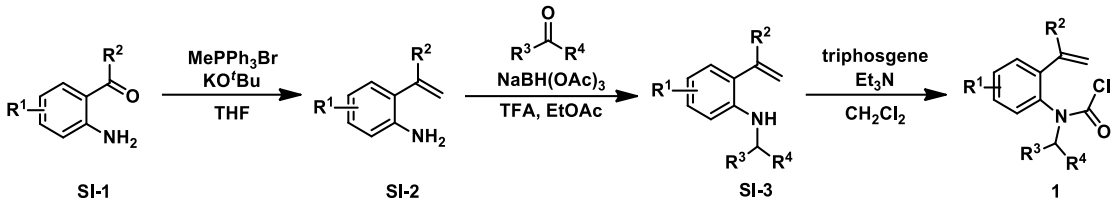
Entry	Ligand	Base	Solvent	Yield[b](%)
1	$P(2\text{-}CH_3\text{-}C_6H_4)_3$	KOPiv/$PhNEt_2$(1:1)	MeCN	10%
2	$P(2\text{-}CH_3\text{-}C_6H_4)_3$	KOPiv/$PhNEt_2$(1:1)	DCE	5%
3	$P(2\text{-}CH_3\text{-}C_6H_4)_3$	KOPiv/$PhNEt_2$(1:1)	DMA	0%
4	$P(2\text{-}CH_3\text{-}C_6H_4)_3$	KOPiv/$PhNEt_2$(1:1)	THF	10%
5	$P(2\text{-}CH_3\text{-}C_6H_4)_3$	KOPiv/$PhNEt_2$(1:1)	1,4-Dioxane	30%
6	$P(4\text{-}OCH_3\text{-}C_6H_4)_3$	KOPiv/$PhNEt_2$(1:1)	1,4-Dioxane	25%
7	$P(4\text{-}CF_3\text{-}C_6H_4)_3$	KOPiv/$PhNEt_2$(1:1)	1,4-Dioxane	30%
8	DPPE	KOPiv/$PhNEt_2$(1:1)	1,4-Dioxane	35%
9	DPPB	KOPiv/$PhNEt_2$(1:1)	1,4-Dioxane	30%
10	$P(2\text{-}OCH_3\text{-}C_6H_4)_3$	KOPiv/$PhNEt_2$(1:1)	1,4-Dioxane	40%
11	PCy_3HBF_4	KOPiv/$PhNEt_2$(1:1)	1,4-Dioxane	0%
12	**$P(2\text{-}OCH_3\text{-}C_6H_4)_3$**	**KOPiv/Et_3N(1:1)**	**1,4-Dioxane**	**70%**
13	$P(2\text{-}OCH_3\text{-}C_6H_4)_3$	KOPiv/ DIPEA(1:1)	1,4-Dioxane	60%
14	$P(2\text{-}OCH_3\text{-}C_6H_4)_3$	Cs_2CO_3/ Et_3N(1:1)	1,4-Dioxane	10%
15	$P(2\text{-}OCH_3\text{-}C_6H_4)_3$	CsOAc/ Et_3N(1:1)	1,4-Dioxane	63%

[a] The reactions were conducted with **1** (0.2 mmol), $Pd(OAc)_2$ (0.02 mmol), ligand (0.04 mmol), base (0.8 mmol), and indicated

solvent (2.0 mL) under N_2 atmosphere at 110 °C for 12 h. [b] Isolated yield.

Preparation of Starting Materials:

General Procedure 1:

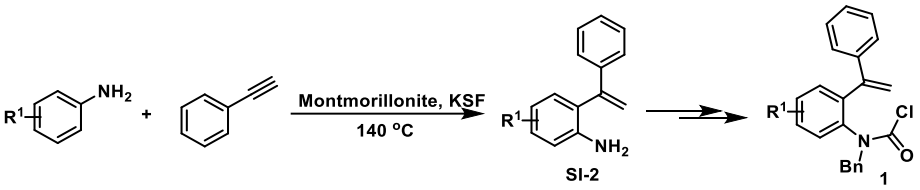


A mixture of $MePPh_3Br$ (1.5 equiv) and KO^tBu (1.5 equiv) in THF (0.3 mmol/mL) was stirred at room temperature for 1 h. Then **SI-1** (1.0 equiv) was added dropwise to the reaction mixture at 0 °C. The reaction was stirred at room temperature until the starting material was disappeared. After that the solvents were evaporated under reduced pressure. The residue was purified by column chromatography to give **SI-2** (**1a-1e**, **1i**, **1j**, **1m, 1n**).

The **SI-2** (1.0 equiv) was dissolved in ethyl acetate (0.25 M). The aldehyde or ketone (1.2 equiv) was added followed by trifluoroacetic acid (2.0 equiv). The reaction was stirred for 30 minutes then sodium triacetoxyborohydride (2.0 equiv) was added. The reduction was stirred for 2 h then quenched with 4 M NaOH. The reaction was diluted with ethyl acetate and washed twice with brine. The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude was purified by flash column chromatography to give **SI-3**.

The **SI-3** (1.0 equiv) was dissolved in dichloromethane (0.3 M) and cooled to 0 °C. Then triethylamine (2.0 equiv) was added followed by triphosgene (0.5 equiv). The reaction was warmed to room temperature and stirred until completion indicated by TLC. The reaction was quenched with water and extracted twice with dichloromethane. The organic layers were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The crude starting materials were purified by flash column chromatography in ethyl acetate/petroleum ether mixtures to give **1**.

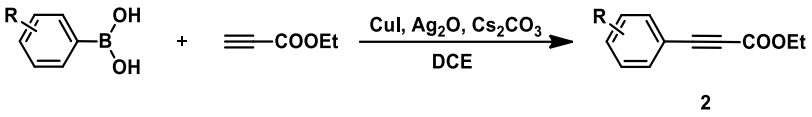
General Procedure 2：



Aniline (1.0 equiv), phenylacetylene (1.1 equiv) and montraorillonite KSF (100.0 mg/mmol) are introduced in a round bottomed flask equipped with magnetic stirrer and a reflux condenser. The reaction mixture is heated at 140 °C for 5 hours and then cooled to room temperature. The crude mixtures were dissolved with dichloromethane and filtered. Then the solvents were concentrated in vacuo and the crude was purified by column chromatography (silica gel, appropriate mixture of petroleum ether/ethyl acetate) to give **SI-2** (**1f**–**1h**, **1k, 1l, 1o**).

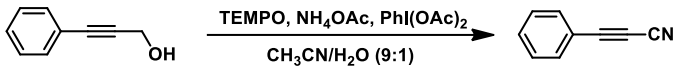
(Note: The remaining procedure follows the **General Procedure 1**.)

General Procedure 3:



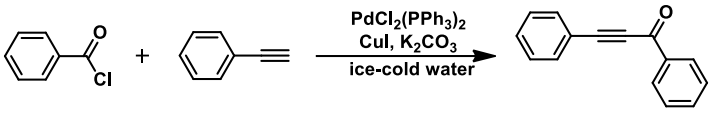
Under air atmosphere, a reaction tube was charged with arylboronic acid (1.0 equiv), alkyne (1.5 equiv), CuI (0.2 equiv), Ag_2O (2.0 equiv), Cs_2CO_3 (2.0 equiv), and DCE (0.1 M). After the mixture was heated at 80 °C for 36 h, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the product **2** (**2a**–**2i**).

General Procedure 4:



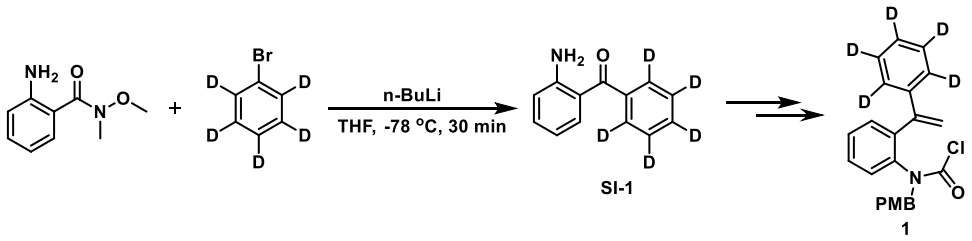
To a solution of 3-phenylprop-2-yn-1-ol (1.0 equiv) in acetonitrile/water (9:1, 0.3 M) was added TEMPO (5.0 mol%), ammonium acetate (4.0 equiv) and iodobenzene diacetate (2.2 equiv) at room temperature under nitrogen atmosphere. The reaction mixture was stirred for 2-6 h until the raw material is completely transfommed and then concentrated in vacuo on rotavapor. The resultant crude was extracted between water and ethyl acetate. The organic layer was washed with brine, dried over magnesium sulfate and concentrated in vacuo on rotavapor. The crude was purified by column chromatography on a silica gel column to give the desired product **2k**.

General Procedure 5:



Terminal alkynes(1.0 equiv), acid chloride(2.0 equiv), sodium lauryl sulfate (7.0 mol%), $PdCl_2(PPh_3)_4$ (2.0 mol%) and CuI (5.0 mol%) were added in a test tube that was cooled by ice-water bath then ice-cold water (3.0 M) that dissovled K_2CO_3 (3.0 equiv) was added to the test tube in small portions while stirring. After the addition was completed, the reaction mixture was capped, then heated and stirred at 65 ^oC for 4 hours. Then the reaction mixture was cooled and extracted with ethyl ether (3 x 10 mL) and concentrated in vacuo. The residue was purified by silica gel column chromatography to give the pure product **2l**.

General Procedure 6:



In a flame dried round-bottomed flask at -78 ^oC, the N-methoxy-Nmethylbenzamide (1.0 equiv) and bromobenzene-d5 (1.0 equiv) in THF (0.2 M) were stirred vigorously under nitrogen. N-butyllithium (2.0 equiv) was added slowly via a syringe. After the addition was complete, 2 mL of 1.0 N HCl per 1.0 mL of n-butyllithium was added to the flask while the mixture was still at -78 ^oC. The reaction mixture was allowed to warm up with stirring, and the THF was removed in vacuo. The resulting mixture was extracted with ethyl acetate, and the combined organic phase was dried over anhydrous sodium sulfate. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel chromatography to give the desired products (**SI-1**).

(Note: The remaining procedure follows the **General Procedure 1**.

General Procedure for the Synthesis of Spirooxindoles:

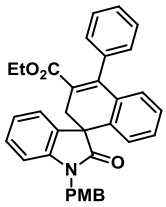
In a 38 mL sealed tube, the mixture of **1** (0.20 mmol), **2** (0.40 mmol), $Pd(PPh_3)_4$

(11.6 mg, 0.01 mmol), Cs_2CO_3 (97.8 mg, 0.30 mmol) were dissolved in anhydrous toluene (2.0 mL). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was heated to 110 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum Ether) to give the products **3**.

General Procedure for the Synthesis of [3,4]-fused oxindoles:

In a 38 mL sealed tube, the mixture of **1** (0.20 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), P(2-OMe-C_6H_4)$_3$ (14.1 mg, 0.04 mmol), KOPiv (56.0 mg, 0.4 mmol), Et_3N (40.5 mg, 0.4 mmol) were dissolved in anhydrous 1,4-Dixoane (2.0 mL). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was heated to 110 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/Petroleum Ether) to give the products **4**.

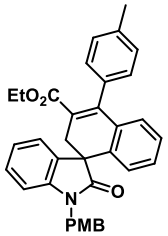
Characterization of Products:



ethyl 1-(4-methoxybenzyl)-2-oxo-4'-phenyl-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (**3aa**)

White solid (80 mg, 78%), M.P.: 167-168 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 4H), 7.24 – 7.20 (m, 4H), 7.09 – 7.00 (m, 3H), 6.86 – 6.74 (m, 6H), 4.89 (s, 2H), 3.80 (q, *J* = 7.2 Hz, 2H), 3.68 (s, 3H), 3.39 (d, *J* = 16.8 Hz, 1H), 2.89 (d, *J* = 16.8 Hz, 1H), 0.76 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.0, 168.2, 159.2,

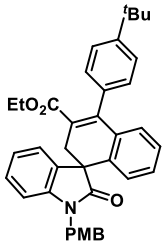
145.3, 141.3, 139.1, 136.4, 135.3, 133.3, 130.0, 129.4, 128.8, 128.5, 128.2, 128.0, 127.9, 127.6, 125.8, 124.0, 123.8, 123.0, 114.4, 109.7, 60.4, 55.4, 52.0, 43.6, 35.3, 13.6. **ESI-MS**: Calcd for $C_{34}H_{29}NO_4$: [M+H$^+$] 516.2169, found 516.2175.



ethyl

1-(4-methoxybenzyl)-2-oxo-4'-(p-tolyl)-2'H-spiro[indoline-3,1'-naphthalene]-3'-carbo xylate (**3ab**)

White solid (79 mg, 75%), M.P.: 178-179 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.12 – 7.01 (m, 5H), 6.86 (d, *J* = 7.2 Hz, 2H), 6.80 – 6.73 (m, 4H), 4.89 (s, 2H), 3.82 (q, *J* = 7.2 Hz, 2H), 3.68 (s, 3H), 3.38 (d, *J* = 16.8 Hz, 1H), 2.86 (d, *J* = 16.8 Hz, 1H), 2.33 (s, 3H), 0.81 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.0, 168.2, 159.2, 145.3, 141.2, 137.2, 136.4, 136.0, 135.4, 133.3, 129.9, 129.4, 128.9, 128.8, 128.5, 128.0, 127.8, 125.7, 123.9, 123.8, 123.0, 114.4, 109.7, 60.4, 55.4, 52.0, 43.6, 35.4, 21.4, 13.7. **ESI-MS**: Calcd for $C_{35}H_{31}NO_4$: [M+H$^+$] 530.2326, found 530.2326.

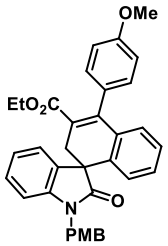


ethyl

4'-(4-(tert-butyl)phenyl)-1-(4-methoxybenzyl)-2-oxo-2'H-spiro[indoline-3,1'-naphthal ene]-3'-carboxylate (**3ac**)

Yellow oil (83 mg, 73%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.19 – 7.11 (m, 3H), 6.98 – 6.92 (m, 2H), 6.90 – 6.82 (m, 4H), 4.99 (s, 2H), 3.87 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.47 (d, *J* = 16.4 Hz, 1H), 2.93 (d, *J* = 16.4 Hz, 1H), 1.39 (s, 9H), 0.79 (t,

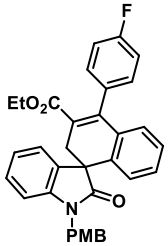
J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.1, 168.7, 159.3, 150.6, 145.0, 141.3, 136.5, 136.0, 135.4, 133.3, 129.9, 129.5, 128.8, 128.7, 128.5, 128.1, 127.9, 125.8, 125.1, 124.2, 123.8, 123.0, 114.5, 109.7, 60.4, 55.4, 52.1, 43.7, 35.5, 34.8, 31.6, 13.5. **ESI-MS**: Calcd for $C_{38}H_{37}NO_4$: [M+H$^+$] 572.2795, found 572.2791.



ethyl

1-(4-methoxybenzyl)-4'-(4-methoxyphenyl)-2-oxo-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (**3ad**)

White solid (91 mg, 83%), M.P.: 165-166 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.12 (m, 5H), 7.00 – 6.92 (m, 4H), 6.90 – 6.82 (m, 4H), 4.98 (s, 2H), 3.92 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 3.79 (s, 3H), 3.46 (d, *J* = 16.4 Hz, 1H), 2.93 (d, *J* = 16.4 Hz, 1H), 0.93 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.1, 168.4, 159.3, 144.9, 141.3, 136.5, 135.5, 133.3, 131.2, 130.2, 123.0, 129.4, 128.9, 128.5, 128.1, 127.9, 125.7, 124.1, 123.8, 123.0, 114.4, 113.7, 109.7, 60.4, 55.5, 55.4, 52.0, 43.6, 35.5, 13.9. **ESI-MS**: Calcd for $C_{35}H_{31}NO_5$: [M+H$^+$] 546.2275, found 546.2270.

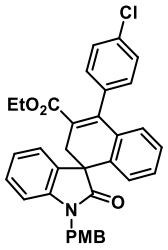


ethyl

4'-(4-fluorophenyl)-1-(4-methoxybenzyl)-2-oxo-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (**3ae**)

White solid (65 mg, 61%), M.P.: 183-184 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 5H), 7.22 – 7.13 (m, 5H), 7.00 – 6.95 (m, 1H), 6.91 – 6.84 (m, 5H), 5.00 (d, *J* = 16.0 Hz, 1H), 4.96 (d, *J* = 16.4 Hz, 1H), 3.93 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H),

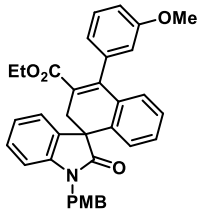
3.45 (d, *J* = 16.8 Hz, 1H), 3.00 (d, *J* = 16.8 Hz, 1H), 0.93 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.8, 168.0, 162.5 (d, *J* = 245.0 Hz), 159.3, 144.4, 141.5, 136.4, 135.3, 134.9, 133.2, 130.1, 129.3, 128.8, 128.6, 128.0, 128.0, 125.9, 124.6, 123.8, 123.1, 115.4, 115.2, 114.4, 109.8, 60.6, 55.4, 51.9, 43.6, 35.3, 13.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.66. **ESI-MS**: Calcd for $C_{34}H_{28}FNO_4$: [M+H$^+$] 534.2075, found 534.2073.



ethyl

4'-(4-chlorophenyl)-1-(4-methoxybenzyl)-2-oxo-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (**3af**)

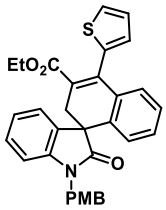
White solid (60 mg, 55%), M.P.: 200-201 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.24 – 7.15 (m, 5H), 7.12 – 7.02 (m, 3H), 6.91 – 6.86 (m, 1H), 6.81 – 6.74 (m, 5H), 4.90 (d, *J* = 15.6 Hz, 1H), 4.86 (d, *J* = 15.6 Hz, 1H), 3.84 (q, *J* = 6.8 Hz, 2H), 3.69 (s, 3H), 3.34 (d, *J* = 16.8 Hz, 1H), 2.92 (d, *J* = 16.8 Hz, 1H), 0.84 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.7, 167.8, 159.2, 144.4, 141.4, 137.6, 136.4, 135.1, 133.6, 133.1, 130.3, 130.2, 129.2, 128.8, 128.6, 128.5, 128.0, 128.0, 125.9, 124.4, 123.7, 123.1, 114.4, 109.8, 60.6, 55.4, 51.8, 43.6, 35.2, 13.7. **ESI-MS**: Calcd for $C_{34}H_{28}ClNO_4$: [M+H$^+$] 550.1780, found 550.1781.



ethyl

1-(4-methoxybenzyl)-4'-(3-methoxyphenyl)-2-oxo-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (**3ag**)

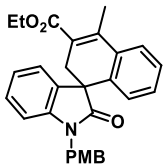
Yellow oil (83 mg, 76%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 4H), 7.21 – 7.13 (m, 3H), 6.99 – 6.85 (m, 9H), 5.00 (s, 2H), 3.97 – 3.89 (m, 2H), 3.86 (s, 3H), 3.79 (s, 3H), 3.48 (d, *J* = 16.4 Hz, 1H), 2.98 (d, *J* = 16.8 Hz, 1H), 0.91 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.0, 168.1, 159.6, 159.2, 144.9, 141.2, 140.4, 136.3, 135.1, 133.3, 130.0, 129.4, 129.3, 128.8, 128.5, 128.0, 127.9, 125.7, 124.0, 123.8, 123.0, 114.7, 114.7, 114.4, 109.7, 60.4, 55.4, 55.4, 51.9, 43.6, 35.3, 13.7. **ESI-MS**: Calcd for $C_{35}H_{31}NO_5$: [M+H$^+$] 546.2275, found 546.2276.



ethyl

1-(4-methoxybenzyl)-2-oxo-4'-(thiophen-2-yl)-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (**3ai**)

White solid (90 mg, 86%), M.P.: 158-159 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 1H), 7.36 – 7.30 (m, 3H), 7.20 – 7.12 (m, 5H), 7.08 – 7.04 (m, 1H), 6.97 – 6.83 (m, 5H), 4.99 (s, 2H), 4.04 – 3.94 (m, 2H), 3.80 (s, 3H), 3.47 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.92 (dd, *J* = 16.8, 5.6 Hz, 1H), 1.04 – 0.96 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.9, 168.1, 159.3, 141.2, 138.8, 137.3, 136.1, 135.0, 133.0, 130.2, 128.9, 128.8, 128.6, 128.0, 127.7, 127.6, 126.9, 126.1, 125.7, 123.8, 123.1, 114.4, 109.7, 60.7, 55.3, 51.8, 43.6, 35.6, 13.8. **ESI-MS**: Calcd for $C_{32}H_{27}NO_4S$: [M+H$^+$] 522.1734, found 522.1734.

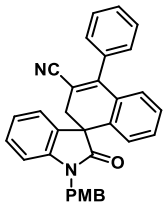


ethyl

1-(4-methoxybenzyl)-4'-methyl-2-oxo-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (**3aj**)

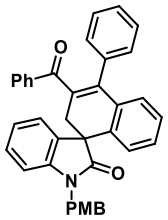
Yellow oil (77 mg, 85%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 1H), 7.22 – 7.17 (m, 3H), 7.10 – 7.01 (m, 3H), 6.80 – 6.71 (m, 5H), 4.89 (d, *J* = 15.2 Hz, 1H),

4.82 (d, *J* = 15.6 Hz, 1H), 4.15 – 4.05 (m, 2H), 3.66 (s, 3H), 3.17 (d, *J* = 16.8 Hz, 1H), 2.77 (d, *J* = 16.8 Hz, 1H), 2.53 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.1, 168.2, 159.2, 141.8, 141.1, 136.4, 135.6, 133.2, 129.8, 128.8, 128.3, 128.0, 126.2, 125.6, 123.7, 122.8, 122.7, 114.3, 109.5, 60.6, 55.3, 51.8, 43.5, 34.9, 16.3, 14.3. **ESI-MS**: Calcd for $C_{29}H_{27}NO_4$: [M+H$^+$] 454.2013, found 454.2015.



1-(4-methoxybenzyl)-2-oxo-4'-phenyl-2'H-spiro[indoline-3,1'-naphthalene]-3'-carbonitrile (**3ak**)

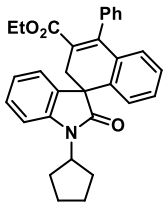
Yellow oil (82 mg, 88%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 5H), 7.31 – 7.19 (m, 6H), 7.06 – 7.03 (m, 1H), 7.00 – 6.95 (m, 1H), 6.91 – 6.85 (m, 4H), 4.99 (d, *J* = 15.2 Hz, 1H), 4.95 (d, *J* = 15.6 Hz, 1H), 3.79 (s, 3H), 3.36 (d, *J* = 16.4 Hz, 1H), 2.85 (d, *J* = 16.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.9, 159.4, 153.5, 141.3, 136.5, 136.2, 133.5, 132.1, 131.3, 129.5, 129.5, 129.4, 129.1, 128.9, 128.8, 128.3, 127.8, 126.2, 123.7, 123.3, 119.1, 114.5, 110.1, 104.3, 55.4, 51.3, 43.7, 35.7. **ESI-MS**: Calcd for $C_{32}H_{24}N_2O_2$: [M+H$^+$] 469.1911, found 469.1912.



3'-benzoyl-1-(4-methoxybenzyl)-4'-phenyl-2'H-spiro[indoline-3,1'-naphthalen]-2-one (**3al**)

Yellow oil (79 mg, 72%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.80 (m, 2H), 7.50 – 7.45 (m, 1H), 7.36 – 7.31 (m, 1H), 7.27 – 7.21 (m, 7H), 7.20 – 7.13 (m, 5H), 7.09 – 7.01 (m, 2H), 6.87 – 6.77 (m, 4H), 4.95 (d, *J* = 15.2 Hz, 1H), 4.88 (d, *J* = 15.6 Hz, 1H), 3.75 (s, 3H), 3.25 (d, *J* = 16.8 Hz, 1H), 3.17 (d, *J* = 16.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.5, 178.3, 159.2, 142.1, 140.9, 137.5, 137.3, 135.9, 135.4, 133.3, 132.6, 132.4, 130.3, 129.5, 129.4, 128.7, 128.2, 128.1, 128.0, 126.1, 124.3, 123.2,

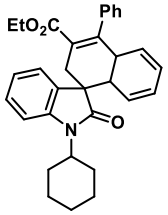
114.4, 109.6, 55.3, 51.8, 43.4, 37.2. **ESI-MS**: Calcd for $C_{38}H_{29}NO_3$: [M+H$^+$] 548.2220, found 548.2224.



ethyl

1-cyclopentyl-2-oxo-4'-phenyl-4a',8a'-dihydro-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (**3ba**)

White solid (78 mg, 84%), M.P.: 158-159 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 4H), 7.24 – 7.15 (m, 3H), 7.10 – 7.00 (m, 2H), 6.96 – 6.87 (m, 2H), 6.81 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.74 (dd, *J* = 7.6, 1.6 Hz, 1H), 4.93 – 4.83 (m, 1H), 3.81 (q, *J* = 7.2 Hz, 2H), 3.34 (d, *J* = 16.8 Hz, 1H), 2.84 (d, *J* = 16.8 Hz, 1H), 2.14 – 2.08 (m, 2H), 1.96 – 1.90 (m, 4H), 1.71 – 1.68 (m, 2H), 0.79 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.1, 168.2, 145.1, 140.6, 139.2, 136.8, 135.2, 133.9, 130.0, 129.4, 128.3, 128.2, 127.8, 127.6, 125.7, 124.2, 124.0, 122.6, 110.3, 60.4, 52.8, 51.8, 35.2, 27.7, 25.4, 13.7. **ESI-MS**: Calcd for $C_{31}H_{29}NO_3$: [M+H$^+$] 464.2220, found 464.2219.

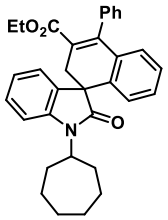


ethyl

1-cyclohexyl-2-oxo-4'-phenyl-4a',8a'-dihydro-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (**3ca**)

White solid (60 mg, 63%), M.P.: 200-201 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 4H), 7.32 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 7.16 – 7.07 (m, 3H), 6.98 – 6.93 (m, 1H), 6.88 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.82 (dd, *J* = 7.2, 1.2 Hz, 1H), 4.37 – 4.30 (m, 1H), 3.88 (q, *J* = 7.2 Hz, 2H), 3.41 (d, *J* = 16.8 Hz, 1H), 2.92 (d, *J* = 16.8 Hz, 1H), 2.32 – 2.22 (m, 2H), 1.96 – 1.85 (m, 4H), 1.77 (d, *J* = 12.8 Hz, 1H), 1.52 – 1.41 (m, 2H), 1.36 – 1.27 (m, 1H), 0.86 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ

178.9, 168.2, 145.1, 141.1, 139.2, 136.8, 135.2, 133.9, 130.0, 129.3, 128.9, 128.3, 128.2, 127.8, 127.5, 125.6, 124.2, 123.9, 122.4, 110.6, 60.4, 52.7, 51.6, 35.2, 29.3, 26.1, 25.5, 13.6. **ESI-MS**: Calcd for $C_{32}H_{31}NO_3$: [M+H$^+$] 478.2377, found 478.2379.

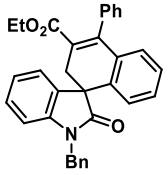


ethyl

1-cycloheptyl-2-oxo-4'-phenyl-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate

(**3da**)

White solid (71 mg, 72%), M.P.: 156-157 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 4H), 7.32 – 7.28 (m, 2H), 7.25 – 7.21 (m, 1H), 7.17 – 7.07 (m, 3H), 6.98 – 6.93 (m, 1H), 6.90 – 6.87 (m, 1H), 6.82 – 6.79 (m, 1H), 4.56 (s, 1H), 3.88 (q, *J* = 7.2 Hz, 2H), 3.40 (d, *J* = 16.8 Hz, 1H), 2.91 (d, *J* = 16.8 Hz, 1H), 2.36 – 2.25 (m, 2H), 1.96 – 1.92 (m, 2H), 1.90 – 1.85 (m, 2H), 1.77 – 1.62 (m, 6H), 0.85 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.2, 168.2, 145.2, 140.7, 139.2, 136.7, 135.2, 133.9, 123.0, 129.4, 128.2, 128.2, 127.8, 127.5, 125.6, 124.1, 123.9, 122.4, 110.7, 60.4, 54.2, 51.6, 35.2, 32.1, 31.7, 27.8, 27.7, 26.2, 13.6. **ESI-MS**: Calcd for $C_{33}H_{33}NO_3$: [M+H$^+$] 492.2533, found 492.2534.

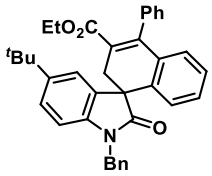


ethyl 1-benzyl-2-oxo-4'-phenyl-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate

(**3ea**)

White solid (78 mg, 80%), M.P.: 179-180 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.30 (m, 11H), 7.21 – 7.12 (m, 3H), 7.00 – 6.88 (m, 3H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.07 (s, 2H), 3.91 (q, *J* = 7.2 Hz, 2H), 3.50 (d, *J* = 16.8 Hz, 1H), 3.01 (d, *J* = 16.8 Hz, 1H), 0.88 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.1, 168.2, 145.3, 141.3, 139.1, 136.4, 135.9, 135.3, 133.2, 130.0, 129.5, 129.0, 128.6, 128.2, 128.0,

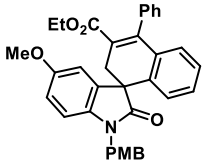
127.8, 127.6, 127.4, 125.8, 124.0, 123.8, 123.1, 109.7, 60.4, 52.0, 44.1, 35.4, 13.7. **ESI-MS**: Calcd for $C_{33}H_{27}NO_3$: [M+H$^+$] 486.2064, found 486.2065.



ethyl

1-benzyl-5-(tert-butyl)-2-oxo-4'-phenyl-2'H-spiro[indoline-3,1'-naphthalene]-3'-carbo xylate (**3fa**)

White solid (71 mg, 66%), M.P.: 205-206 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 2.0 Hz, 1H), 7.39 – 7.28 (m, 6H), 7.26 – 7.18 (m, 4H), 7.12 – 7.03 (m, 3H), 6.86 – 6.83 (m, 2H), 6.66 (d, *J* = 8.0 Hz, 1H), 4.98 (d, *J* = 15.6 Hz, 1H), 4.92 (d, *J* = 15.6 Hz, 1H), 3.80 – 3.73 (m, 2H), 3.42 (d, *J* = 16.4 Hz, 1H), 2.84 (d, *J* = 16.4 Hz, 1H), 1.13 (s, 9H), 0.72 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.1, 168.7, 146.1, 145.0, 139.2, 138.8, 137.0, 136.2, 135.3, 132.5, 130.0, 129.4, 129.0, 128.2, 127.9, 127.8, 127.7, 127.5, 125.8, 125.2, 124.6, 121.0, 109.0, 60.4, 52.2, 44.2, 35.7, 34.7, 31.6, 13.6. **ESI-MS**: Calcd for $C_{37}H_{35}NO_3$: [M+H$^+$] 542.2690, found 542.2690.

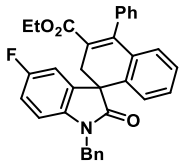


ethyl

5-methoxy-1-(4-methoxybenzyl)-2-oxo-4'-phenyl-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (**3ga**)

Yellow oil (57 mg, 52%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 3H), 7.33 – 7.28 (m, 4H), 7.19 – 7.11 (m, 2H), 7.04 (d, *J* = 2.0 Hz, 1H), 6.93 – 6.87 (m, 4H), 6.74 – 6.69 (m, 2H), 4.97 (s, 2H), 3.89 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.69 (s, 3H), 3.49 (d, *J* = 16.8 Hz, 1H), 2.96 (d, *J* = 16.8 Hz, 1H), 0.85 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.7, 168.3, 159.3, 156.1, 145.1, 139.2, 136.5, 135.3, 134.7, 134.5, 130.1, 129.5, 128.8, 128.3, 128.1, 128.0, 127.6, 125.9, 124.2, 114.4, 113.2,

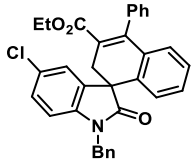
111.0, 110.2, 60.4, 55.8, 55.4, 52.4, 43.7, 35.4, 13.7. **ESI-MS**: Calcd for $C_{35}H_{31}NO_5$: [M+H$^+$] 546.2275, found 546.2272.



ethyl

1-benzyl-5-fluoro-2-oxo-4'-phenyl-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (**3ha**)

White solid (69 mg, 69%), M.P.: 189-190 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 3H), 7.39 – 7.35 (m, 4H), 7.34 – 7.30 (m, 3H), 7.23 – 7.13 (m, 3H), 6.96 – 6.85 (m, 3H), 6.75 – 6.71 (m, 1H), 5.08 (d, *J* = 15.6 Hz, 1H), 5.04 (d, *J* = 15.6 Hz, 1H), 3.91 (q, *J* = 7.2 Hz, 2H), 3.51 (d, *J* = 16.8 Hz, 1H), 3.00 (d, *J* = 16.8 Hz, 1H), 0.86 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.8, 168.1, 160.2 (d, *J* = 240.0 Hz), 145.3, 138.9, 137.1 (d, *J* = 2.0 Hz), 135.7, 135.6, 135.2, 134.6, 134.5, 130.2, 129.6, 129.1, 128.3, 128.2, 128.0, 127.7, 127.4, 125.8, 123.8, 114.9 (d, *J* = 23.0 Hz), 112.0 (d, *J* = 25.0 Hz), 110.3 (d, *J* = 8.0 Hz), 60.5, 52.4, 44.3, 35.3, 13.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.37. **ESI-MS**: Calcd for $C_{33}H_{26}FNO_3$: [M+H$^+$] 504.1969, found 504.1964.

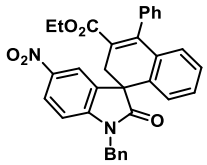


ethyl

1-benzyl-5-chloro-2-oxo-4'-phenyl-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (**3ia**)

White solid (56 mg, 54%), M.P.: 156-157 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 3H), 7.40 – 7.30 (m, 8H), 7.23 – 7.14 (m, 3H), 6.98 – 6.92 (m, 1H), 6.91 – 6.83 (m, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 5.04 (s, 2H), 3.91 (q, *J* = 6.8 Hz, 2H), 3.48 (d, *J* = 16.8 Hz, 1H), 3.01 (d, *J* = 16.8 Hz, 1H), 0.86 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.5, 168.0, 145.4, 139.9, 138.9, 135.6, 135.5, 135.3, 134.8, 130.1, 129.7, 129.1, 128.9, 128.6, 128.4, 128.3, 128.0, 127.7, 127.4, 125.8, 124.5, 124.5,

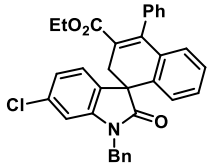
123.8, 110.7, 110.7, 60.5, 52.2, 44.3, 35.3, 13.6. **ESI-MS**: Calcd for $C_{33}H_{26}ClNO_3$: [M+H$^+$] 520.1674, found 520.1678.



ethyl

1-benzyl-5-nitro-2-oxo-4'-phenyl-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (**3ja**)

Yellow oil (53 mg, 50%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 2.0 Hz, 1H), 8.15 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.41 – 7.33 (m, 7H), 7.23 – 7.20 (m, 2H), 7.02 – 6.99 (m, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.87 – 6.84 (m, 1H), 5.13 (d, *J* = 16.0 Hz, 1H), 5.09 (d, *J* = 16.4 Hz, 1H), 3.88 (q, *J* = 7.2 Hz, 2H), 3.50 (d, *J* = 16.8 Hz, 1H), 3.04 (d, *J* = 16.8 Hz, 1H), 0.82 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.9, 167.9, 146.9, 145.6, 143.6, 138.6, 135.3, 134.8, 134.7, 133.5, 130.2, 129.9, 129.3, 128.8, 128.7, 128.6, 128.3, 127.7, 127.3, 125.7, 125.5, 123.5, 119.8, 109.4, 60.6, 51.8, 44.5, 35.2, 13.5. **ESI-MS**: Calcd for $C_{33}H_{26}N_2O_5$: [M+H$^+$] 531.1914, found 531.1912.

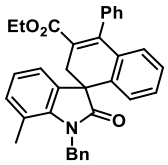


ethyl

1-benzyl-6-chloro-2-oxo-4'-phenyl-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (**3ka**)

Yellow oil (73 mg, 70%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 5H), 7.19 – 7.09 (m, 5H), 7.07 – 6.98 (m, 3H), 6.93 – 6.90 (m, 1H), 6.86 – 6.82 (m, 1H), 6.62 – 6.57 (m, 2H), 4.80 (d, *J* = 15.6 Hz, 1H), 4.74 (d, *J* = 15.6 Hz, 1H), 3.84 – 3.72 (m, 3H), 2.97 (d, *J* = 17.6 Hz, 1H), 0.71 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.2, 167.9, 145.6, 144.8, 139.5, 136.4, 135.4, 132.7, 131.3, 130.0, 129.9, 129.8, 129.3, 129.0, 128.9, 128.1, 127.8, 127.1, 125.5, 124.2, 124.1, 122.6, 107.9, 60.2, 52.1,

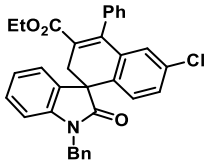
43.7, 31.5, 13.5. **ESI-MS**: Calcd for $C_{33}H_{26}ClNO_3$: [M+H$^+$] 520.1674, found 520.1674.



ethyl

1-benzyl-7-methyl-2-oxo-4'-phenyl-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxyla te (**3la**)

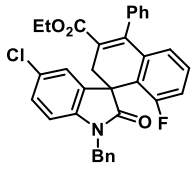
White solid (78 mg, 78%), M.P.: 195-196 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 3H), 7.38 – 7.30 (m, 6H), 7.25 – 7.21 (m, 2H), 7.21 – 7.12 (m, 2H), 6.99 – 6.91 (m, 4H), 5.38 (d, *J* = 16.8 Hz, 1H), 5.30 (d, *J* = 17.2 Hz, 1H), 3.91 (q, *J* = 7.2 Hz, 2H), 3.49 (d, *J* = 16.8 Hz, 1H), 3.07 (d, *J* = 16.8 Hz, 1H), 2.35 (s, 3H), 0.87 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 180.0, 168.2, 145.3, 139.5, 139.2, 137.8, 136.6, 135.4, 134.0, 132.5, 130.0, 129.5, 129.0, 128.2, 127.9, 127.5, 127.3, 125.9, 125.7, 123.9, 123.2, 121.9, 120.3, 60.4, 51.2, 45.3, 36.0, 19.0, 13.6. **ESI-MS**: Calcd for $C_{34}H_{29}NO_3$: [M+H$^+$] 500.2220, found 500.2226.



ethyl

1-benzyl-6'-chloro-2-oxo-4'-phenyl-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxyla te (**3ma**)

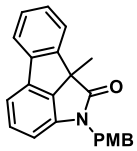
Yellow oil (33 mg, 32%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.40 (m, 3H), 7.39 – 7.26 (m, 8H), 7.23 – 7.18 (m, 1H), 7.14 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.02 – 6.97 (m, 1H), 6.90 (d, *J* = 2.0 Hz, 1H), 6.85 – 6.79 (m, 2H), 5.06 (d, *J* = 16.0 Hz, 1H), 5.02 (d, *J* = 15.6 Hz, 1H), 3.90 (q, *J* = 6.8 Hz, 2H), 3.45 (d, *J* = 16.8 Hz, 1H), 3.00 (d, *J* = 16.8 Hz, 1H), 0.86 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.5, 168.0, 143.9, 141.4, 138.2, 137.3, 137.2, 135.9, 134.7, 134.0, 132.9, 132.9, 129.7, 129.1, 129.1, 128.8, 128.5, 128.0, 127.4, 127.2, 125.6, 123.8, 123.3, 109.9, 60.6, 51.5, 44.2, 35.4, 13.6. **ESI-MS**: Calcd for $C_{33}H_{26}ClNO_3$: [M+H$^+$] 520.1674, found 520.1674.



ethyl

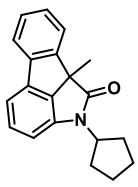
1-benzyl-5-chloro-8'-fluoro-2-oxo-4'-phenyl-2'H-spiro[indoline-3,1'-naphthalene]-3'-carboxylate (**3na**)

White solid (62 mg, 58%), M.P.: 200-201 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.41 (m, 3H), 7.40 – 7.34 (m, 4H), 7.31 – 7.25 (m, 3H), 7.21 – 7.11 (m, 3H), 6.99 – 6.93 (m, 1H), 6.76 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 5.11 (d, *J* = 15.6 Hz, 1H), 5.00 (d, *J* = 15.6 Hz, 1H), 3.89 (q, *J* = 7.2 Hz, 2H), 3.52 (d, *J* = 16.4 Hz, 1H), 2.87 (d, *J* = 16.4 Hz, 1H), 0.85 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.0, 167.7, 159.1 (d, *J* = 247.0 Hz), 144.2, 140.0, 138.6, 137.5, 137.5, 135.5, 132.8, 129.4, 129.3, 129.1, 128.8, 128.4, 128.0, 127.9, 127.5, 125.6, 124.9, 124.0, 124.0, 122.4 (d, *J* = 15.0 Hz), 117.3 (d, *J* = 23.0 Hz), 110.8, 60.7, 48.5, 44.6, 36.0, 13.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.75. **ESI-MS**: Calcd for $C_{33}H_{25}ClFNO_3$: [M+H$^+$] 538.1580, found 538.1581.



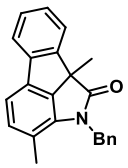
2-(4-methoxybenzyl)-9b-methyl-2,9b-dihydro-1H-indeno[1,2,3-cd]indol-1-one (**4a**)

Colorless oil (48 mg, 70%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.25 (m, 4H), 7.22 – 7.14 (m, 2H), 6.90 – 6.85 (m, 2H), 6.48 (dd, *J* = 5.6, 2.0 Hz, 1H), 5.08 (d, *J* = 15.2 Hz, 1H), 4.32 (d, *J* = 15.2 Hz, 1H), 3.79 (s, 3H), 1.82 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.3, 159.2, 150.2, 146.8, 143.9, 142.9, 142.6, 131.5, 129.1, 128.7, 128.2, 127.1, 125.3, 122.3, 115.9, 114.3, 108.3, 57.3, 55.4, 43.9, 27.3. **ESI-MS**: Calcd for $C_{23}H_{19}NO_2$: [M+H$^+$] 342.1489, found 342.1489.



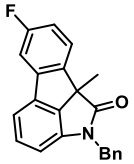
2-cyclopentyl-9b-methyl-2,9b-dihydro-1H-indeno[1,2,3-cd]indol-1-one (**4b**)

Colorless oil (36 mg, 62%), **^{1}H NMR** (400 MHz, CDCl3) δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.18 – 7.08 (m, 3H), 6.61 (d, *J* = 7.6 Hz, 1H), 4.61 – 4.52 (m, 2H), 2.10 – 1.94 (m, 2H), 1.89 – 1.68 (m, 4H), 1.68 (s, 3H), 1.64 – 1.58 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.0, 150.3, 147.0, 142.9, 142.5, 142.5, 131.0, 128.1, 127.0, 125.2, 122.2, 115.4, 109.4, 57.2, 53.3, 29.2, 28.0, 27.5, 25.2, 25.1. **ESI-MS**: Calcd for $C_{20}H_{19}NO$: [M+H$^+$] 290.1539, found 290.1538.



2-benzyl-3,9b-dimethyl-2,9b-dihydro-1H-indeno[1,2,3-cd]indol-1-one (**4l**)

White solid (49 mg, 75%), M.P.: 163-164 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.19 – 7.11 (m, 4H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 5.22 (d, *J* = 16.4 Hz, 1H), 4.67 (d, *J* = 16.4 Hz, 1H), 2.12 (s, 3H), 1.75 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.4, 149.9, 147.0, 142.8, 141.0, 139.4, 138.1, 134.1, 128.9, 128.2, 127.4, 126.7, 126.3, 125.1, 122.0, 119.9, 116.1, 56.9, 45.1, 28.3, 17.6, 17.5. **ESI-MS**: Calcd for $C_{23}H_{19}NO$: [M+H$^+$] 326.1539, found 326.1539.

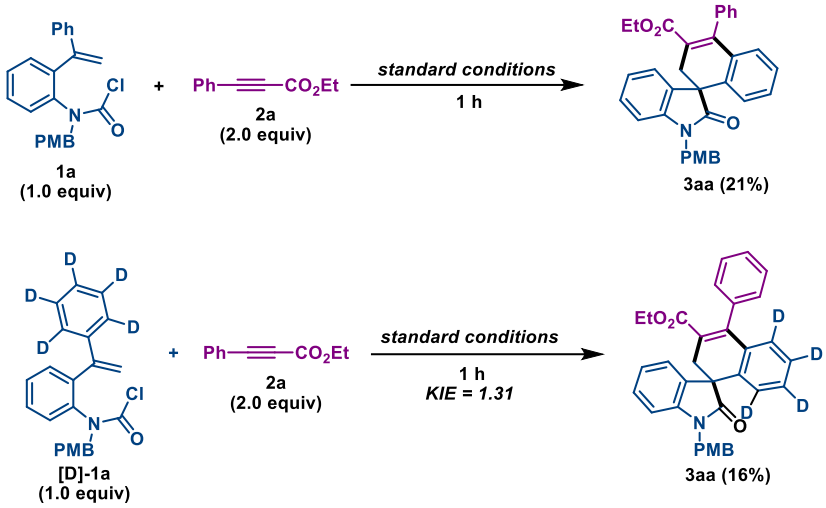


2-benzyl-7-fluoro-9b-methyl-2,9b-dihydro-1H-indeno[1,2,3-cd]indol-1-one (**4o**)

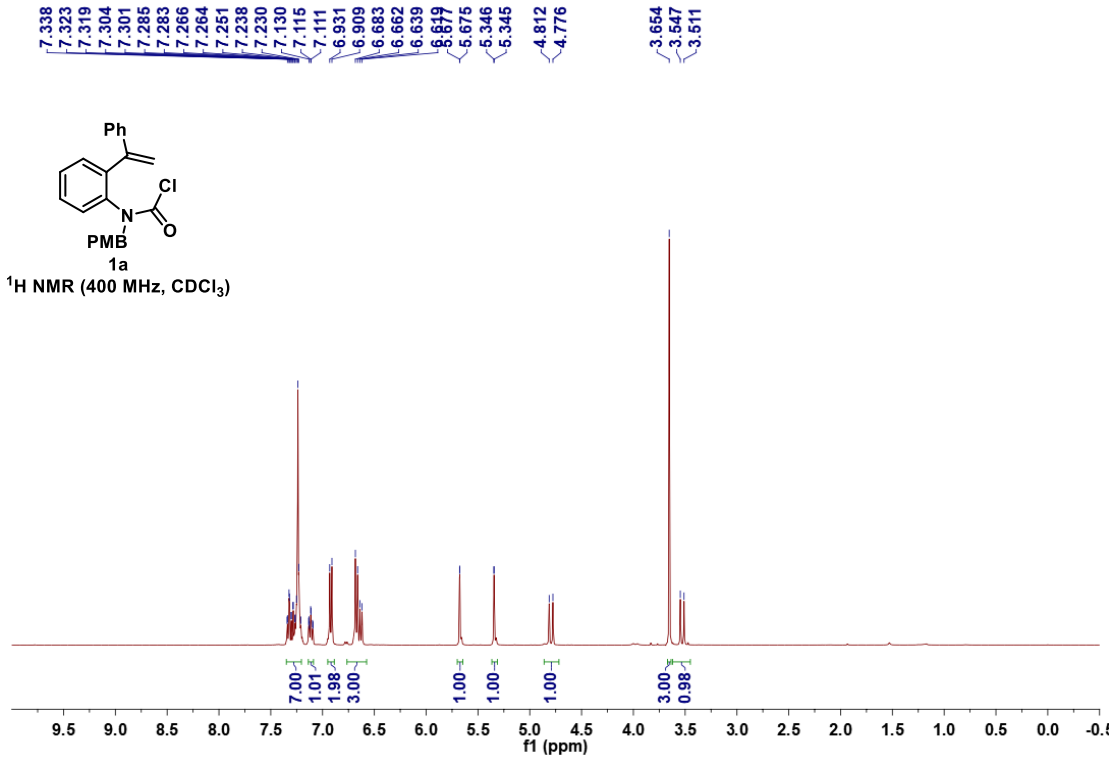
Colorless oil (38 mg, 58%), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.4, 5.2 Hz, 1H), 7.33 – 7.15 (m, 6H), 7.13 – 7.04 (m, 2H), 6.88 – 6.82 (m, 1H), 6.41 (d, *J* = 7.2 Hz, 1H), 5.08 (d, *J* = 15.6 Hz, 1H), 4.26 (d, *J* = 15.2 Hz, 1H), 1.74 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.2, 163.2 (d, *J* = 244.0 Hz), 147.7, 145.7, 144.9, 143.9, 141.6, 136.5, 131.7, 129.0, 127.9, 127.7, 126.1, 116.1, 113.6 (d, *J* = 20.0 Hz), 109.7 (d, *J* = 24.0 Hz), 108.8, 56.7, 44.4, 27.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.54. **ESI-MS**: Calcd for $C_{22}H_{16}FNO$: [M+H$^+$] 330.1289, found 330.1286.

Control Experiments:

KIE by parallel experiments:

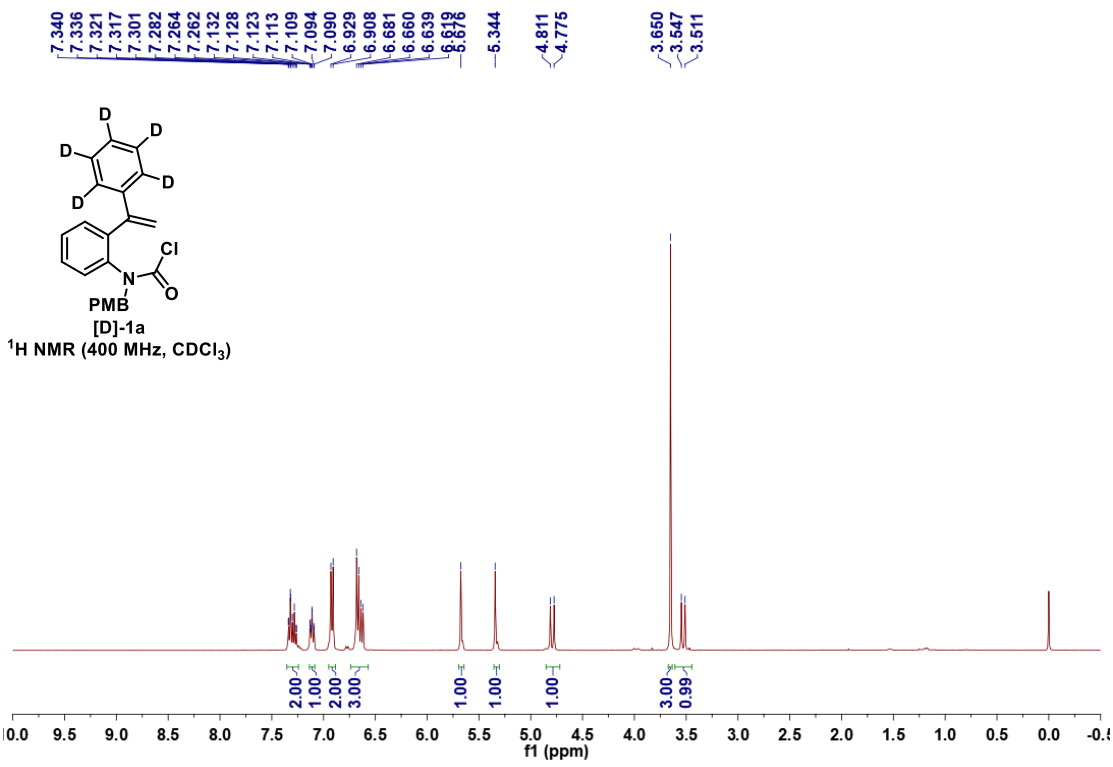


A sealed tube contained **1a** (75.4 mg, 0.2 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol, 5 mol%), Cs_2CO_3 (97.8 mg, 0.30 mmol, 1.5 equiv) was evacuate and purged with nitrogen gas three times. Then, **2a** (69.6 mg, 0.4 mmol, 2.0 equiv) in toluene (2.0 mL) were added to the system via syringe under a nitrogen atmosphere. In another sealed tube **[D]-1a** (75.4 mg, 0.2 mmol, 1.0 equiv) was used instead of **1a**. The two reactions were heated by an electric heating mantle to 110 °C for 1 h, the ^1H NMR was using 1-chloro-2,4-dinitrobenzene (46.4 mg, 0.2 mmol) as the internal standard. Thus the KIE values were found to be 1.31. The KIE values suggested that the C-H bond activation step is not the rate-determining step of this reaction (the ^1H NMR spectrum of the crude product is shown below).



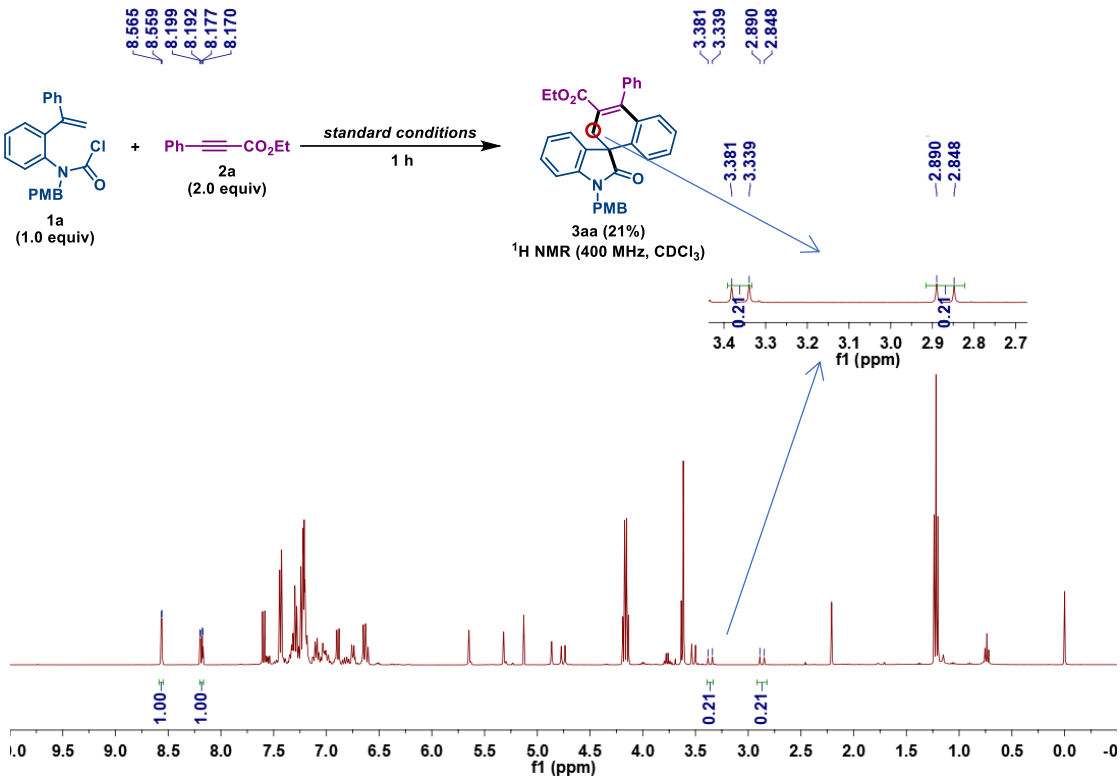
1a

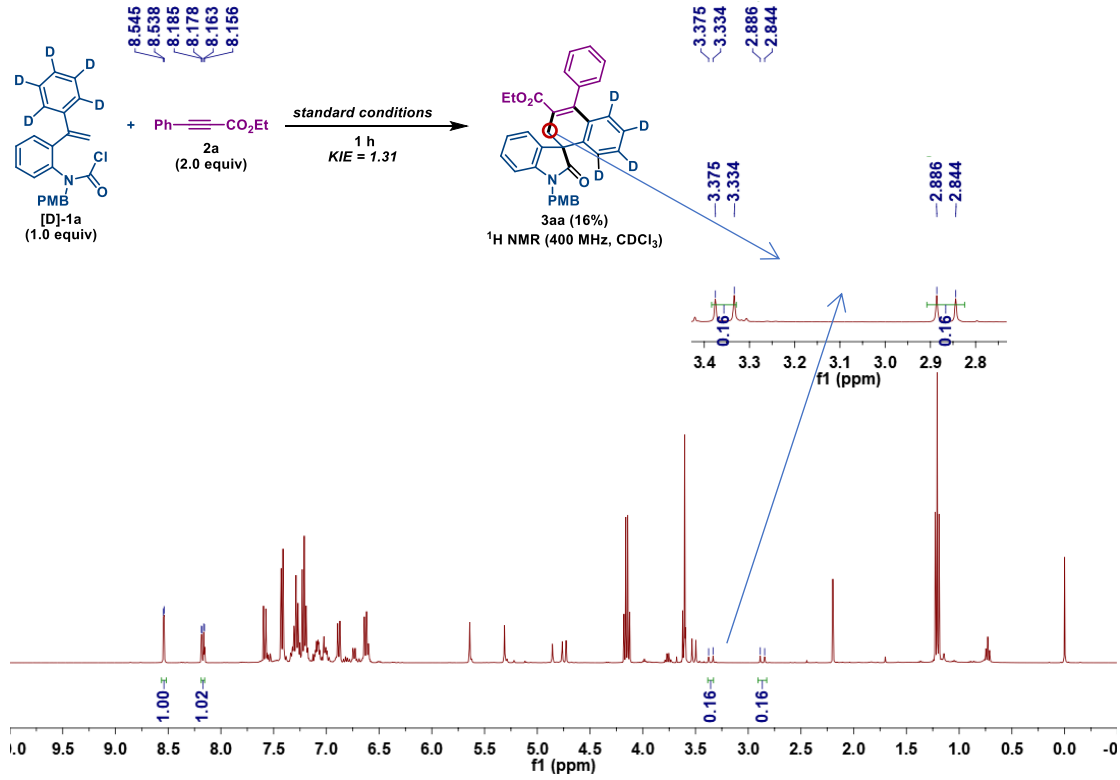
^{1}H NMR (400 MHz, $CDCl_3$)



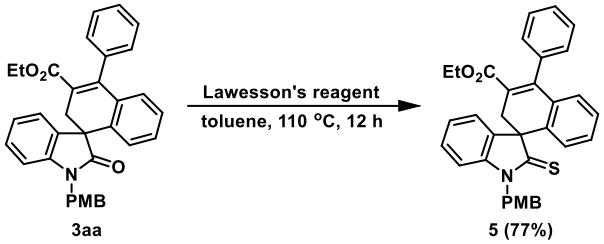
[D]-1a

^{1}H NMR (400 MHz, $CDCl_3$)


8.565
8.559
8.199
8.192
8.177
8.170
3.381
3.339
2.890
2.848
Ph
Cl
N
O
PMB
1a
(1.0 equiv)
+
Ph—≡—CO2Et
2a
(2.0 equiv)
standard conditions
1 h
EtO2C
Ph
O
N
O
PMB
3aa (21%)
1H NMR (400 MHz, CDCl3)
0.21
0.21
3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7
f1 (ppm)
1.00
1.00
0.21
0.21
f1 (ppm)

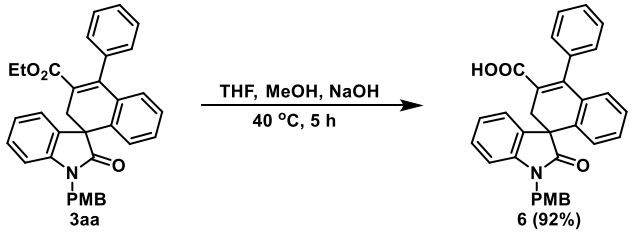

8.545
8.538
8.185
8.178
8.163
8.156
3.375
3.334
2.886
2.844
D
D
D
D
D
Cl
N
O
PMB
[D]-1a
(1.0 equiv)
+
Ph—≡—CO2Et
2a
(2.0 equiv)
standard conditions
1 h
KIE = 1.31
EtO2C
D
D
D
D
D
O
N
O
PMB
3aa (16%)
1H NMR (400 MHz, CDCl3)
0.16
0.16
3.4 3.3 3.2 3.1 3.0 2.9 2.8
f1 (ppm)
1.00
1.02
0.16
0.16
f1 (ppm)

Synthetic Transformations:



A solution of **3aa** (82.4 mg, 0.16 mmol) and Lawesson's reagent (97.1 mg, 0.24 mmol) in toluene (2.0 mL) was stirred and refluxed. After 12 h, the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford of **5** (65.4 mg, 77% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.39 – 7.28 (m, 5H), 7.26 – 7.22 (m, 2H), 7.16 – 7.12 (m, 1H), 7.06 – 6.93 (m, 4H), 6.83 – 6.78 (m, 3H), 6.74 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.51 (d, *J* = 14.8 Hz, 1H), 5.49 (d, *J* = 14.8 Hz, 1H), 3.83 – 3.73 (m, 2H), 3.75 (d, *J* = 16.8 Hz, 1H), 3.69 (s, 3H), 2.74 (d, *J* = 16.4 Hz, 1H), 0.78 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 209.5, 168.2, 159.4, 144.8, 142.3, 139.1, 138.1, 137.9, 134.8, 130.0, 129.3, 128.9, 128.6, 128.3, 127.8, 127.6, 127.0, 126.8, 124.6, 124.5, 123.9, 114.4, 111.0, 62.6, 60.4, 55.4, 48.1, 39.8, 13.7. **ESI-MS**: Calcd for $C_{34}H_{29}NO_3S$: [M+H$^+$] 532.1941, found 532.1941.

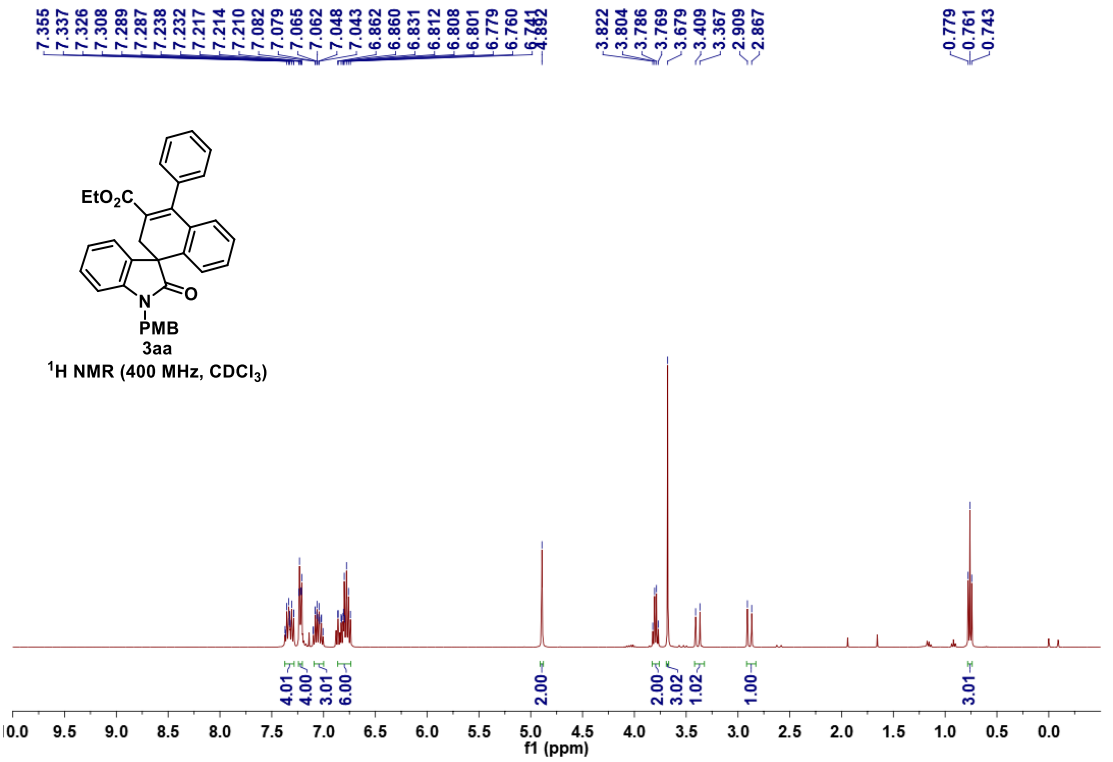


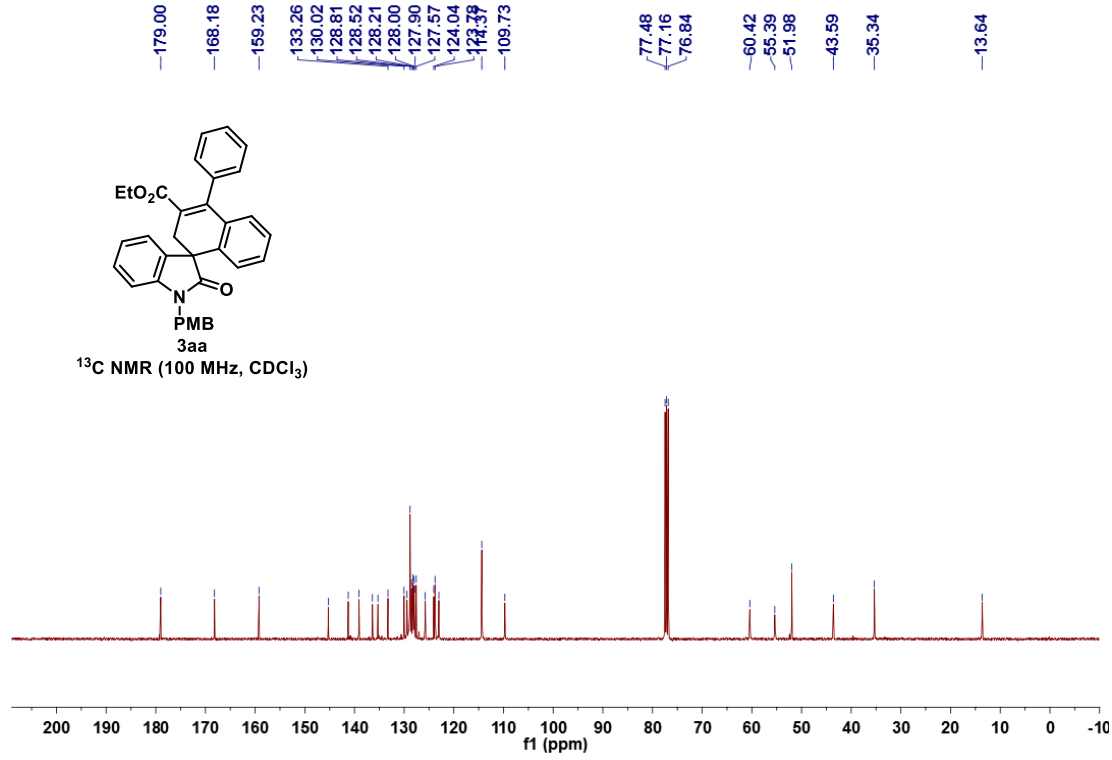
3aa (51.5 mg, 0.10 mmol) was dissolved in 0.5 mL of THF and 0.5 mL MeOH, and 1.0 mL of a 2M NaOH aqueous solution was added. Reaction was performed at 40 °C for 5 h. 1M HCl acidified. The reaction was diluted with ethyl acetate. The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give **6** (44.8 mg, 92% yield) as a yellow oil.

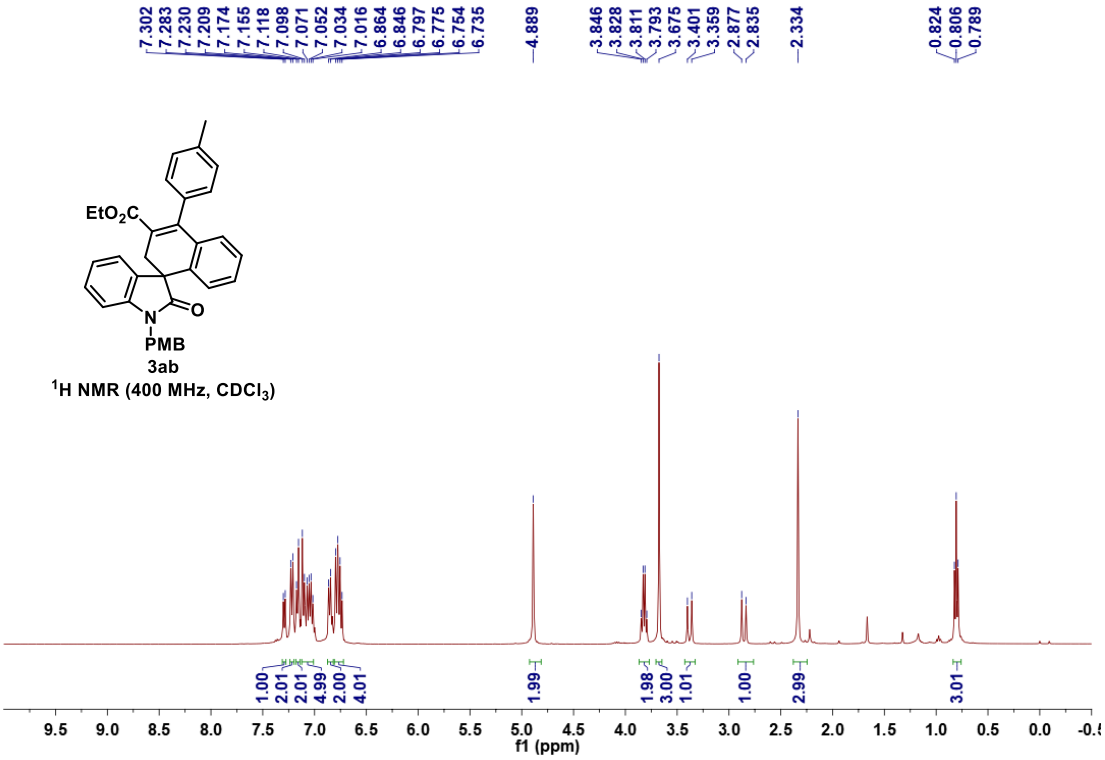
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.29 (m, 3H), 7.27 – 7.17 (m, 5H), 7.16 – 6.93 (m, 3H), 6.89 – 6.84 (m, 5H), 6.86 – 6.65 (m, 5H), 4.89 (s, 2H), 3.72 (s, 3H), 3.33 (d, *J* = 16.8 Hz, 1H), 2.90 (d, *J* = 16.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.9,

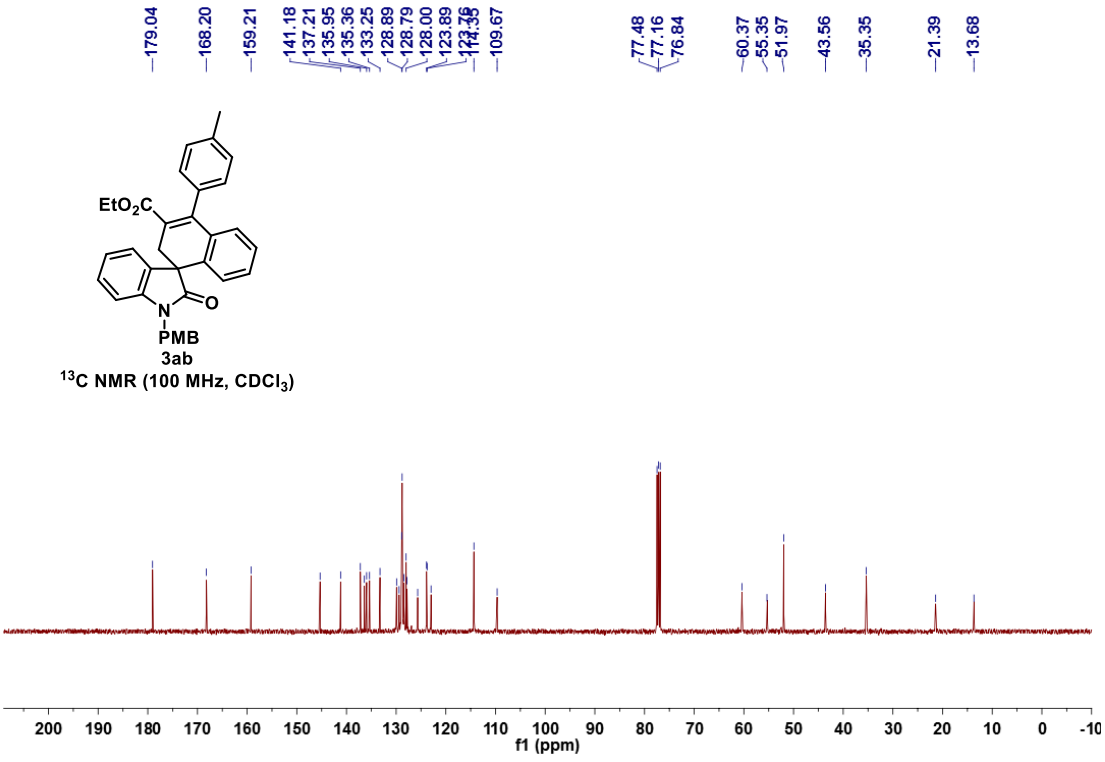
171.7, 159.3, 147.8, 141.4, 138.4, 136.8, 135.4, 133.1, 130.5, 129.9, 128.9, 128.6, 128.4, 128.0, 128.0, 125.9, 123.8, 123.1, 122.7, 114.5, 109.8, 55.5, 51.9, 43.7, 35.2. **ESI-MS**: Calcd for $C_{32}H_{25}NO_4$: [M+H$^+$] 488.1856, found 488.1858.

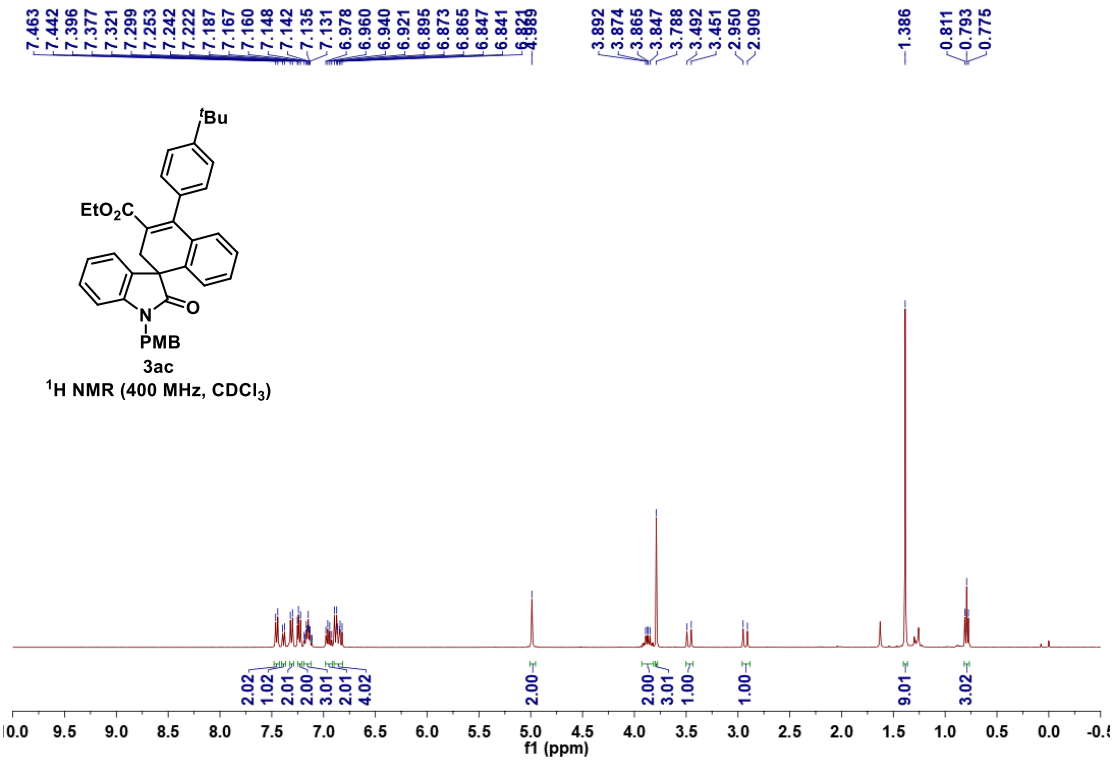
NMR Spectra:

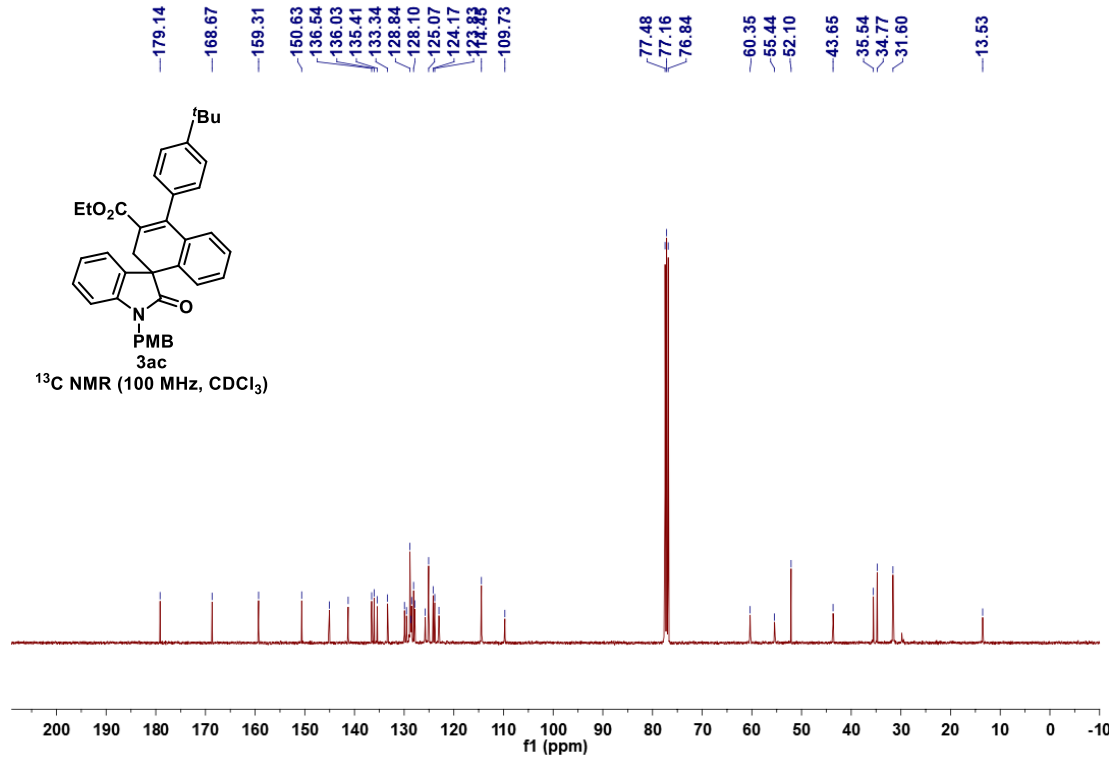

7.355
7.337
7.326
7.308
7.289
7.287
7.238
7.232
7.217
7.214
7.210
7.082
7.079
7.065
7.062
7.048
7.043
6.862
6.860
6.831
6.812
6.808
6.801
6.779
6.760
3.822
3.804
3.786
3.769
3.679
3.409
3.367
2.909
2.867
0.779
0.761
0.743
EtO2C
N
O
PMB
3aa
1H NMR (400 MHz, CDCl3)
4.01
4.00
3.01
6.00
2.00
2.00
3.02
1.02
1.00
3.01
f1 (ppm)


179.00
168.18
159.23
133.26
130.02
128.81
128.52
128.21
128.00
127.90
127.57
124.04
109.73
77.48
77.16
76.84
60.42
55.39
51.98
43.59
35.34
13.64
EtO2C
N
O
PMB
3aa
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.302
7.283
7.230
7.209
7.174
7.155
7.118
7.098
7.071
7.052
7.034
7.016
6.864
6.846
6.797
6.775
6.754
6.735
4.889
3.846
3.828
3.811
3.793
3.675
3.401
3.359
2.877
2.835
2.334
0.824
0.806
0.789
EtO2C
N
O
PMB
3ab
1H NMR (400 MHz, CDCl3)
1.00
2.01
2.01
4.99
2.00
4.01
1.99
1.98
3.00
1.01
1.00
2.99
3.01
f1 (ppm)


179.04
168.20
159.21
141.18
137.21
135.95
135.36
133.25
128.89
128.79
128.00
123.89
109.67
77.48
77.16
76.84
60.37
55.35
51.97
43.56
35.35
21.39
13.68
EtO2C
N
O
PMB
3ab
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.463
7.442
7.396
7.377
7.321
7.299
7.253
7.242
7.222
7.187
7.167
7.160
7.148
7.142
7.135
7.131
6.978
6.960
6.940
6.921
6.895
6.873
6.865
6.847
6.841
3.892
3.874
3.865
3.847
3.788
3.492
3.451
2.950
2.909
1.386
0.811
0.793
0.775
tBu
EtO2C
N
O
PMB
3ac
1H NMR (400 MHz, CDCl3)
2.02
1.02
2.01
2.00
3.01
2.01
4.02
2.00
2.00
3.01
1.00
1.00
9.01
3.02
f1 (ppm)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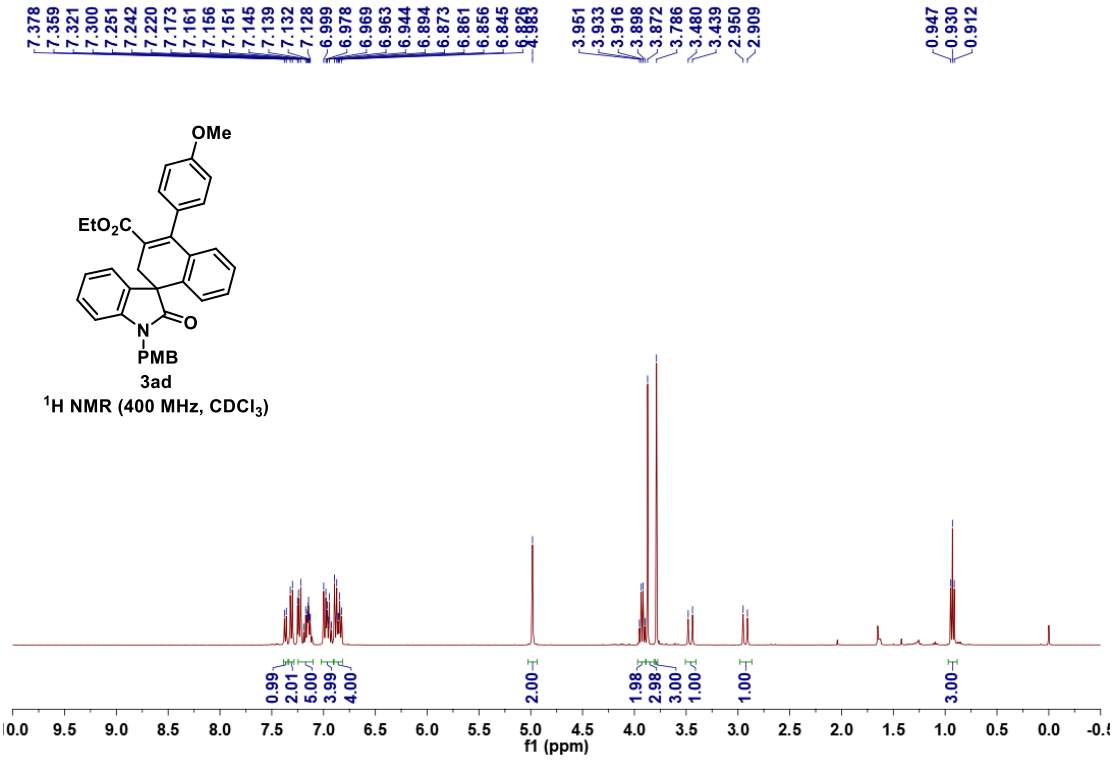
159.31
150.63
136.54
136.03
135.41
133.34
128.84
128.10
125.07
124.17
109.73
77.48
77.16
76.84
60.35
55.44
52.10
43.65
35.54
34.77
31.60
13.53
tBu
EtO2C
N
O
PMB
3ac
13C NMR (100 MHz, CDCl3)
f1 (ppm)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7.321
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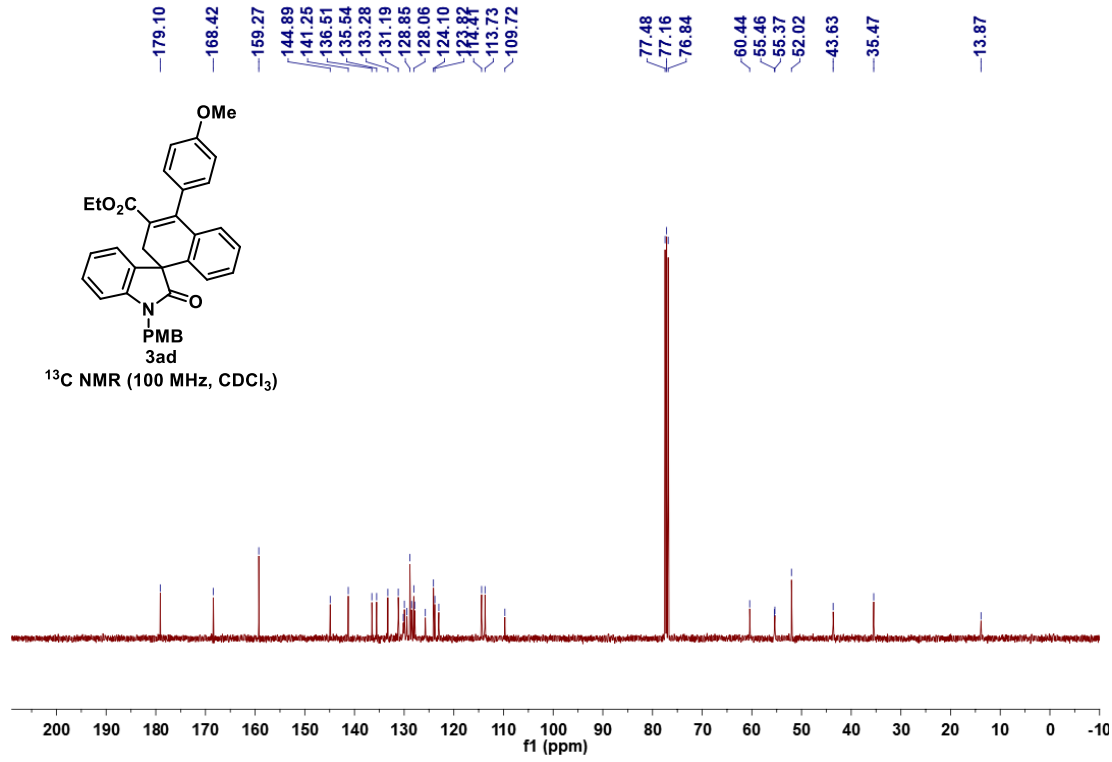
7.242
7.220
7.173
7.161
7.156
7.151
7.145
7.139
7.132
7.128
6.999
6.978
6.969
6.963
6.944
6.894
6.873
6.861
6.856
6.845
3.951
3.933
3.916
3.898
3.872
3.786
3.480
3.439
2.950
2.909
0.947
0.930
0.912
OMe
EtO2C
N
O
PMB
3ad
1H NMR (400 MHz, CDCl3)
0.99
2.01
5.00
3.99
4.00
2.00
1.98
2.98
3.00
1.00
1.00
3.00
f1 (ppm)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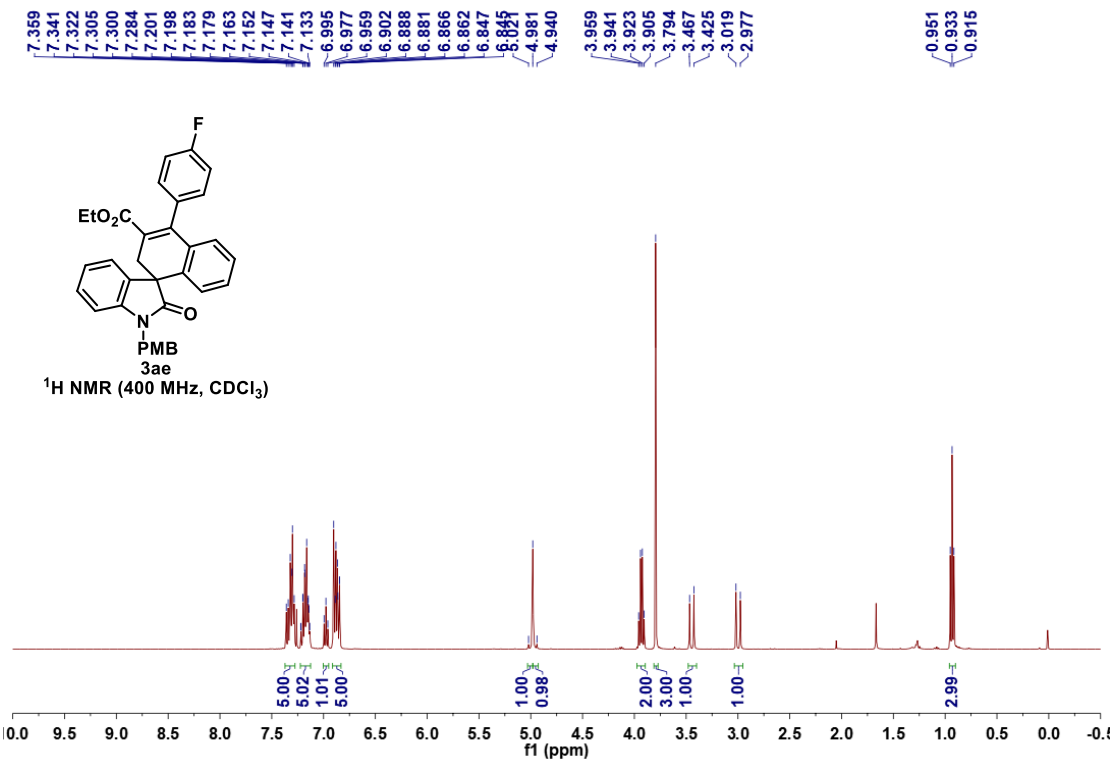
136.51
135.54
133.28
131.19
128.85
128.06
124.10
113.73
109.72
77.48
77.16
76.84
60.44
55.46
55.37
52.02
43.63
35.47
13.87
OMe
EtO2C
N
O
PMB
3ad
13C NMR (100 MHz, CDCl3)
f1 (ppm)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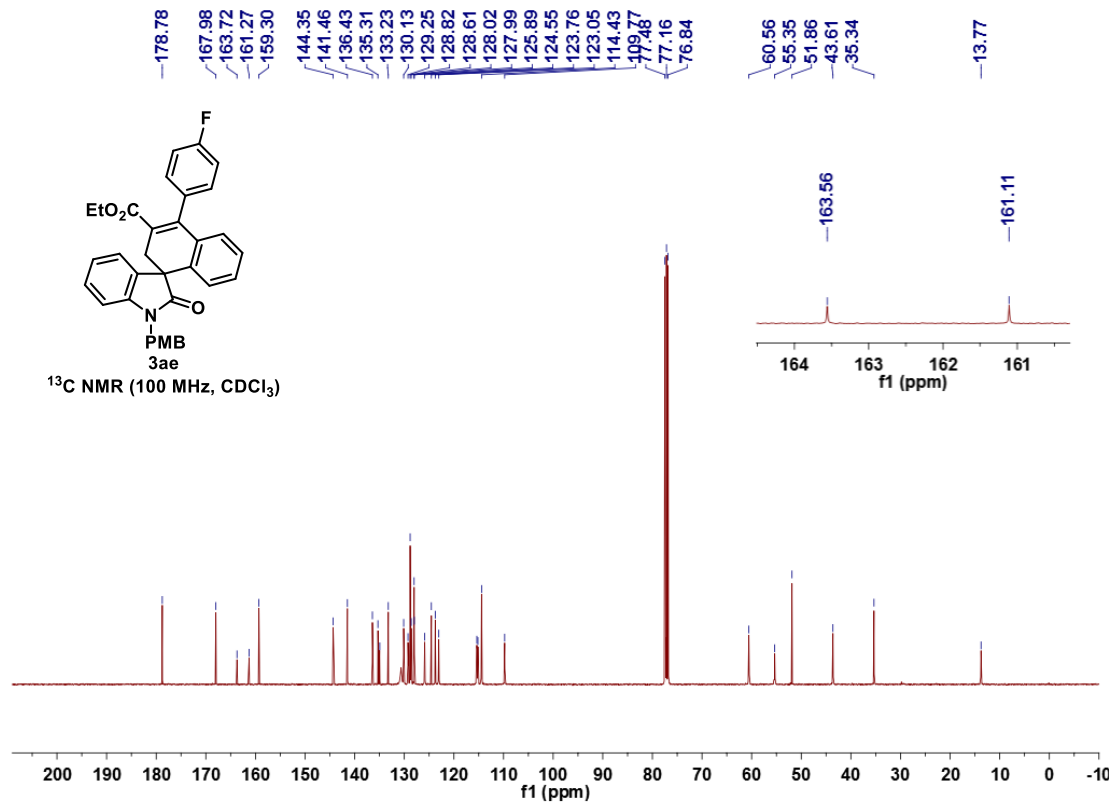
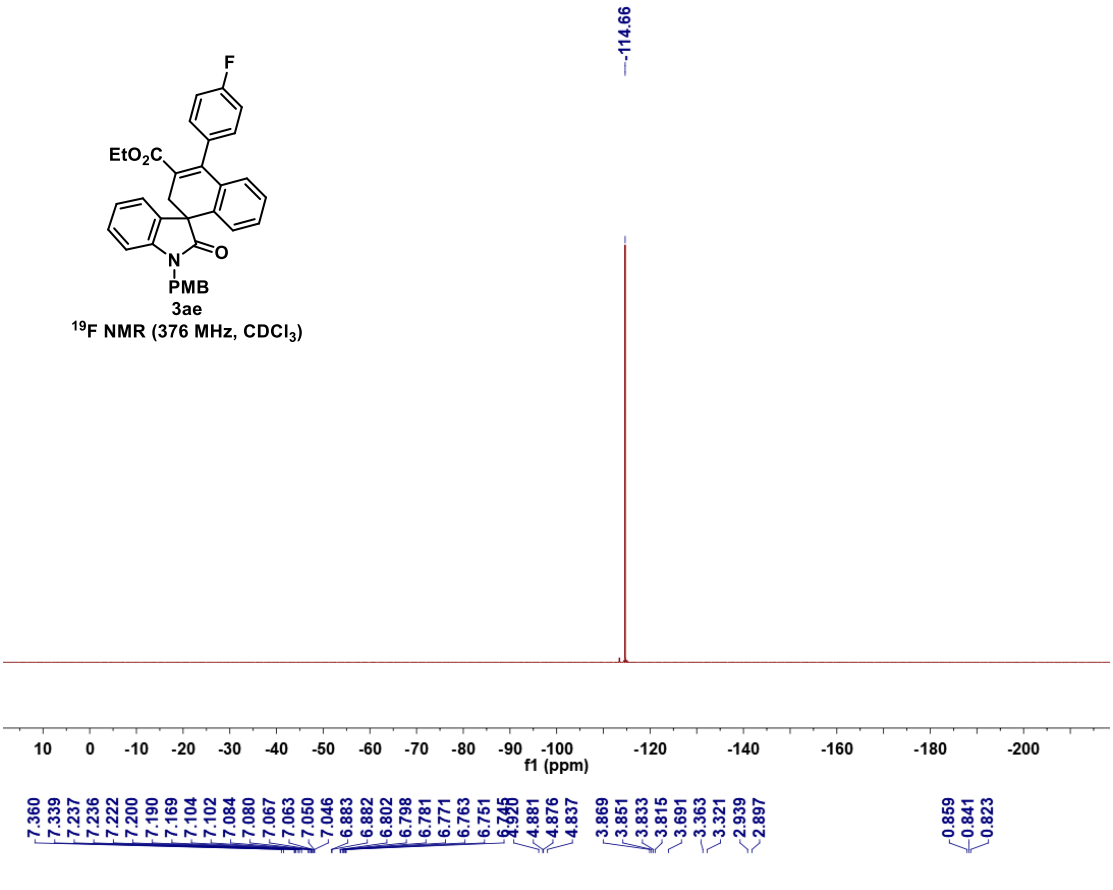
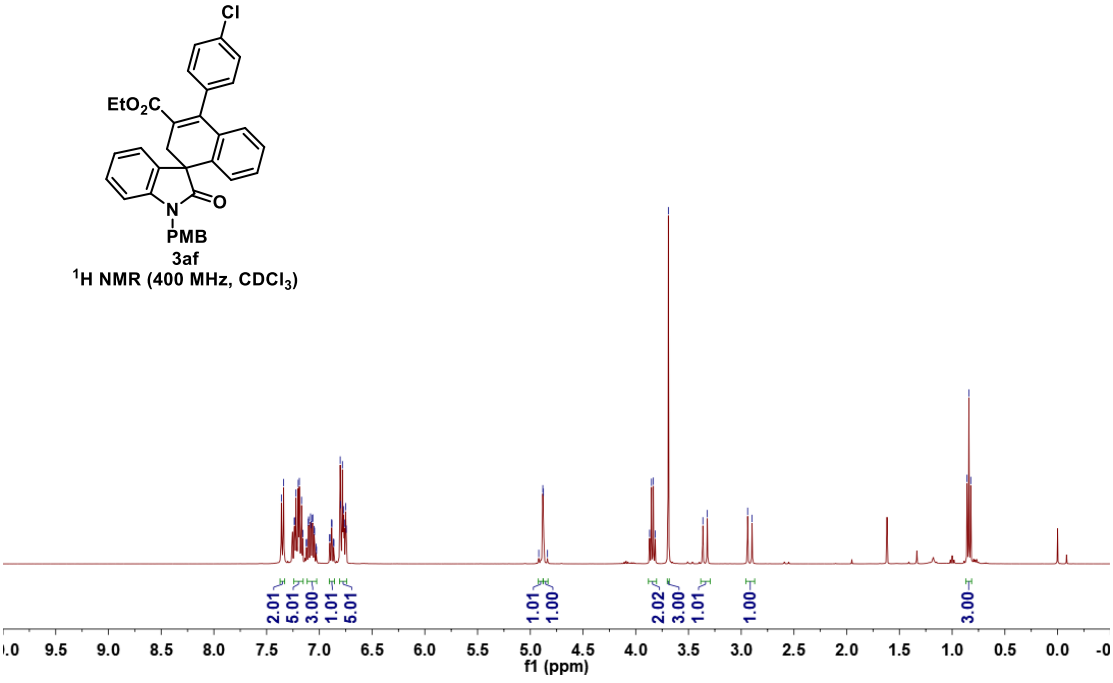
7.322
7.305
7.300
7.284
7.201
7.198
7.183
7.179
7.163
7.152
7.147
7.141
7.133
6.995
6.977
6.959
6.902
6.888
6.881
6.866
6.862
6.847
6.845
6.021
4.981
4.940
3.959
3.941
3.923
3.905
3.794
3.467
3.425
3.019
2.977
0.951
0.933
0.915
F
EtO2C
N
O
PMB
3ae
1H NMR (400 MHz, CDCl3)
5.00
5.02
1.01
5.00
1.00
0.98
2.00
3.00
1.00
1.00
2.99
f1 (ppm)


178.78
167.98
163.72
161.27
159.30
144.35
141.46
136.43
135.31
133.23
130.13
129.25
128.82
128.61
128.02
127.99
125.89
124.55
123.76
123.05
114.43
77.48
77.16
76.84
60.56
55.35
51.86
43.61
35.34
13.77
F
EtO2C
N
O
PMB
3ae
13C NMR (100 MHz, CDCl3)
163.56
161.11
f1 (ppm)



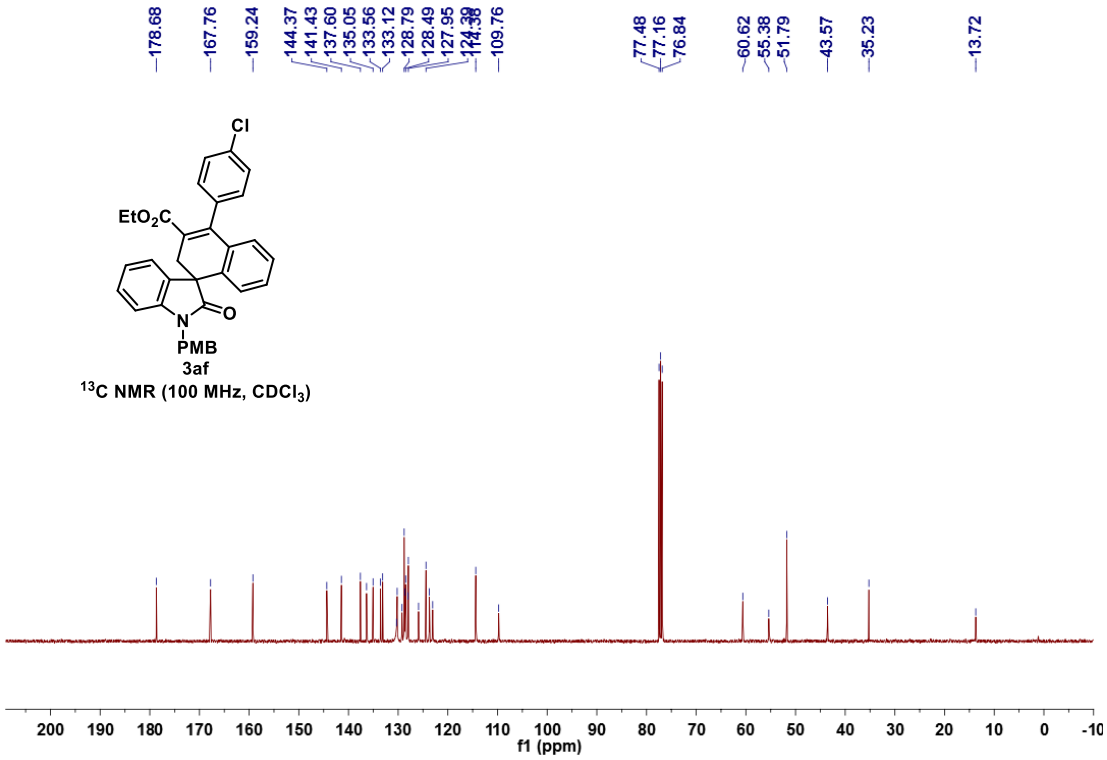
3ae

^{19}F NMR (376 MHz, $CDCl_3$)



3af

^{1}H NMR (400 MHz, $CDCl_3$)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137.60
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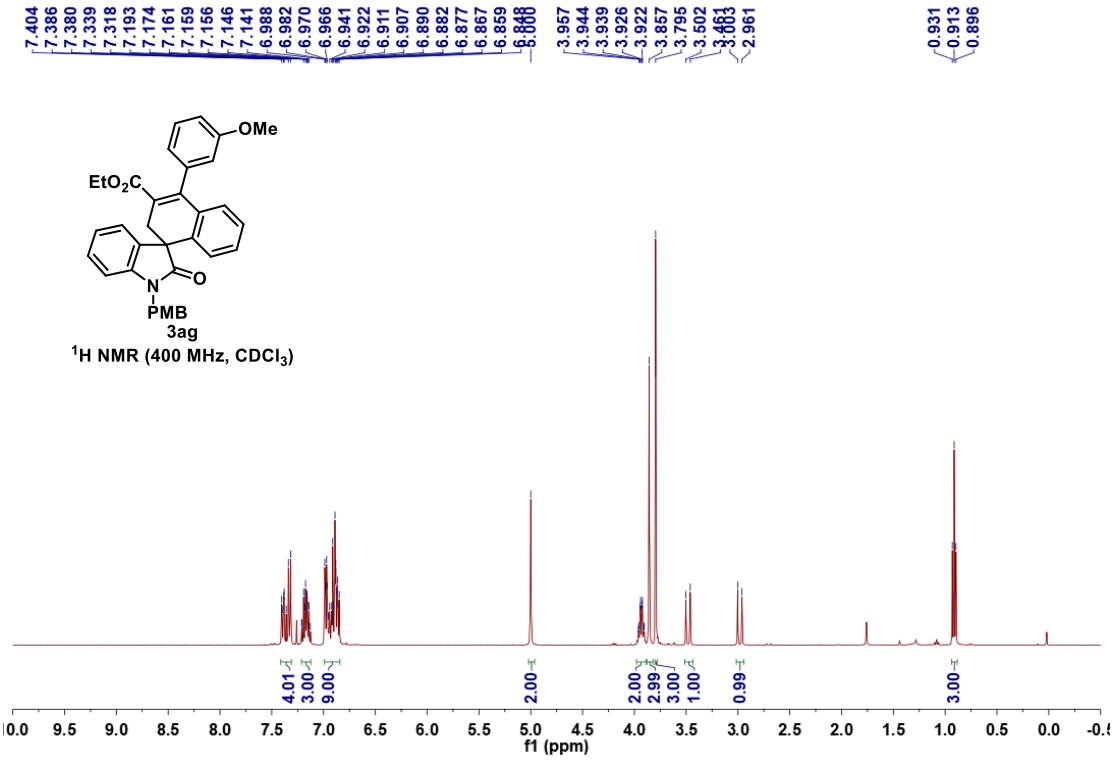
133.56
133.12
128.79
128.49
127.95
109.76
77.48
77.16
76.84
60.62
55.38
51.79
43.57
35.23
13.72
Cl
EtO2C
N
O
PMB
3af
13C NMR (100 MHz, CDCl3)
f1 (ppm)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7.386
7.380
7.339
7.318
7.193
7.174
7.161
7.159
7.156
7.146
7.141
6.988
6.982
6.970
6.966
6.941
6.922
6.911
6.907
6.890
6.882
6.877
6.867
6.859
3.957
3.944
3.939
3.926
3.922
3.857
3.795
3.502
2.961
0.931
0.913
0.896
OMe
EtO2C
N
O
PMB
3ag
1H NMR (400 MHz, CDCl3)
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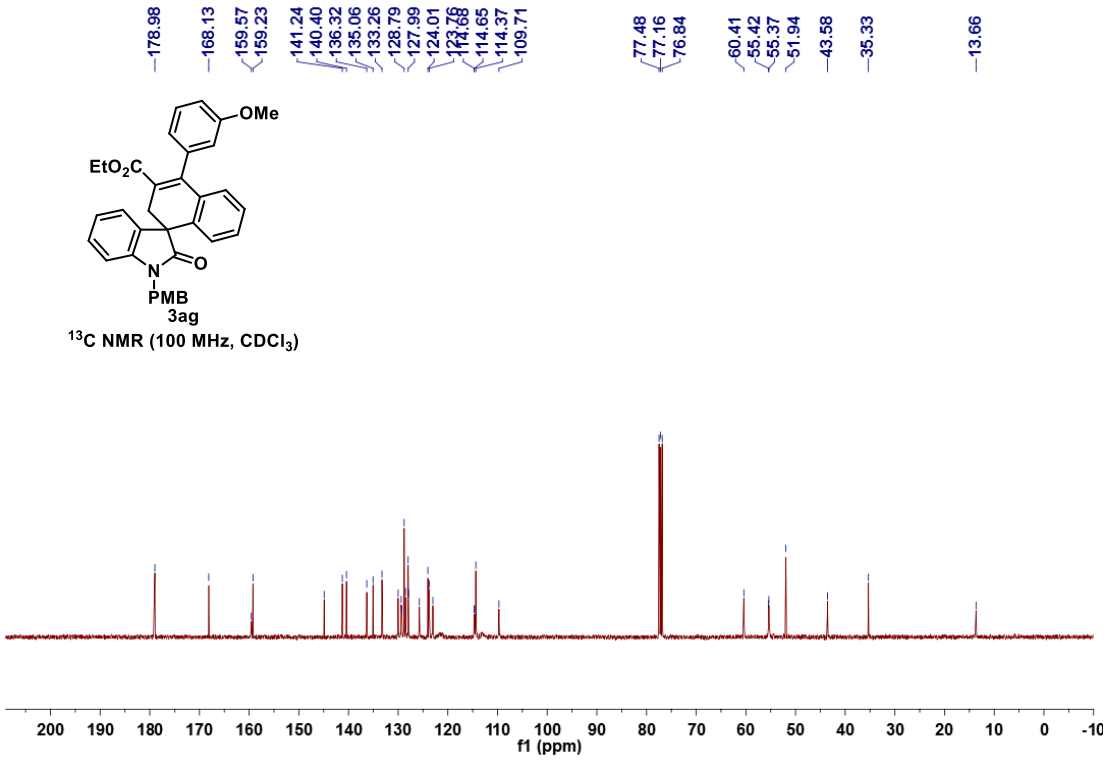
3.00
9.00
2.00
2.00
2.99
3.00
1.00
0.99
3.00
f1 (ppm)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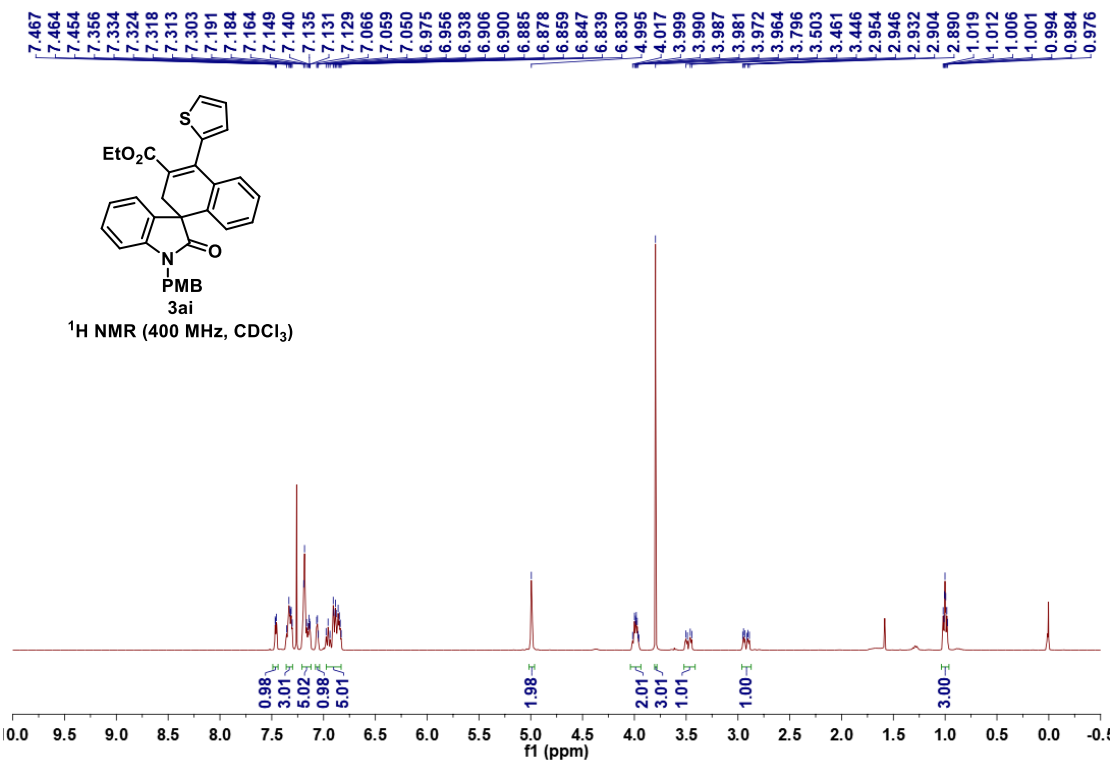
168.13
159.57
159.23
141.24
140.40
136.32
135.06
133.26
128.79
127.99
124.01
114.65
114.37
109.71
77.48
77.16
76.84
60.41
55.42
55.37
51.94
43.58
35.33
13.66
OMe
EtO2C
O
N
PMB
3ag
13C NMR (100 MHz, CDCl3)
f1 (ppm)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7.454
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7.334
7.324
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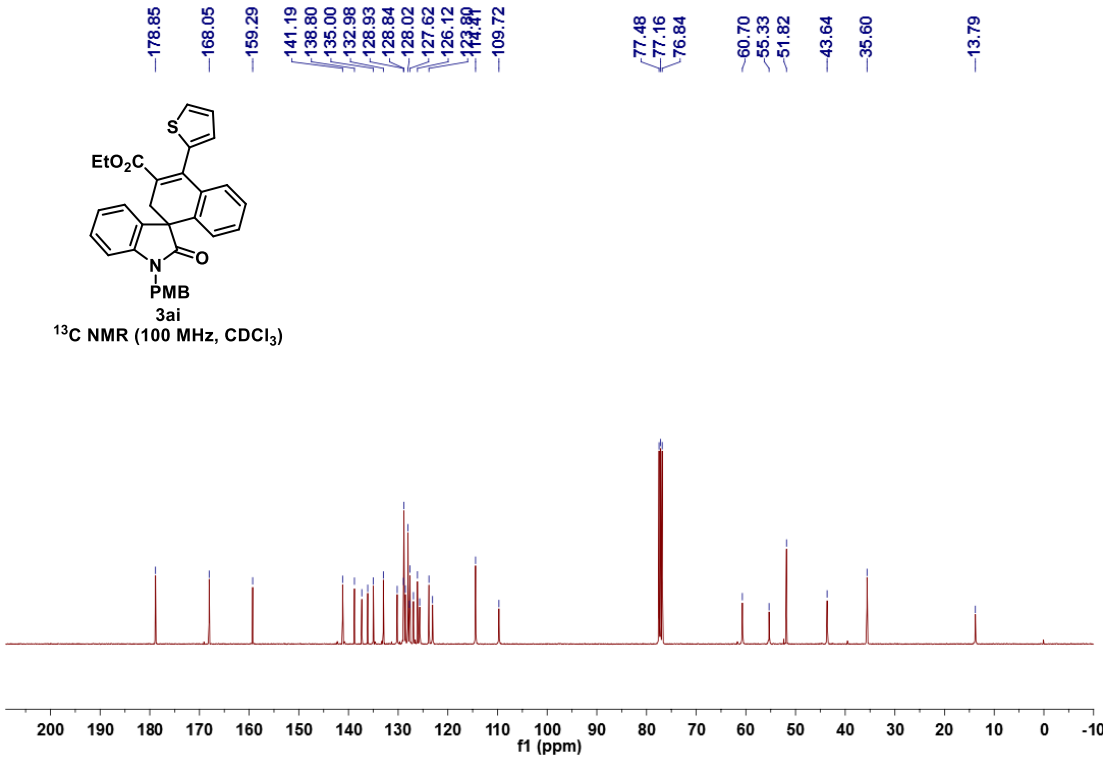
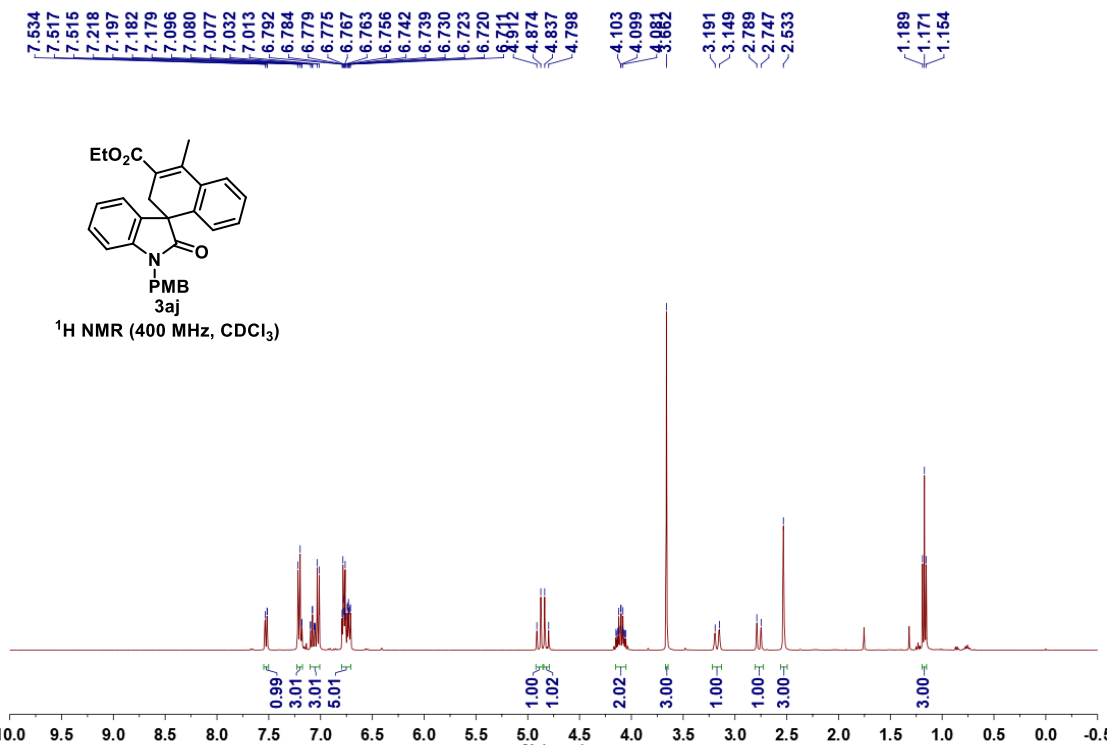
7.303
7.191
7.184
7.164
7.149
7.140
7.135
7.131
7.129
7.066
7.059
7.050
6.975
6.956
6.938
6.906
6.900
6.885
6.878
6.859
6.847
6.839
6.830
4.995
4.017
3.999
3.990
3.987
3.981
3.972
3.964
3.796
3.503
3.461
3.446
2.954
2.946
2.932
2.904
2.890
1.019
1.012
1.006
1.001
0.994
0.984
0.976
S
EtO2C
O
N
PMB
3ai
1H NMR (400 MHz, CDCl3)
0.98
3.01
5.02
0.98
5.01
1.98
2.01
3.01
1.01
1.00
3.00
f1 (ppm)



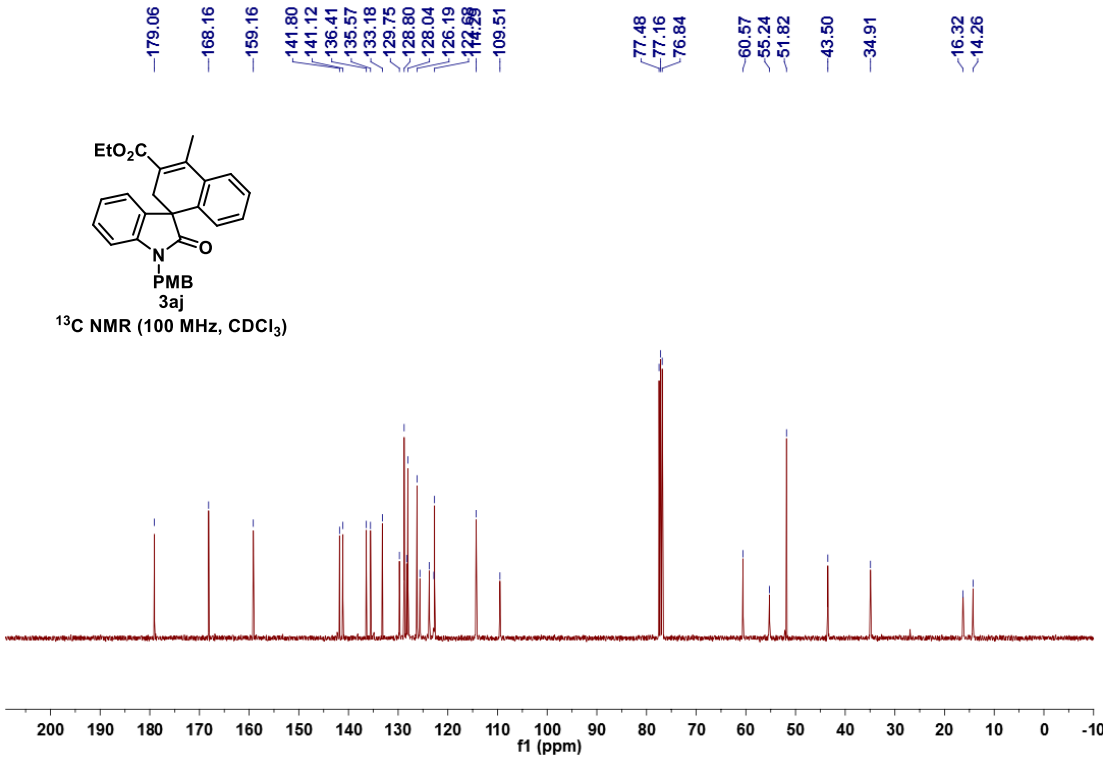
3ai

^{13}C NMR (100 MHz, $CDCl_3$)



3aj

^{1}H NMR (400 MHz, $CDCl_3$)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135.57
133.18
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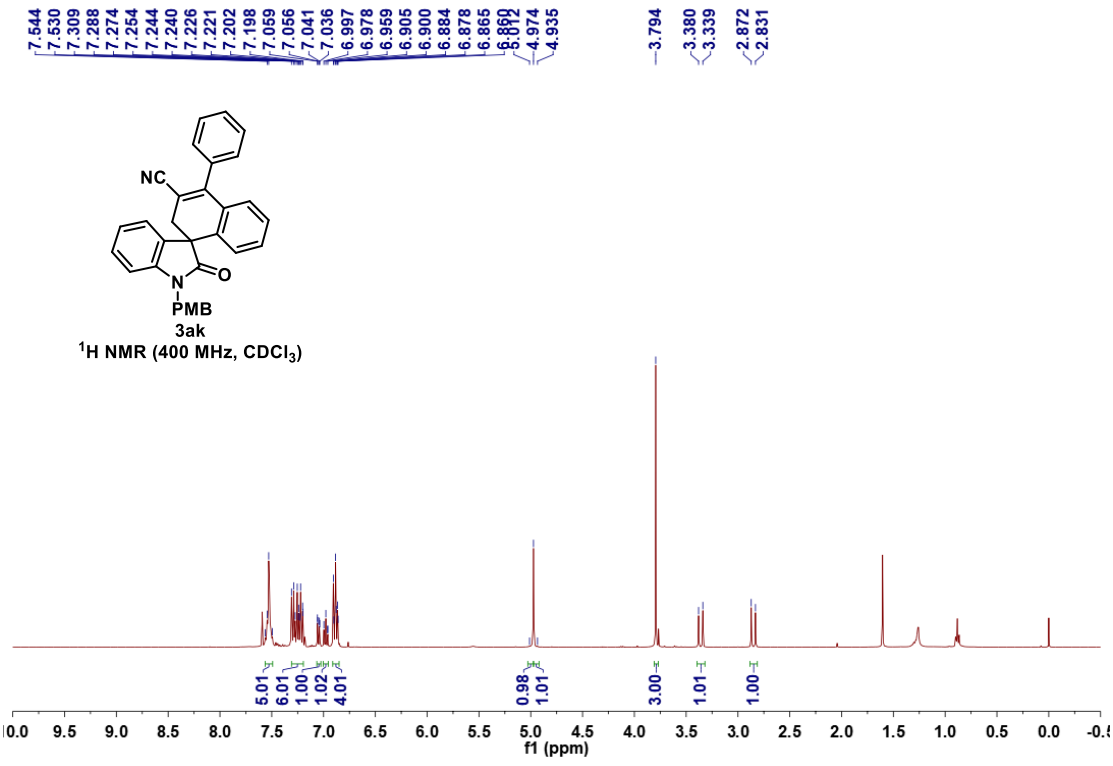
128.80
128.04
126.19
109.51
77.48
77.16
76.84
60.57
55.24
51.82
43.50
34.91
16.32
14.26
EtO2C
N
O
PMB
3aj
13C NMR (100 MHz, CDCl3)
f1 (ppm)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7.254
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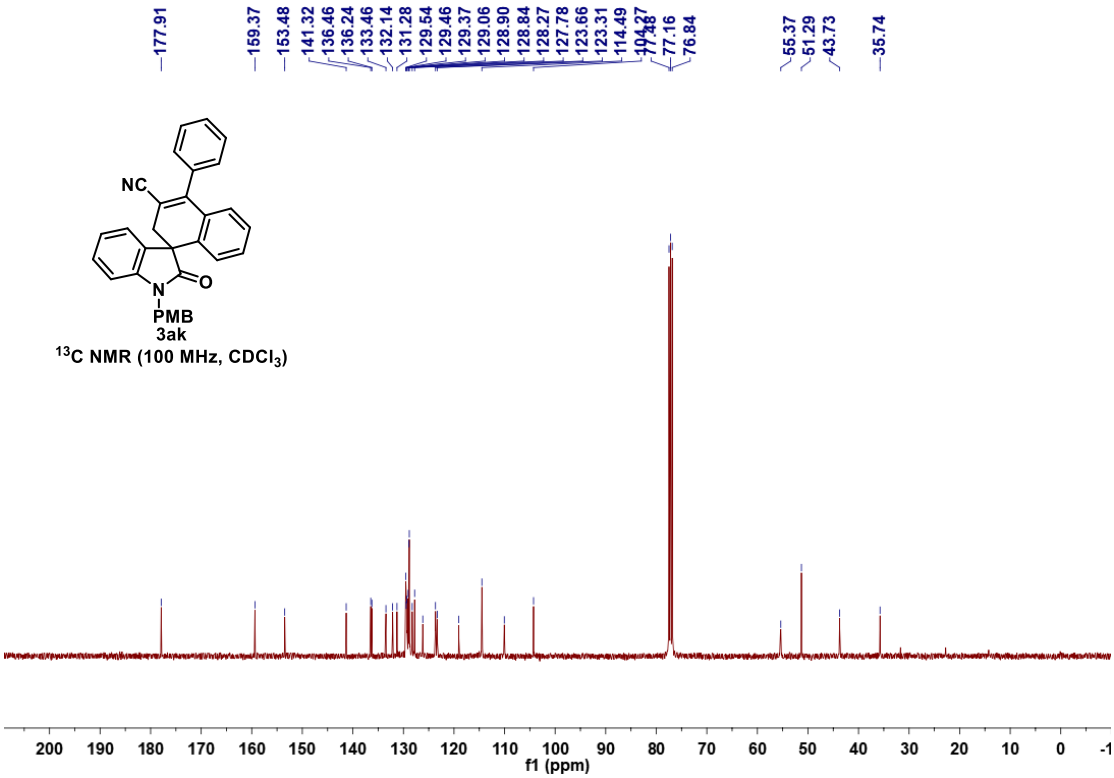
7.240
7.226
7.221
7.202
7.198
7.059
7.056
7.041
7.036
6.997
6.978
6.959
6.905
6.900
6.884
6.878
6.865
4.974
4.935
3.794
3.380
3.339
2.872
2.831
NC
N
O
PMB
3ak
1H NMR (400 MHz, CDCl3)
5.01
6.01
1.00
1.02
4.01
0.98
1.01
3.00
1.01
1.00
f1 (ppm)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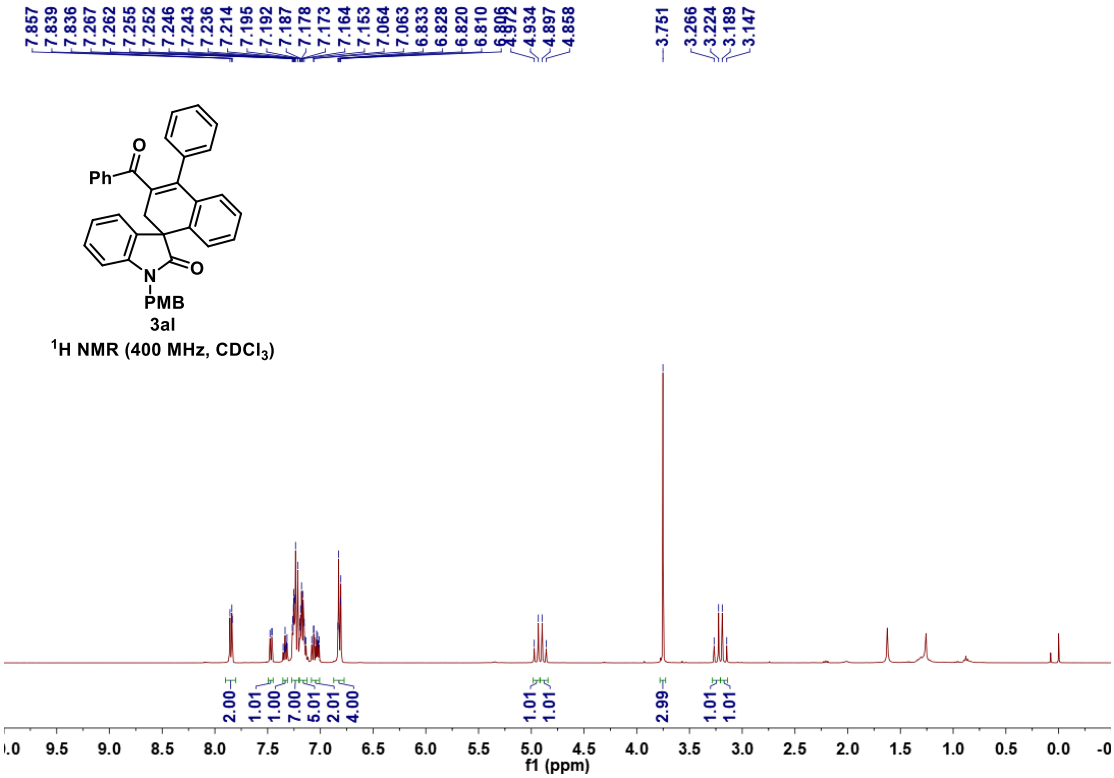
153.48
141.32
136.46
136.24
133.46
132.14
131.28
129.54
129.46
129.37
129.06
128.90
128.84
128.27
127.78
123.66
123.31
114.49
104.27
77.48
77.16
76.84
55.37
51.29
43.73
35.74
NC
O
N
PMB
3ak
13C NMR (100 MHz, CDCl3)
f1 (ppm)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7.836
7.267
7.262
7.255
7.252
7.246
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7.236
7.214
7.195
7.192
7.187
7.178
7.173
7.164
7.153
7.064
7.063
6.833
6.828
6.820
6.810
4.934
4.897
4.858
3.751
3.266
3.224
3.189
3.147
Ph
O
O
N
PMB
3al
1H NMR (400 MHz, CDCl3)
2.00
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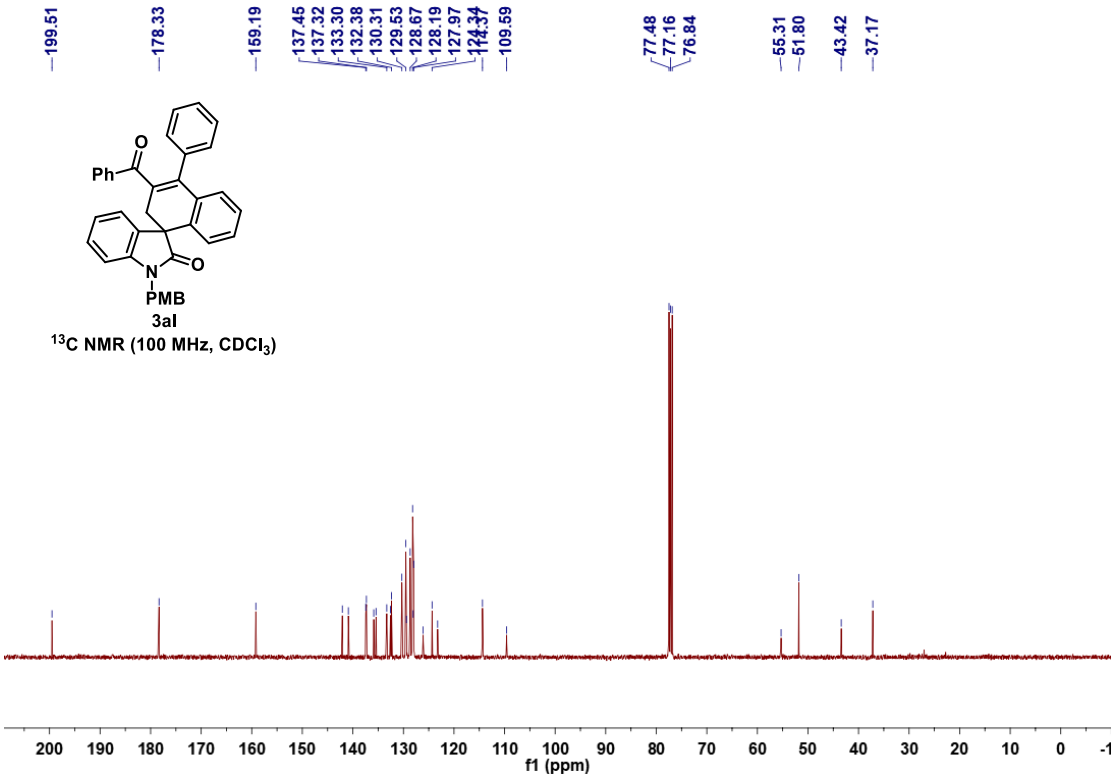
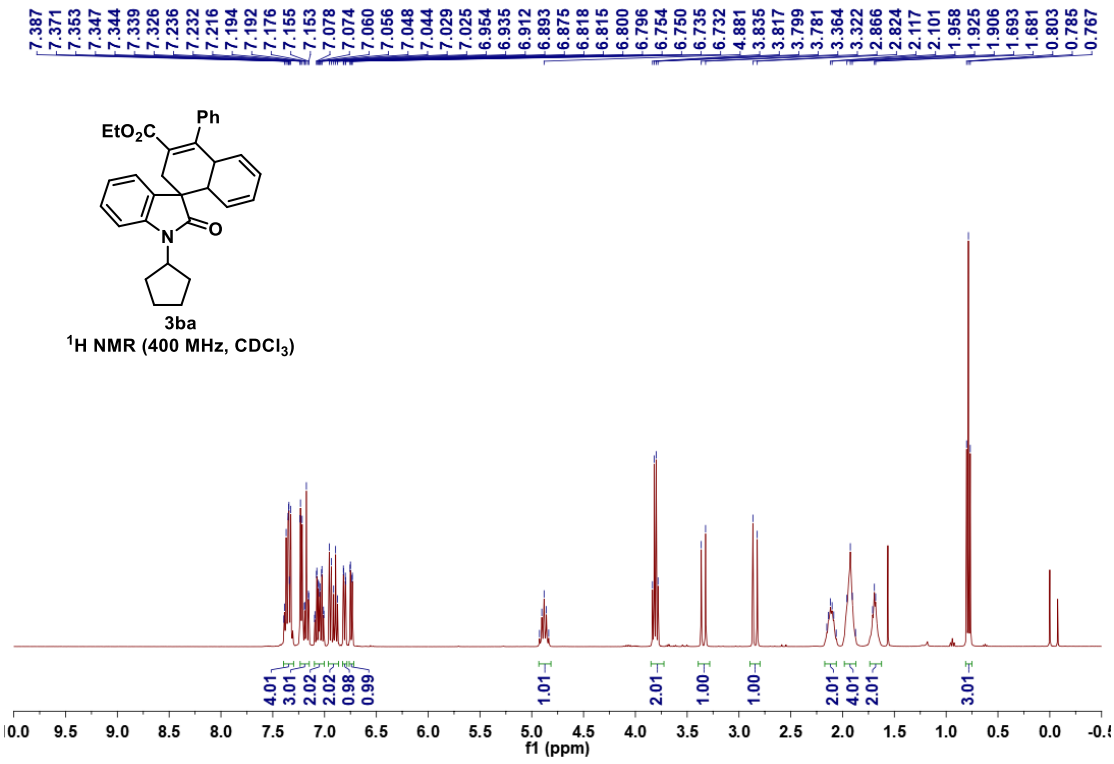
1.00
7.00
5.01
2.01
4.00
1.01
1.01
2.99
1.01
1.01
f1 (ppm)



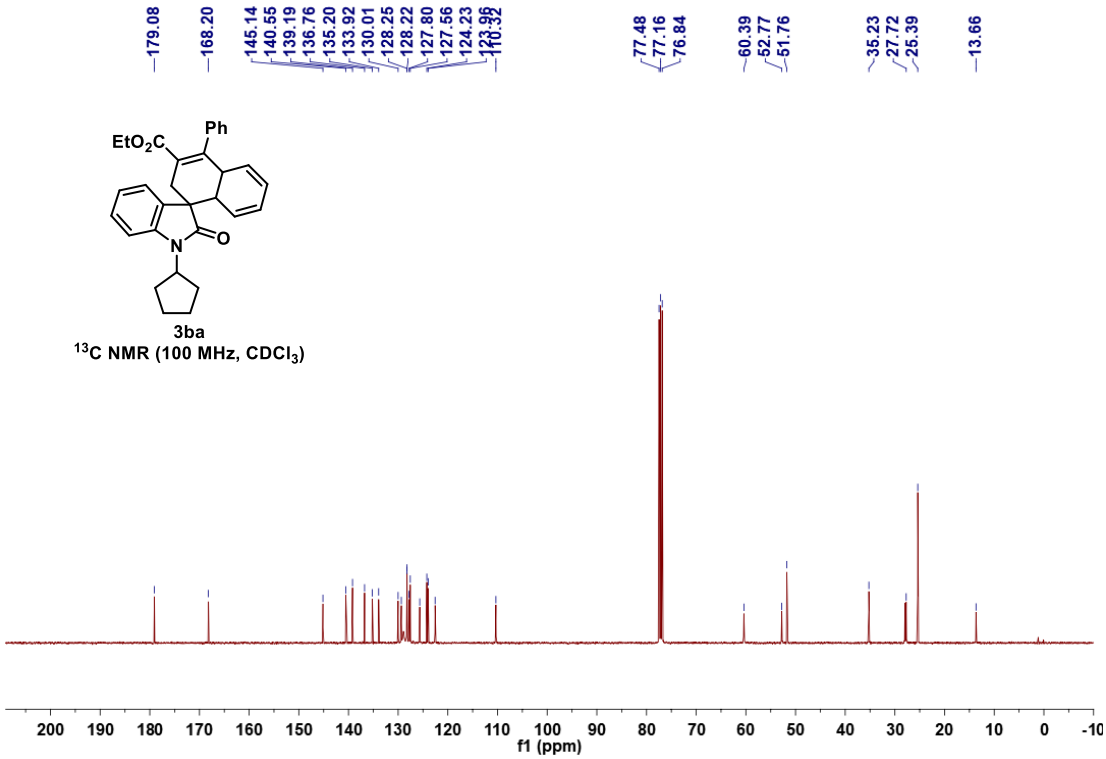
3aI

^{13}C NMR (100 MHz, $CDCl_3$)



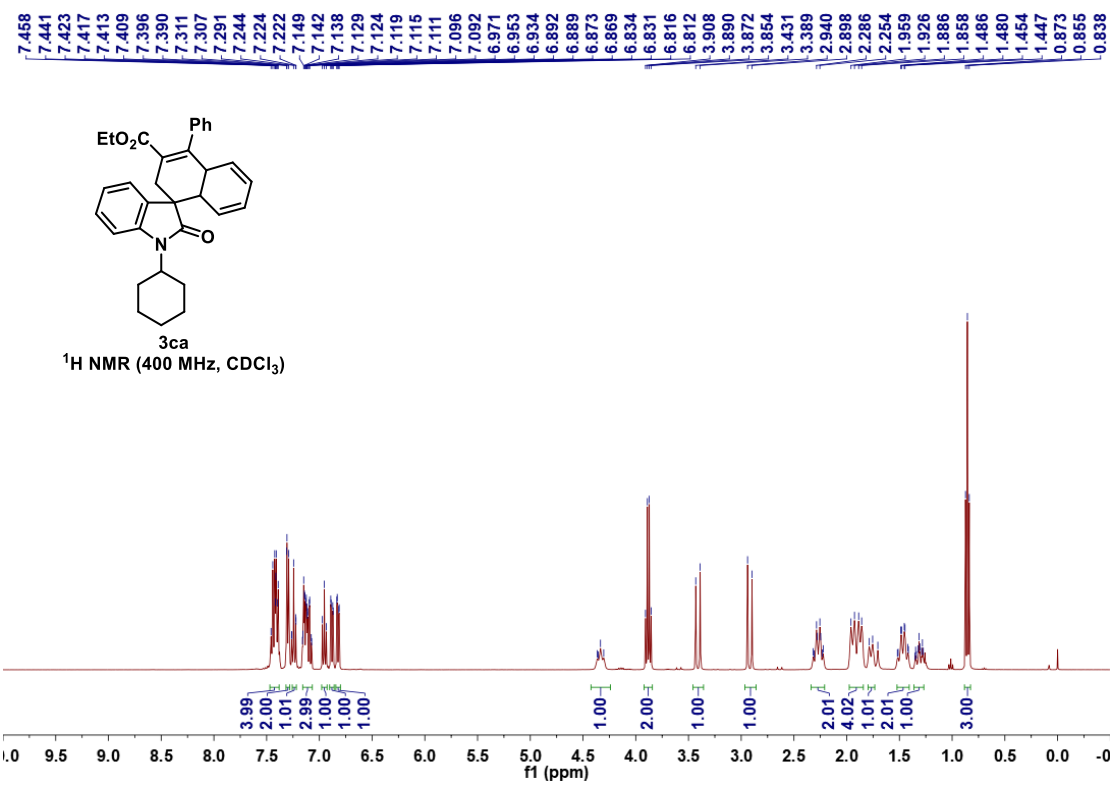
3ba

^{1}H NMR (400 MHz, $CDCl_3$)



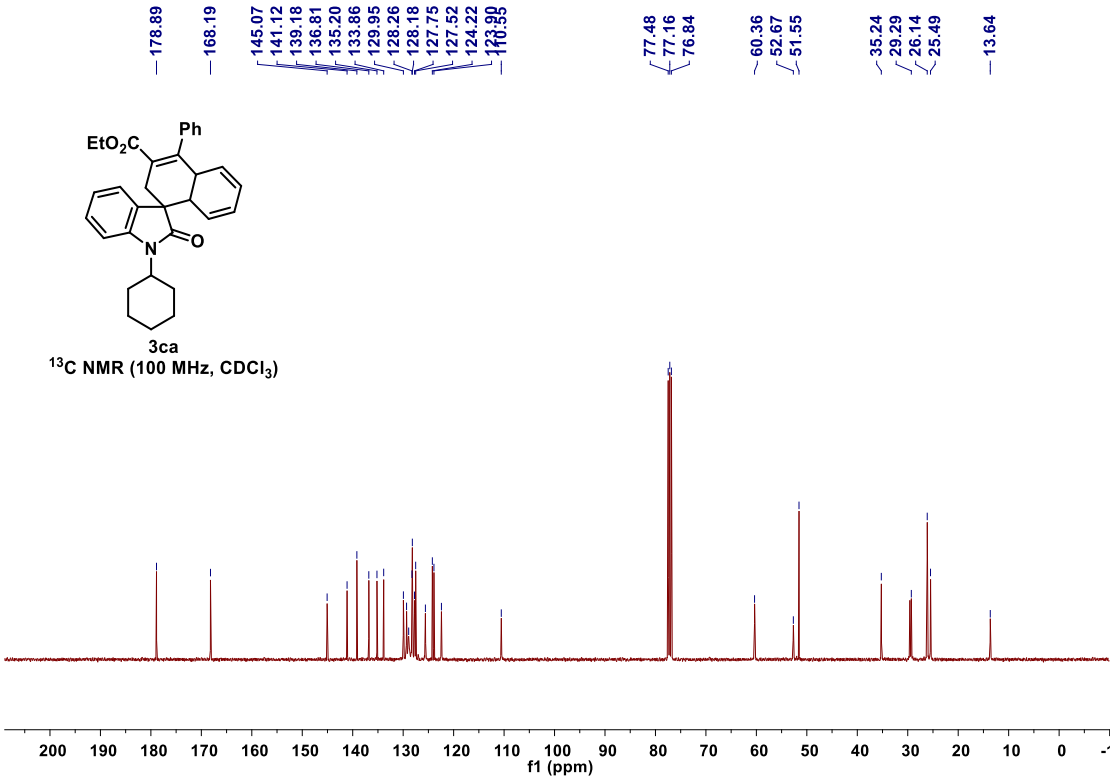
3ba

^{13}C NMR (100 MHz, $CDCl_3$)



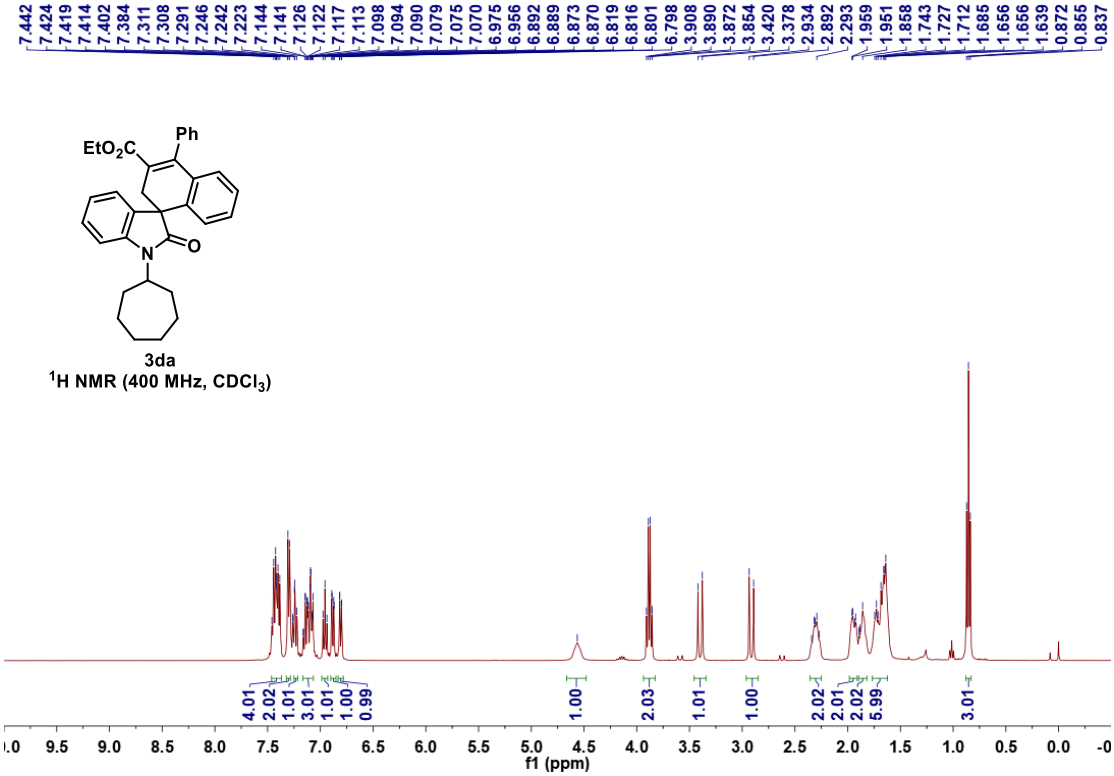
3ca

^{1}H NMR (400 MHz, $CDCl_3$)



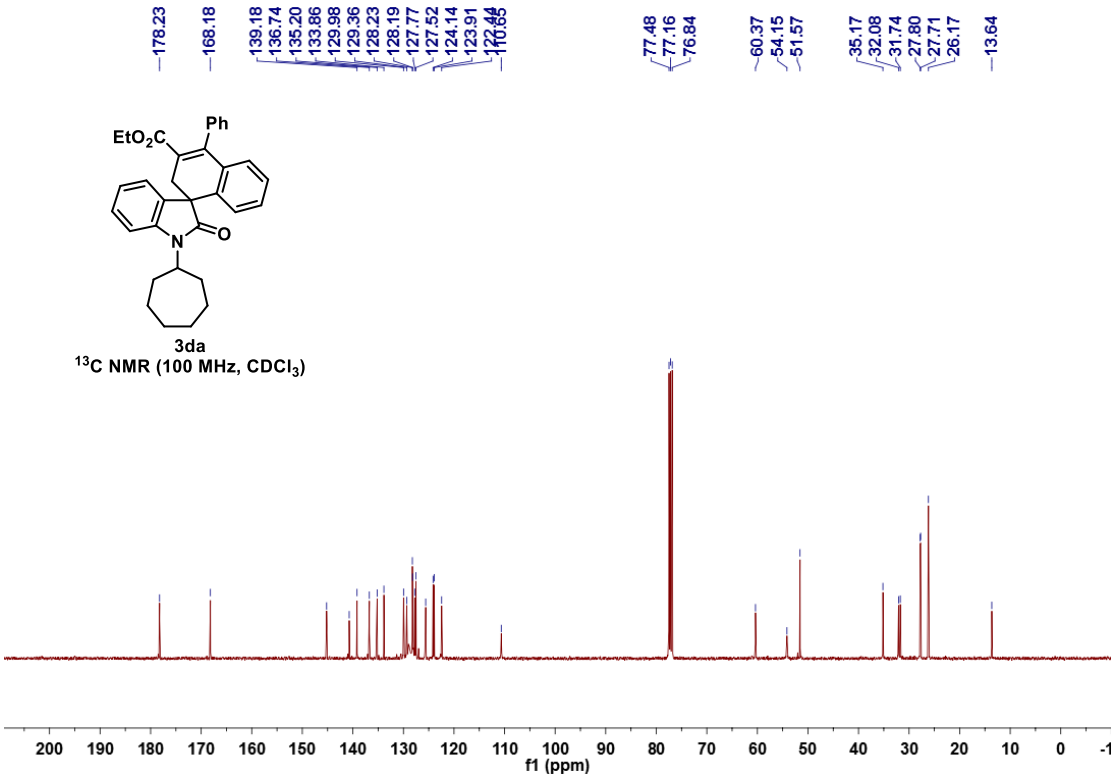
3ca

^{13}C NMR (100 MHz, $CDCl_3$)



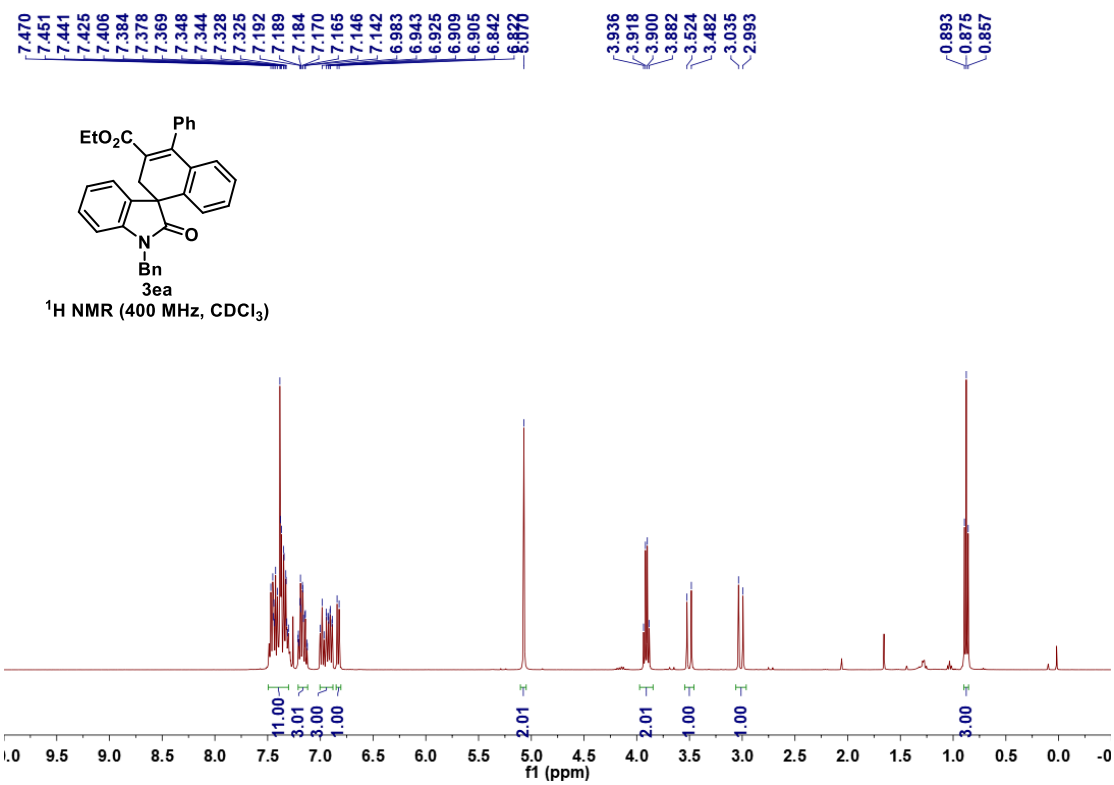
3da

^{1}H NMR (400 MHz, $CDCl_3$)



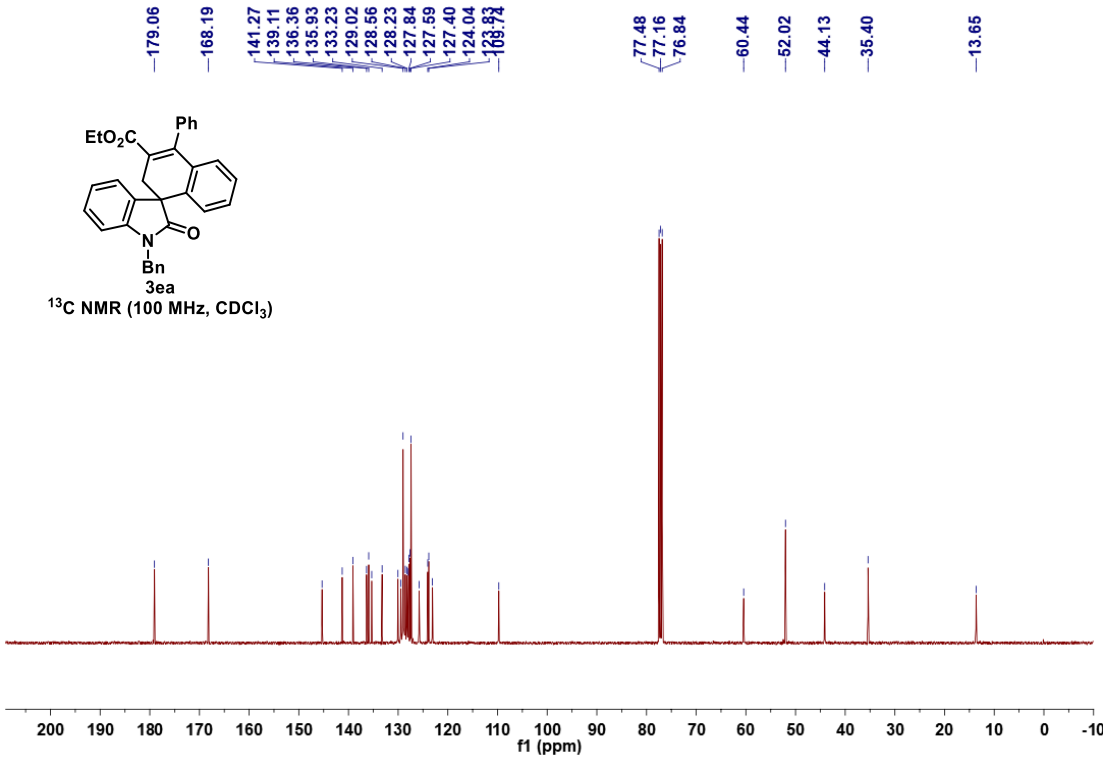
3da

^{13}C NMR (100 MHz, $CDCl_3$)



3ea

^{1}H NMR (400 MHz, $CDCl_3$)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139.11
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135.93
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129.02
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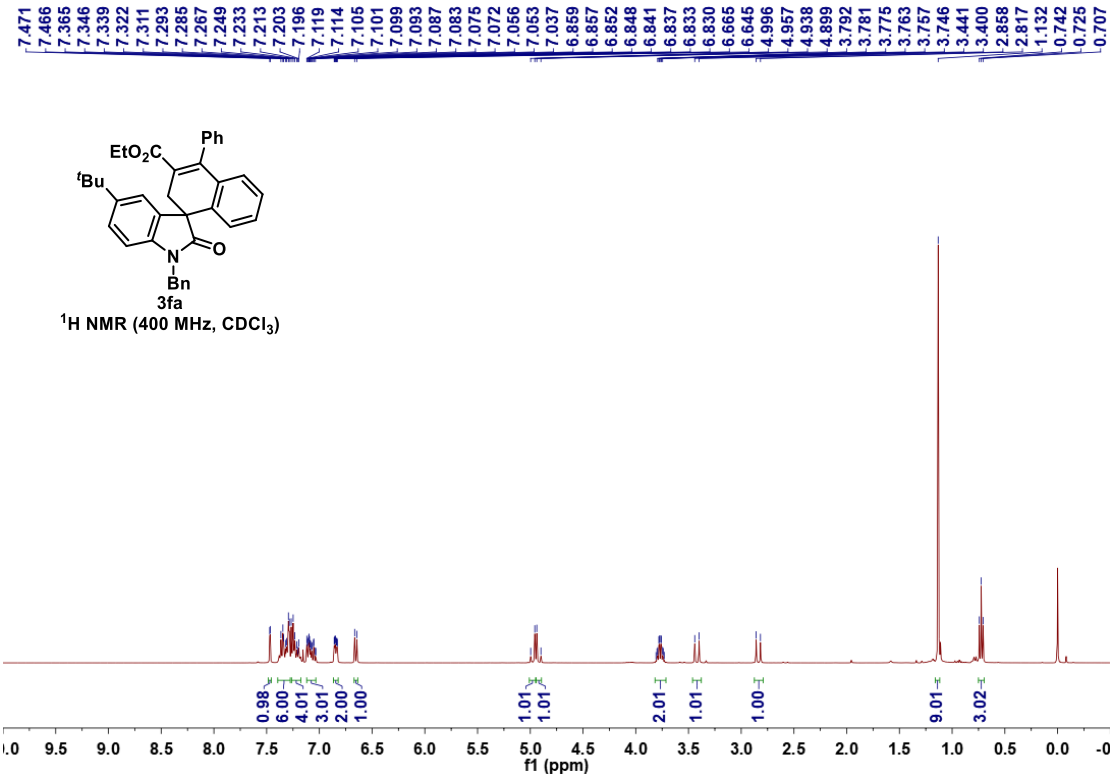
128.23
127.84
127.59
127.40
124.04
77.48
77.16
76.84
60.44
52.02
44.13
35.40
13.65
EtO2C
Ph
N
O
Bn
3ea
13C NMR (100 MHz, CDCl3)
f1 (ppm)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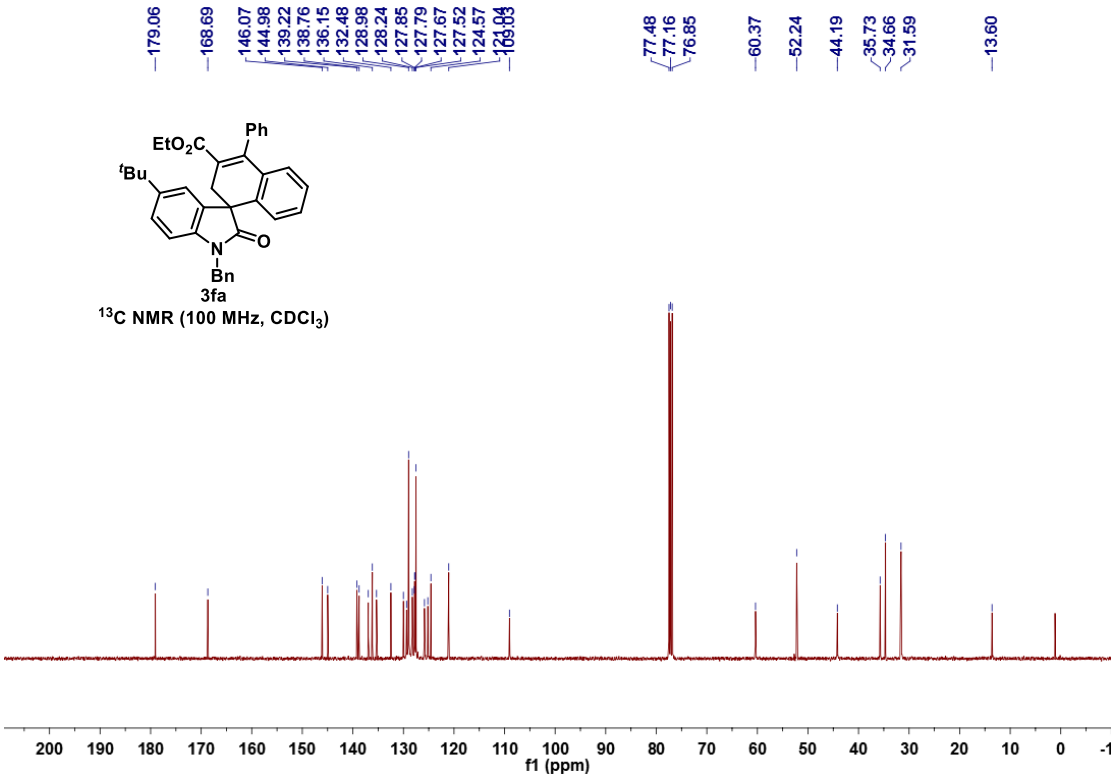
7.249
7.233
7.213
7.203
7.196
7.119
7.114
7.105
7.101
7.099
7.093
7.087
7.083
7.075
7.072
7.056
7.053
7.037
6.859
6.857
6.852
6.848
6.841
6.837
6.833
6.830
6.665
6.645
4.996
4.957
4.938
4.899
3.792
3.781
3.775
3.763
3.757
3.746
3.441
3.400
2.858
2.817
1.132
0.742
0.725
0.707
EtO2C
Ph
tBu
N
O
Bn
3fa
1H NMR (400 MHz, CDCl3)
0.98
6.00
4.01
3.01
2.00
1.00
1.01
1.01
2.01
1.01
1.00
9.01
3.02
f1 (ppm)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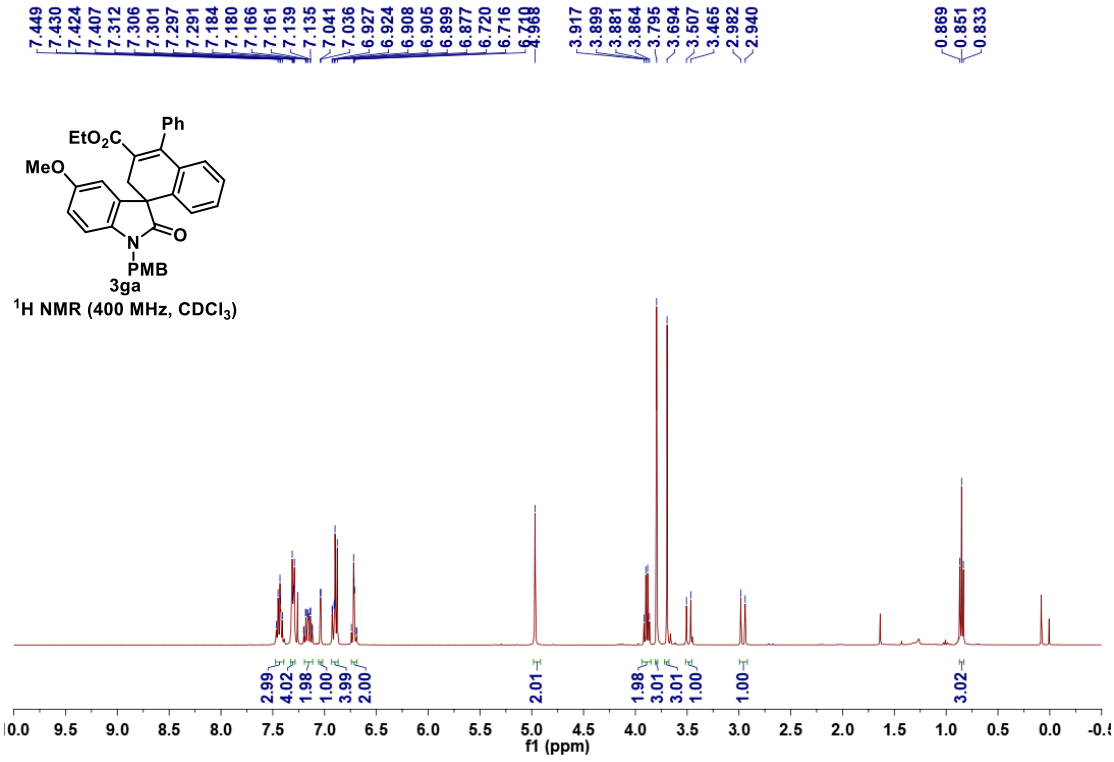
127.67
127.52
124.57
77.48
77.16
76.85
60.37
52.24
44.19
35.73
34.66
31.59
13.60
EtO2C
Ph
tBu
O
N
Bn
3fa
13C NMR (100 MHz, CDCl3)
f1 (ppm)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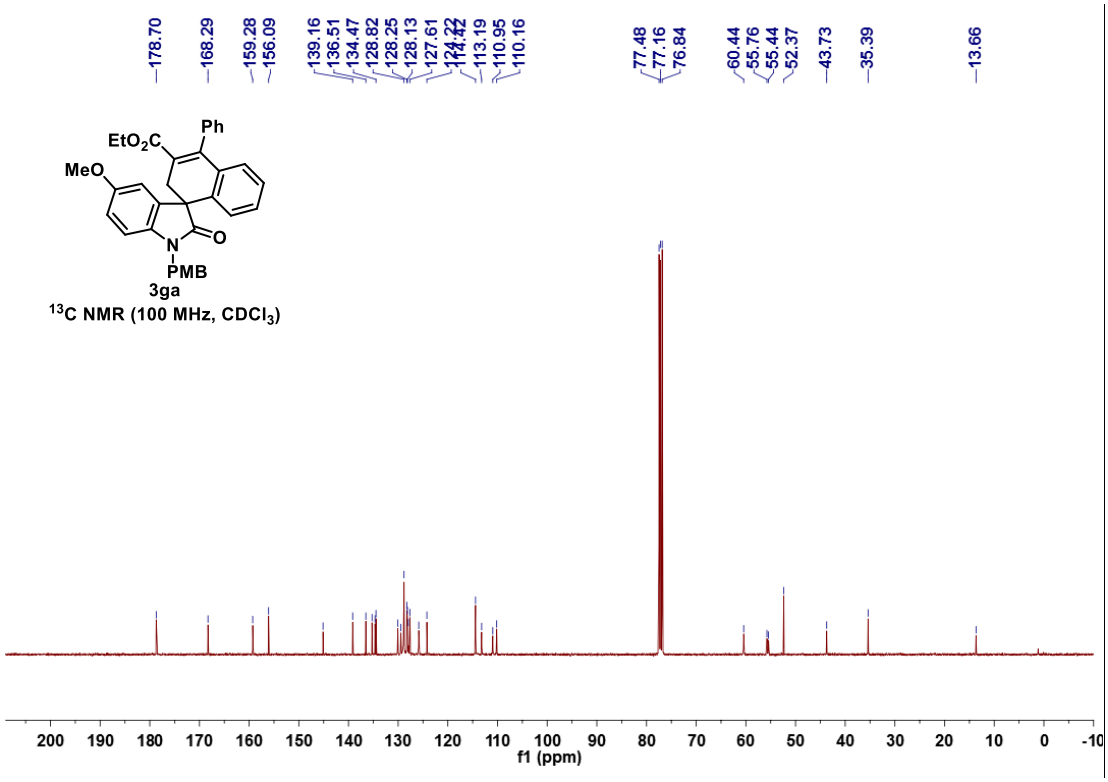
7.161
7.139
7.135
7.041
7.036
6.927
6.924
6.908
6.905
6.899
6.877
6.720
6.716
3.917
3.899
3.881
3.864
3.795
3.694
3.507
3.465
2.982
2.940
0.869
0.851
0.833
EtO2C
Ph
MeO
O
N
PMB
3ga
1H NMR (400 MHz, CDCl3)
2.99
4.02
1.98
1.00
3.99
2.00
2.01
1.98
3.01
3.01
1.00
1.00
3.02
f1 (ppm)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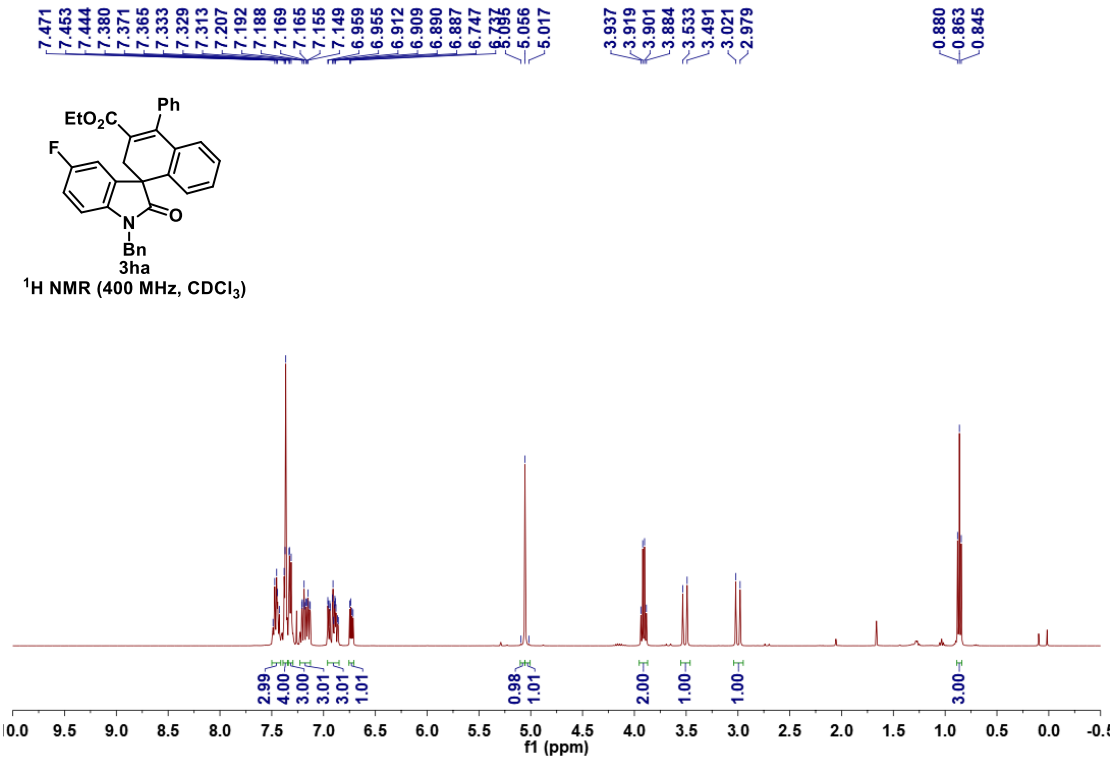
168.29
159.28
156.09
139.16
136.51
134.47
128.82
128.25
128.13
127.61
113.19
110.95
110.16
77.48
77.16
76.84
60.44
55.76
55.44
52.37
43.73
35.39
13.66
EtO2C
Ph
MeO
N
O
PMB
3ga
13C NMR (100 MHz, CDCl3)
f1 (ppm)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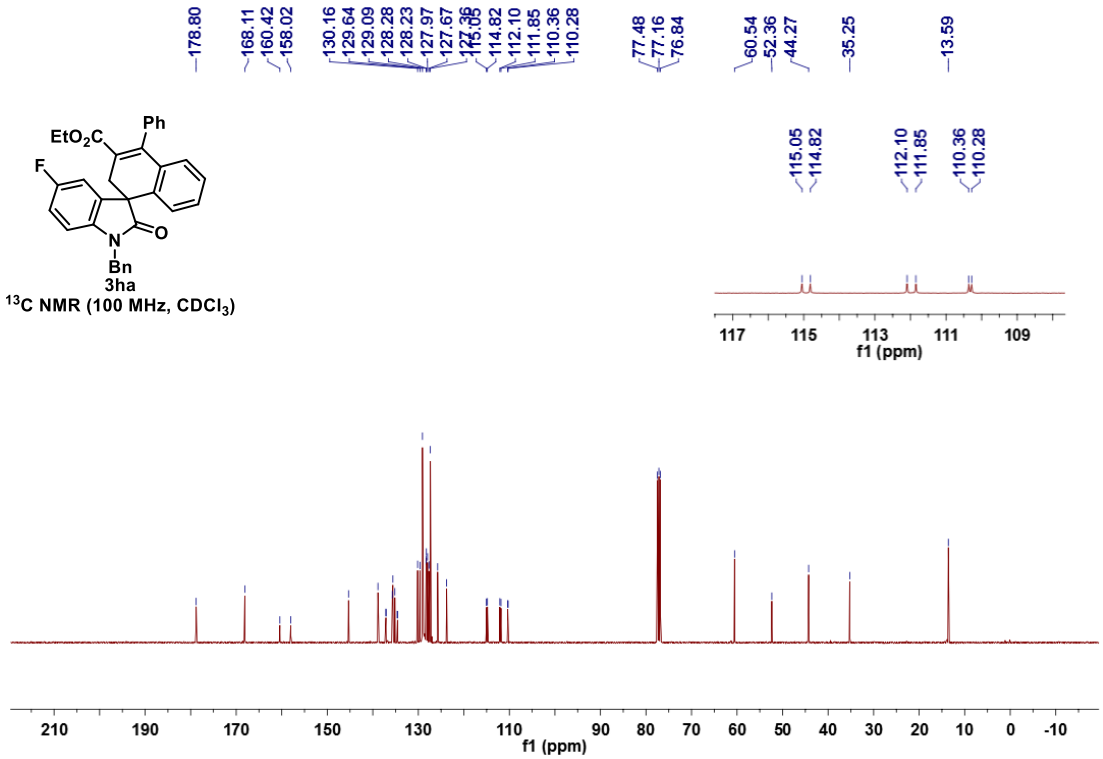
7.371
7.365
7.333
7.329
7.313
7.207
7.192
7.188
7.169
7.165
7.155
7.149
6.959
6.955
6.912
6.909
6.890
6.887
6.747
5.095
5.056
5.017
3.937
3.919
3.901
3.884
3.533
3.491
3.021
2.979
0.880
0.863
0.845
EtO2C
Ph
F
N
O
Bn
3ha
1H NMR (400 MHz, CDCl3)
2.99
4.00
3.00
3.01
3.01
1.01
0.98
1.01
2.00
1.00
1.00
3.00
f1 (ppm)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160.42
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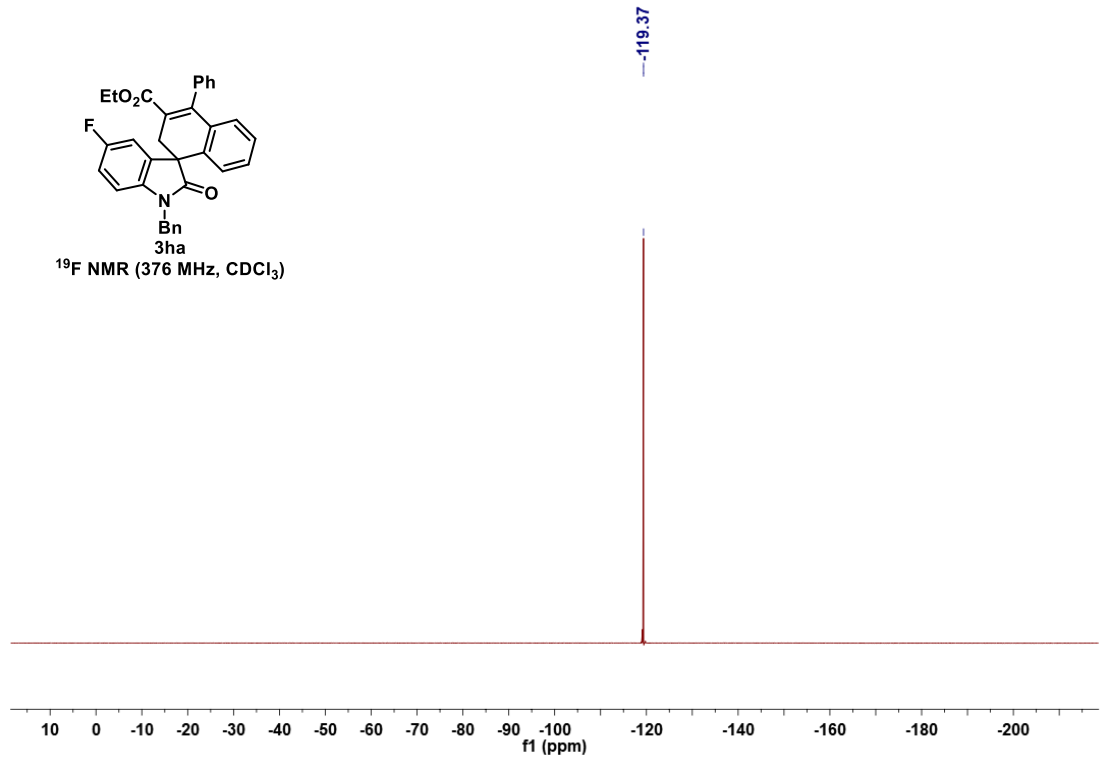
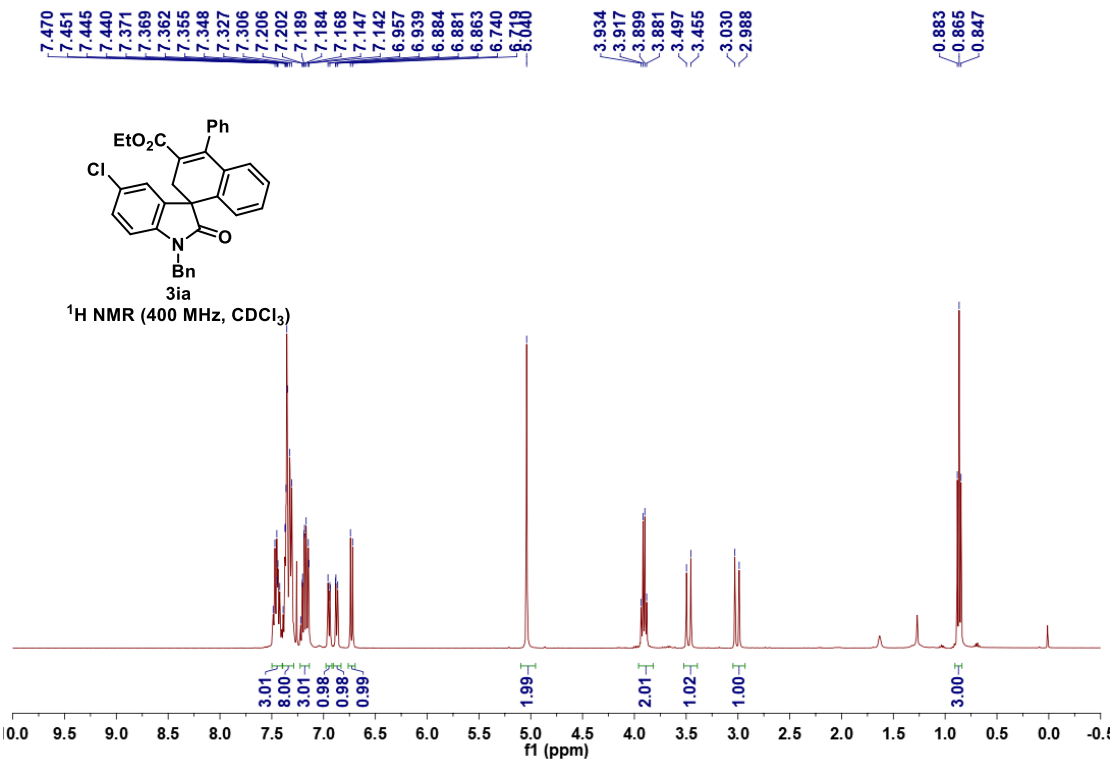
130.16
129.64
129.09
128.28
128.23
127.97
127.67
114.82
112.10
111.85
110.36
110.28
77.48
77.16
76.84
60.54
52.36
44.27
35.25
13.59
115.05
114.82
112.10
111.85
110.36
110.28
EtO2C
Ph
F
N
O
Bn
3ha
13C NMR (100 MHz, CDCl3)
117
115
113
111
109
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-119.37
EtO2C
Ph
F
N
O
Bn
3ha
19F NMR (376 MHz, CDCl3)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)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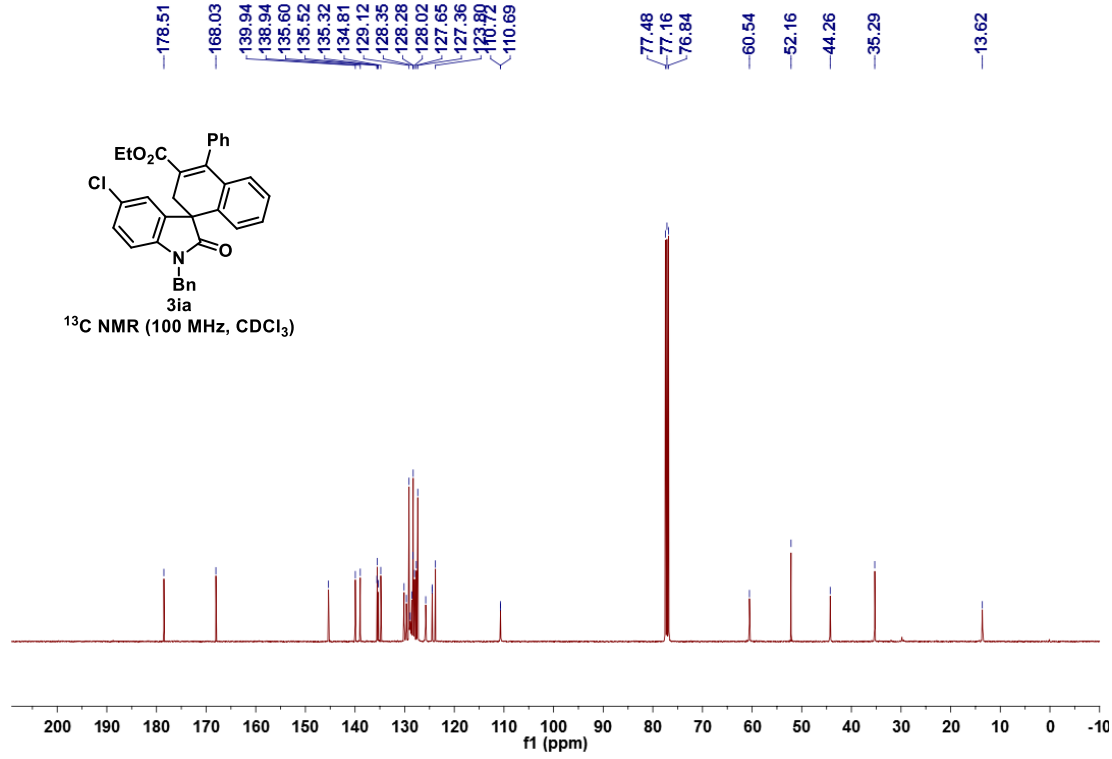
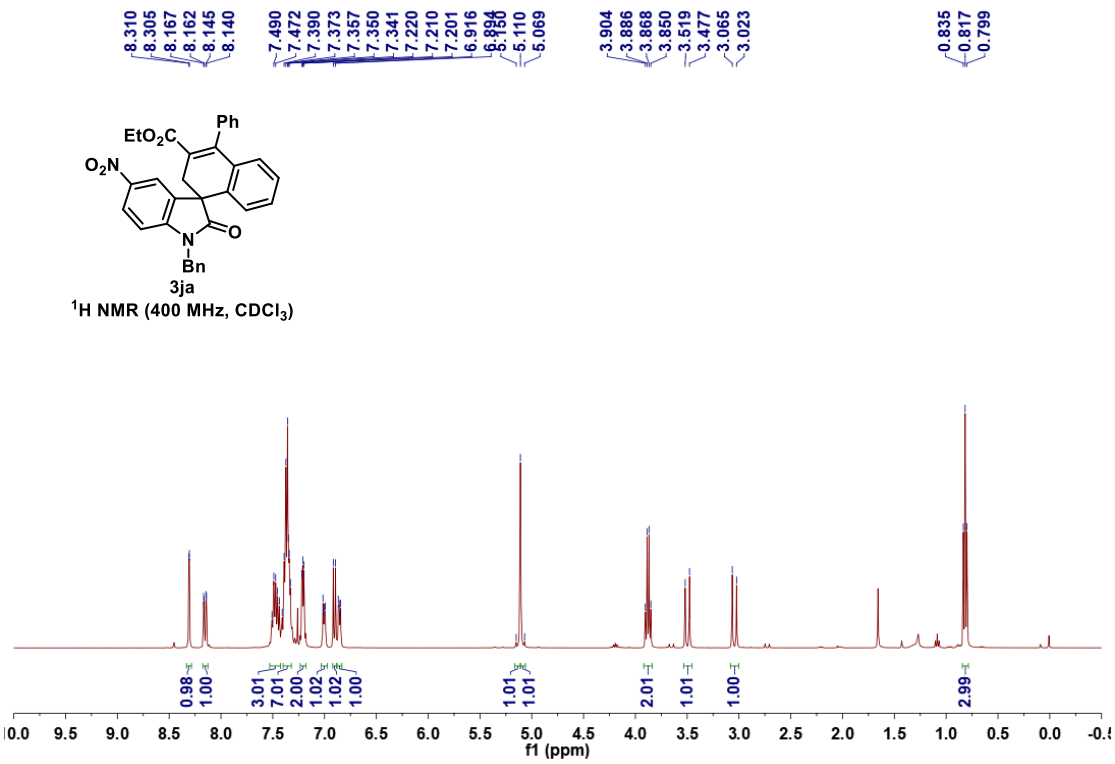
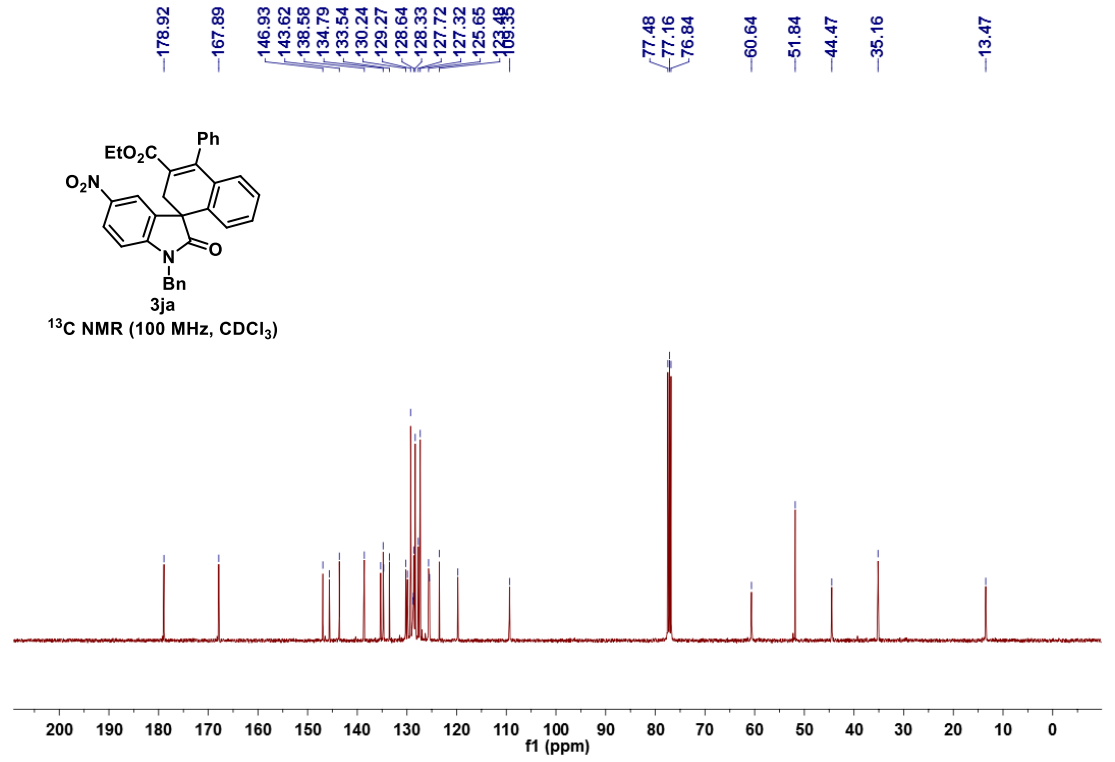
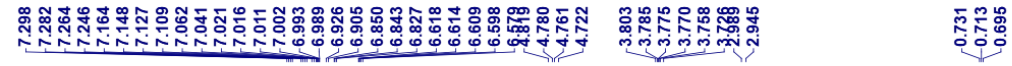
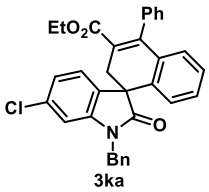
7.451
7.445
7.440
7.371
7.369
7.362
7.355
7.348
7.327
7.306
7.206
7.202
7.189
7.184
7.168
7.147
7.142
6.957
6.939
6.884
6.881
6.863
6.740
6.719
6.040
3.934
3.917
3.899
3.881
3.497
3.455
3.030
2.988
0.883
0.865
0.847
EtO2C
Ph
Cl
N
O
Bn
3ia
1H NMR (400 MHz, CDCl3)
3.01
8.00
3.01
0.98
0.98
0.99
1.99
2.01
1.02
1.00
3.00
f1 (ppm)


178.51
168.03
139.94
138.94
135.60
135.52
135.32
134.81
129.12
128.35
128.28
128.02
127.65
127.36
110.72
110.69
77.48
77.16
76.84
60.54
52.16
44.26
35.29
13.62
EtO2C
Ph
Cl
N
O
Bn
3ia
13C NMR (100 MHz, CDCl3)
f1 (ppm)


8.310
8.305
8.167
8.162
8.145
8.140
7.490
7.472
7.390
7.373
7.357
7.350
7.341
7.220
7.210
7.201
6.916
5.110
5.069
3.904
3.886
3.868
3.850
3.519
3.477
3.065
3.023
0.835
0.817
0.799
EtO2C
Ph
O2N
N
O
Bn
3ja
1H NMR (400 MHz, CDCl3)
0.98
1.00
3.01
7.01
2.00
1.02
1.02
1.00
1.01
1.01
2.01
1.01
1.00
2.99
f1 (ppm)

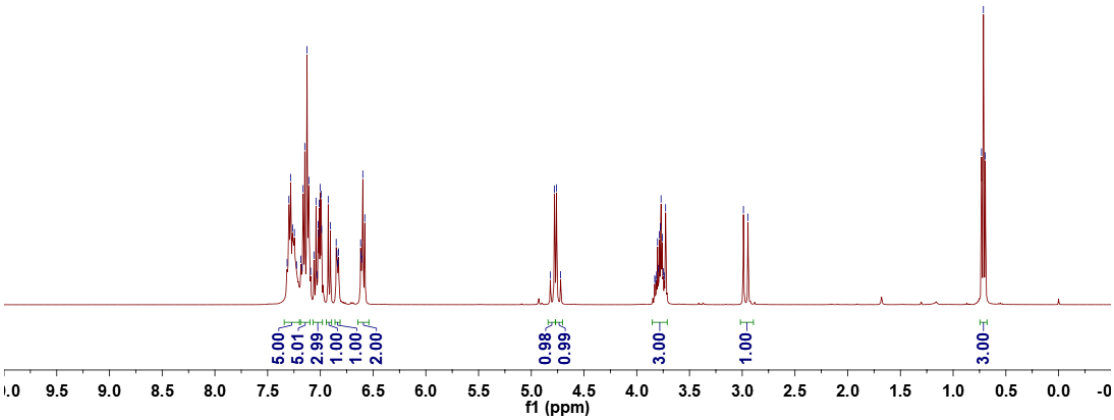

178.92
167.89
146.93
143.62
138.58
134.79
133.54
130.24
129.27
128.64
128.33
127.72
127.32
125.65
77.48
77.16
76.84
60.64
51.84
44.47
35.16
13.47
EtO2C
Ph
O2N
N
O
Bn
3ja
13C NMR (100 MHz, CDCl3)
f1 (ppm)

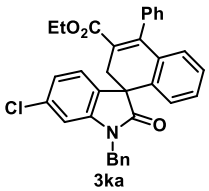




3ka

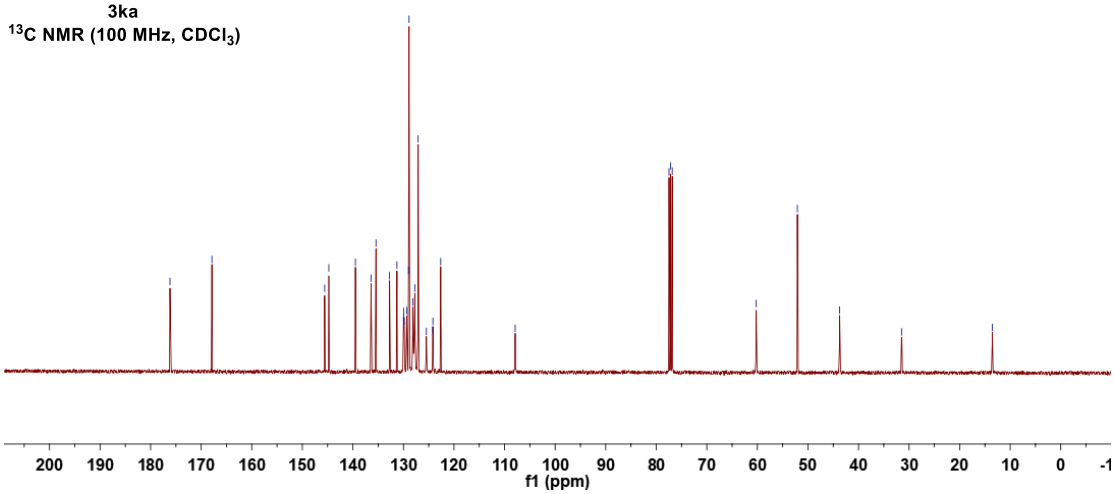
^{1}H NMR (400 MHz, $CDCl_3$)

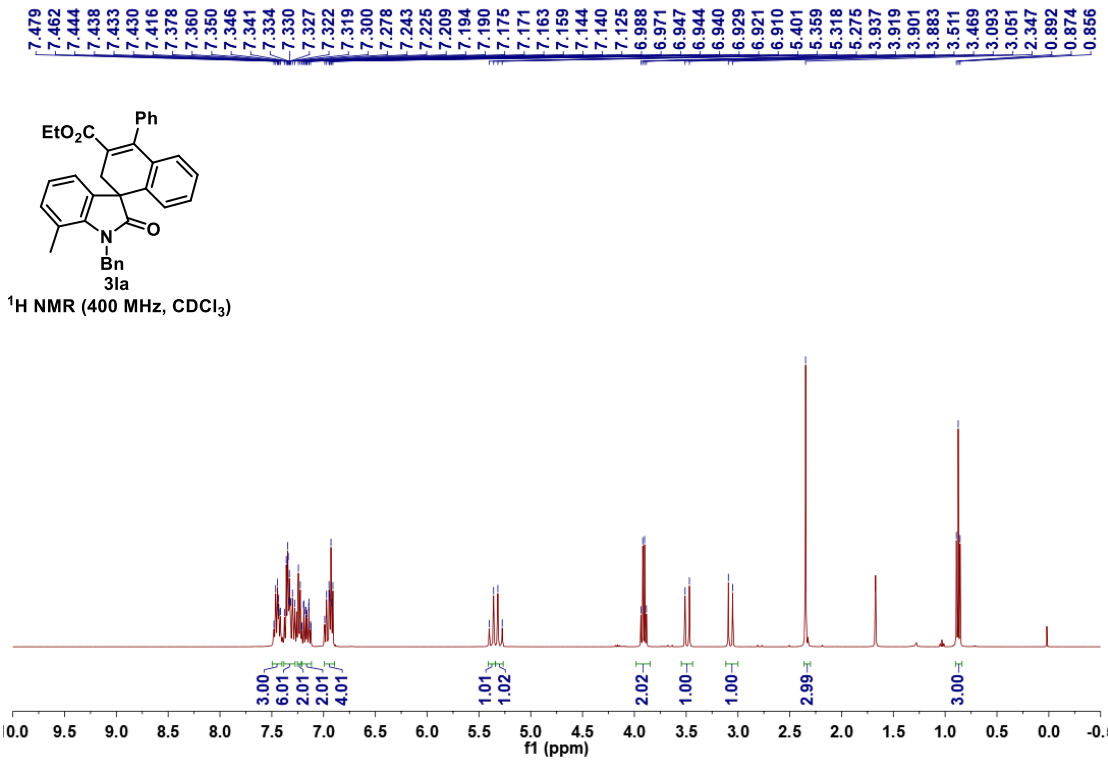




3ka

^{13}C NMR (100 MHz, $CDCl_3$)

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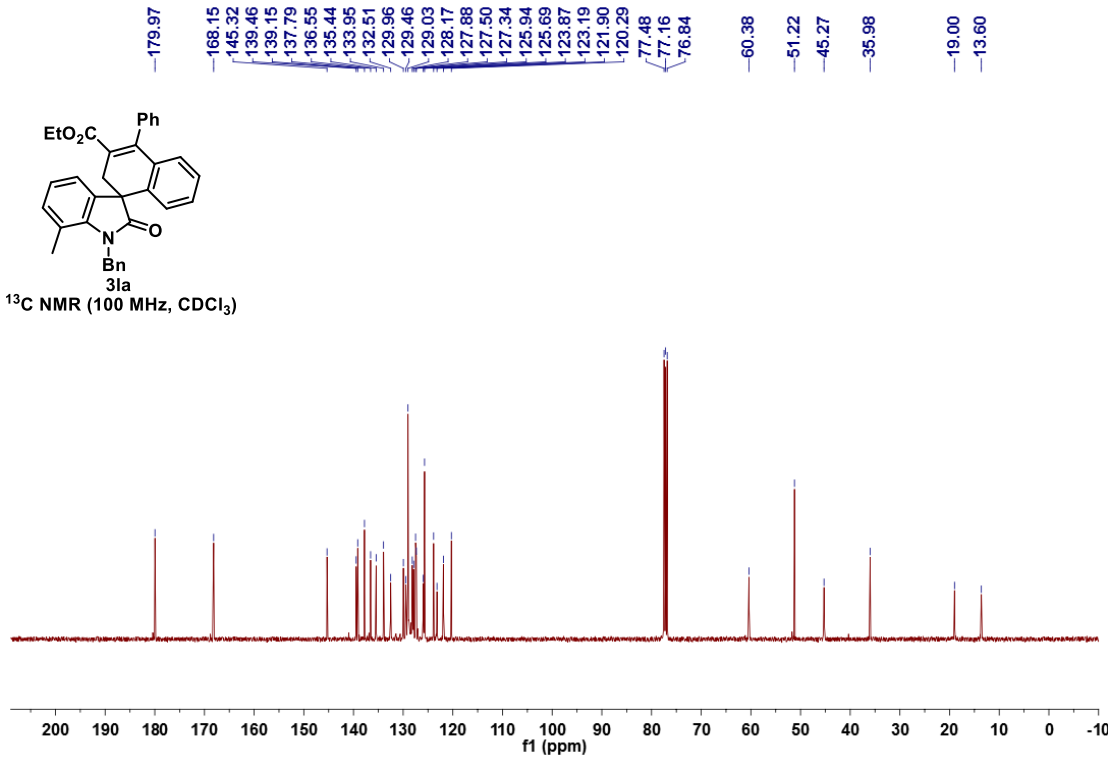
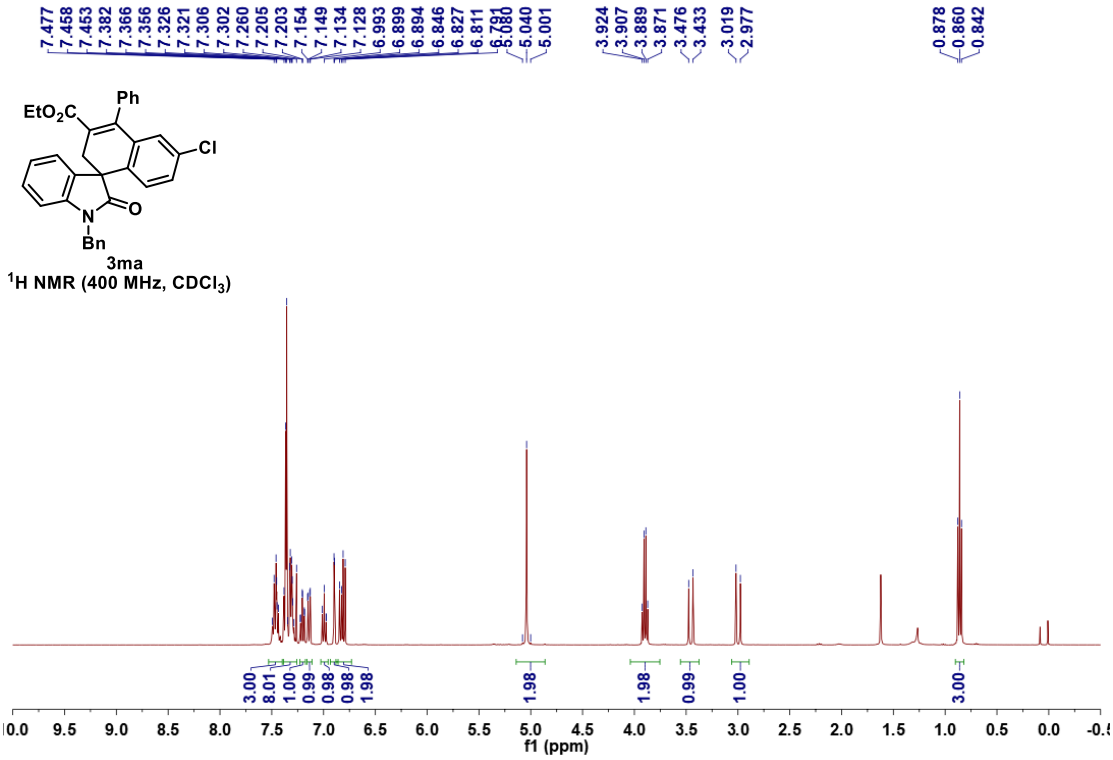
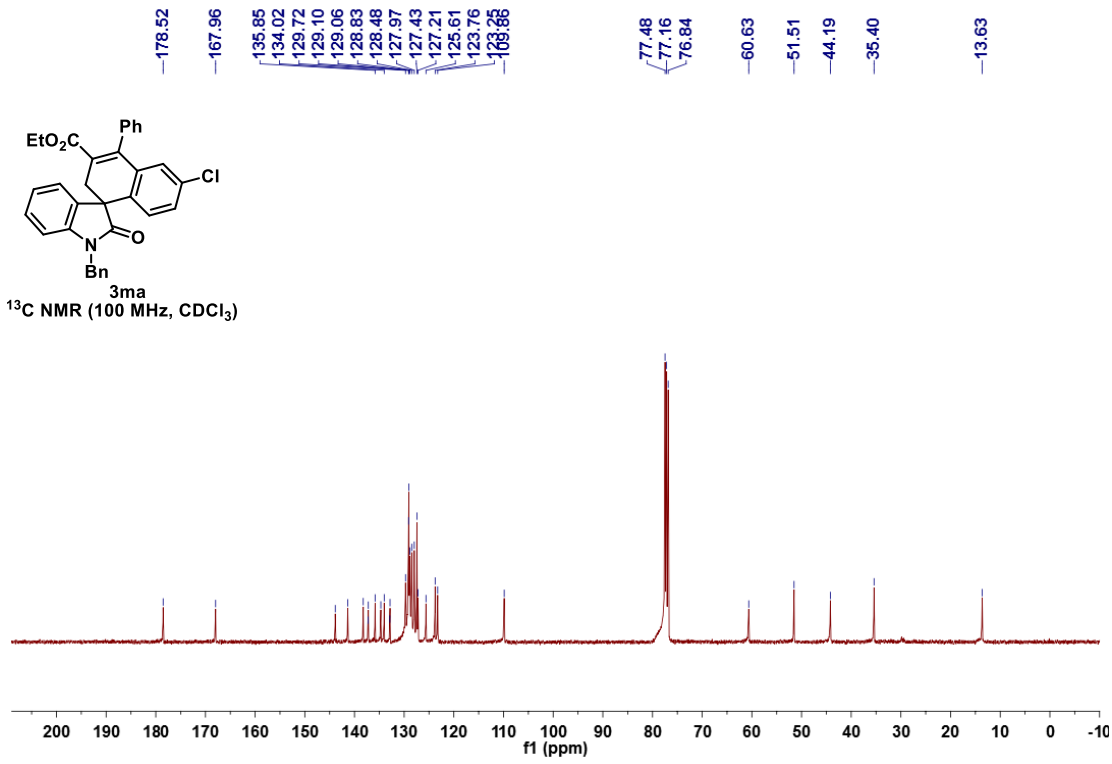
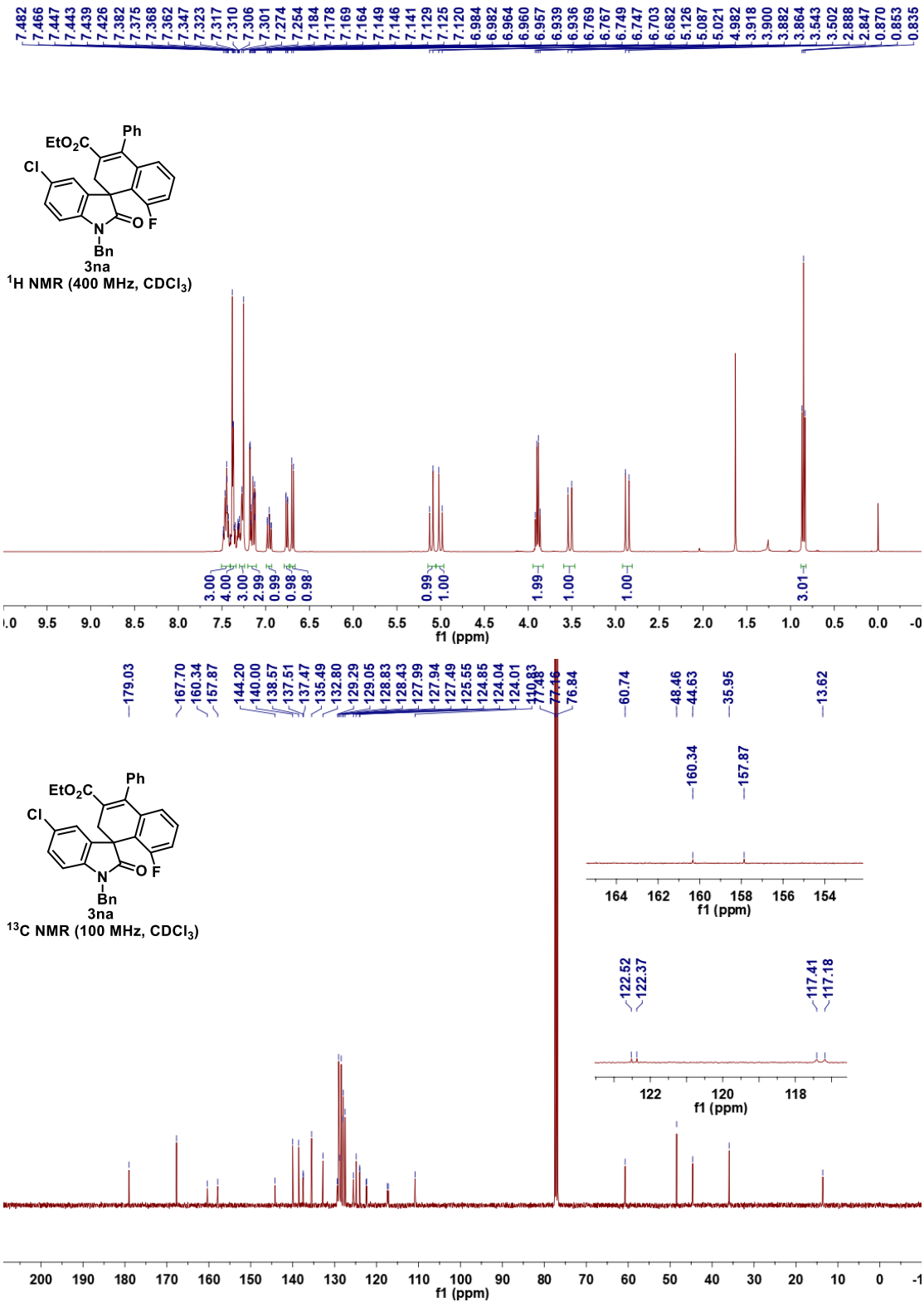
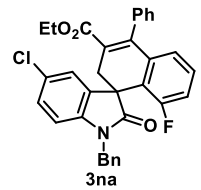
7.444
7.438
7.433
7.430
7.416
7.378
7.360
7.350
7.346
7.341
7.334
7.330
7.327
7.322
7.319
7.300
7.278
7.243
7.225
7.209
7.194
7.190
7.175
7.171
7.163
7.159
7.144
7.140
7.125
6.988
6.971
6.947
6.944
6.940
6.929
6.921
6.910
5.401
5.359
5.318
5.275
3.937
3.919
3.901
3.883
3.511
3.469
3.093
3.051
2.347
0.892
0.874
0.856
EtO2C
Ph
N
O
Bn
3la
1H NMR (400 MHz, CDCl3)
3.00
6.01
2.01
2.01
4.01
1.01
1.02
2.02
1.00
1.00
2.99
3.00
f1 (ppm)


179.97
168.15
145.32
139.46
139.15
137.79
136.55
135.44
133.95
132.51
129.96
129.46
129.03
128.17
127.88
127.50
127.34
125.94
125.69
123.87
123.19
121.90
120.29
77.48
77.16
76.84
60.38
51.22
45.27
35.98
19.00
13.60
EtO2C
Ph
N
O
Bn
3la
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.477
7.458
7.453
7.382
7.366
7.356
7.326
7.321
7.306
7.302
7.260
7.205
7.203
7.154
7.149
7.134
7.128
6.993
6.899
6.894
6.846
6.827
6.811
6.781
6.080
5.040
5.001
3.924
3.907
3.889
3.871
3.476
3.433
3.019
2.977
0.878
0.860
0.842
EtO2C
Ph
Cl
O
N
Bn
3ma
1H NMR (400 MHz, CDCl3)
3.00
8.01
1.00
0.99
0.98
0.98
1.98
1.98
1.98
0.99
1.00
3.00
f1 (ppm)

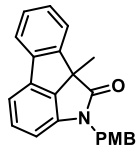

178.52
167.96
135.85
134.02
129.72
129.10
129.06
128.83
128.48
127.97
127.43
127.21
125.61
123.76
77.48
77.16
76.84
60.63
51.51
44.19
35.40
13.63
EtO2C
Ph
Cl
O
N
Bn
3ma
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.482 7.466 7.447 7.443 7.439 7.426 7.382 7.375 7.368 7.362 7.347 7.323 7.317 7.310 7.306 7.301 7.274 7.254 7.184 7.178 7.169 7.164 7.149 7.146 7.141 7.129 7.125 7.120 6.984 6.982 6.964 6.960 6.957 6.939 6.936 6.769 6.767 6.749 6.747 6.703 6.682 5.126 5.087 5.021 4.982 3.918 3.900 3.882 3.864 3.543 3.502 2.888 2.847 0.870 0.853 0.835
EtO2C
Ph
Cl
O F
N
Bn
3na
1H NMR (400 MHz, CDCl3)
3.00 4.00 3.00 2.99 0.99 0.98 0.98 0.99 1.00 1.99 1.00 1.00 3.01
f1 (ppm)
179.03 167.70 160.34 157.87 144.20 140.00 138.57 137.51 137.47 135.49 132.80 129.29 129.05 128.83 128.43 127.99 127.94 127.49 125.55 124.85 124.04 124.01 77.48 77.16 76.84 60.74 48.46 44.63 35.95 13.62
160.34 157.87
164 162 160 158 156 154
f1 (ppm)
122.52 122.37 117.41 117.18
122 120 118
f1 (ppm)
13C NMR (100 MHz, CDCl3)
f1 (ppm)



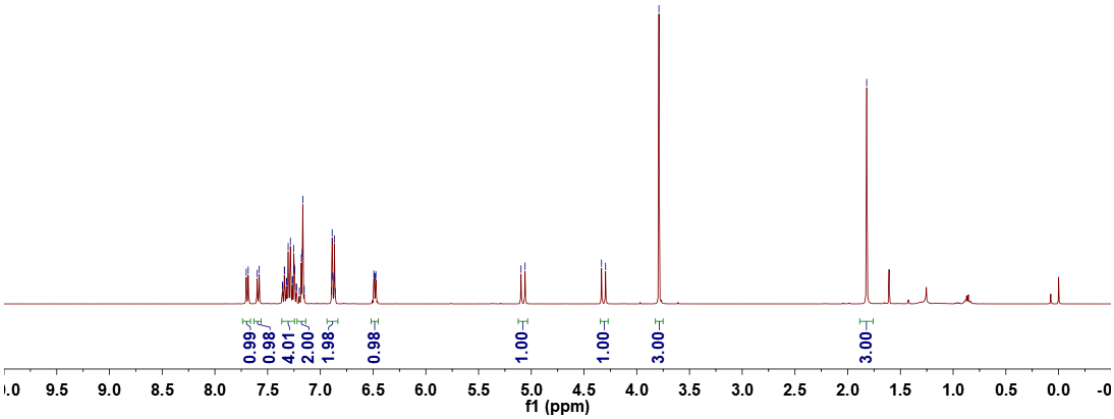
3na

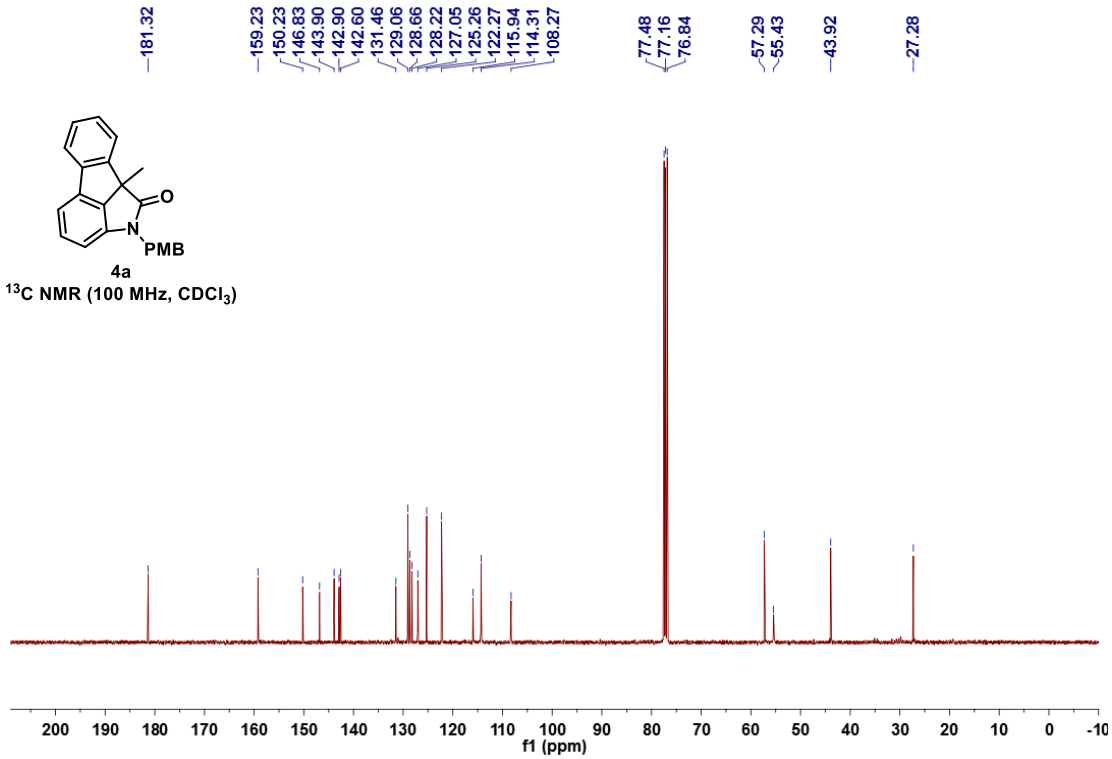
^{19}F NMR (376 MHz, $CDCl_3$)



4a

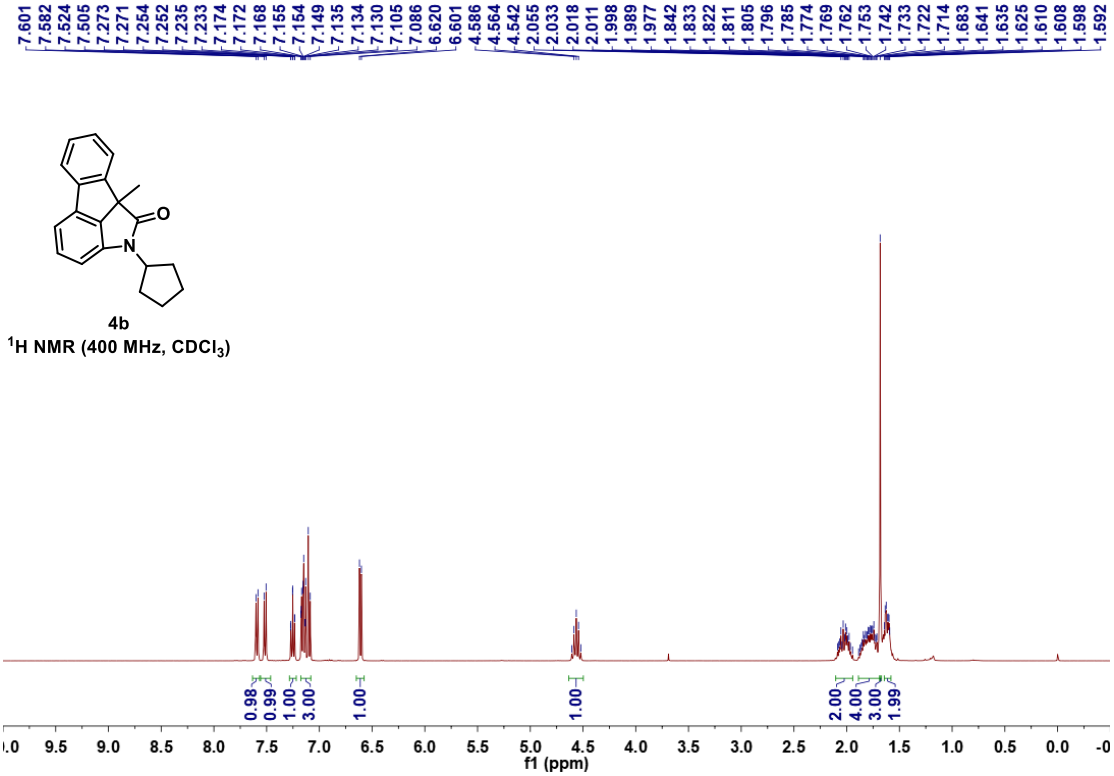
^{1}H NMR (400 MHz, $CDCl_3$)





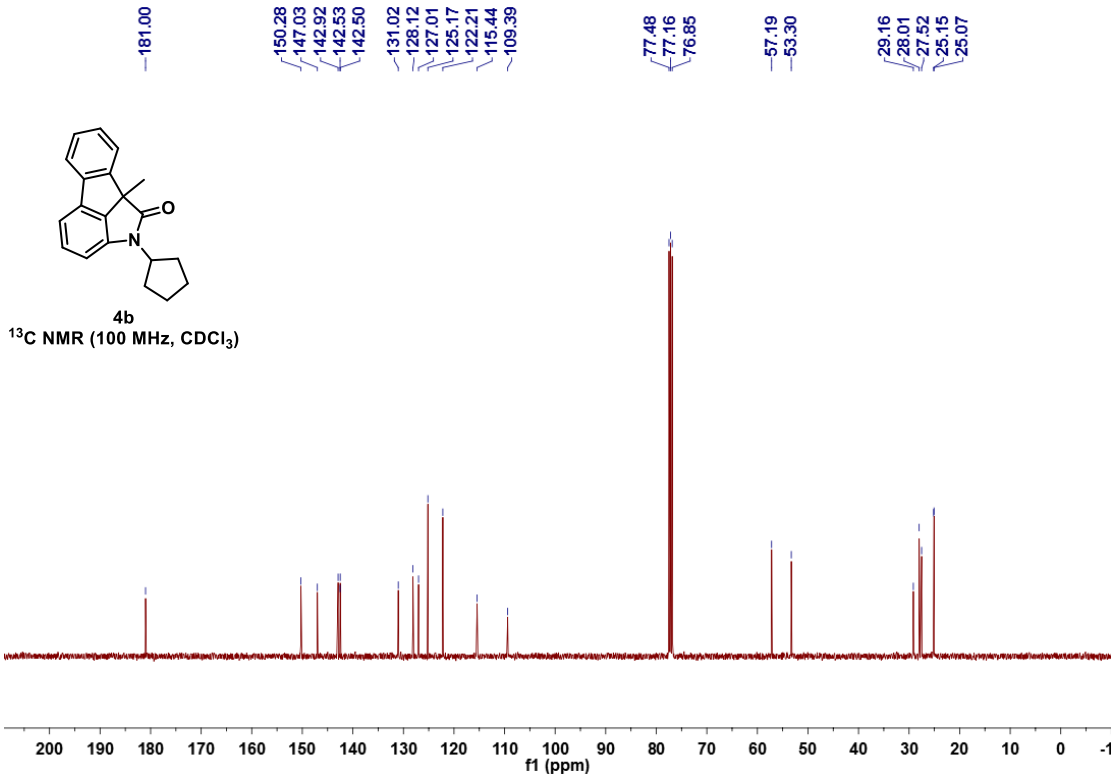
4a

^{13}C NMR (100 MHz, $CDCl_3$)



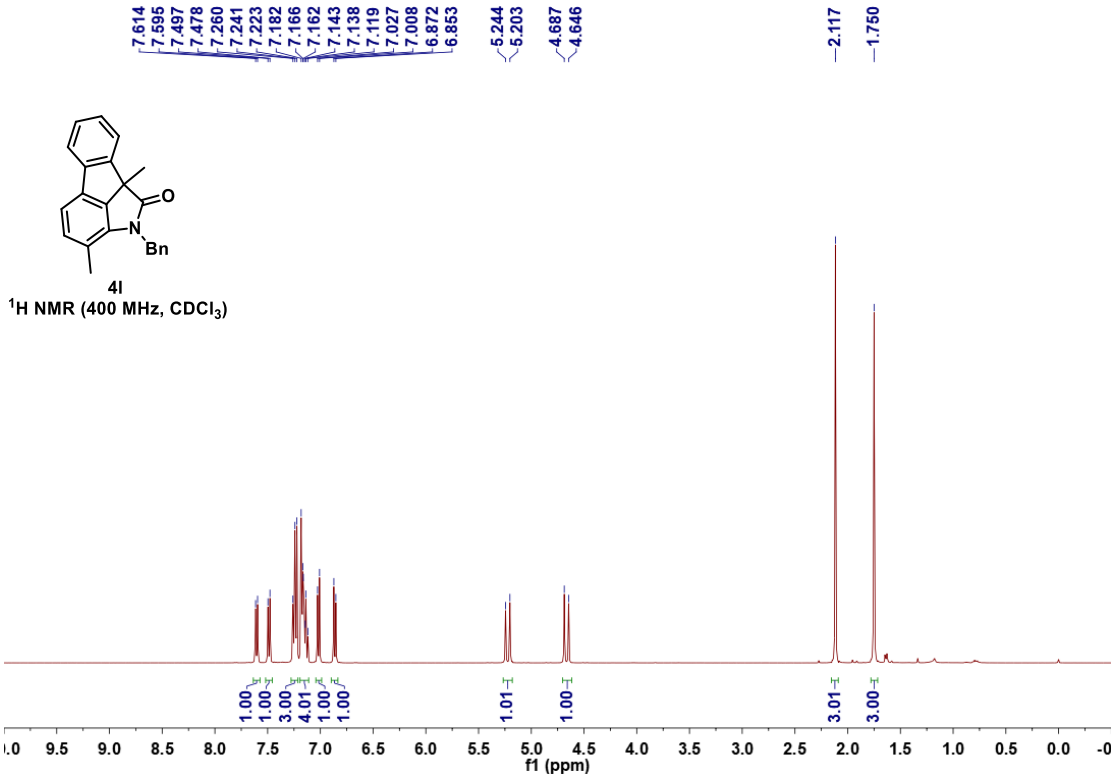
4b

^{1}H NMR (400 MHz, $CDCl_3$)



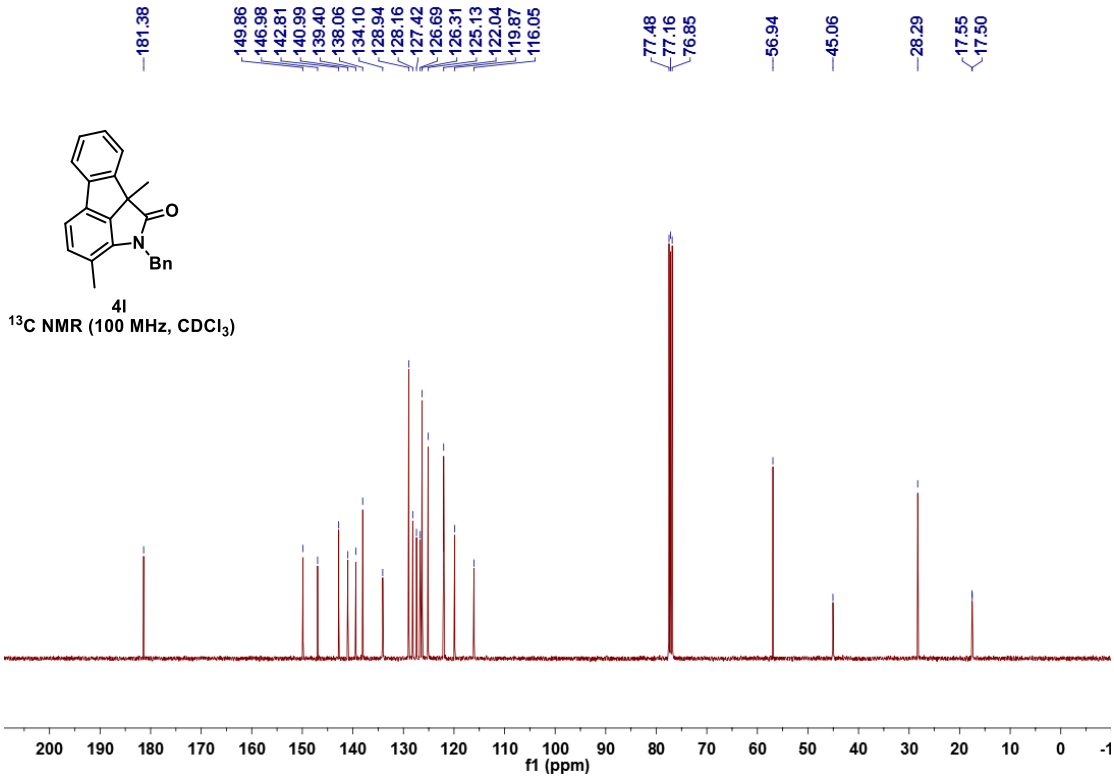
4b

^{13}C NMR (100 MHz, $CDCl_3$)



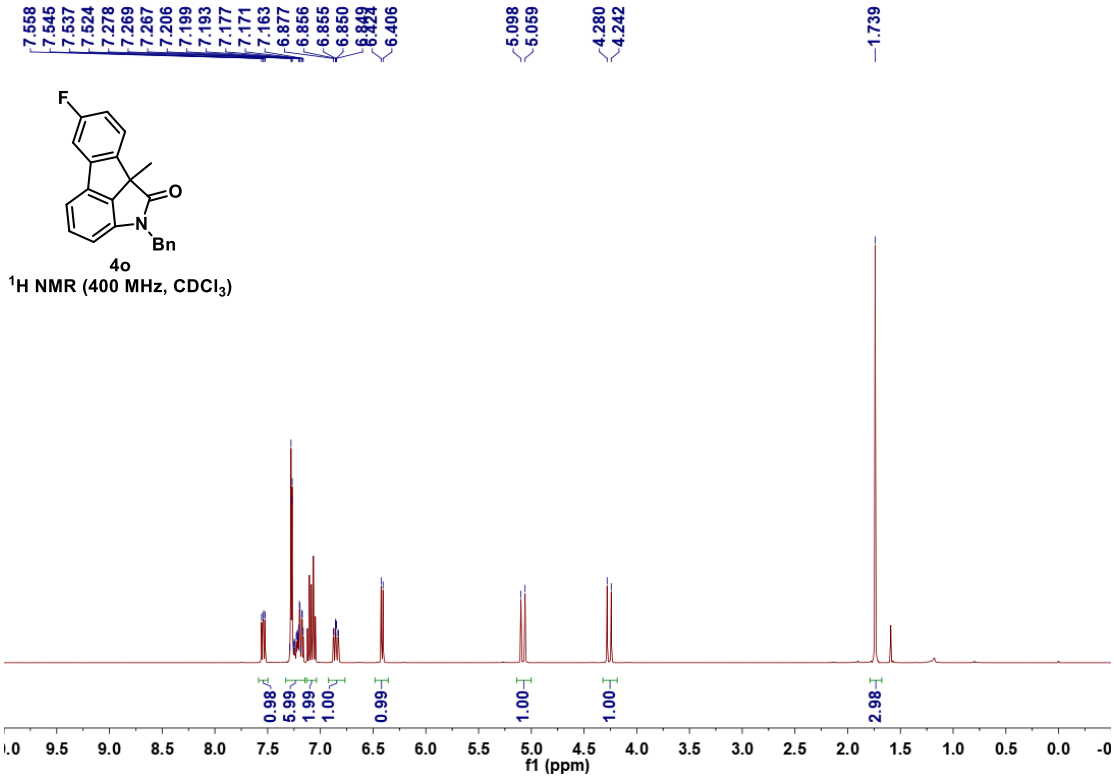
4l

^{1}H NMR (400 MHz, $CDCl_3$)



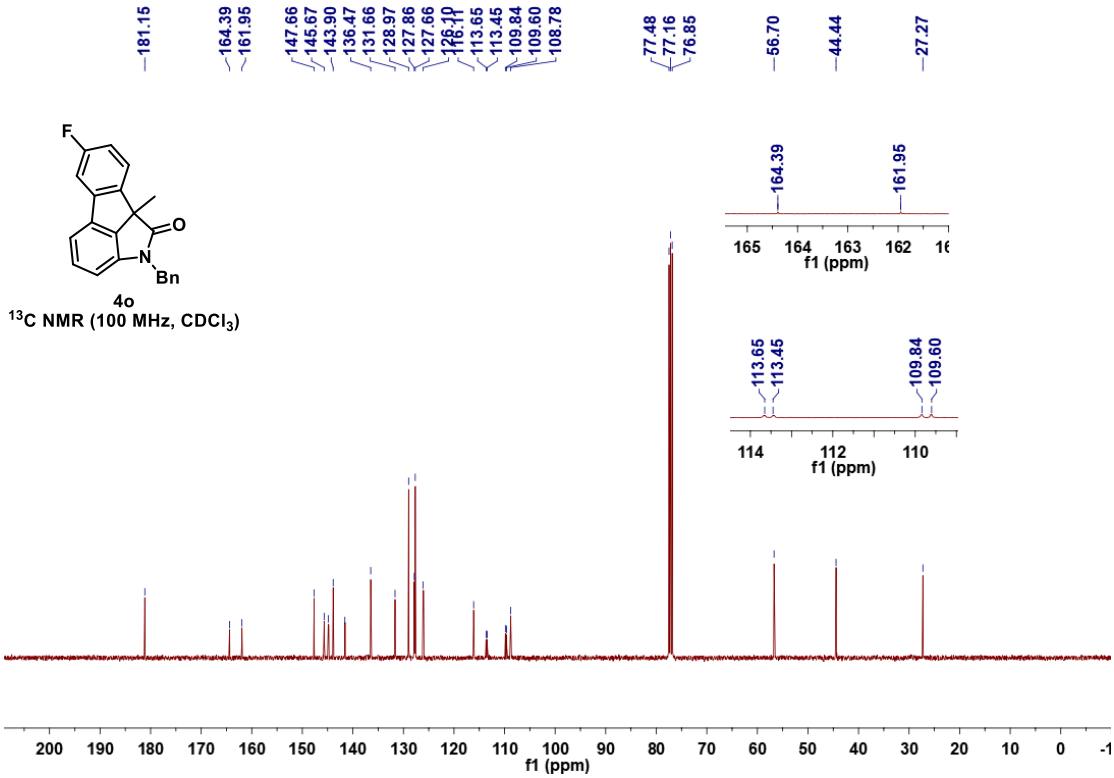
4l

^{13}C NMR (100 MHz, $CDCl_3$)



4o

^{1}H NMR (400 MHz, $CDCl_3$)


181.15
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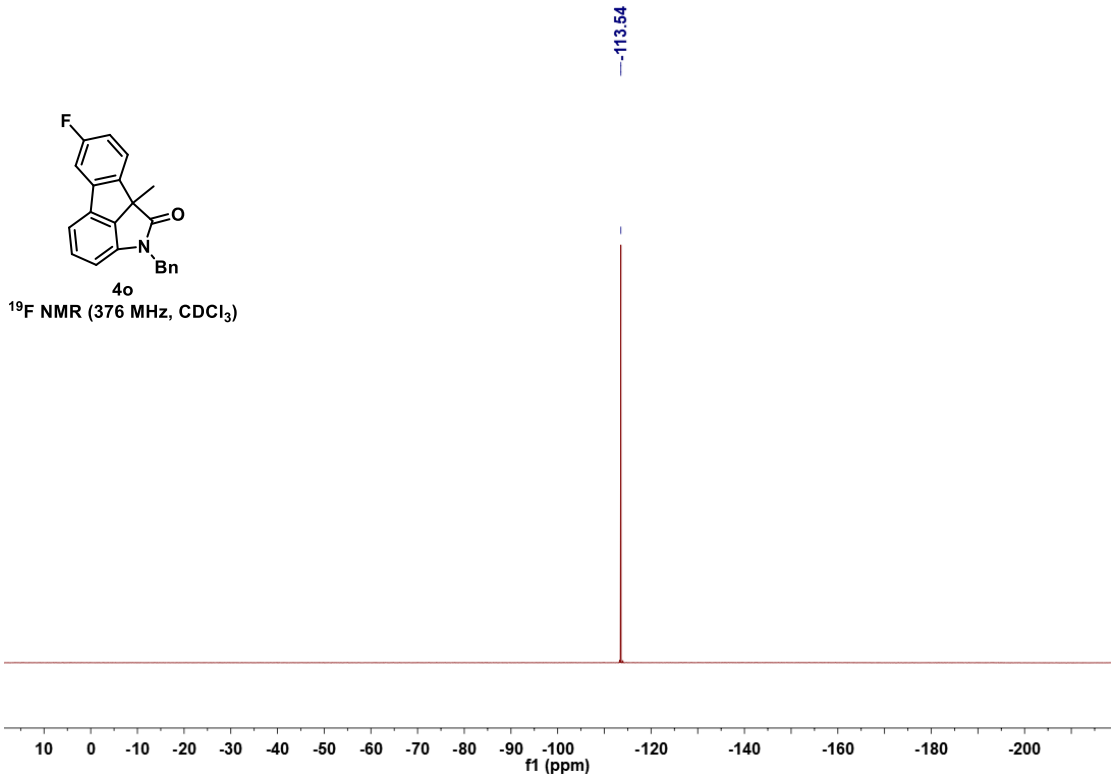
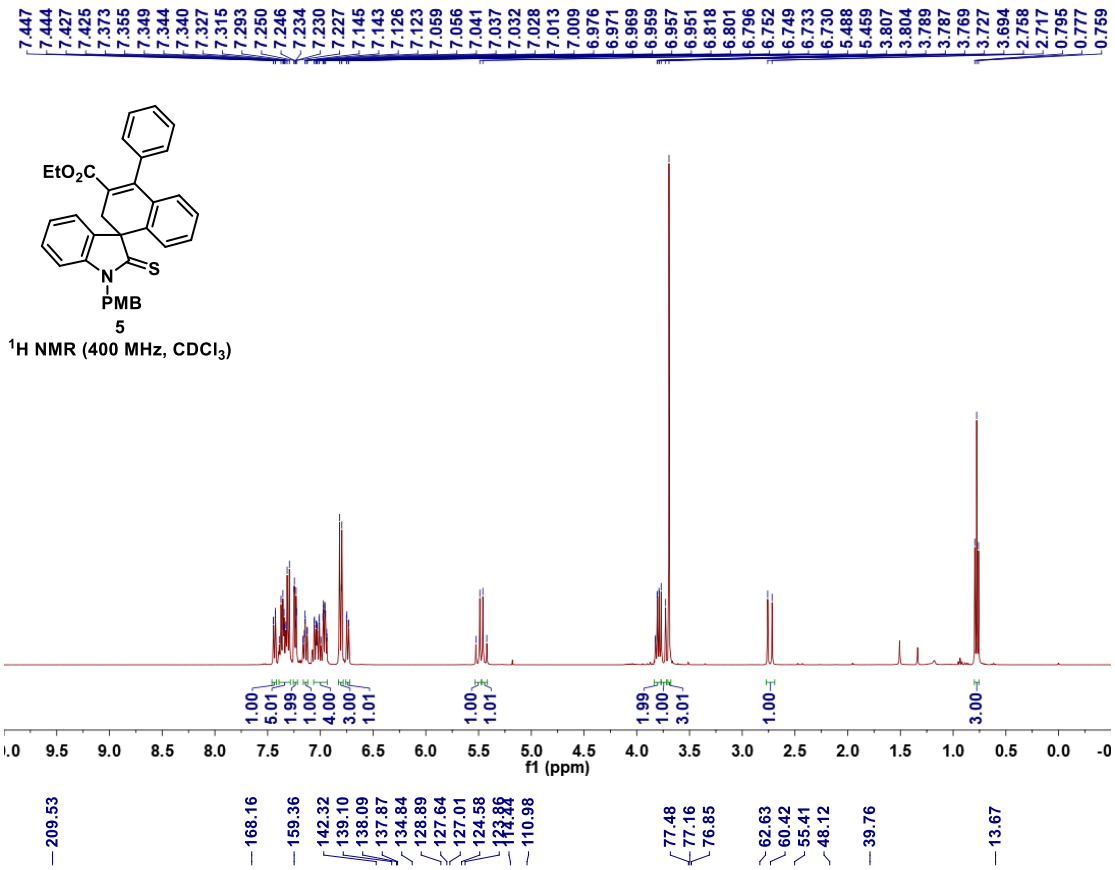
161.95
147.66
145.67
143.90
136.47
131.66
128.97
127.86
127.66
126.10
126.11
113.65
113.45
109.84
109.60
108.78
77.48
77.16
76.85
56.70
44.44
27.27
F
O
N
Bn
4o
13C NMR (100 MHz, CDCl3)
164.39
161.95
165
164
163
162
f1 (ppm)
113.65
113.45
109.84
109.60
114
112
110
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-113.54
F
O
N
Bn
4o
19F NMR (376 MHz, CDCl3)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)


7.447
7.444
7.427
7.425
7.373
7.355
7.349
7.344
7.340
7.327
7.315
7.293
7.250
7.246
7.234
7.230
7.227
7.145
7.143
7.126
7.123
7.059
7.056
7.041
7.037
7.032
7.028
7.013
7.009
6.976
6.971
6.969
6.959
6.957
6.951
6.818
6.801
6.796
6.752
6.749
6.733
6.730
5.488
5.459
3.807
3.804
3.789
3.787
3.769
3.727
3.694
2.758
2.717
0.795
0.777
0.759
EtO2C
N
S
PMB
5
1H NMR (400 MHz, CDCl3)
1.00
5.01
1.99
1.00
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1.01
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1.00
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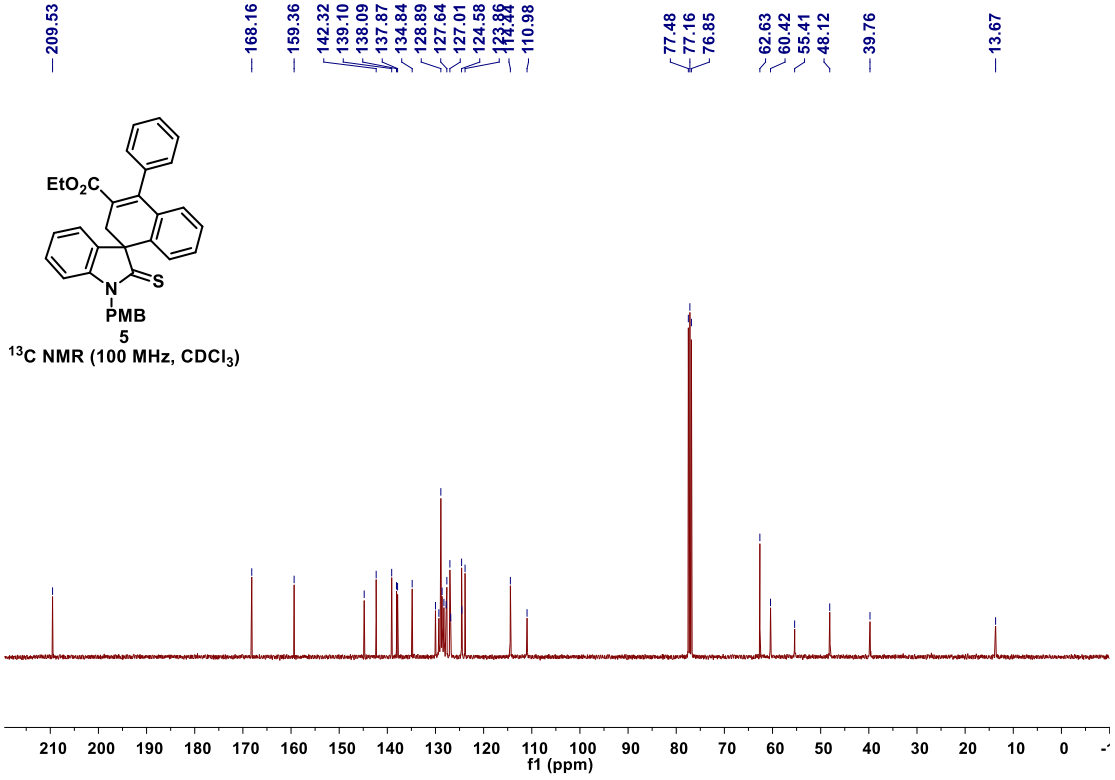
f1 (ppm)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134.84
128.89
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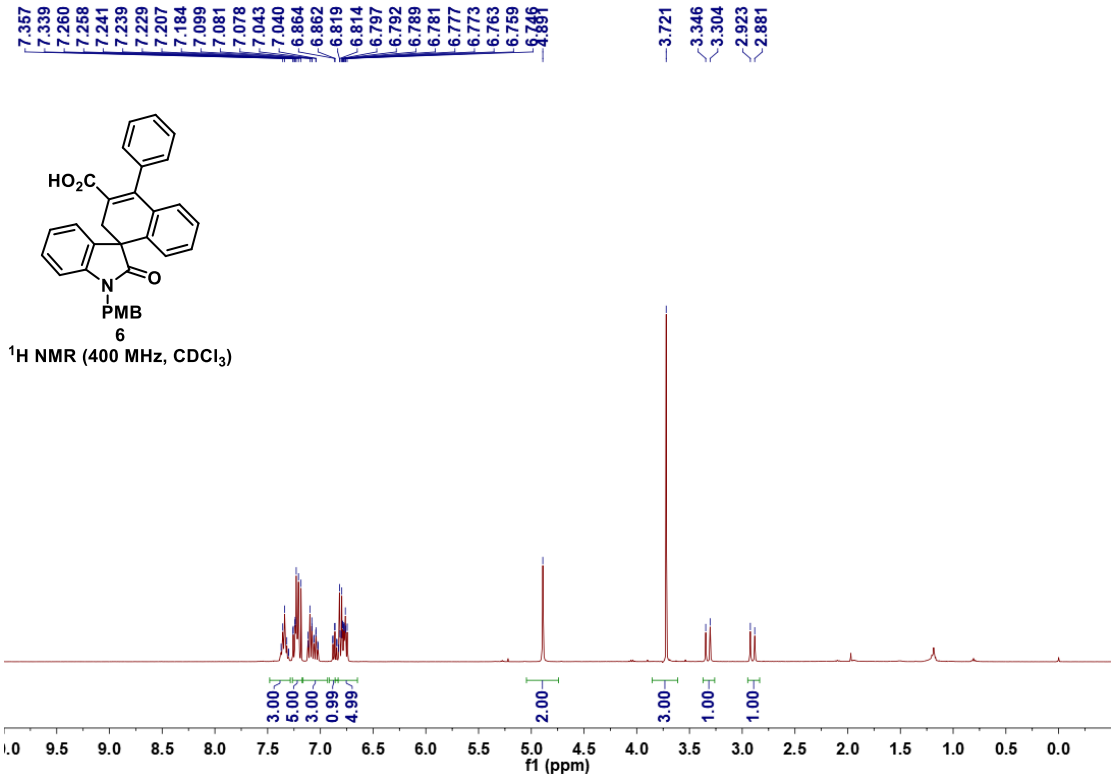
110.98
77.48
77.16
76.85
62.63
60.42
55.41
48.12
39.76
13.67
EtO2C
N
S
PMB
5
13C NMR (100 MHz, CDCl3)
f1 (ppm)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7.040
6.864
6.862
6.819
6.814
6.797
6.792
6.789
6.781
6.777
6.773
6.763
6.759
6.746
4.891
3.721
3.346
3.304
2.923
2.881
HO2C
N
O
PMB
6
1H NMR (400 MHz, CDCl3)
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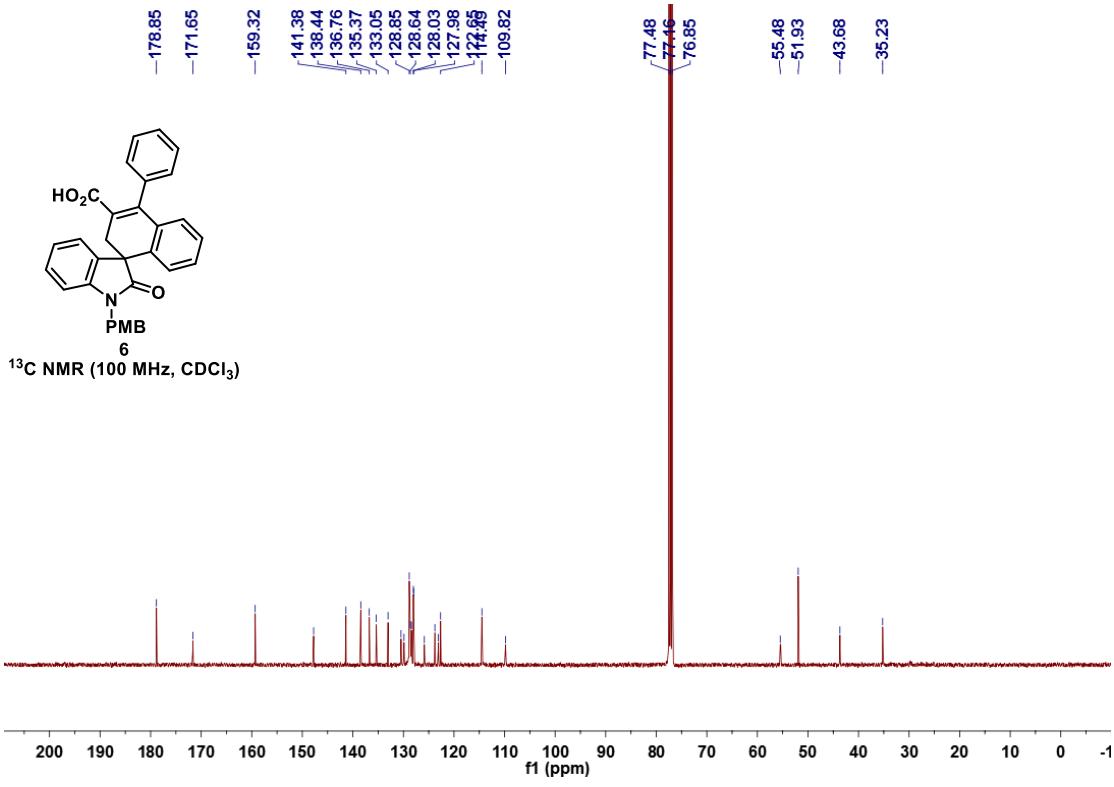
5.00
3.00
0.99
4.99
2.00
3.00
1.00
1.00
f1 (ppm)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141.38
138.44
136.76
135.37
133.05
128.85
128.64
128.03
127.98
109.82
77.48
77.16
76.85
55.48
51.93
43.68
35.23
HO2C
N
O
PMB
6
13C NMR (100 MHz, CDCl3)
f1 (ppm)

Crystallography:

Single crystals of complexes **3ad** (CCDC reference number **2033127**) suitable for X-ray diffraction were obtained by crystallization from n-hexane/CH_2Cl_2 (2:1). Data collection was performed on a Bruker SMART 1000, using graphite- monochromated Mo Ko radiation (ω-2θ scans, λ = 0.71073 Å). Semiempirical absorption corrections were applied for these complexes. The structures were solved by direct methods and refined by full-matrix least squares. All calculations were using the SHELXL-97 program system. The crystal data and summary of X-ray data collection are presented in **Tables 1-8**.

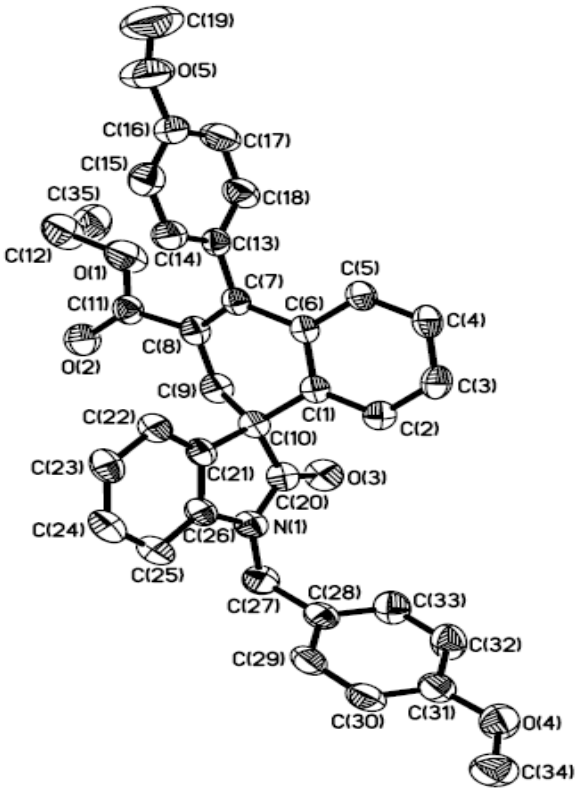

Figure 1. X-ray crystal structures of **3ad**.

X-Ray Crystal Structure of 3ad

Table 1 Crystal data and structure refinement for 2033127.

Empirical formula	$C_{35}H_{31}NO_5$
Formula weight	545.61
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.0610(7)
b/Å	12.6713(7)
c/Å	16.0933(8)
α/°	90
β/°	90.8880(10)
γ/°	90
Volume/Å^3	2867.0(3)
Z	4
ρ_{calc}g/cm^3	1.264
μ/mm^{-1}	0.084
F(000)	1152.0
Crystal size/mm^3	0.22 × 0.21 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.818 to 50.02
Index ranges	$-16 \leq h \leq 16$, $-15 \leq k \leq 13$, $-19 \leq l \leq 19$
Reflections collected	16204
Independent reflections	5051 [R_{int} = 0.0216, R_{sigma} = 0.0215]
Data/restraints/parameters	5051/137/389
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0559, wR_2 = 0.1582

Final R indexes [all data] $R_1 = 0.0744$, $wR_2 = 0.1762$

Largest diff. peak/hole / e $Å^{-3}$ 0.40/-0.38

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 2033127. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
N1	7499.5(10)	4655.8(9)	7880.9(8)	20.2(3)
N2	6731.8(11)	5909.1(8)	7249.8(7)	18.6(3)
N3	6627.0(12)	6788.6(9)	7343.1(8)	25.1(4)
C1	7641.5(13)	5482.2(11)	7714.4(9)	20.4(4)
C2	8347.8(13)	4226.2(12)	8303.6(10)	25.9(4)
C3	9341.2(15)	4595.6(14)	8582.0(12)	37.3(5)
C4	9459.8(17)	5465.9(15)	8412.0(14)	48.1(6)
C5	8602.6(16)	5922.8(13)	7973.7(12)	37.4(5)
C6	5670.3(15)	6970.7(10)	6893.7(10)	24.7(4)
C7	5145.4(14)	6234.9(11)	6508.3(9)	22.8(4)
C8	5846.6(12)	5558.7(10)	6742.1(9)	17.4(4)
C9	5741.7(12)	4649.6(10)	6455.2(8)	16.7(4)
C10	6579.3(12)	4322.8(10)	6077.7(9)	16.4(4)
C11	7111.4(12)	3539.1(10)	6314.2(9)	20.6(4)
C12	7822.6(13)	3208.9(11)	5916.2(10)	25.3(4)
C13	8023.2(13)	3658.3(12)	5279.9(11)	26.8(4)
C14	7519.7(13)	4446.3(11)	5052.9(10)	25.1(4)
C15	6810.9(13)	4784.6(10)	5457(1)	20.6(4)
C16	4857.0(12)	4206.6(10)	6478.2(9)	17.4(4)
C17	4468.9(11)	3366.5(10)	6113.9(9)	16.6(4)
C18	4672.0(12)	3072.2(10)	5409.4(9)	18.8(4)
C19	4223.9(13)	2306.8(11)	5059.7(9)	21.7(4)

C20	3555.5(13)	1817.5(11)	5396.4(10)	23.8(4)
C21	3342.0(13)	2098.8(11)	6091.4(10)	24.7(4)
C22	3794.7(12)	2862.1(11)	6445.7(9)	21.1(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 2033127. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O3	96.4(13)	69.3(12)	85.8(12)	-14.2(9)	15.6(10)	20.0(10)
O4	124.3(18)	89.1(15)	120.7(17)	7.7(12)	-38.9(15)	-17.8(13)
N1	73.7(13)	68.9(13)	57.2(11)	-0.6(9)	10.6(9)	4.7(10)
C1	67.5(13)	38.5(10)	49.0(11)	-9.3(8)	-5.5(10)	6.0(9)
C2	67.9(14)	53.6(13)	61.7(13)	-10.7(10)	-7.4(11)	0.7(10)
C3	74.4(16)	72.0(16)	62.9(14)	-12.2(12)	-21.2(12)	7.1(13)
C4	83.2(17)	77.6(17)	47.6(12)	-0.7(11)	-13.4(12)	12.2(13)
C5	72.5(14)	60.8(14)	49.4(12)	-0.1(10)	-4.0(10)	6.8(11)
C6	66.6(13)	42.7(11)	46.8(11)	-5.4(8)	-6.9(9)	6.2(9)
C7	67.9(13)	41.5(11)	54.2(12)	-1.0(9)	-11.4(10)	1.5(9)
C8	75.2(15)	52.7(12)	52.3(12)	-6.2(9)	-11.9(11)	0.3(11)
C9	87.4(17)	61.5(14)	48.7(12)	-12.8(10)	-7.7(11)	2.4(12)
C10	68.1(13)	48.7(12)	49.0(11)	-6.7(9)	0.8(10)	3.6(10)
C11	83.1(15)	76.4(15)	56.6(13)	3.9(11)	-18.7(11)	-6.0(13)
C20	76.0(15)	61.3(14)	52.4(12)	-9.6(10)	1.1(11)	8.9(12)
C21	72.0(14)	51.6(12)	40.8(10)	-1.9(9)	-3.4(9)	4.9(10)
C22	79.3(15)	56.7(13)	56.9(12)	1.4(10)	6.3(11)	7.3(11)
C23	97.9(19)	58.0(14)	64.7(14)	1.1(11)	2.5(13)	19.5(13)
C24	112(2)	55.1(15)	73.0(16)	11.7(12)	4.5(15)	7.4(15)
C25	98(2)	66.2(16)	68.7(15)	14.5(12)	9.6(14)	-2.4(14)

C26	76.4(15)	61.0(14)	45.9(11)	1.0(10)	3.6(10)	4.2(11)
C27	84.6(17)	99(2)	50.9(13)	0.4(12)	13.6(12)	3.1(15)
C28	80.4(16)	72.7(16)	46.9(12)	3.6(11)	13.1(11)	1.5(13)
C29	94(2)	76.3(18)	72.6(16)	24.7(13)	7.3(15)	0.6(15)
C30	108(2)	64.4(17)	83.3(18)	15.7(13)	4.9(16)	-14.3(15)
C31	97(2)	72.7(17)	69.4(15)	3.6(13)	-4.8(14)	-7.8(15)
C32	117(3)	67.8(18)	114(2)	2.6(16)	-33(2)	6.2(17)
C33	106(2)	63.2(16)	95(2)	-8.2(14)	-14.5(17)	1.9(15)
C34	138(3)	103(3)	99(2)	0.1(19)	-12(2)	-43(2)
O1	85.2(17)	89.6(19)	69.8(15)	-0.5(14)	-23.2(13)	-14.5(14)
O2	92(2)	107(4)	62.8(19)	9(2)	-17.8(17)	2(3)
O5	84.1(19)	148(5)	106(3)	0(3)	26(2)	-12(3)
C12	92(2)	102(2)	84(2)	2.0(18)	-29.1(18)	-18.6(19)
C13	63.2(15)	55(2)	52(2)	10.1(16)	-13.3(11)	-4.6(13)
C14	56(3)	69.5(18)	100(3)	19.3(17)	-2(3)	9.3(16)
C15	60(3)	83(4)	109(4)	13(4)	-2(3)	6(3)
C16	66.2(17)	74(4)	65(3)	1(2)	0.5(16)	-3(2)
C17	69(3)	77(3)	68(3)	3(2)	13(2)	-2(2)
C18	58(4)	66.5(16)	68(3)	8.5(15)	8(3)	-15(2)
C19	111(4)	168(5)	162(5)	12(4)	32(4)	-14(4)
C35	123(3)	158(4)	149(4)	15(3)	-34(3)	-12(3)
O1'	85.2(17)	89.6(19)	69.8(15)	-0.5(14)	-23.2(13)	-14.5(14)
O2'	92(2)	107(4)	62.8(19)	9(2)	-17.8(17)	2(3)
O5'	84.1(19)	148(5)	106(3)	0(3)	26(2)	-12(3)
C12'	92(2)	102(2)	84(2)	2.0(18)	-29.1(18)	-18.6(19)
C13'	63.2(15)	55(2)	52(2)	10.1(16)	-13.3(11)	-4.6(13)
C14'	56(3)	69.5(18)	100(3)	19.3(17)	-2(3)	9.3(16)

C15'	60(3)	83(4)	109(4)	13(4)	-2(3)	6(3)
C16'	66.2(17)	74(4)	65(3)	1(2)	0.5(16)	-3(2)
C17'	69(3)	77(3)	68(3)	3(2)	13(2)	-2(2)
C18'	58(4)	66.5(16)	68(3)	8.5(15)	8(3)	-15(2)
C19'	111(4)	168(5)	162(5)	12(4)	32(4)	-14(4)
C35'	123(3)	158(4)	149(4)	15(3)	-34(3)	-12(3)

Table 4 Bond Lengths for 2033127.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O3	C20	1.218(3)	C24	C25	1.387(4)
O4	C31	1.370(3)	C25	C26	1.377(3)
O4	C34	1.414(4)	C27	C28	1.502(4)
N1	C20	1.362(3)	C28	C29	1.367(4)
N1	C26	1.407(3)	C28	C33	1.379(4)
N1	C27	1.463(3)	C29	C30	1.383(4)
C1	C2	1.382(3)	C30	C31	1.364(4)
C1	C6	1.399(3)	C31	C32	1.381(4)
C1	C10	1.522(3)	C32	C33	1.372(4)
C2	C3	1.386(3)	O1	C12	1.477(6)
C3	C4	1.373(4)	O5	C16	1.413(5)
C4	C5	1.379(3)	O5	C19	1.430(7)
C5	C6	1.396(3)	C12	C35	1.613(8)
C6	C7	1.482(3)	C13	C14	1.3900
C7	C8	1.341(3)	C13	C18	1.3900
C7	C13	1.558(4)	C14	C15	1.3900
C7	C13'	1.433(6)	C15	C16	1.3900
C8	C9	1.496(3)	C16	C17	1.3900
C8	C11	1.486(3)	C17	C18	1.3900
C9	C10	1.534(3)	O1'	C12'	1.454(7)

C10	C20	1.530(3)	O5'	C16'	1.344(6)
C10	C21	1.516(3)	O5'	C19'	1.410(8)
C11	O1	1.354(4)	C12'	C35'	1.542(8)
C11	O2	1.216(5)	C13'	C14'	1.3900
C11	O1'	1.282(5)	C13'	C18'	1.3900
C11	O2'	1.235(7)	C14'	C15'	1.3900
C21	C22	1.378(3)	C15'	C16'	1.3900
C21	C26	1.384(3)	C16'	C17'	1.3900
C22	C23	1.389(3)	C17'	C18'	1.3900
C23	C24	1.360(4)			

Table 5 Bond Angles for 2033127.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C31	O4	C34	119.0(3)	C23	C24	C25	121.5(2)
C20	N1	C26	111.08(19)	C26	C25	C24	117.4(2)
C20	N1	C27	123.1(2)	C21	C26	N1	109.5(2)
C26	N1	C27	125.6(2)	C25	C26	N1	128.4(2)
C2	C1	C6	119.89(19)	C25	C26	C21	122.1(2)
C2	C1	C10	121.2(2)	N1	C27	C28	114.46(19)
C6	C1	C10	118.88(18)	C29	C28	C27	121.7(2)
C1	C2	C3	120.7(2)	C29	C28	C33	117.2(3)
C4	C3	C2	120.0(2)	C33	C28	C27	121.0(3)
C3	C4	C5	119.8(2)	C28	C29	C30	122.5(3)
C4	C5	C6	121.3(2)	C31	C30	C29	119.5(3)
C1	C6	C7	120.73(18)	O4	C31	C32	115.7(3)
C5	C6	C1	118.34(19)	C30	C31	O4	125.3(3)
C5	C6	C7	120.9(2)	C30	C31	C32	119.0(3)
C6	C7	C13	116.5(6)	C33	C32	C31	120.6(3)
C8	C7	C6	119.0(2)	C32	C33	C28	121.1(3)

C8	C7	C13	124.5(6)	C11	O1	C12	122.5(4)
C8	C7	C13'	122.3(9)	C16	O5	C19	114.7(5)
C13'	C7	C6	118.3(9)	O1	C12	C35	99.0(5)
C7	C8	C9	120.37(19)	C14	C13	C7	111.6(5)
C7	C8	C11	125.2(2)	C14	C13	C18	120.0
C11	C8	C9	114.40(19)	C18	C13	C7	128.4(5)
C8	C9	C10	113.23(17)	C15	C14	C13	120.0
C1	C10	C9	109.18(18)	C14	C15	C16	120.0
C1	C10	C20	113.13(18)	C15	C16	O5	116.0(4)
C20	C10	C9	106.44(17)	C17	C16	O5	124.0(4)
C21	C10	C1	112.36(16)	C17	C16	C15	120.0
C21	C10	C9	113.92(18)	C18	C17	C16	120.0
C21	C10	C20	101.57(18)	C17	C18	C13	120.0
O1	C11	C8	115.8(2)	C11	O1'	C12'	114.1(5)
O2	C11	C8	122.8(5)	C16'	O5'	C19'	123.3(8)
O2	C11	O1	121.3(5)	O1'	C12'	C35'	109.2(6)
O1'	C11	C8	112.9(3)	C14'	C13'	C7	129.5(8)
O2'	C11	C8	119.3(5)	C14'	C13'	C18'	120.0
O2'	C11	O1'	127.4(6)	C18'	C13'	C7	110.3(8)
O3	C20	N1	125.2(2)	C13'	C14'	C15'	120.0
O3	C20	C10	126.0(2)	C14'	C15'	C16'	120.0
N1	C20	C10	108.74(19)	O5'	C16'	C15'	117.3(6)
C22	C21	C10	131.6(2)	O5'	C16'	C17'	122.7(6)
C22	C21	C26	119.4(2)	C15	C16'	C17'	120.0
C26	C21	C10	109.08(19)	C18'	C17'	C16'	120.0
C21	C22	C23	119.1(2)	C17'	C18'	C13'	120.0
C24	C23	C22	120.6(2)				

Table 6 Torsion Angles for 2033127.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O4	C31	C32	C33	178.8(3)	C10	C21	C26	C25	-178.9(2)
N1	C27	C28	C29	98.5(3)	C11	C8	C9	C10	-146.2(2)
N1	C27	C28	C33	-83.7(3)	C11	O1	C12	C35	-84.8(6)
C1	C2	C3	C4	-0.1(3)	C11	O1'	C12'	C35'	138.7(8)
C1	C6	C7	C8	-16.7(3)	C20	N1	C26	C21	-0.2(3)
C1	C6	C7	C13	162.4(4)	C20	N1	C26	C25	179.5(2)
C1	C6	C7	C13'	156.8(6)	C20	N1	C27	C28	93.2(3)
C1	C10	C20	O3	-61.3(3)	C20	C10	C21	C22	178.9(2)
C1	C10	C20	N1	121.7(2)	C20	C10	C21	C26	-1.1(2)
C1	C10	C21	C22	57.8(3)	C21	C10	C20	O3	178.1(2)
C1	C10	C21	C26	-122.3(2)	C21	C10	C20	N1	1.0(2)
C2	C1	C6	C5	0.9(3)	C21	C22	C23	C24	0.4(4)
C2	C1	C6	C7	-178.53(18)	C22	C21	C26	N1	-179.19(19)
C2	C1	C10	C9	-149.8(2)	C22	C21	C26	C25	1.0(3)
C2	C1	C10	C20	-31.5(3)	C22	C23	C24	C25	0.1(4)
C2	C1	C10	C21	82.8(2)	C23	C24	C25	C26	-0.1(4)
C2	C3	C4	C5	0.9(4)	C24	C25	C26	N1	179.8(2)
C3	C4	C5	C6	-0.7(4)	C24	C25	C26	C21	-0.5(4)
C4	C5	C6	C1	-0.2(3)	C26	N1	C20	O3	-177.6(2)
C4	C5	C6	C7	179.3(2)	C26	N1	C20	C10	-0.6(2)
C5	C6	C7	C8	163.9(2)	C26	N1	C27	C28	-93.0(3)
C5	C6	C7	C13	-17.1(5)	C26	C21	C22	C23	-1.0(3)
C5	C6	C7	C13'	-22.6(6)	C27	N1	C20	O3	-3.0(4)
C6	C1	C2	C3	-0.8(3)	C27	N1	C20	C10	174.03(19)
C6	C1	C10	C9	33.4(2)	C27	N1	C26	C21	-174.6(2)
C6	C1	C10	C20	151.71(19)	C27	N1	C26	C25	5.1(4)
C6	C1	C10	C21	-94.0(2)	C27	C28	C29	C30	178.1(2)

C6	C7	C8	C9	-1.0(3)	C27	C28	C33	C32	-177.8(3)
C6	C7	C8	C11	179.9(2)	C28	C29	C30	C31	-0.4(4)
C6	C7	C13	C14	-88.8(5)	C29	C28	C33	C32	0.2(4)
C6	C7	C13	C18	92.8(9)	C29	C30	C31	O4	-178.4(3)
C6	C7	C13'	C14'	-95.1(11)	C29	C30	C31	C32	0.3(4)
C6	C7	C13'	C18'	90.0(8)	C30	C31	C32	C33	0.0(5)
C7	C8	C9	C10	34.7(3)	C31	C32	C33	C28	-0.3(5)
C7	C8	C11	O1	17.8(4)	C33	C28	C29	C30	0.1(4)
C7	C8	C11	O2	-165.3(4)	C34	O4	C31	C30	-4.9(5)
C7	C8	C11	O1'	51.5(4)	C34	O4	C31	C32	176.4(3)
C7	C8	C11	O2'	-135.3(5)	O2	C11	O1	C12	1.7(6)
C7	C13	C14	C15	-178.6(10)	O5	C16	C17	C18	179.5(7)
C7	C13	C18	C17	178.4(12)	C13	C7	C8	C9	-180.0(4)
C7	C13'	C14'	C15'	-174.5(18)	C13	C7	C8	C11	1.0(5)
C7	C13'	C18'	C17'	175.5(15)	C13	C14	C15	C16	0.0
C8	C7	C13	C14	90.2(5)	C14	C13	C18	C17	0.0
C8	C7	C13	C18	-88.3(9)	C14	C15	C16	O5	-179.6(6)
C8	C7	C13'	C14'	78.2(12)	C14	C15	C16	C17	0.0
C8	C7	C13'	C18'	-96.8(8)	C15	C16	C17	C18	0.0
C8	C9	C10	C1	-48.7(2)	C16	C17	C18	C13	0.0
C8	C9	C10	C20	-171.11(19)	C18	C13	C14	C15	0.0
C8	C9	C10	C21	77.8(2)	C19	O5	C16	C15	-165.6(6)
C8	C11	O1	C12	178.6(4)	C19	O5	C16	C17	14.8(8)
C8	C11	O1'	C12'	-173.3(5)	O2'	C11	O1'	C12'	14.1(9)
C9	C8	C11	O1	-161.3(3)	O5'	C16'	C17'	C18'	180.0(10)
C9	C8	C11	O2	15.6(5)	C13'	C7	C8	C9	-174.3(6)
C9	C8	C11	O1'	-127.6(4)	C13'	C7	C8	C11	6.7(7)
C9	C8	C11	O2'	45.7(6)	C13'	C14'	C15'	C16'	0.0
C9	C10	C20	O3	58.6(3)	C14'	C13'	C18'	C17'	0.0

C9	C10	C20	N1	-118.4(2)	C14'	C15'	C16'	O5'	-180.0(9)
C9	C10	C21	C22	-67.1(3)	C14'	C15'	C16'	C17'	0.0
C9	C10	C21	C26	112.9(2)	C15'	C16'	C17'	C18'	0.0
C10	C1	C2	C3	-177.58(19)	C16'	C17'	C18'	C13'	0.0
C10	C1	C6	C5	177.79(18)	C18'	C13'	C14'	C15'	0.0
C10	C1	C6	C7	-1.7(3)	C19'	O5'	C16'	C15'	-12.8(12)
C10	C21	C22	C23	178.9(2)	C19'	O5'	C16'	C17'	167.2(9)
C10	C21	C26	N1	0.9(2)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2033127.

Atom	x	y	z	U(eq)
H2	-2291.14	2484.86	25.55	73
H3	-2290.52	2999.01	-1352.33	84
H4	-929.38	3685.54	-1921.88	84
H5	439.81	3817.85	-1126.72	73
H9A	-476.82	3845.82	1767.29	79
H9B	-105.47	2835.72	2230.86	79
H22	516.78	974.83	696.32	77
H23	502.73	-822.05	976.98	88
H24	-723.88	-1559.05	1677.47	96
H25	-1987.91	-536.55	2128.23	93
H27A	-3102.32	2066.76	2702.97	94
H27B	-2857.47	864.04	2766.56	94
H29	-3815.91	-384.93	2020.79	97
H30	-5191.35	-795.76	1300.84	102
H32	-5617.79	2267.34	883.1	120
H33	-4238.02	2659.94	1591.58	106
H34A	-6243.12	-854.21	119.76	170

H34B	-7299.42	-460.11	124.96	170
H34C	-6810.32	-852.81	950.26	170
H12A	3809.99	3919.51	1727.65	112
H12B	3317.86	3344.19	2483.14	112
H14	1820.73	1855.64	-83.29	90
H15	3250.1	1772.85	-781.31	101
H17	3370.85	4940.76	-822.76	85
H18	1941.47	5023.58	-124.74	77
H19A	4580.87	4657.03	-1700.91	220
H19B	5498.3	3973.02	-1560.08	220
H19C	4965.48	4445.45	-796.67	220
H35A	2921.94	5537.71	2041.21	216
H35B	3520.51	5233.18	2835.42	216
H35C	2431.89	4969.02	2786.32	216
H12C	3093.65	3468.12	2460.31	112
H12D	2883.74	4645.01	2706.72	112
H14'	2134.8	1827.67	-17.6	90
H15'	3594.13	2174.76	-612.79	101
H17'	2987.71	5273.72	-634.99	85
H18'	1528.37	4926.65	-39.81	77
H19D	4708.49	2456.62	-1186.41	220
H19E	5319	3080.8	-527.83	220
H19F	5447.16	3300.42	-1478.18	220
H35D	3889.47	4038.88	1261.62	216
H35E	4359.27	4590.41	2037.31	216
H35F	3643.5	5216.3	1466.34	216

Table 8 Atomic Occupancy for 2033127.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
O1	0.562(4)	O2	0.562(4)	O5	0.573(3)
C12	0.562(4)	H12A	0.562(4)	H12B	0.562(4)
C13	0.573(3)	C14	0.573(3)	H14	0.573(3)
C15	0.573(3)	H15	0.573(3)	C16	0.573(3)
C17	0.573(3)	H17	0.573(3)	C18	0.573(3)
H18	0.573(3)	C19	0.573(3)	H19A	0.573(3)
H19B	0.573(3)	H19C	0.573(3)	C35	0.562(4)
H35A	0.562(4)	H35B	0.562(4)	H35C	0.562(4)
O1'	0.438(4)	O2'	0.438(4)	O5'	0.427(3)
C12'	0.438(4)	H12C	0.438(4)	H12D	0.438(4)
C13'	0.427(3)	C14'	0.427(3)	H14'	0.427(3)
C15'	0.427(3)	H15'	0.427(3)	C16'	0.427(3)
C17'	0.427(3)	H17'	0.427(3)	C18'	0.427(3)
H18'	0.427(3)	C19'	0.427(3)	H19D	0.427(3)
H19E	0.427(3)	H19F	0.427(3)	C35'	0.438(4)
H35D	0.438(4)	H35E	0.438(4)	H35F	0.438(4)