Supporting Information

Substrate-directed divergent annulations of sulfur ylides: synthesis of functionalized bispirocyclopentane and bispirocyclopropane derivatives

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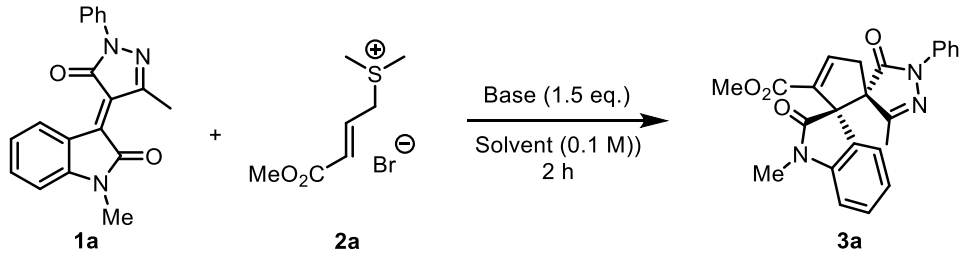
1. General information

Commercially available materials purchased from Alfa Aesar or Sigma-Aldrich were used as received. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a JEOL (600 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ = 7.26, singlet). ^{1}H NMR splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets); m (multiplet), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as m (multiplet) or br (broad). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a JEOL (151 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on Finnigan MAT 95 XP mass spectrometer (Thermo Electron Corporation). X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp.

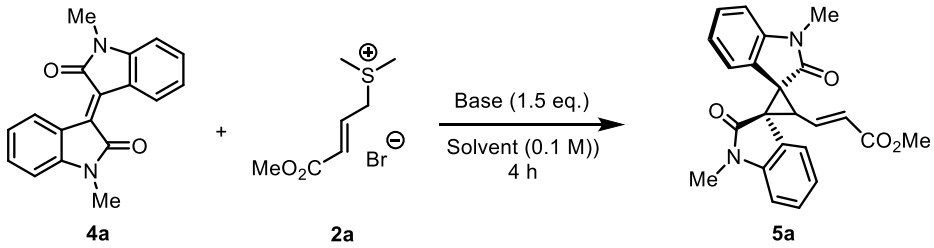
2. Screening of conditions for the [2+3] annulation[a]



Entry	Base	Solvent	Temp(°C)	Yield (%)[b]	dr[c]
1	K_2CO_3	CH_2Cl_2	rt	81	>20:1
2	K_2CO_3	THF	rt	42	>20:1
3	K_2CO_3	Toluene	rt	12	-
4	K_2CO_3	DMF	rt	43	>20:1
5	K_2CO_3	MeOH	rt	39	>20:1
6	**K_2CO_3**	**MeCN**	**rt**	**92**	**>20:1**
7	Na_2CO_3	MeCN	rt	47	>20:1
8	Cs_2CO_3	MeCN	rt	68	>20:1
9	DBU	MeCN	rt	35	-
10	DABCO	MeCN	rt	34	-
11	Et_3N	MeCN	rt	70	>20:1
12	DMAP	MeCN	rt	40	>20:1
13	NaOH	MeCN	rt	15	-
14	K_2CO_3	MeCN	0	40	>20:1
15	K_2CO_3	MeCN	50	91	>20:1
15[d]	K_2CO_3	MeCN	rt	85	>20:1

[a] General conditions (unless otherwise specified): **1a** (0.1 mmol), **2a** (0.15 mmol), Base (1.5 equiv), solvent (1.0 mL), rt, 2 h. [b] Isolated yield. [c] The diastereomeric ratio was determined by ^{1}H NMR spectroscopy. [d] 1.0 eq. K_2CO_3 was used

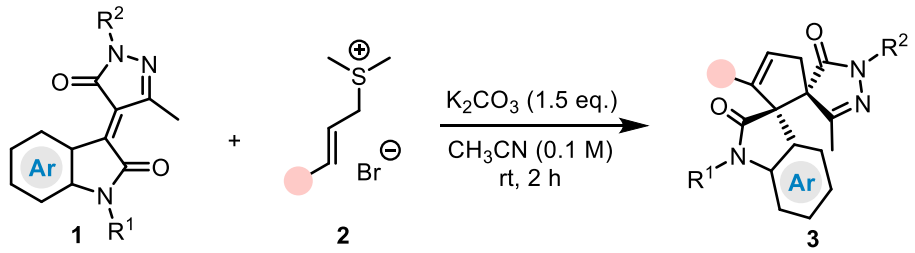
3. Screening of conditions for the [2+1] annulation [a]



Entry	Base	Solvent	Temp(°C)	Yield (%)[b]	E:Z[c]
1	K_2CO_3	CH_2Cl_2	rt	62	>20:1
2	K_2CO_3	THF	rt	88	>20:1
3	K_2CO_3	Toluene	rt	<15	-
4	K_2CO_3	DMF	rt	80	>20:1
5	K_2CO_3	MeOH	rt	<10	>20:1
6	K_2CO_3	MeCN	rt	71	>20:1
7	Na_2CO_3	THF	rt	51	>20:1
8	**Cs_2CO_3**	**THF**	**rt**	**93**	**>20:1**
9	DBU	THF	rt	90	>20:1
10	DABCO	THF	rt	42	-
11	Et_3N	THF	rt	38	-
12	NaOH	THF	rt	45	-
13	Cs_2CO_3	THF	0	45	>20:1
14	Cs_2CO_3	THF	50	90	>20:1

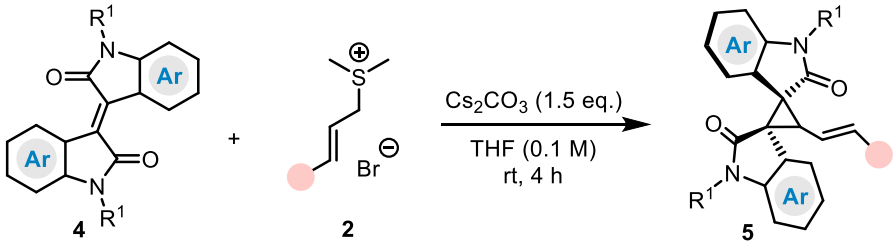
[a] General conditions (unless otherwise specified): **4a** (0.1 mmol), **2a** (0.15 mmol), Base (1.5 equiv), solvent (1.0 mL), rt, 4 h. [b] Isolated yield. [c] The E:Z ratio was determined by ^{1}H NMR spectroscopy.

4. General procedure for the synthesis of 3



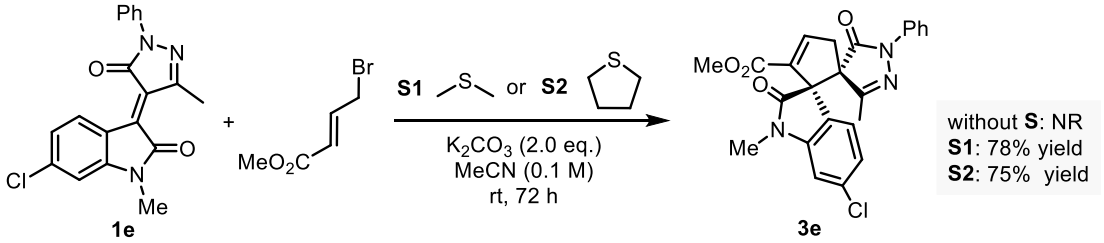
To a solution of oxindole-derived pyrazolones **1**[1] (0.10 mmol, 1.0 equiv.) in MeCN (1.0 mL) were added the sulfonium salts **2** (0.15 mmol, 1.5 equiv.) and K_2CO_3 (0.15 mmol, 1.5 equiv.). The reaction mixture was stirred at room temperature 2 h and monitored by TLC. After that solvent removal in vacuo gave the crude product **3**, which was directly purified by flash chromatography (FC). The yield of cycloaddition products **3** and diastereomeric ratio were determined at this stage.

5. General procedure for the synthesis of 5

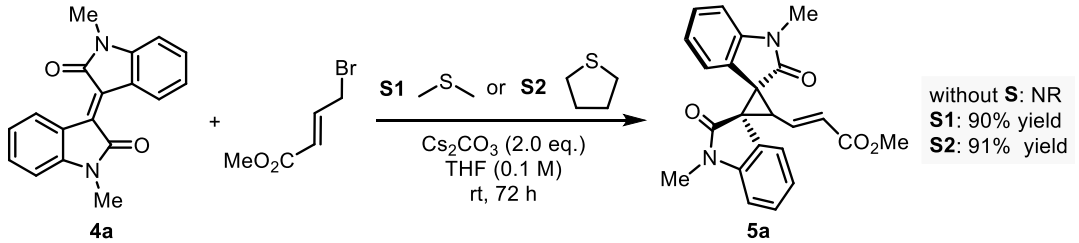


To a solution of isoindigos **4**[2] (0.10 mmol, 1.0 equiv.) in THF (1.0 mL) were added the sulfonium salts **2** (0.15 mmol, 1.5 equiv.) and Cs_2CO_3 (0.15 mmol, 1.5 equiv.). The reaction mixture was stirred at room temperature 4 h and monitored by TLC. After that solvent removal in vacuo gave the crude product **5**, which was directly purified by flash chromatography (FC). The yield of [2+1] annulation adducts **5** were determined at this stage and the structure were confirmed by ^{1}H NMR, ^{13}C NMR spectrum.

6. General procedure for the multi-component reaction

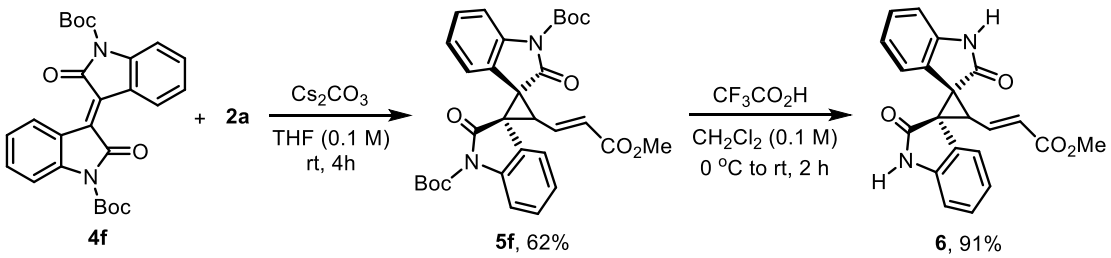


To a solution of **1e** (0.10 mmol, 35.1 mg, 1.0 equiv.) in MeCN (1.0 mL) were added the thioether **S** (0.6 mmol, 6.0 equiv.), methyl-4-bromobut-2-enoate (0.2 mmol, 35.8 mg, 2.0 equiv.) and K_2CO_3 (0.20 mmol, 27.6 mg, 2.0 equiv.). The reaction mixture was stirred at room temperature 72 h and monitored by TLC. After the given reaction time, solvent removal in vacuo gave the crude product **3e**, which was directly purified by flash chromatography (FC).



To a solution of or **4a** (0.10 mmol, 29.0 mg, 1.0 equiv.) in THF (1.0 mL) were added the thioether **S** (0.6 mmol, 6.0 equiv.), methyl-4-bromobut-2-enoate (0.2 mmol, 35.8 mg, 2.0 equiv.) and Cs_2CO_3 (0.20 mmol, 65.1 mg, 2.0 equiv.). The reaction mixture was stirred at room temperature 72 h and monitored by TLC. After the given reaction time, solvent removal in vacuo gave the crude product or **5a**, which was directly purified by flash chromatography (FC).

7. Scale-up synthesis and deprotection of 5f



To a solution of Isoindigos **4f** (1.0 mmol, 462.5 mg, 1.0 equiv.) in THF (10.0 mL) were added the sulfonium salts **2a** (1.5 mmol, 361.5 mg, 1.5 equiv.) and Cs_2CO_3 (1.5 mmol, 488.7 mg, 1.5 equiv.). The reaction mixture was stirred at room temperature 4 h and monitored by TLC. After that solvent removal in vacuo gave the crude product **5**, which was directly purified by flash chromatography (FC). The [2+1] annulation adducts **5f** were isolated in 62% yield (347.2 mg).

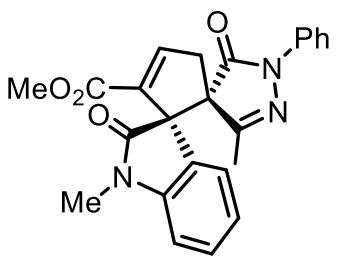
To a solution of cycloaddition products **5f** (0.5 mmol, 280.0 mg, 1.0 equiv.) in CH_2Cl_2 (5.0 mL) was added CF_3COOH (2.5 mmol, 185.7 μL, 5.0 equiv.) at 0 ℃, maintaining the temperature and stirring for 30 minutes. After that, the reaction was allowed to stir at room temperature for another 2 h. The solvent was then removed in vacuo and the residue was purified by flash column chromatography to give the desired deprotection product **6** (91% yield, 163.8 mg) as a white solid.

8. Stereochemistry determination and X-ray structures

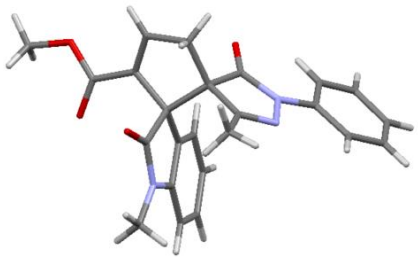
Configurations of the products **3** were assigned based on the crystal X-ray structure of **3a** (CCDC number 2305021) which was obtained as colorless solid *via* evaporation of a hexane/CH_2Cl_2 solution.

Configurations of the products **5** were assigned based on the crystal X-ray structure of **5a** (CCDC number 2305023) which was obtained as colorless needles *via* evaporation of a hexane/CH_2Cl_2 solution.

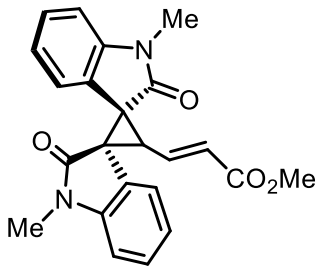
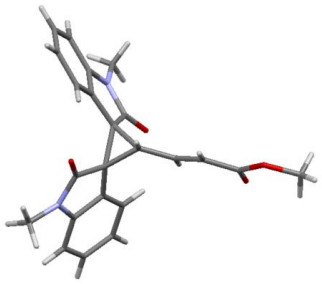
These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



3a

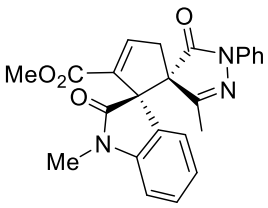


3a, CCDC 2305021

 **5a**	 **5a**, CCDC 2305023

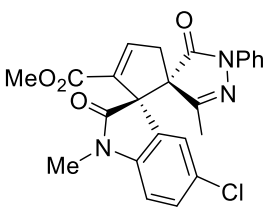
9. Compound characterization

Methyl 1,3''-dimethyl-2,5''-dioxo-1''-phenyl-1'',5''-dihydrodispiro[indoline-3,2'-cyclopentane-1',4''-pyrazol]-3'-ene-3'-carboxylate



Cycloaddition product **3a** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 10:1 to 2:1) in 92% yield (38.1 mg, >20:1 dr). White solid, melting point: 160-161 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 3.08 (dd, *J* = 1.8, 8.1 Hz, 2H), 3.21 (s, 3H), 3.59 (s, 3H), 6.79 (d, *J* = 7.2 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.24-7.32 (m, 4H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 16.3, 26.6, 37.8, 51.8, 65.0, 65.0, 108.2, 118.9 (2C), 122.6, 125.0, 125.2, 125.7, 128.6 (2C), 129.6, 136.6, 137.4, 143.6, 145.1, 159.5, 162.5, 171.7, 174.0; HRMS calcd. for $C_{24}H_{22}N_3O_4$ $[M + H]^+$: 416.1605, found: 416.1605.

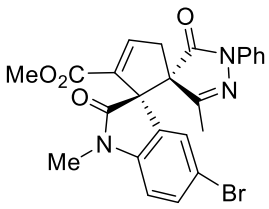
Methyl 5-chloro-1,3''-dimethyl-2,5''-dioxo-1''-phenyl-1'',5''-dihydrodispiro [indoline-3,2'-cyclopentane-1',4''-pyrazol]-3'-ene-3'-carboxylate



Cycloaddition product **3b** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 10:1 to 2:1) in 80% yield (35.9 mg, >20:1 dr). White solid, melting point: 197-198 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.21 (s, 3H), 3.02 (dd, *J* = 3.0, 18.0 Hz, 1H), 3.14 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.19 (s, 3H),

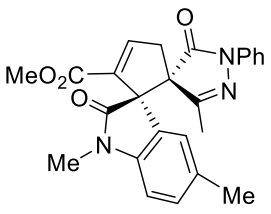
3.62 (s, 3H), 6.70 (d, *J* = 8.4 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.22 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.31-7.34 (m, 3H), 7.38 (d, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 16.3, 26.8, 37.8, 52.0, 64.8, 65.0, 109.1, 119.0 (2C), 125.3, 126.2, 127.0, 128.1, 128.8 (2C), 129.5, 136.2, 137.2, 142.2, 145.5, 159.2, 162.4, 171.5, 173.7; HRMS calcd. for $C_{24}H_{21}ClN_3O_4$ $[M + H]^+$: 450.1215, found: 450.1218.

Methyl 5-bromo-1,3''-dimethyl-2,5''-dioxo-1''-phenyl-1'',5''-dihydrodispiro [indoline-3,2'-cyclopentane-1',4''-pyrazol]-3'-ene-3'-carboxylate



Cycloaddition product **3c** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 10:1 to 2:1) in 92% yield (45.4 mg, >20:1 dr). White solid, melting point: 196-197 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.21 (s, 3H), 3.01 (dd, *J* = 3.0, 18.0 Hz, 1H), 3.14 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.19 (s, 3H), 3.63 (s, 3H), 6.66 (d, *J* = 8.4 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.32-7.35 (m, 3H), 7.37 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.51 (d, *J* = 2.4 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 16.3, 26.7, 37.7, 52.0, 64.8, 64.9, 109.6, 115.4, 119.1 (2C), 125.3, 127.3, 128.8 (2C), 128.9, 132.4, 136.1, 137.1, 142.7, 145.6, 159.2, 162.4, 171.5, 173.6; HRMS calcd. for $C_{24}H_{21}BrN_3O_4$ $[M + H]^+$: 494.0710, found: 494.0712.

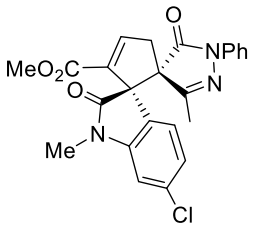
Methyl 1,3'',5-trimethyl-2,5''-dioxo-1''-phenyl-1'',5''-dihydrodispiro[indoline-3, 2'-cyclopentane-1',4''-pyrazol]-3'-ene-3'-carboxylate



Cycloaddition product **3d** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 10:1 to 2:1) in 79% yield (33.9 mg, >20:1 dr). White solid, melting point: 194-195 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.18 (s, 3H), 2.20 (s, 3H), 2.96 (dd, *J* = 3.0, 18.0 Hz, 1H), 3.17 (dd, *J* = 3.0, 18.6 Hz, 1H), 3.19 (s, 3H), 3.59 (s, 3H), 6.66 (d, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.18 (s, 1H), 7.29-7.32 (m, 3H), 7.65 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR

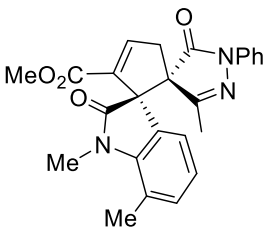
(151 MHz, $CDCl_3$): δ = 16.1, 21.0, 26.6, 37.4, 51.8, 65.1, 65.2, 107.8, 118.8 (2C), 125.0, 125.0, 126.4, 128.6 (2C), 129.8, 132.0, 136.3, 137.3, 141.3, 145.4, 159.2, 162.6, 172.1, 173.9; HRMS calcd. for $C_{25}H_{24}N_3O_4$ $[M + H]^+$: 430.1761, found: 430.1763.

Methyl 6-chloro-1,3''-dimethyl-2,5''-dioxo-1''-phenyl-1'',5''-dihydrodispiro [indo line-3,2'-cyclopentane-1',4''-pyrazol]-3'-ene-3'-carboxylate



Cycloaddition product **3e** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 10:1 to 2:1) in 90% yield (40.4 mg, >20:1 dr). White solid, melting point: 169-170 ℃. ^1H NMR (600 MHz, $CDCl_3$): δ = 2.21 (s, 3H), 3.01 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.14 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.20 (s, 3H), 3.61 (s, 3H), 6.80 (d, *J* = 1.2 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.31-7.34 (m, 3H), 7.68 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 16.3, 26.8, 37.9, 51.9, 64.6, 64.9, 109.1, 118.8 (2C), 122.5, 123.7, 125.2, 126.7, 128.8 (2C), 135.4, 136.4, 137.3, 144.8, 145.2, 159.4, 162.4, 171.5, 174.1; HRMS calcd. for $C_{24}H_{21}ClN_3O_4$ $[M + H]^+$: 450.1215, found: 450.1214.

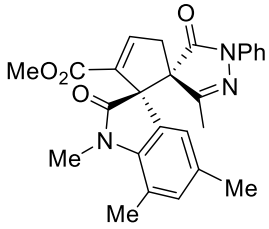
Methyl 1,3'',7-trimethyl-2,5''-dioxo-1''-phenyl-1'',5''-dihydrodispiro [indoline -3, 2'-cyclopentane-1',4''-pyrazol]-3'-ene-3'-carboxylate



Cycloaddition product **3f** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 10:1 to 2:1) in 83% yield (35.6 mg, >20:1 dr). White solid, melting point: 195-196 ℃. ^1H NMR (600 MHz, $CDCl_3$): δ = 2.24 (s, 3H), 2.51 (s, 3H), 3.01 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.09 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.47 (s, 3H), 3.61 (s, 3H), 6.86 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.19 (d, 7.8 Hz, 1H), 7.28-7.31 (m, 3H), 7.67 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 16.4, 19.1, 30.0, 37.8, 51.8, 64.7, 65.1, 118.9 (2C), 119.5, 122.2, 123.6, 125.0, 125.7, 128.6 (2C), 133.5, 136.9, 137.4, 141.2, 144.7, 159.8,

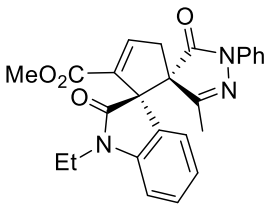
162.5, 171.5, 174.7; HRMS calcd. for $C_{25}H_{24}N_3O_4$ $[M + H]^+$: 430.1761, found: 430.1762.

Methyl 1,3'',5,7-tetramethyl-2,5''-dioxo-1''-phenyl-1'',5''-dihydrodispiro [indoline-3,2'-cyclopentane-1',4''-pyrazol]-3'-ene-3'-carboxylate



Cycloaddition product **3g** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 10:1 to 2:1) in 68% yield (30.1 mg, >20:1 dr). White solid, melting point: 203-204 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.14 (s, 3H), 2.21 (s, 3H), 2.46 (s, 3H), 2.96 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.13 (dd, *J* = 2.4, 17.4 Hz, 1H), 3.45 (s, 3H), 3.61 (s, 3H), 6.75 (s, 1H), 7.00 (s, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.29-7.31 (m, 3H), 7.65 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 16.2, 18.9, 20.7, 30.0, 37.4, 51.8, 64.9, 65.3, 118.9 (2C), 119.1, 124.2, 125.0, 125.6, 128.6 (2C), 131.6, 134.0, 136.7, 137.4, 138.9, 145.1, 159.5, 162.6, 171.9, 174.7; HRMS calcd. for $C_{26}H_{26}N_3O_4$ $[M + H]^+$: 444.1918, found: 444.1921.

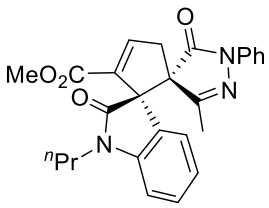
Methyl 1-ethyl-3''-methyl-2,5''-dioxo-1''-phenyl-1'',5''-dihydrodispiro [indoline-3,2'-cyclopentane-1',4''-pyrazol]-3'-ene-3'-carboxylate



Cycloaddition product **3h** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 10:1 to 2:1) in 84% yield (36.0 mg, >20:1 dr). White solid, melting point: 191-192 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.20 (t, *J* = 7.2 Hz, 3H), 2.26 (s, 3H), 3.03 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.11 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.57 (s, 3H), 3.74 (q, *J* = 7.2 Hz, 2H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.23-7.26 (m, 1H), 7.28-7.32 (m, 3H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 12.1, 16.4, 35.0, 37.7, 51.7, 65.0, 65.1, 108.3, 118.9 (2C), 122.3, 125.0, 125.6, 125.9, 128.6 (2C), 129.5, 136.9, 137.4, 142.6, 144.9, 159.9, 162.4, 171.6, 173.7;

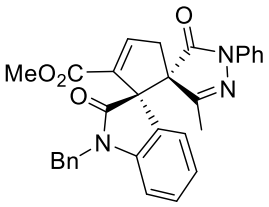
HRMS calcd. for $C_{25}H_{24}N_3O_4$ [M + H]$^+$: 430.1761, found: 430.1763.

Methyl 3''-methyl-2,5''-dioxo-1''-phenyl-1-propyl-1'',5''-dihydrodispiro [indoline -3, '-cyclopentane-1',4''-pyrazol]-3'-ene-3'-carboxylate



Cycloaddition product **3i** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 10:1 to 2:1) in 80% yield (35.4 mg, >20:1 dr). White solid, melting point: 162-163 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.8 Hz, 3H), 1.65 (t, *J* = 6.6 Hz, 2H), 2.26 (s, 3H), 3.06 (dd, *J* = 2.4, 5.4 Hz, 2H), 3.57 (s, 3H), 3.61-3.68 (m, 2H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.28-7.34 (m, 4H), 7.65 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 11.2, 16.5, 20.5, 37.7, 41.9, 51.8, 65.1, 65.2, 108.5, 118.9 (2C), 122.2, 125.0, 125.5, 125.8, 128.6 (2C), 129.5, 137.0, 137.4, 143.0, 144.8, 160.2, 162.4, 171.4, 173.9; HRMS calcd. for $C_{26}H_{26}N_3O_4$ [M + H]$^+$: 444.1918, found: 444.1918.

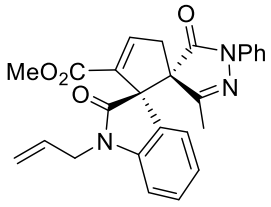
Methyl 1-benzyl-3''-methyl-2,5''-dioxo-1''-phenyl-1'',5''-dihydrodispiro [indoline -3,2'-cyclopentane-1',4''-pyrazol]-3'-ene-3'-carboxylate



Cycloaddition product **3j** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 10:1 to 2:1) in 76% yield (37.3 mg, >20:1 dr). White solid, melting point: 57-58 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.27 (s, 3H), 3.03 (dd, *J* = 3.0, 18.6 Hz, 1H), 3.14 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.58 (s, 3H), 4.78 (d, *J* = 15.6, 1H), 5.01 (d, *J* = 15.6, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 2H), 7.11-7.16 (m, 5H), 7.30-7.34 (m, 4H), 7.68 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 16.7, 37.7, 43.9, 51.9, 65.0, 65.6, 109.3, 118.9 (2C), 122.4, 125.0, 125.3, 125.8, 126.8 (2C), 127.4, 128.7 (2C), 128.7 (2C), 129.6, 135.1, 137.1, 137.5, 142.4, 144.7, 160.7, 162.4, 171.0, 174.1; HRMS calcd. for

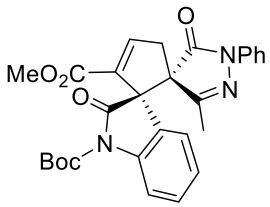
$C_{30}H_{26}N_3O_4$ [M + H]$^+$: 492.1918, found: 492.1917.

Methyl 1-allyl-3''-methyl-2,5''-dioxo-1''-phenyl-1'',5''-dihydrodispiro [indoline-3, 2'-cyclopentane-1',4''-pyrazol]-3'-ene-3'-carboxylate



Cycloaddition product **3k** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 10:1 to 2:1) in 78% yield (34.4 mg, >20:1 dr). White solid, melting point: 154-155 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.24 (s, 3H), 3.04 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.12 (dd, *J* = 3.0, 18.0 Hz, 1H), 3.59 (s, 3H), 4.26 (dd, *J* = 4.8, 16.2 Hz, 1H), 4.38 (dd, *J* = 4.8, 16.2 Hz, 1H), 5.11 (d, *J* = 10.2 Hz, 1H), 5.18 (d, *J* = 16.8 Hz, 1H), 5.74-5.80 (m, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.28-7.33 (m, 3H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 16.4, 37.7, 42.5, 51.8, 65.1, 65.2, 109.1, 117.5, 118.9 (2C), 122.5, 125.0, 125.3, 125.8, 128.6 (2C), 129.5, 130.5, 136.7, 137.4, 142.7, 145.1, 159.8, 162.4, 171.6, 173.8; HRMS calcd. for $C_{26}H_{24}N_3O_4$ [M + H]$^+$: 442.1761, found: 442.1762.

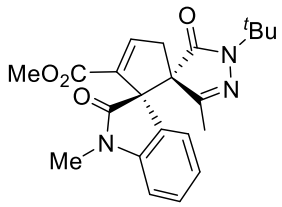
1-(*Tert*-butyl) 3'-methyl 3''-methyl-2,5''-dioxo-1''-phenyl-1'',5''-dihydrodispiro [indoline-3,2'-cyclopentane-1',4''-pyrazol]-3'-ene-1,3'-dicarboxylate



Cycloaddition product **3l** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 10:1 to 2:1) in 52% yield (26.1 mg, >20:1 dr). White solid, melting point: 54-55 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.61 (s, 9H), 2.24 (s, 3H), 2.96 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.15 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.59 (s, 3H), 7.05 (t, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.25-7.31 (m, 3H), 7.36 (t, *J* = 2.4 Hz, 1H), 7.39 (d, *J* = 6.6 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 16.0, 28.0 (3C), 37.4, 51.9, 65.7, 66.0, 84.8, 114.8, 119.1 (2C), 124.0, 124.3, 125.3, 125.5, 128.7 (2C), 129.8, 135.8, 137.1, 139.7,

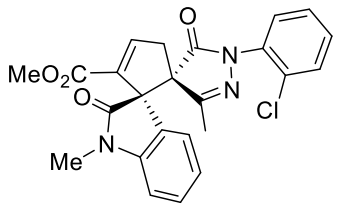
146.2, 148.6, 158.4, 162.4, 171.6, 172.8; HRMS calcd. for $C_{28}H_{27}N_3NaO_6$ $[M + Na]^+$: 524.1792, found: 524.1793.

Methyl 1''-(*tert*-butyl)-1,3''-dimethyl-2,5''-dioxo-1'',5''-dihydrodispiro[indoline-3, 2'-cyclopentane-1',4''-pyrazol]-3'-ene-3'-carboxylate



Cycloaddition product **3m** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 10:1 to 2:1) in 71% yield (28.0 mg, >20:1 dr). White solid, melting point: 114-115 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.26 (s, 9H), 2.02 (s, 3H), 2.78 (dd, *J* = 3.0, 18.0 Hz, 1H), 3.10 (dd, *J* = 1.8, 17.4 Hz, 1H), 3.21 (s, 3H), 3.55 (s, 3H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.98 (t, *J* = 8.4 Hz, 1H), 7.26-7.29 (m, 2H), 7.37 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 15.9, 26.4, 27.8 (3C), 37.1, 51.6, 57.0, 64.6, 64.9, 107.9, 122.4, 125.6, 126.1, 129.2, 135.9, 143.8, 146.0, 156.0, 162.7, 173.8, 174.4; HRMS calcd. for $C_{22}H_{26}N_3O_4$ $[M + H]^+$: 396.1918, found: 396.1918.

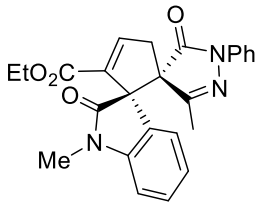
Methyl 1''-(2-chlorophenyl)-1,3''-dimethyl-2,5''-dioxo-1'',5''-dihydrodispiro[indo line-3,2'-cyclopentane-1',4''-pyrazol]-3'-ene-3'-carboxylate



Cycloaddition product **3n** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 8:1 to 1:1) in 72% yield (32.3 mg, >20:1 dr). White solid, melting point: 182-183 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 3.08 (dd, *J* = 3.0, 18.6 Hz, 1H), 3.15 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.24 (s, 3H), 3.60 (s, 3H), 6.82 (d, *J* = 7.8 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 7.10-7.12 (m, 1H), 7.23-7.24 (m, 2H), 7.28-7.32 (m, 3H), 7.36-7.38 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 16.5, 26.6, 37.5, 51.9, 63.6, 65.3, 108.1, 122.4, 125.4, 126.1, 127.3, 128.4, 129.6, 129.7, 130.2, 131.6, 134.1, 137.0, 143.5, 144.6, 160.6, 162.4, 171.8, 173.9; HRMS calcd. for $C_{24}H_{21}ClN_3O_4$ $[M + H]^+$: 450.1215, found:

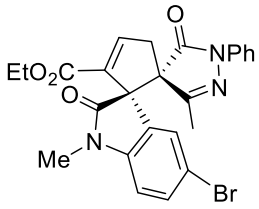
450.1218.

Ethyl 1,3''-dimethyl-2,5''-dioxo-1''-phenyl-1'',5''-dihydrodispiro[indoline-3,2'-cyclopentane-1',4''-pyrazol]-3'-ene-3'-carboxylate



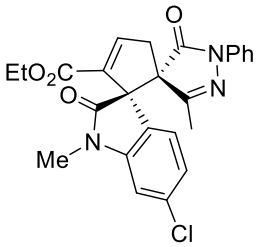
Cycloaddition product **3o** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 10:1 to 2:1) in 86% yield (36.9 mg, >20:1 dr). White solid, melting point: 143-144 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 6.6 Hz, 3H), 2.23 (s, 3H), 3.01 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.14 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.20 (s, 3H), 3.94-4.01 (m, 2H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 7.23-7.29 (m, 1H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 2.4 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 13.8, 16.3, 26.6, 37.8, 60.6, 65.0, 65.1, 108.1, 118.9 (2C), 122.6, 125.0, 125.5, 125.8, 128.6 (2C), 129.5, 137.0, 137.4, 143.6, 144.9, 159.6, 162.0, 171.8, 174.2; HRMS calcd. for $C_{25}H_{24}N_3O_4$ $[M + H]^+$: 430.1761, found: 430.1761.

Ethyl 5-bromo-1,3''-dimethyl-2,5''-dioxo-1''-phenyl-1'',5''-dihydrodispiro [indoline-3,2'-cyclopentane-1',4''-pyrazol]-3'-ene-3'-carboxylate



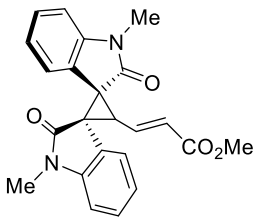
Cycloaddition product **3p** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 10:1 to 2:1) in 84% yield (42.7 mg, >20:1 dr). White solid, melting point: 182-183 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ =1.08 (t, *J* = 7.2 Hz, 3H), 2.21 (s, 3H), 3.00 (dd, *J* = 3.0, 18.0 Hz, 1H), 3.12 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.16 (s, 3H), 3.98-4.05 (m, 2H), 6.62 (d, *J* = 8.4 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.31-7.36 (m, 4H), 7.51 (d, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 13.8, 16.2, 26.6, 37.6, 60.8, 64.9 (2C), 109.5, 115.3, 119.0 (2C), 125.2, 127.5, 128.7 (2C), 128.9, 132.3, 136.4, 137.1, 142.7, 145.5, 159.2, 161.8, 171.5, 173.6; HRMS calcd. for $C_{25}H_{23}BrN_3O_4$ $[M + H]^+$: 508.0866, found: 508.0871.

Ethyl 6-chloro-1,3''-dimethyl-2,5''-dioxo-1''-phenyl-1'',5''-dihydrodispiro [indol ine-3,2'-cyclopentane-1',4''-pyrazol]-3'-ene-3'-carboxylate



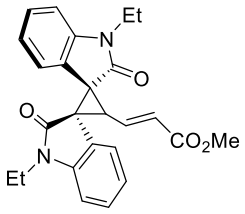
Cycloaddition product **3q** was prepared as described in section 4 and isolated by FC on silica (eluting with PE/EA from 10:1 to 2:1) in 95% yield (44.0 mg, >20:1 dr). White solid, melting point: 176-177 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ =1.08 (t, *J* = 7.2 Hz, 3H), 2.22 (s, 3H), 3.00 (dd, *J* = 3.0, 18.0 Hz, 1H), 3.13 (dd, *J* = 2.4, 18.0 Hz, 1H), 3.18 (s, 3H), 3.98-4.04 (m, 2H), 6.78 (d, *J* = 1.8 Hz, 1H), 6.94 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.28-7.33 (m, 4H), 7.68 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.8, 16.3, 26.7, 37.8, 60.8, 64.5, 64.9, 109.0, 118.8 (2C), 122.5, 123.9, 125.2, 126.7, 128.7 (2C), 135.3, 136.7, 137.3, 144.8, 145.0, 159.4, 161.9, 171.5, 174.1; HRMS calcd. for $C_{25}H_{23}ClN_3O_4$ $[M + H]^+$: 464.1372, found: 464.1372.

Methyl (*E*)-3-(1,1''-dimethyl-2,2''-dioxodispiro[indoline-3,1'-cyclopropane-2',3''-indolin] -3'-yl) acrylate



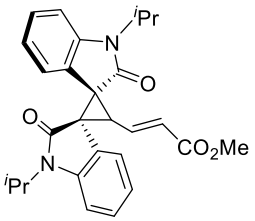
Cycloaddition product **5a** was prepared as described in section 5 and isolated by FC on silica (eluting with PE/CH_2Cl_2 from 5:1 to 1:4) in 93% yield (36.1 mg). White solid, melting point: 231-232 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.17 (s, 3H), 3.19 (s, 3H), 3.73 (d, *J* = 9.0 Hz, 1H), 3.74 (s, 3H), 6.15 (d, *J* = 15.6 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 7.09-7.14 (m, 2H), 7.28-7.34 (m, 2H), 8.07-8.11 (m, 2H), 8.21 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 26.4, 26.8, 40.0, 46.0, 47.5, 51.7, 107.6, 107.9, 121.9, 122.1, 122.1, 124.1, 125.7, 125.8, 127.8, 128.4, 128.5, 137.9, 143.7, 144.1, 165.8, 170.4, 171.3; HRMS calcd. for $C_{23}H_{21}N_2O_4$ $[M + H]^+$: 389.1496, found: 389.1496.

Methyl (*E*)-3-(1,1''-diethyl-2,2''-dioxodispiro[indoline-3,1'-cyclopropane-2',3''-indolin]-3'-yl)acrylate



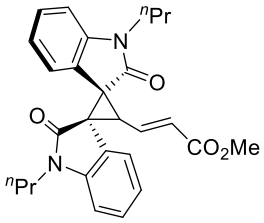
Cycloaddition product **5b** was prepared as described in section 5 and isolated by FC on silica (eluting with PE/CH_2Cl_2 from 2:1 to 1:4) in 91% yield (37.9 mg). White solid, melting point: 232-233 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.21-1.24 (m, 6H), 3.70-3.79 (m, 8H), 6.15 (d, *J* = 15.6 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 7.07-7.12 (m, 2H), 7.27-7.32 (m, 2H), 8.08-8.12 (m, 2H), 8.23 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): = 12.5, 12.6, 35.0, 35.4, 40.2, 46.0, 47.4, 51.7, 107.7, 108.0, 121.7, 121.9, 122.4, 124.3, 125.7, 126.1, 128.0, 128.3, 128.3, 138.1, 142.8, 143.1, 165.8, 170.0, 171.0; HRMS calcd. for $C_{25}H_{25}N_2O_4$ $[M + H]^+$: 417.1809, found: 417.1809.

Methyl (*E*)-3-(1,1''-diisopropyl-2,2''-dioxodispiro[indoline-3,1'-cyclopropane-2',3''-indolin]-3'-yl)acrylate



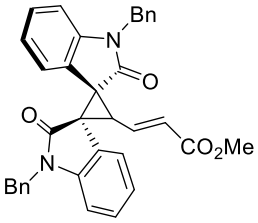
Cycloaddition product **5c** was prepared as described in section 5 and isolated by FC on silica (eluting with PE/CH_2Cl_2 from 4:1 to 1:2) in 90% yield (40.0 mg). White solid, melting point: 221-222 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.42-1.45 (m, 12H), 3.66 (d, *J* = 10.2 Hz, 1H), 3.74 (s, 3H), 4.56-4.64 (m, 2H), 6.15 (d, *J* = 15.6 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 7.04-7.10 (m, 2H), 7.24-7.29 (m, 2H), 8.07-8.12 (m, 2H), 8.24 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 19.1, 19.2, 19.4, 19.4, 40.5, 44.0, 44.5, 46.0, 47.5, 51.6, 109.1, 109.3, 121.2, 121.4, 122.6, 124.6, 125.6, 126.1, 127.9, 128.0, 128.0, 138.3, 142.4, 142.7, 165.8, 169.9, 170.9; HRMS calcd. for $C_{27}H_{29}N_2O_4$ $[M + H]^+$: 445.2122, found: 445.2122.

Methyl (*E*)-3-(2,2''-dioxo-1,1''-dipropyldispiro[indoline-3,1'-cyclopropane-2',3''-indolin]-3'-yl)acrylate



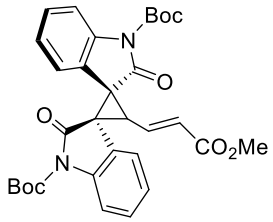
Cycloaddition product **5d** was prepared as described in section 5 and isolated by FC on silica (eluting with PE/CH_2Cl_2 from 4:1 to 1:2) in 90% yield (40.0 mg). White solid, melting point: 171-172 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.87 (q, *J* = 7.2 Hz, 6H), 1.58-1.69 (m, 4H), 3.59-3.68 (m, 4H), 3.73 (s, 3H), 3.74 (d, *J* = 10.2 Hz, 1H), 6.16 (d, *J* = 15.6 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 7.05-7.11 (m, 2H), 7.25-7.31 (m, 2H), 8.08-8.13 (m, 2H), 8.21 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 11.3 (2C), 20.6, 20.7, 40.0, 41.9, 42.2, 46.0, 47.5, 51.6, 107.8, 108.1, 121.6, 121.8, 122.2, 124.2, 125.7, 125.9, 127.9, 128.2, 128.3, 138.1, 143.1, 143.4, 165.8, 170.2, 171.2; HRMS calcd. for $C_{27}H_{29}N_2O_4$ $[M + H]^+$: 445.2122, found: 445.2122.

Methyl (*E*)-3-(1,1''-dibenzyl-2,2''-dioxodispiro[indoline-3,1'-cyclopropane-2',3'' -indolin]-3'-yl)acrylate



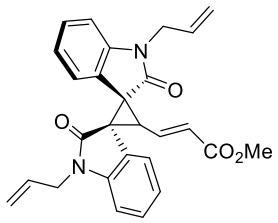
Cycloaddition product **5e** was prepared as described in section 5 and isolated by FC on silica (eluting with PE/CH_2Cl_2 from 2:1 to 1:4) in 89% yield (48.1 mg). White solid, melting point: 65-66 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.76 (s, 3H), 3.88 (d, *J* = 9.6 Hz, 1H), 4.82-4.94 (m, 4H), 6.22 (d, *J* = 15.6 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 7.05-7.13 (m, 6H), 7.17-7.23 (m, 8H), 8.07 (d, *J* = 7.8 Hz, 1H), 8.15 (dd, *J* = 10.2, 15.6 Hz, 1H), 8.21 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 39.9, 43.9, 44.3, 46.4, 47.8, 51.7, 108.6, 108.8, 121.9 (2C), 122.1, 123.7, 125.8, 126.0, 127.1 (2C), 127.1 (2C), 127.5, 127.5, 127.7, 128.3, 128.4, 128.7 (2C), 128.7 (2C), 135.4, 135.5, 137.8, 142.8, 143.1, 165.8, 170.3, 171.2; HRMS calcd. for $C_{35}H_{29}N_2O_4$ $[M + H]^+$: 541.2122, found: 541.2125.

Di-*tert*-butyl (*E*)-3'-(3-methoxy-3-oxoprop-1-en-1-yl)-2,2''-dioxodispiro[indoline -3,1'-cyclopropane-2',3''-indoline]-1,1''-dicarboxylate



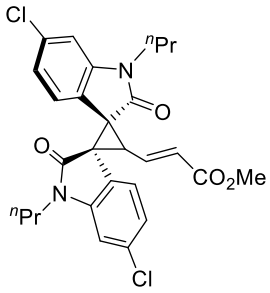
Cycloaddition product **5f** was prepared as described in section 5 and isolated by FC on silica (eluting with PE/CH_2Cl_2 from 4:1 to 1:3) in 65% yield (36.4 mg). White solid, melting point: 101-102 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.58 (s, 18H), 3.75 (s, 3H), 3.79 (d, *J* = 9.6 Hz, 1H), 6.17 (d, *J* = 15.6 Hz, 1H), 7.18-7.23 (m, 2H), 7.31-7.37 (m, 2H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.98-8.03 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 28.0 (3C), 28.0 (3C), 39.4, 47.3, 49.1, 51.7, 84.7, 84.8, 114.1, 114.2, 120.2, 121.9, 123.8, 124.0, 125.4, 126.9, 127.4, 128.8, 128.9, 136.1, 139.8, 140.1, 148.4, 148.5, 165.5, 167.7, 168.6; HRMS calcd. for $C_{31}H_{32}N_2NaO_8$ $[M + Na]^+$: 583.2051, found: 583.2051.

Methyl (*E*)-3-(1,1''-diallyl-2,2''-dioxodispiro[indoline-3,1'-cyclopropane-2',3''-indolin]-3'-yl)acrylate



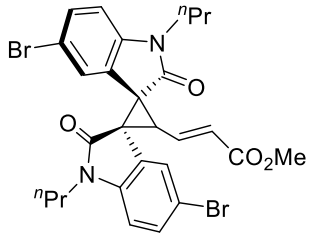
Cycloaddition product **5g** was prepared as described in section 5 and isolated by FC on silica (eluting with PE/CH_2Cl_2 from 2:1 to 1:4) in 85% yield (37.4 mg). White solid, melting point: 176-177 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.74 (s, 3H), 3.75 (d, *J* = 9.6 Hz, 1H), 4.27-4.36 (m, 4H), 5.16-5.19 (m, 4H), 5.74-5.81 (m, 2H), 6.16 (d, *J* = 15.6 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 7.07-7.12 (m, 2H), 7.24-7.30 (m, 2H), 8.07-8.11 (m, 2H), 8.21 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 40.2, 42.7, 43.0, 46.0, 47.5, 51.7, 108.5, 108.7, 117.9, 117.9, 121.8, 122.0, 122.1, 124.0, 125.9, 125.9, 127.9, 128.3, 128.3, 131.2, 131.4, 137.8, 142.9, 143.2, 165.7, 170.0, 171.0; HRMS calcd. for $C_{27}H_{25}N_2O_4$ $[M + H]^+$: 441.1809, found: 441.1810.

Methyl (*E*)-3-(6,6''-dichloro-2,2''-dioxo-1,1''-dipropyldispiro[indoline-3,1'-cyclo propane-2',3''-indolin]-3'-yl)acrylate



Cycloaddition product **5h** was prepared as described in section 5 and isolated by FC on silica (eluting with PE/CH_2Cl_2 from 6:1 to 1:1) in 95% yield (48.7 mg). White solid, melting point: 154-155 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.88 (q, *J* = 7.2 Hz, 6H), 1.60-1.67 (m, 4H), 3.56-3.65 (m, 4H), 3.69 (d, *J* = 9.6 Hz, 1H), 3.74 (s, 3H), 6.16 (d, *J* = 15.6 Hz, 1H), 6.81 (d, *J* = 1.8 Hz, 1H), 6.84 (d, *J* = 2.4 Hz, 1H), 7.03 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.07 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.95-7.99 (m, 2H), 8.08 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 11.3 (2C), 20.6, 20.6, 39.9, 42.1, 42.4, 45.7, 47.2, 51.7, 108.5, 108.8, 120.2, 121.5, 121.8, 122.1, 126.3, 126.9, 128.7, 134.4, 134.6, 137.0, 144.3, 144.6, 165.6, 170.1, 171.1; HRMS calcd. for $C_{27}H_{27}Cl_2N_2O_4$ $[M + H]^+$: 513.1342, found: 513.1343.

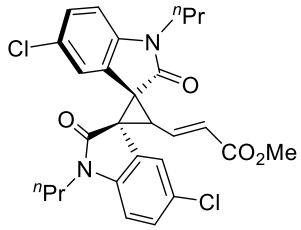
Methyl (*E*)-3-(5,5''-dibromo-2,2''-dioxo-1,1''-dipropyldispiro[indoline-3,1'-cyclopropane-2',3''-indolin]-3'-yl)acrylate



Cycloaddition product **5i** was prepared as described in section 5 and isolated by FC on silica (eluting with PE/CH_2Cl_2 from 6:1 to 1:1) in 76% yield (45.8 mg). White solid, melting point: 201-202 ºC. δ = 0.88 (q, *J* = 7.2 Hz, 6H), 1.58-1.69 (m, 4H), 3.60-3.67 (m, 4H), 3.69 (d, *J* = 10.2 Hz, 1H), 3.76 (s, 3H), 6.17 (d, *J* = 15.6 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 7.40 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.43 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.94 (dd, *J* = 9.6, 15.6 Hz, 1H), 8.24 (d, *J* = 1.8 Hz, 1H), 8.34 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 11.2 (2C), 20.5, 20.6, 40.4, 42.0, 42.3, 45.7, 47.1, 51.8, 109.2, 109.4, 114.5, 114.7, 123.8, 125.8, 126.6, 129.1, 130.8, 131.2, 131.4, 136.7, 142.2, 142.6, 165.5, 169.4, 170.5; HRMS calcd. for $C_{27}H_{27}Br_2N_2O_4$ $[M + H]^+$: 601.0332, found: 601.0327.

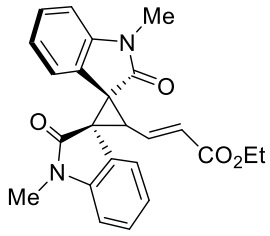
Methyl (*E*)-3-(5,5''-dichloro-2,2''-dioxo-1,1''-dipropyldispiro[indoline-3,1'-cyclo

propane-2',3''-indolin]-3'-yl)acrylate



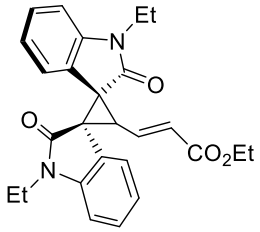
Cycloaddition product **5j** was prepared as described in section 5 and isolated by FC on silica (eluting with PE/CH_2Cl_2 from 6:1 to 1:1) in 75% yield (38.5 mg). White solid, melting point: 187-188 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.88 (q, *J* = 7.2 Hz, 6H), 1.58-1.69 (m, 4H), 3.61-3.68 (m, 4H), 3.69 (d, *J* = 9.6 Hz, 1H), 3.76 (s, 3H), 6.17 (d, *J* = 15.6 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 7.26 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.28 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.96 (dd, *J* = 10.2, 15.6 Hz, 1H), 8.11 (d, *J* = 1.8 Hz, 1H), 8.22 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 11.2 (2C), 20.5, 20.6, 40.4, 42.0, 42.3, 45.7, 47.2, 51.7, 108.7, 108.9, 123.4, 125.5, 126.4, 126.6, 127.2, 127.3, 128.1, 128.2, 128.4, 136.8, 141.7, 142.1, 165.5, 169.6, 170.6; HRMS calcd. for $C_{27}H_{27}Cl_2N_2O_4$ $[M + H]^+$: 513.1342, found: 513.1342.

Ethyl (*E*)-3-(1,1''-dimethyl-2,2''-dioxodispiro[indoline-3,1'-cyclopropane-2',3'' -indolin]-3'-yl)acrylate



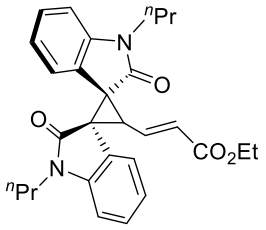
Cycloaddition product **5k** was prepared as described in section 5 and isolated by FC on silica (eluting with PE/CH_2Cl_2 from 2:1 to 1:6) in 88% yield (35.4 mg). White solid, melting point: 219-220 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.27-1.29 (m, 3H), 3.17 (s, 3H), 3.19 (s, 3H), 3.73 (d, *J* = 10.2 Hz, 1H), 4.17-4.22 (m, 2H), 6.14 (d, *J* = 15.6 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 7.08-7.14 (m, 2H), 7.28-7.33 (m, 2H), 8.06-8.10 (m, 2H), 8.21 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 14.2, 26.4, 26.8, 40.0, 46.0, 47.5, 60.5, 107.6, 107.9, 121.9, 122.1, 122.1, 124.1, 125.8, 126.2, 127.8, 128.4, 128.4, 137.6, 143.7, 144.1, 165.3, 170.4, 171.4; HRMS calcd. for $C_{24}H_{23}N_2O_4$ $[M + H]^+$: 403.1652, found: 403.1653.

Ethyl (*E*)-3-(1,1''-diethyl-2,2''-dioxodispiro[indoline-3,1'-cyclopropane-2',3''-indolin]-3'-yl)acrylate



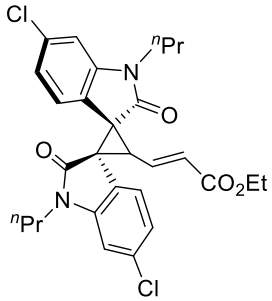
Cycloaddition product **5l** was prepared as described in section 5 and isolated by FC on silica (eluting with PE/CH_2Cl_2 from 4:1 to 1:4) in 94% yield (40.4 mg). White solid, melting point: 227-228 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.20-1.23 (m, 6H), 1.28 (t, *J* = 7.2 Hz, 3H), 3.69-3.81 (m, 5H), 4.16-4.23 (m, 2H), 6.16 (d, *J* = 15.6 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 7.06-7.12 (m, 2H), 7.26-7.32 (m, 2H), 8.07-8.12 (m, 2H), 8.25 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 12.5, 12.6, 14.2, 35.0, 35.3, 40.2, 46.0, 47.4, 60.4, 107.7, 107.9, 121.6, 121.8, 122.4, 124.3, 126.0, 126.1, 128.0, 128.2, 128.3, 137.7, 142.8, 143.1, 165.3, 169.9, 171.0; HRMS calcd. for $C_{26}H_{27}N_2O_4$ $[M + H]^+$: 431.1965, found: 431.1967.

Ethyl (*E*)-3-(2,2''-dioxo-1,1''-dipropyldispiro[indoline-3,1'-cyclopropane-2',3''-indolin]-3'-yl)acrylate



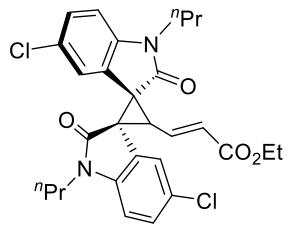
Cycloaddition product **5m** was prepared as described in section 5 and isolated by FC on silica (eluting with PE/CH_2Cl_2 from 6:1 to 1:2) in 90% yield (41.2 mg). White solid, melting point: 155-156 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.87 (q, *J* = 7.8 Hz, 6H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.58-1.69 (m, 4H), 3.58-3.68 (m, 4H), 3.74 (d, *J* = 10.2 Hz, 1H), 4.17-4.22 (m, 2H), 6.16 (d, *J* = 15.6 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 7.05-7.11 (m, 2H), 7.25-7.30 (m, 2H), 8.08-8.12 (m, 2H), 8.22 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 11.2, 11.3, 14.2, 20.6, 20.7, 40.0, 41.8, 42.2, 46.0, 47.5, 60.4, 107.8, 108.0, 121.5, 121.8, 122.2, 124.1, 125.9, 126.1, 127.9, 128.2, 128.2, 137.7, 143.1, 143.4, 165.3, 170.2, 171.2; HRMS calcd. for $C_{28}H_{31}N_2O_4$ $[M + H]^+$: 459.2278, found: 459.2278.

Ethyl (*E*)-3-(6,6''-dichloro-2,2''-dioxo-1,1''-dipropyldispiro[indoline-3,1'-cyclopropane-2',3''-indolin]-3'-yl)acrylate



Cycloaddition product **5n** was prepared as described in section 5 and isolated by FC on silica (eluting with PE/CH_2Cl_2 from 6:1 to 1:2) in 91% yield (48.0 mg). White solid, melting point: 72-73 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.88 (q, *J* = 7.2 Hz, 6H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.59-1.68 (m, 4H), 3.55-3.66 (m, 4H), 3.69 (d, *J* = 10.2 Hz, 1H), 4.18-4.23 (m, 2H), 6.16 (d, *J* = 16.2 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.84 (d, *J* = 1.8 Hz, 1H), 7.03 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.07 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.94-7.98 (m, 2H), 8.09 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 11.2, 11.2, 14.2, 20.6, 20.6, 39.9, 42.0, 42.4, 45.7, 47.2, 60.6, 108.5, 108.8, 120.2, 121.5, 121.8, 122.1, 126.8, 126.9, 128.8, 134.4, 134.6, 136.6, 144.3, 144.6, 165.2, 170.1, 171.1; HRMS calcd. for $C_{28}H_{29}Cl_2N_2O_4$ $[M + H]^+$: 527.1499, found: 527.1498.

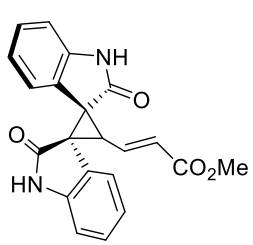
Ethyl (*E*)-3-(5,5''-dichloro-2,2''-dioxo-1,1''-dipropyldispiro[indoline-3,1'-cyclopropane-2',3''-indolin]-3'-yl)acrylate



Cycloaddition product **5o** was prepared as described in section 5 and isolated by FC on silica (eluting with PE/CH_2Cl_2 from 6:1 to 1:2) in 86% yield (45.3 mg). White solid, melting point: 78-79 ℃. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.88 (q, *J* = 7.2 Hz, 6H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.58-1.69 (m, 4H), 3.61-3.68 (m, 4H), 3.70 (d, *J* = 10.2 Hz, 1H), 4.17-4.26 (m, 2H), 6.17 (d, *J* = 15.6 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 7.24-7.29 (m, 2H), 7.95 (dd, *J* = 9.6, 15.6 Hz, 1H), 8.12 (d, *J* = 2.4 Hz, 1H), 8.23 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 11.2, 11.2, 14.2, 20.5, 20.6, 40.3, 42.0, 42.3, 45.7, 47.2, 60.5, 108.6, 108.8, 123.4, 125.4, 126.4, 126.9, 127.1, 127.3, 128.2, 128.2, 128.4, 136.4, 141.7, 142.1, 165.1, 169.5, 170.6; HRMS calcd. for $C_{28}H_{29}Cl_2N_2O_4$ $[M + H]^+$: 527.1499,

found: 527.1497.

Methyl (*E*)-3-(2,2''-dioxodispiro[indoline-3,1'-cyclopropane-2',3''-indolin]-3'-yl) acrylate



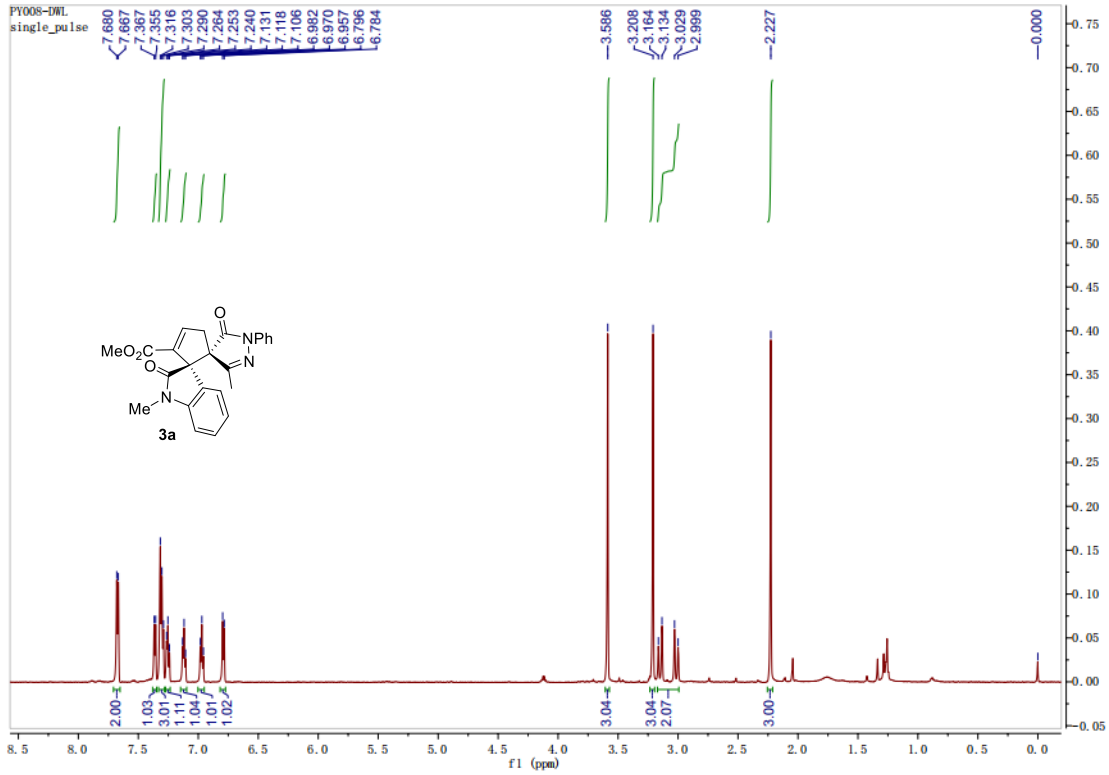
White solid, melting point: 119-120 ℃. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 3.66 (s, 3H), 3.85 (d, *J* = 10.2 Hz, 1H), 6.41 (d, *J* = 15.6 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.96 (td, *J* = 1.8, 7.8 Hz, 1H), 6.01 (td, *J* = 1.8, 7.8 Hz, 1H), 7.21 (td, *J* = 1.8, 7.8 Hz, 1H), 7.25 (td, *J* = 1.8, 7.8 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 8.00 (dd, *J* = 10.2, 15.6 Hz, 1H), 10.76 (s, 1H), 10.79 (s, 1H); ^{13}C NMR (151 MHz, DMSO-d_6): δ = 38.5, 45.9, 47.3, 51.5, 109.3, 109.7, 120.6, 120.8, 122.3, 124.2, 125.3, 125.9, 127.1, 128.3, 128.4, 138.3, 142.1, 142.5, 165.5, 171.7, 171.8; HRMS calcd. for $C_{21}H_{17}N_2O_4$ $[M + H]^+$: 361.1183, found: 361.1185.

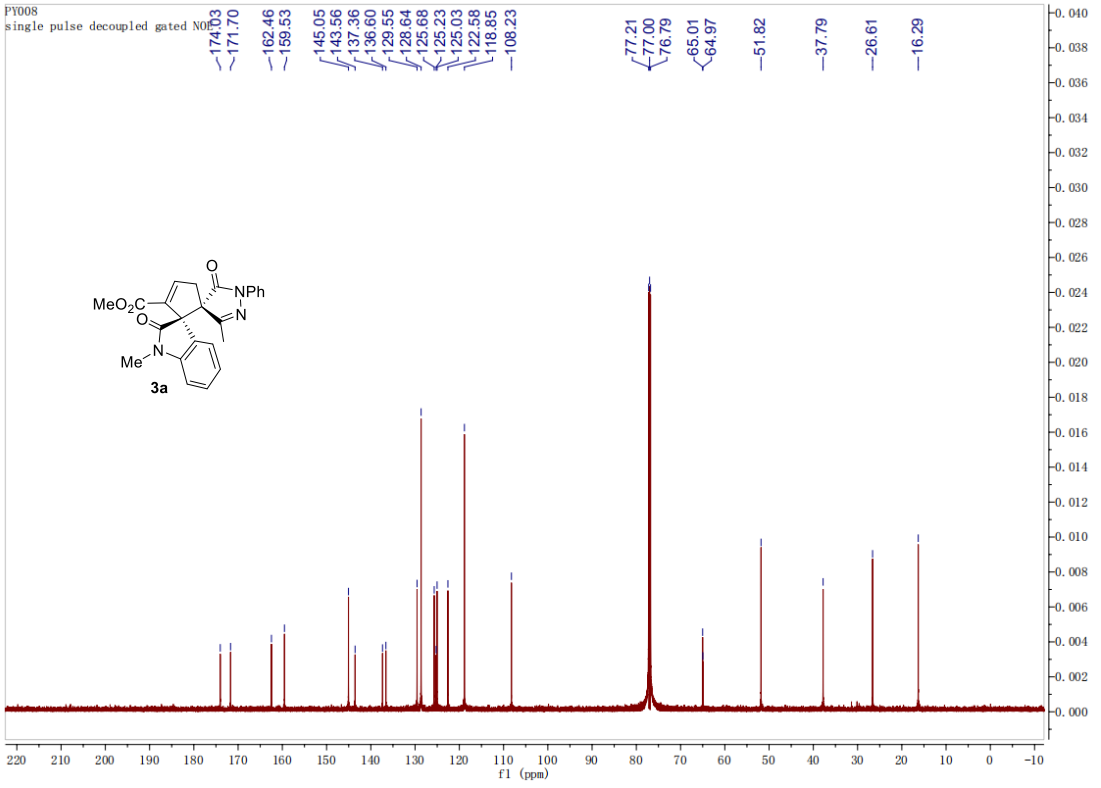
10. References

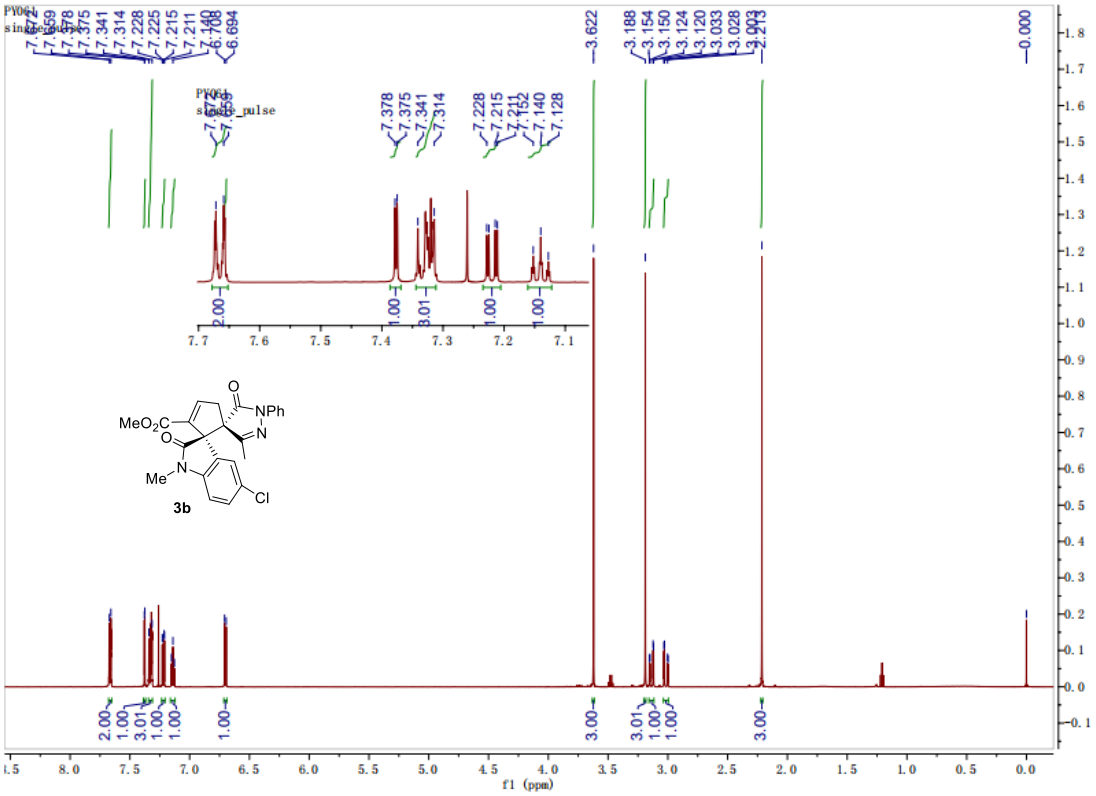
[1] S. Wang, J. Izquierdo, C. Rodríguez-Escrich, and M. A. Pericàs, Asymmetric [4 + 2] Annulation Reactions Catalyzed by a Robust, Immobilized Isothiourea, *ACS Catal.*, 2017, **7**, 2780.

[2] B. M. Trost and M. Osipov, Palladium-Catalyzed Asymmetric Construction of Vicinal All-Carbon Quaternary Stereocenters and its Application to the Synthesis of Cyclotryptamine Alkaloids, *Angew. Chem. Int. Ed.*, 2013, **52**, 9176.

11. ^{1}H and ^{13}C NMR spectra



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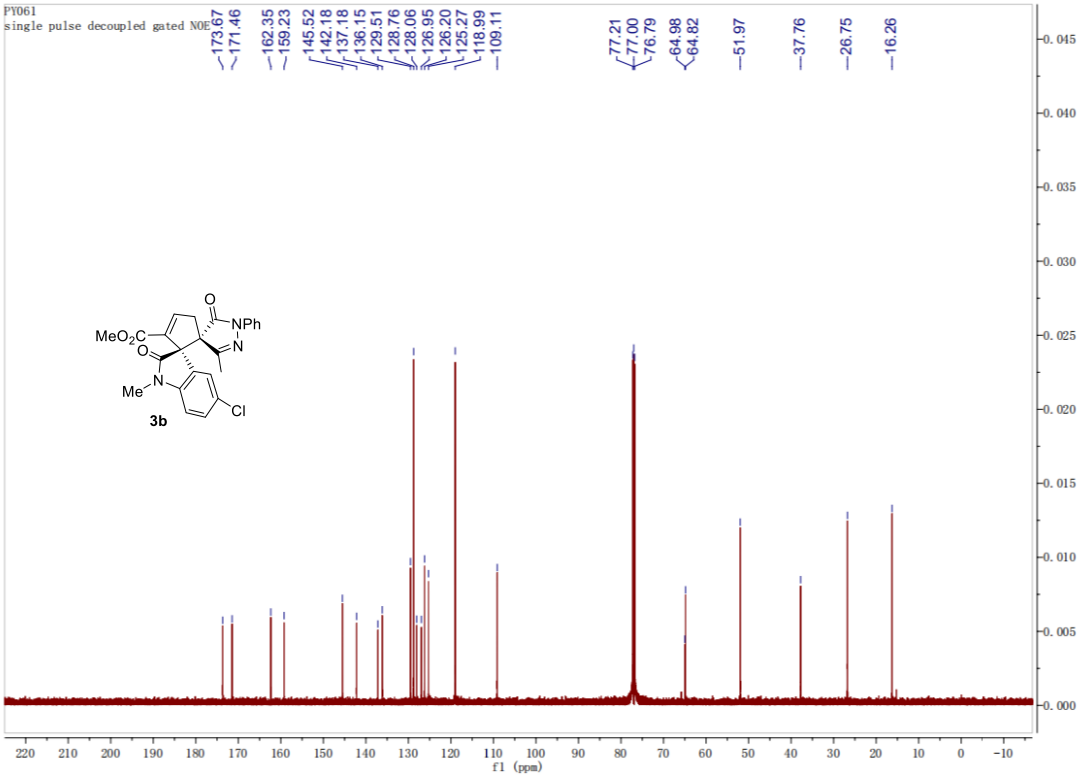
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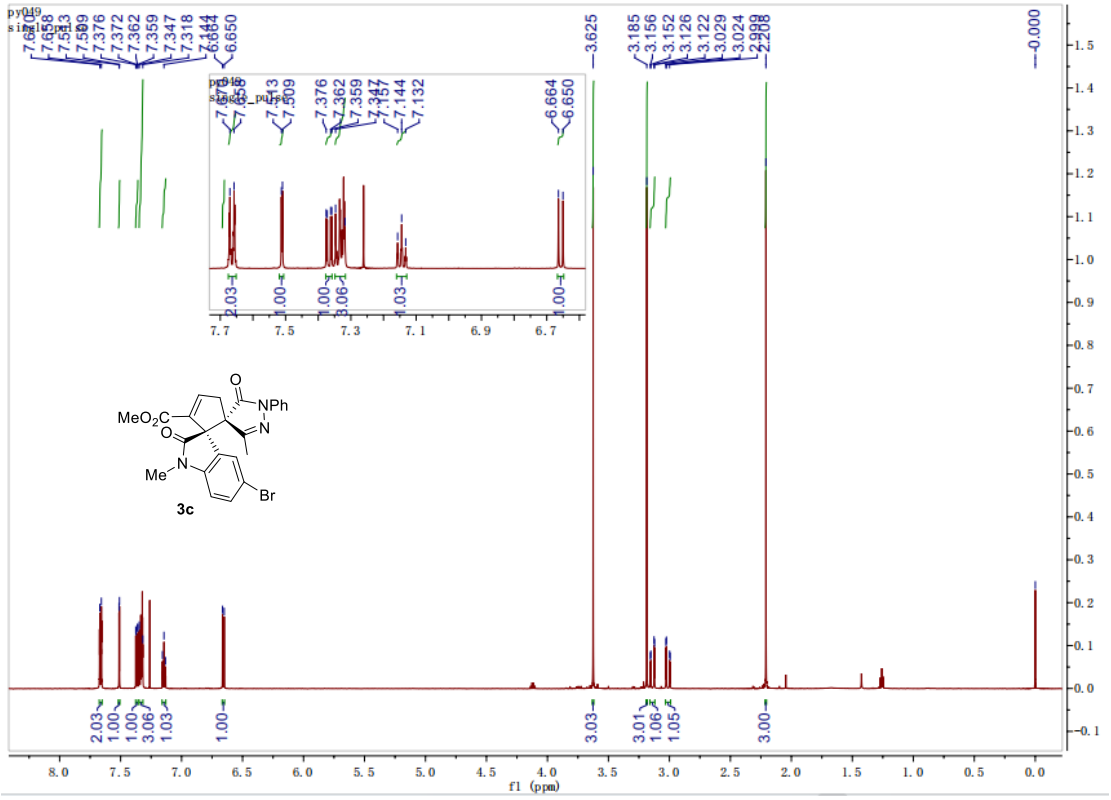
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3.185
3.156
3.152
3.126
3.122
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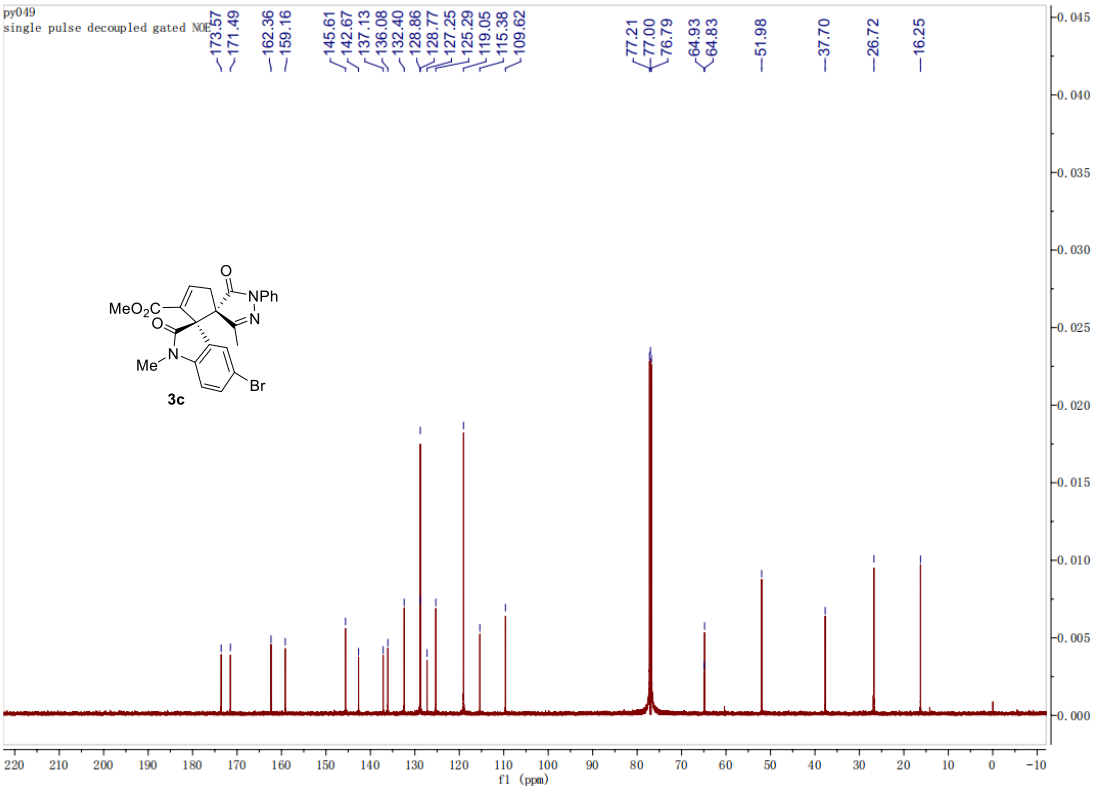
N
Me
N
Br
3c
f1 (ppm)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125.29
119.05
115.38
109.62
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77.00
76.79
64.93
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51.98
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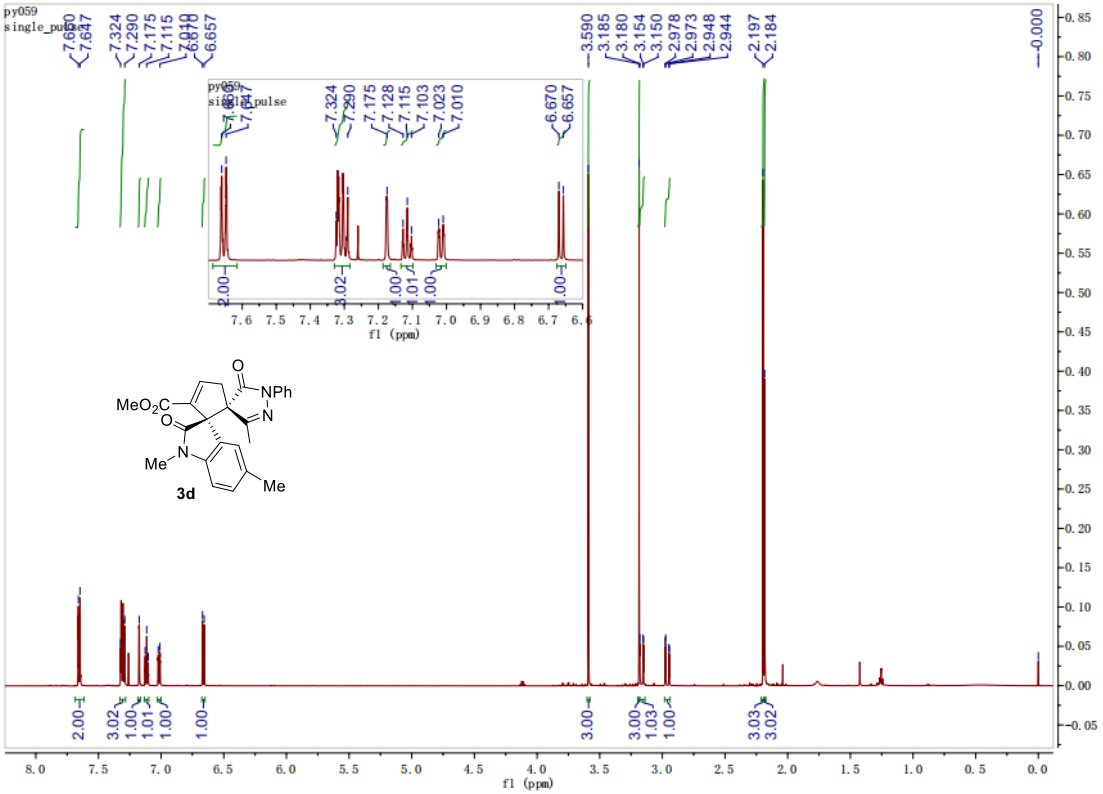
N
Me
N
Br
3c
f1 (ppm)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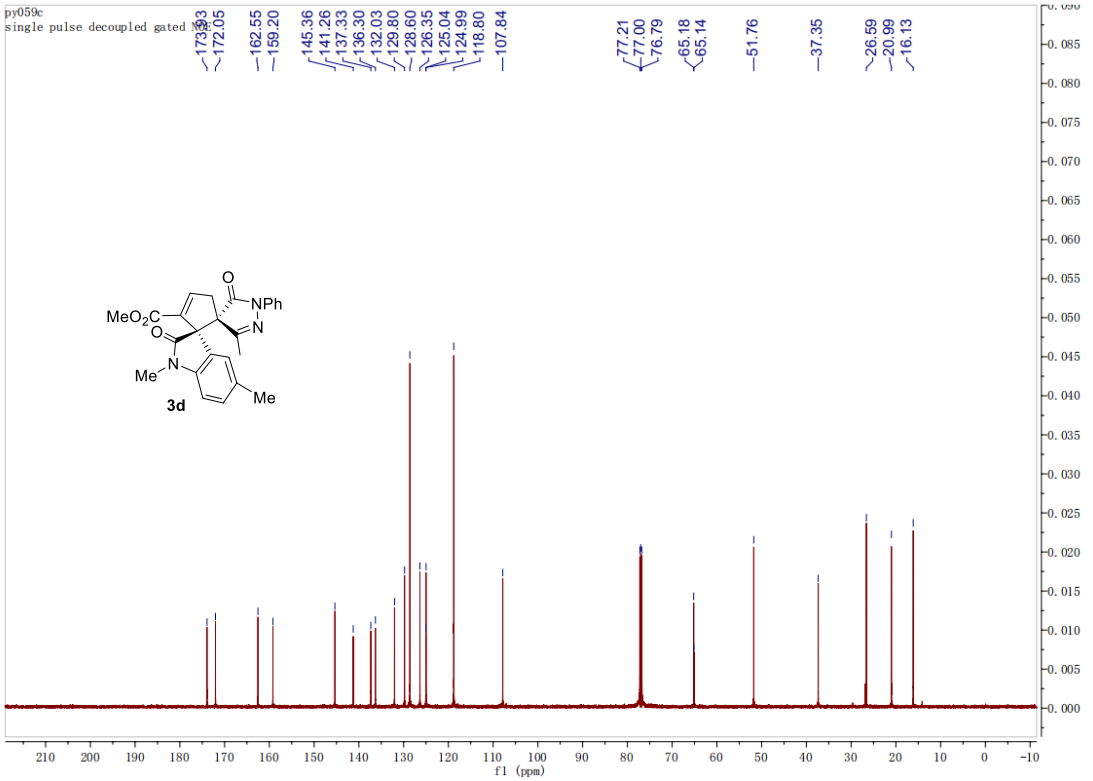
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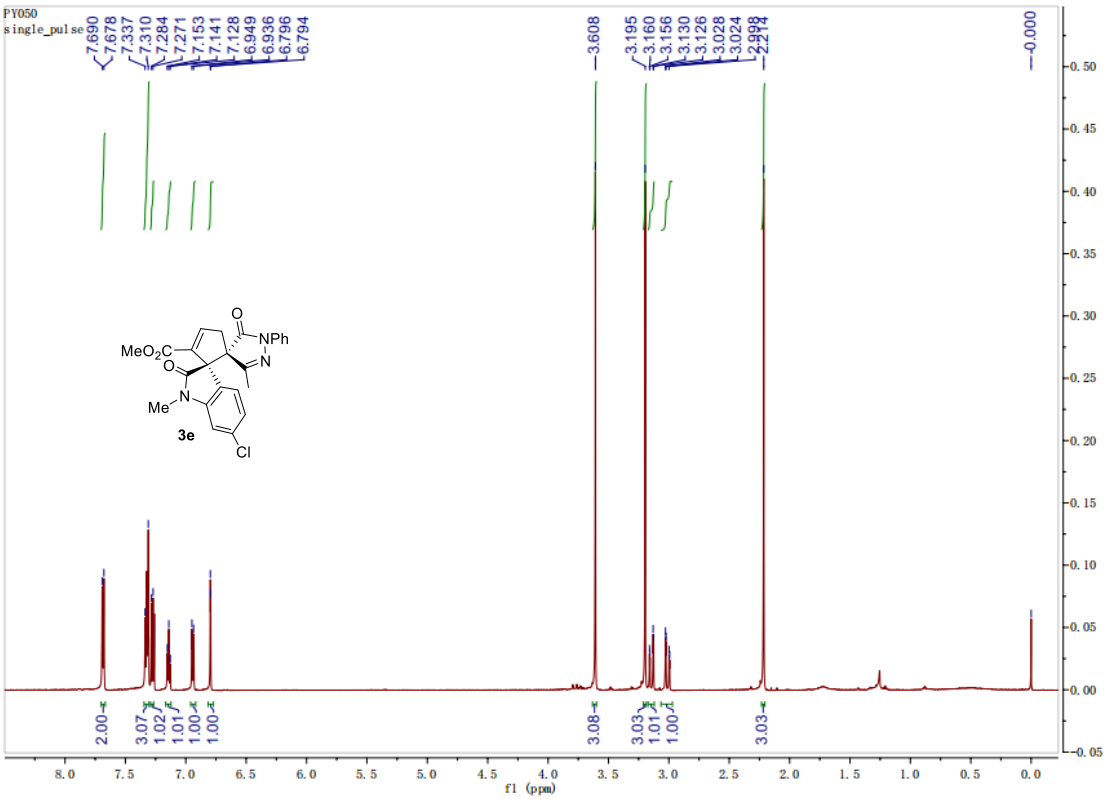
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6.794
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3.195
3.160
3.156
3.130
3.126
3.028
3.024
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2.214
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2.00
3.07
1.02
1.01
1.00
1.00
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1.00
3.03
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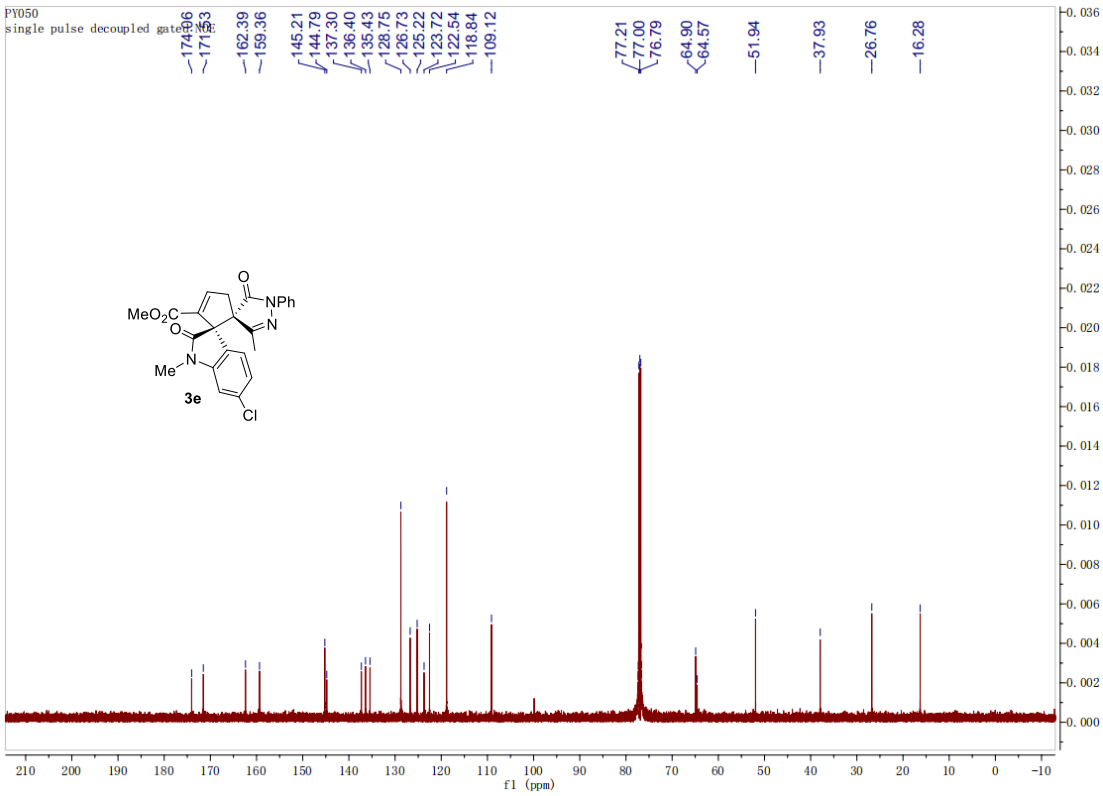
O
NPh
N
Me
N
3e
Cl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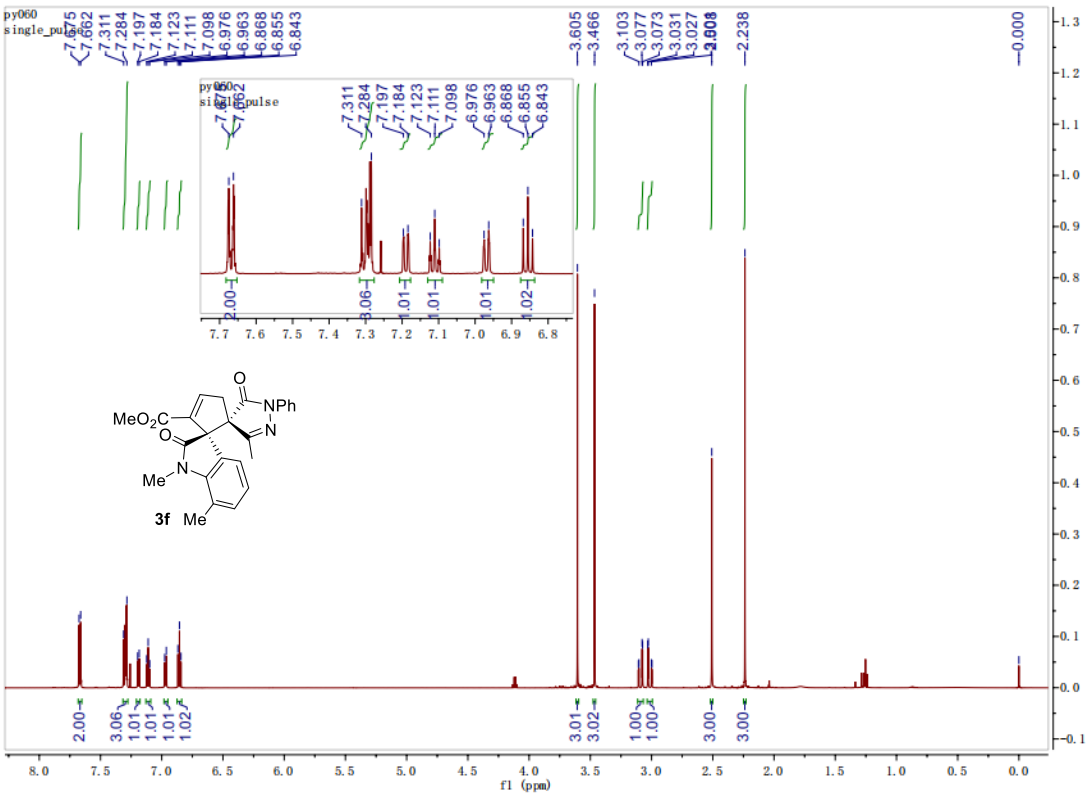
3e
Cl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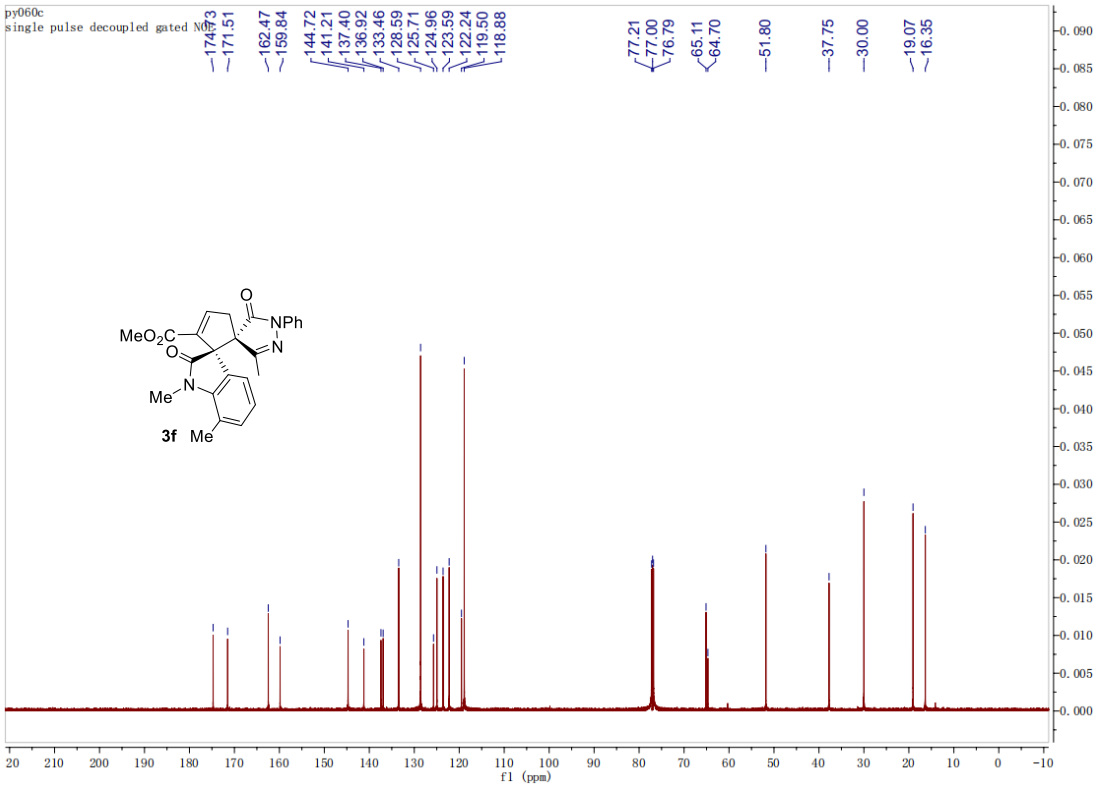
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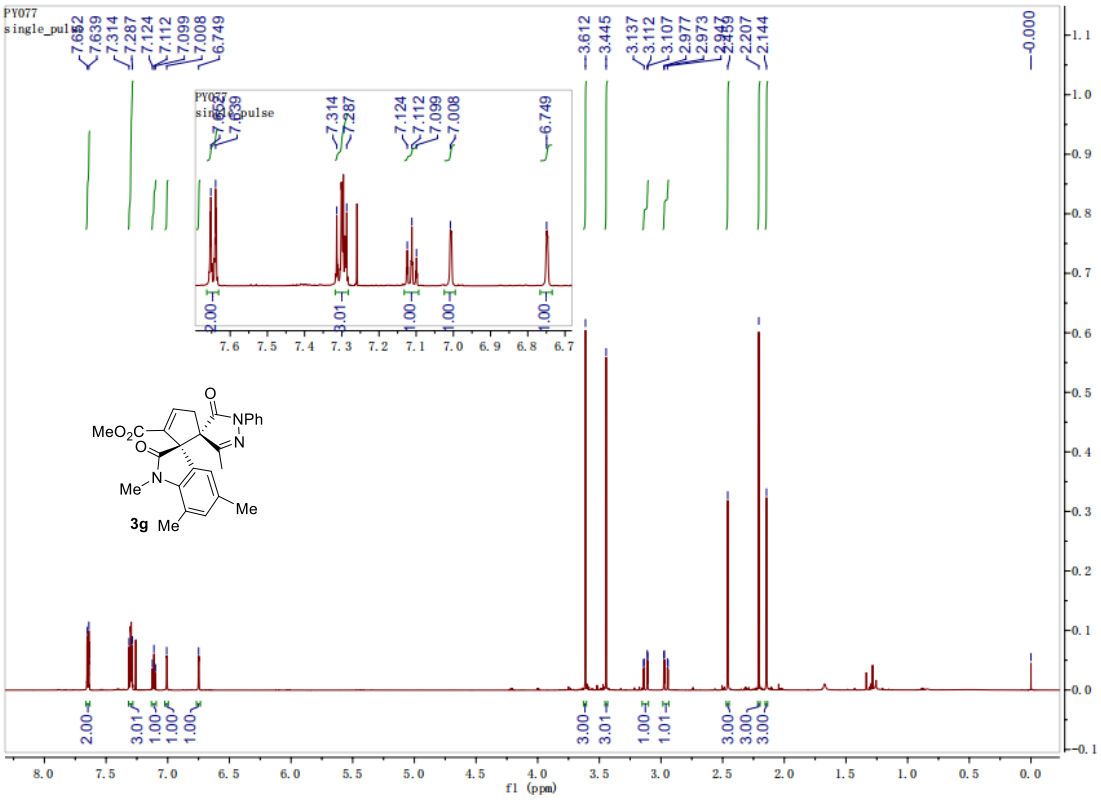
NPh
N
Me
N
3f Me
f1 (ppm)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3.112
3.107
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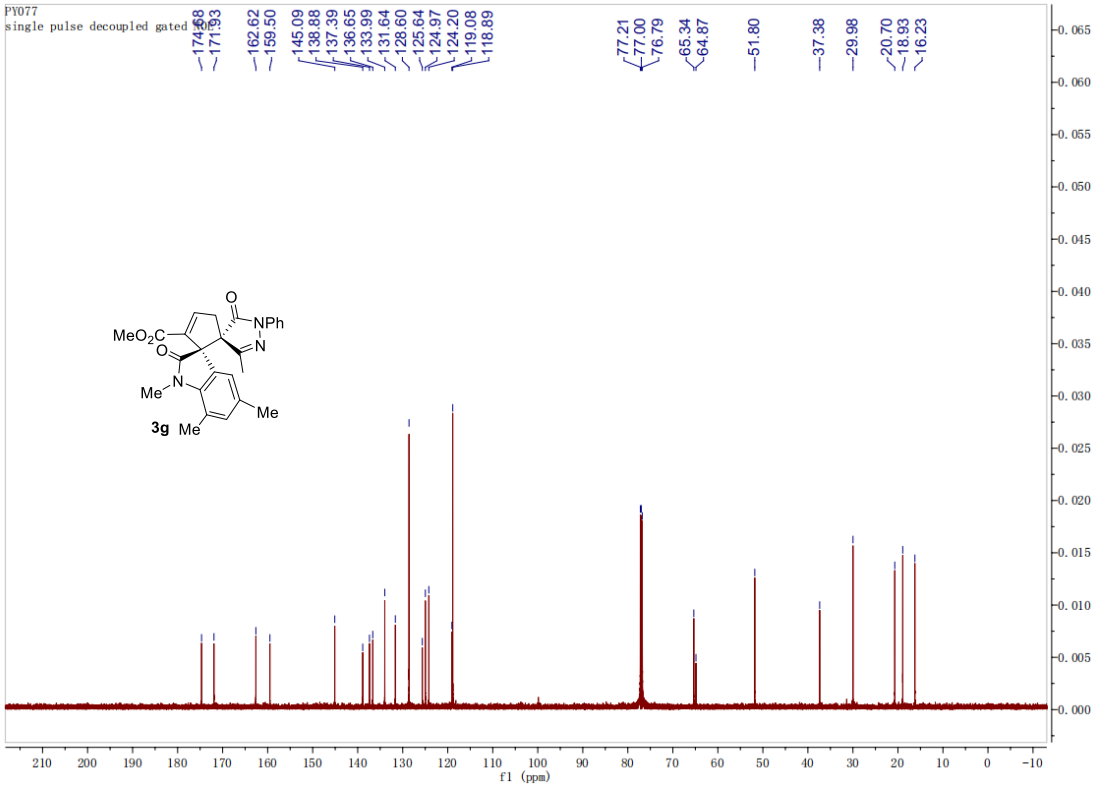
N
Me
N
Me
Me
3g
f1 (ppm)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N
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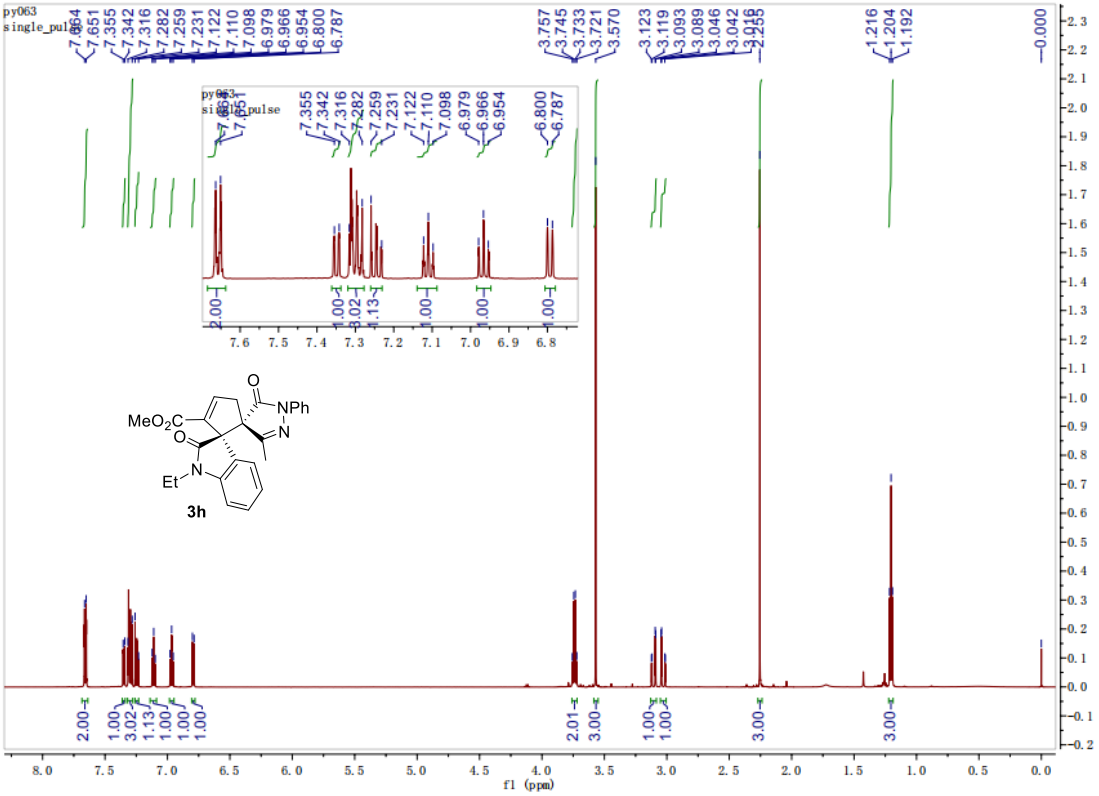
Me
3g
f1 (ppm)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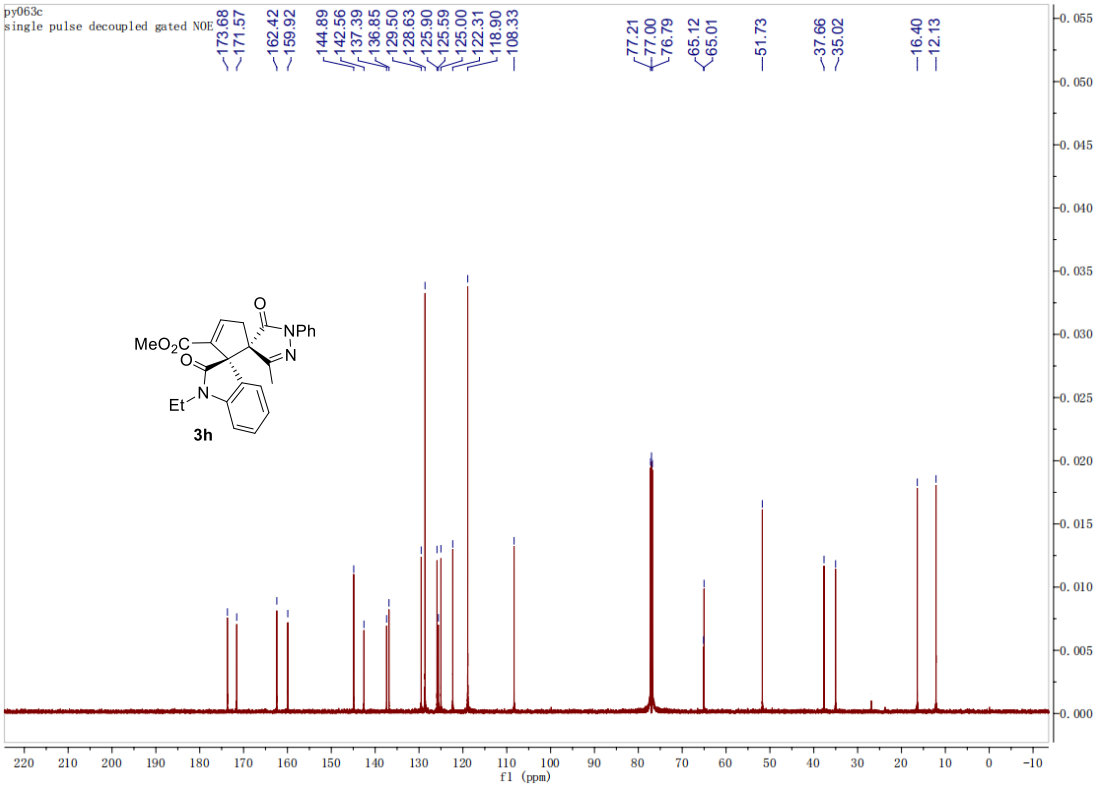
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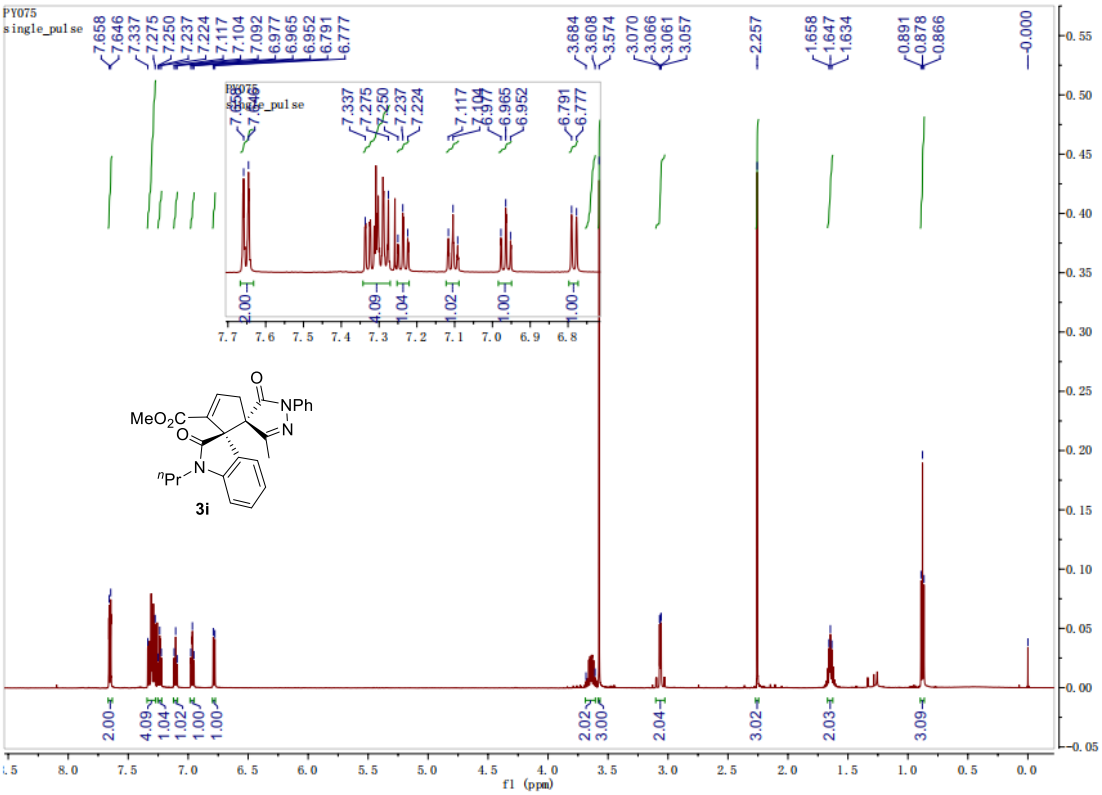
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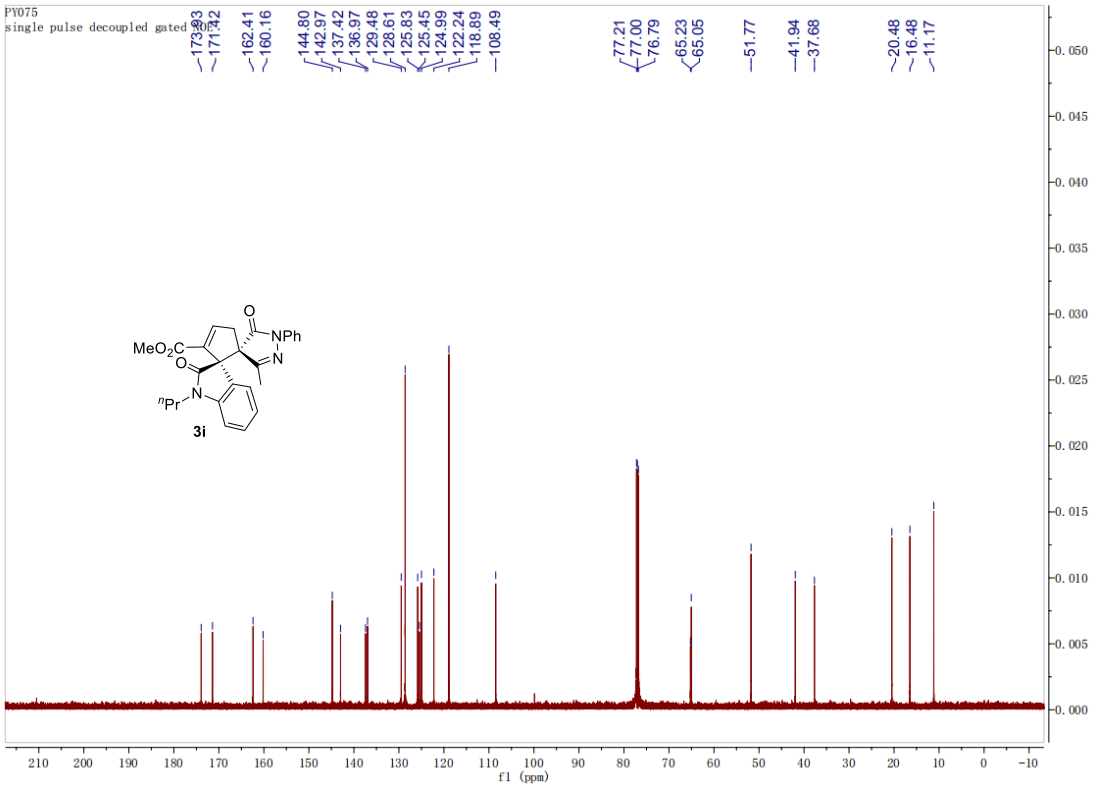
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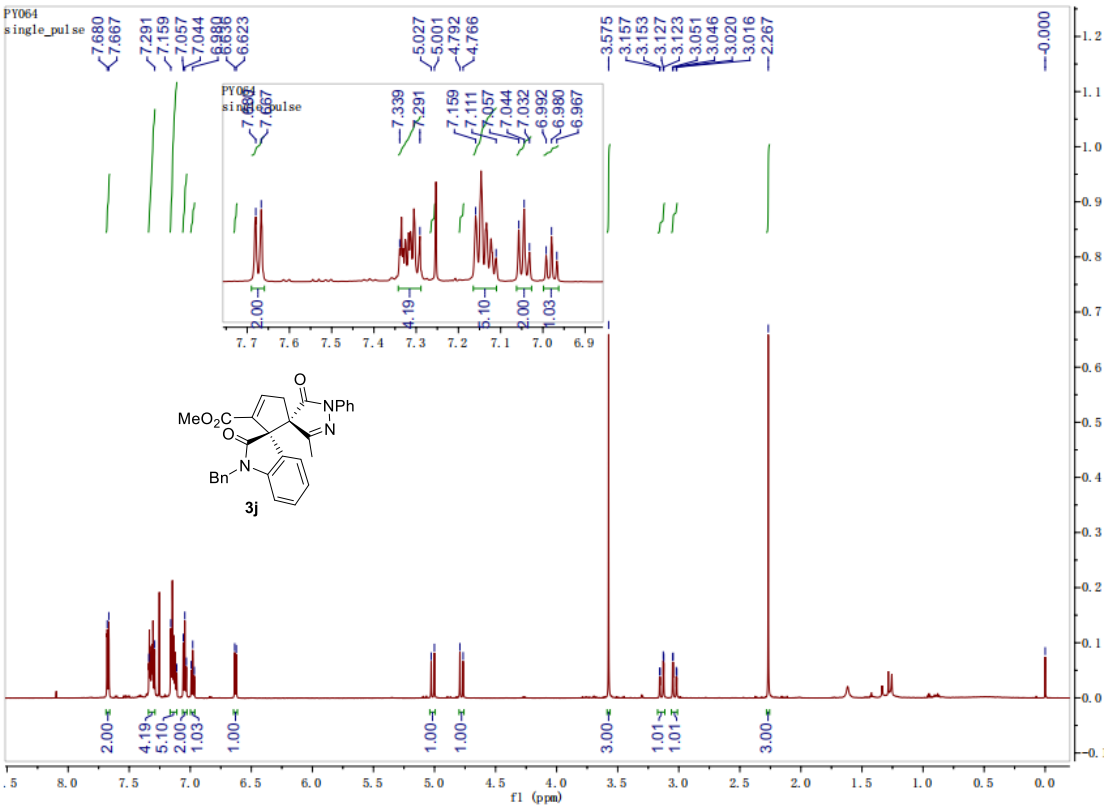
f1 (ppm)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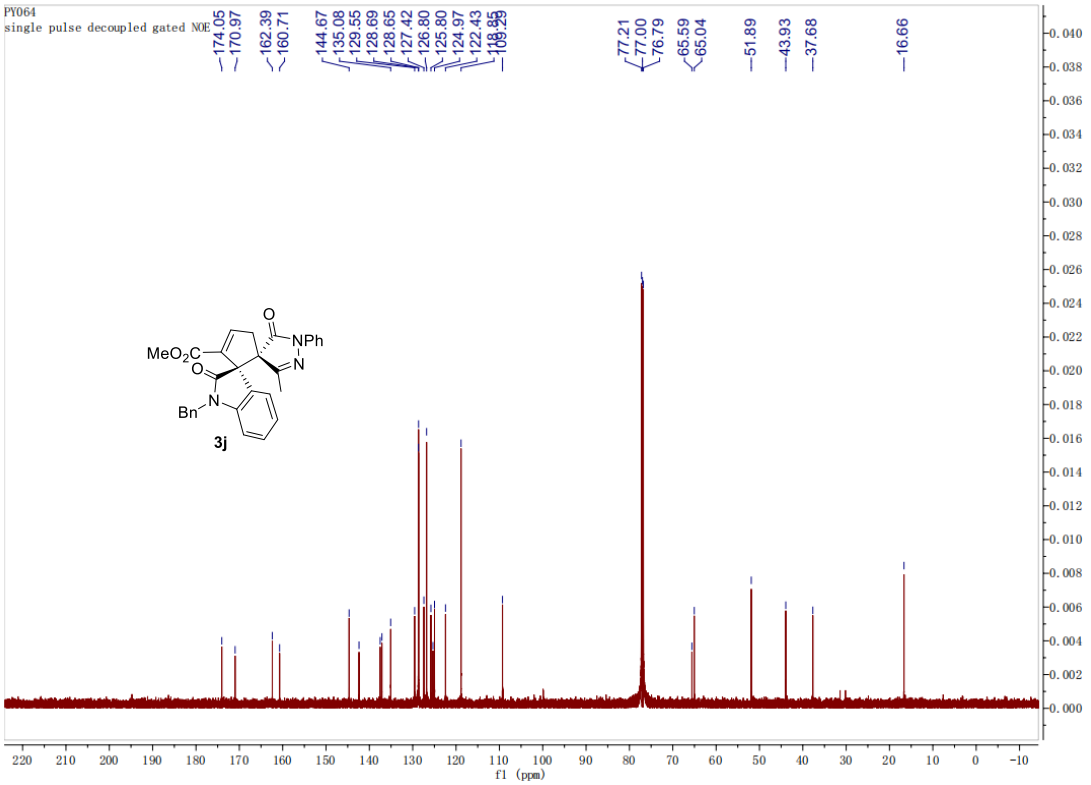
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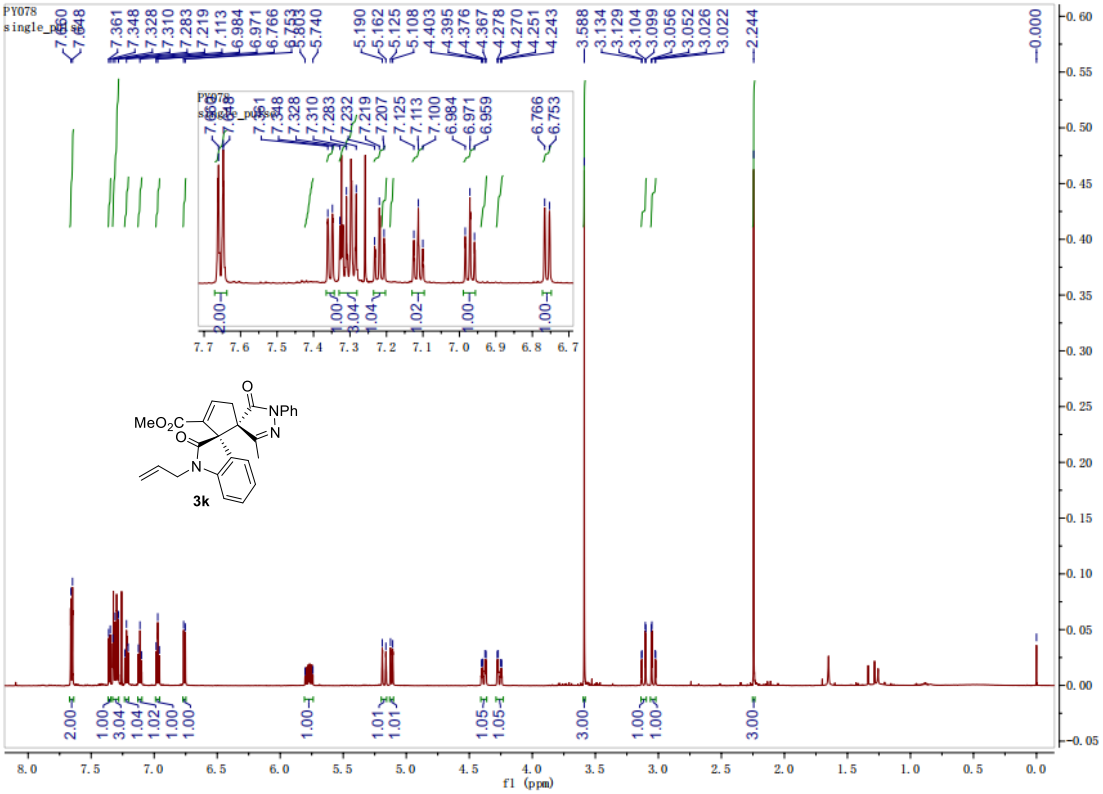
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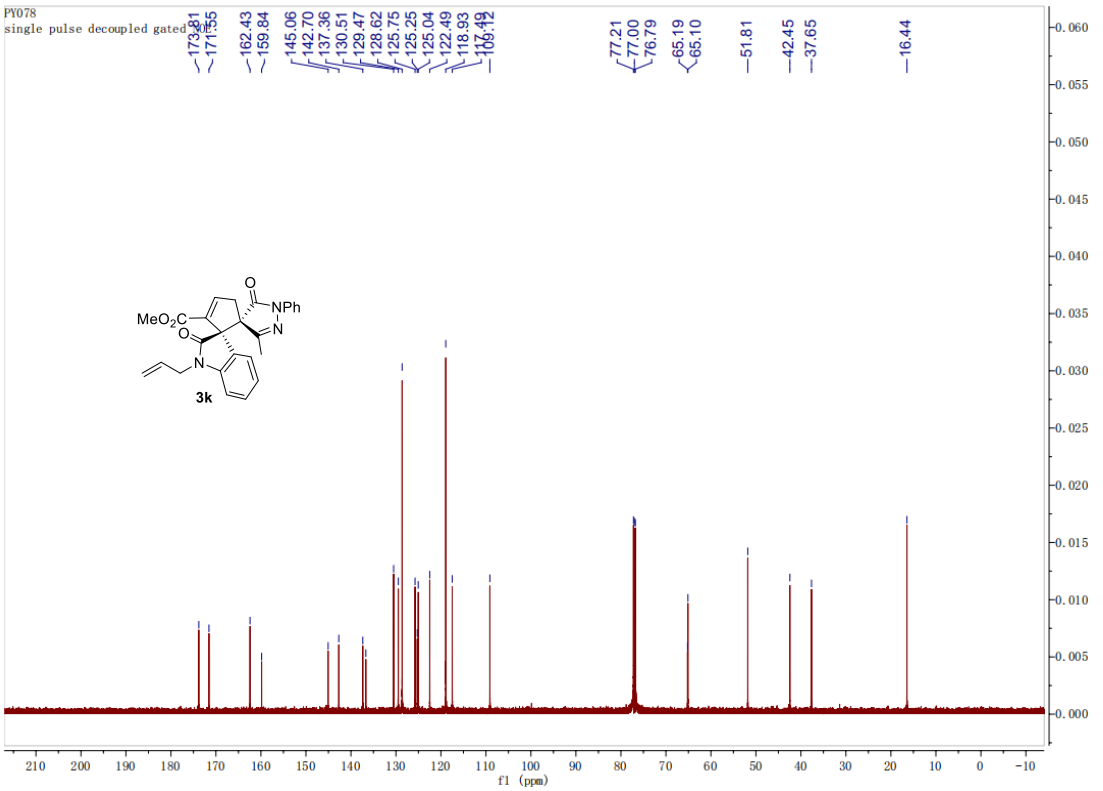
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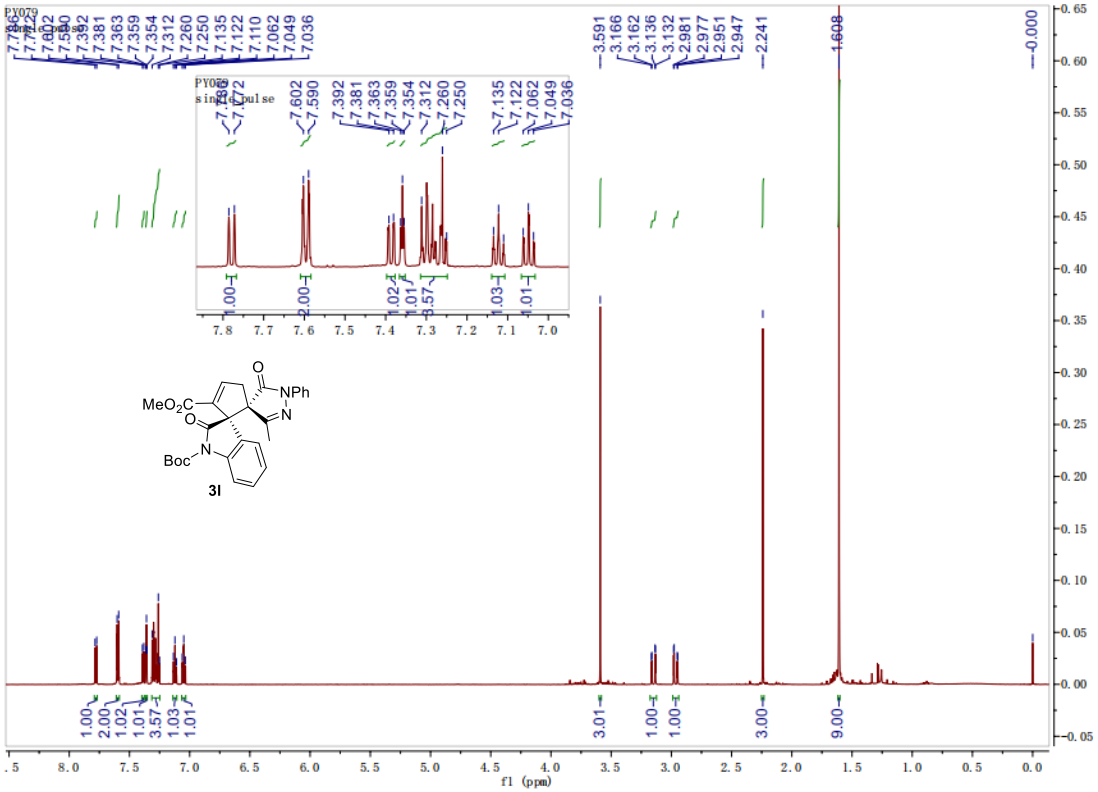
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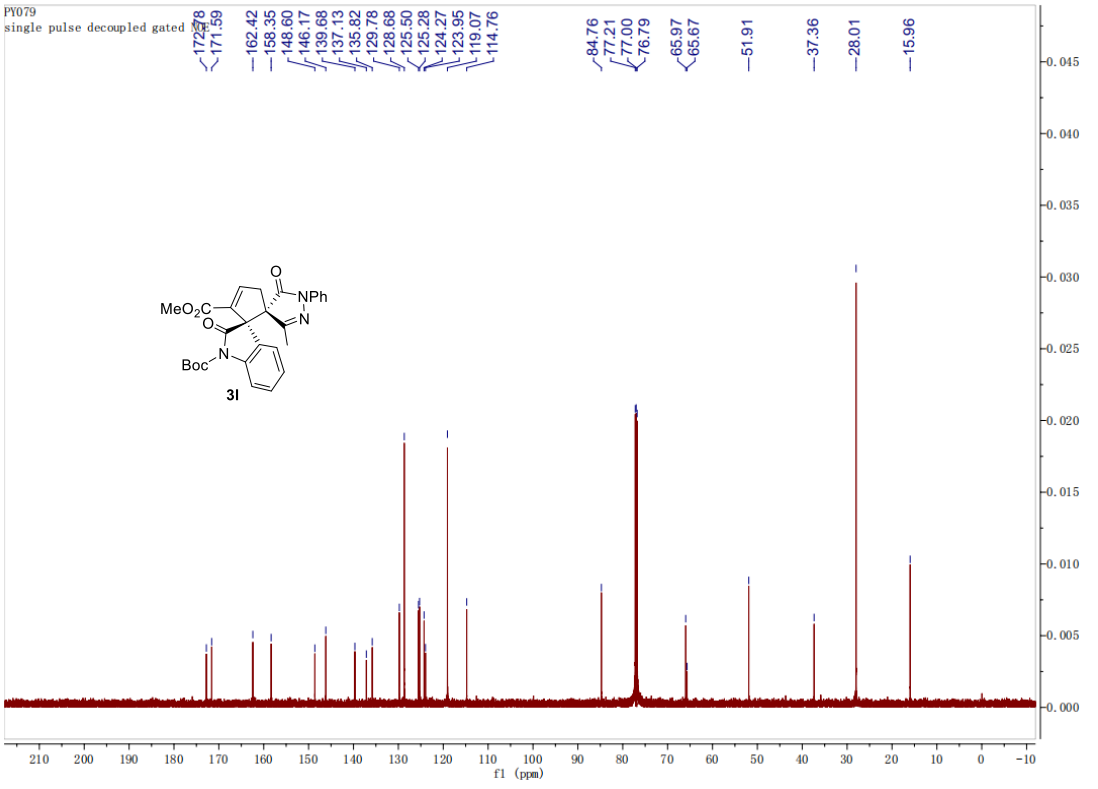
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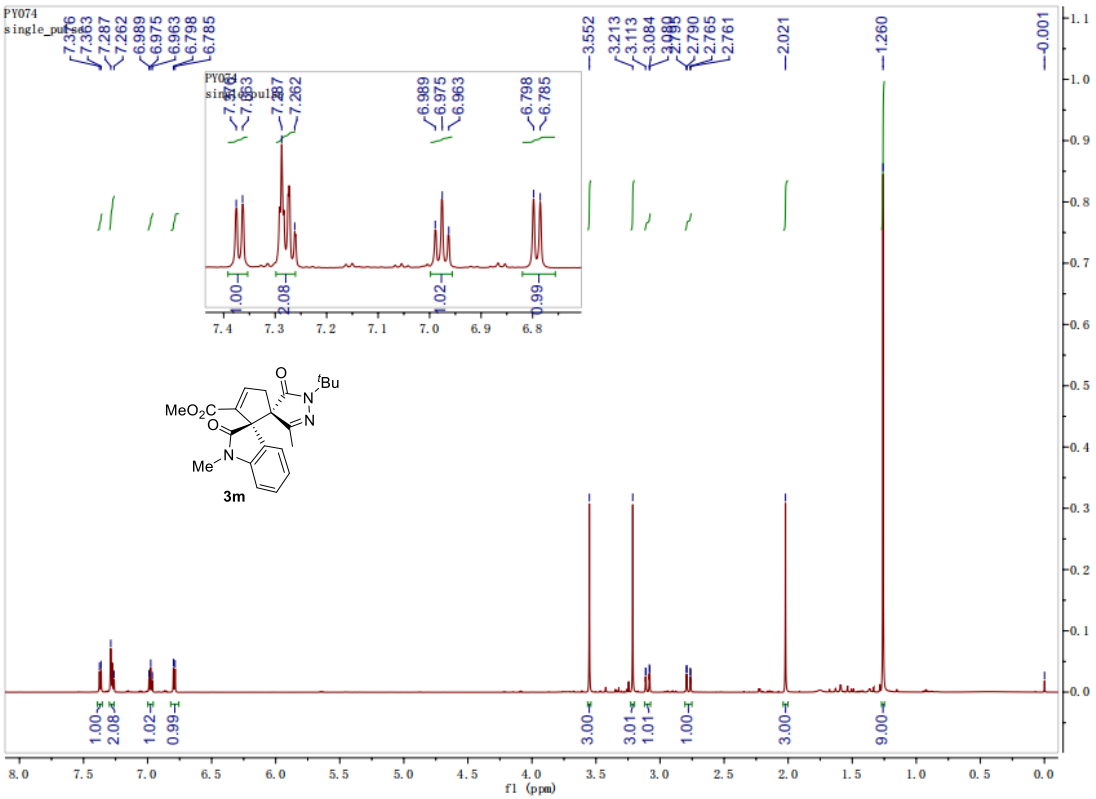
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1.00
2.08
1.02
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1.01
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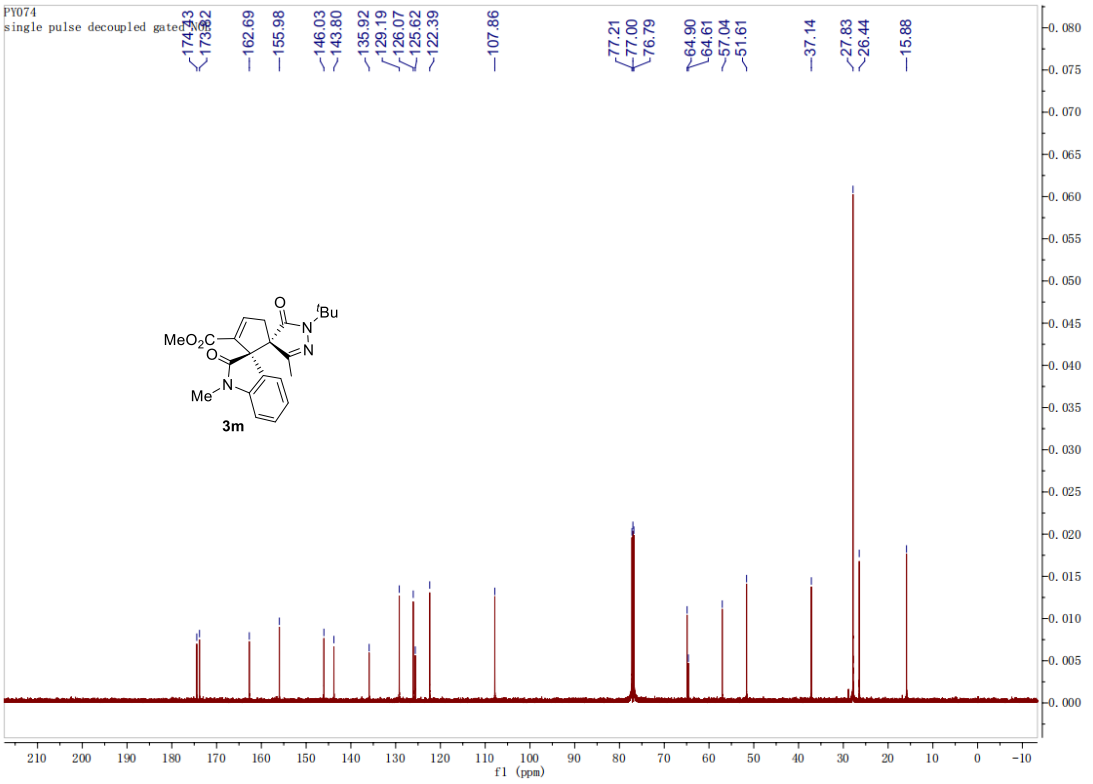
f1 (ppm)
MeO2C
tBu
Me
3m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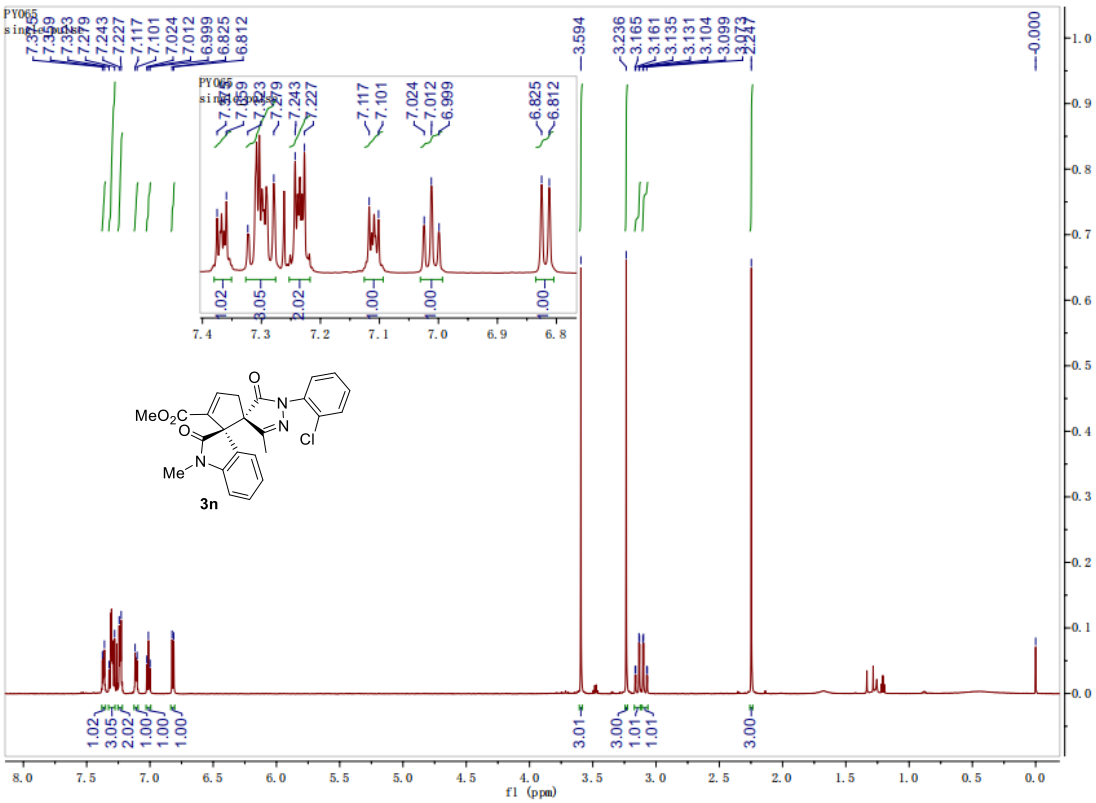
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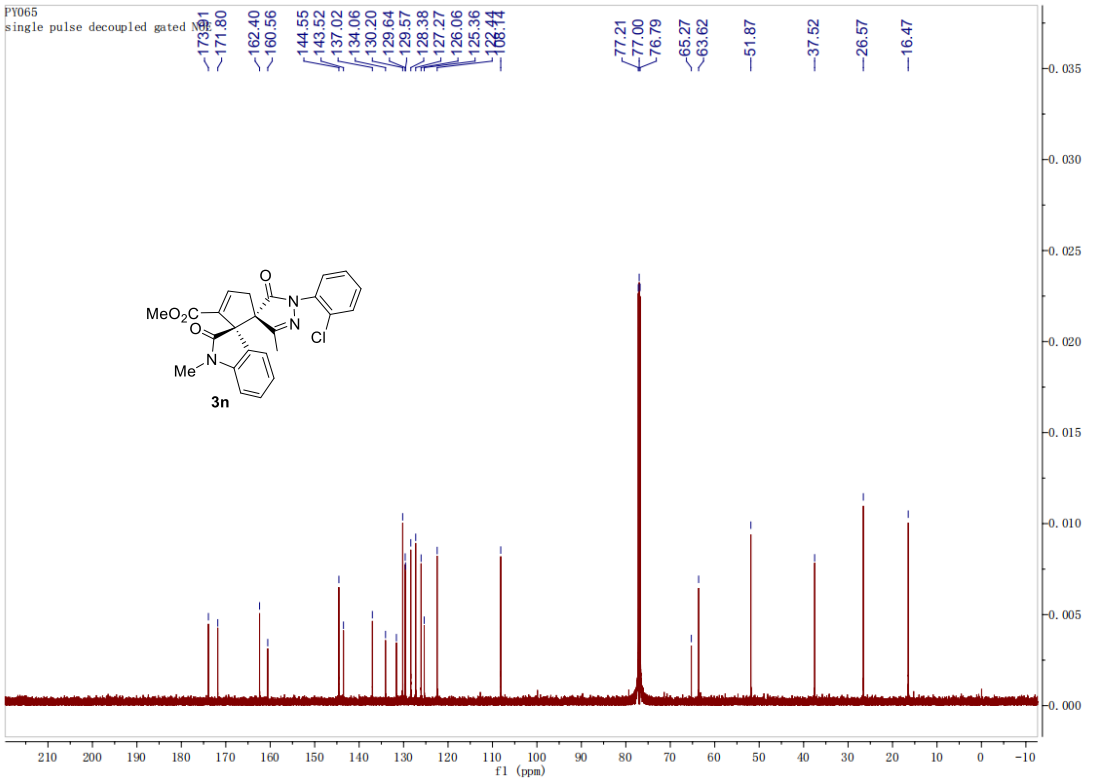
Cl
Me
3n
f1 (ppm)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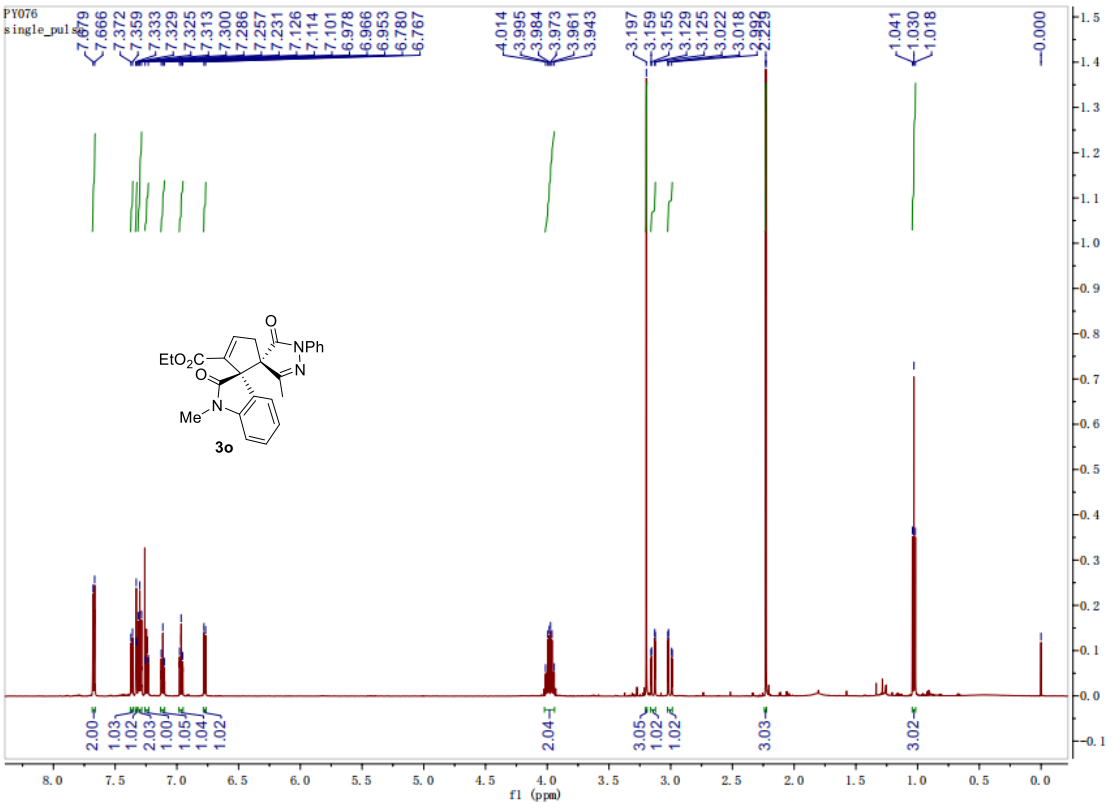
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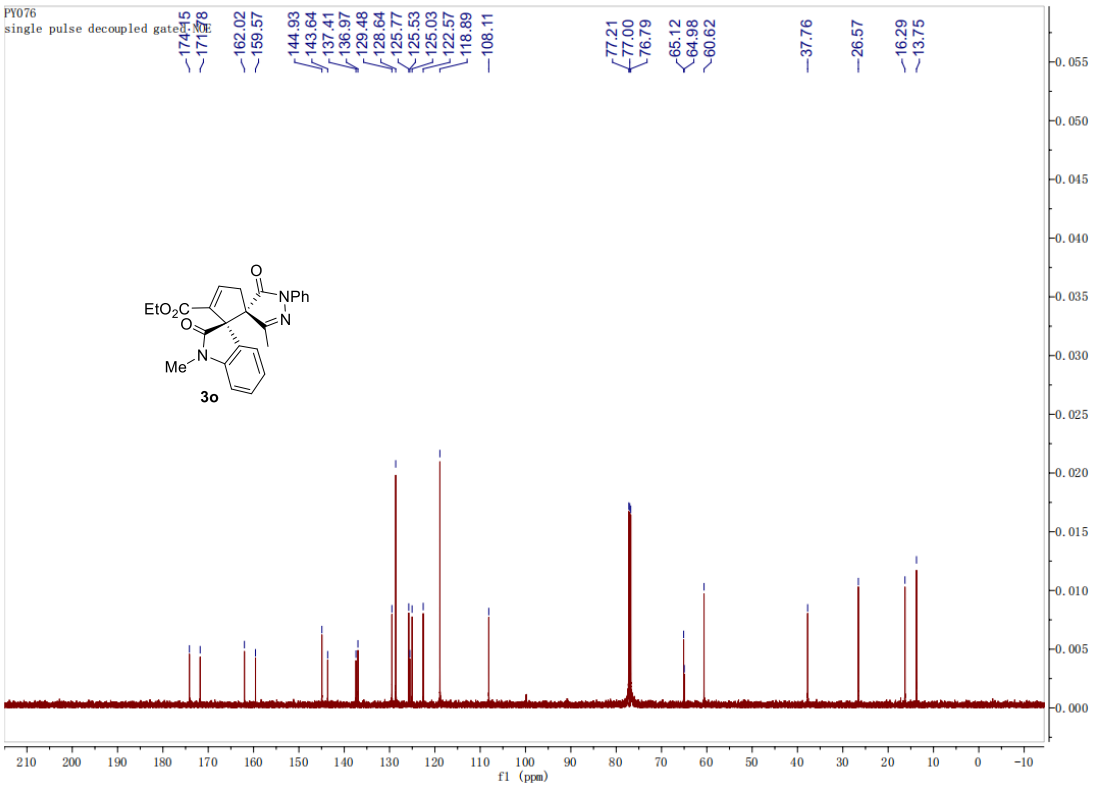
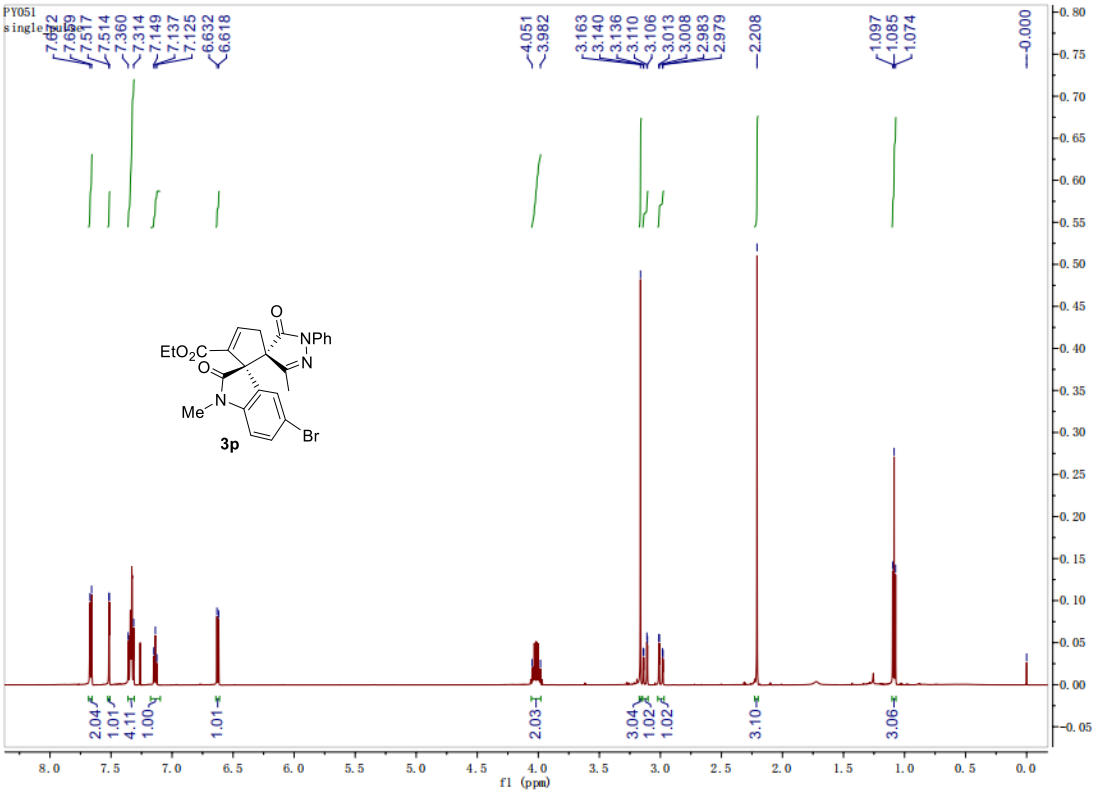
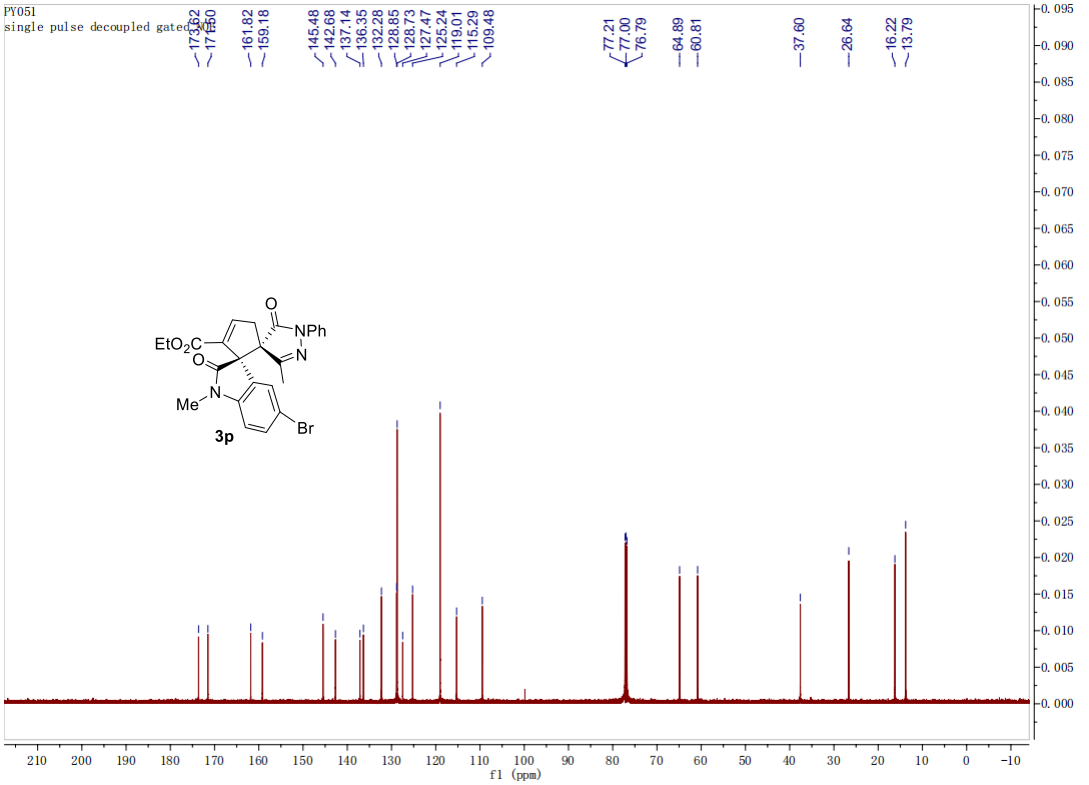
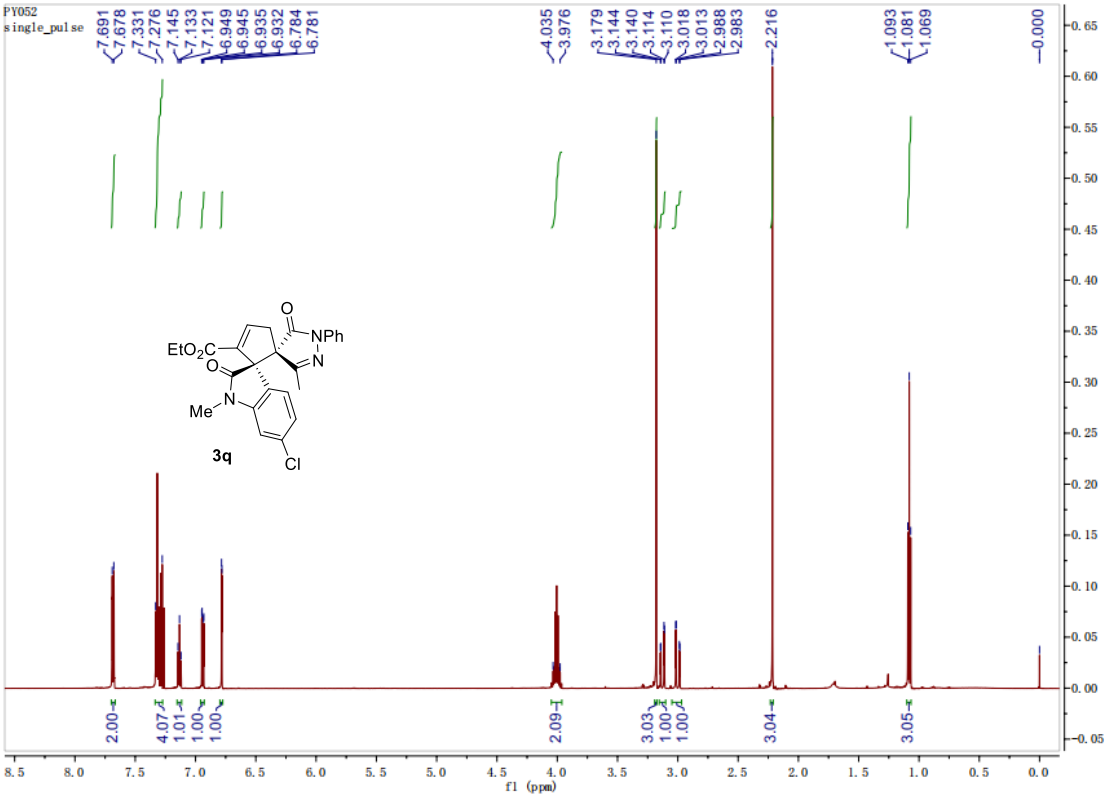
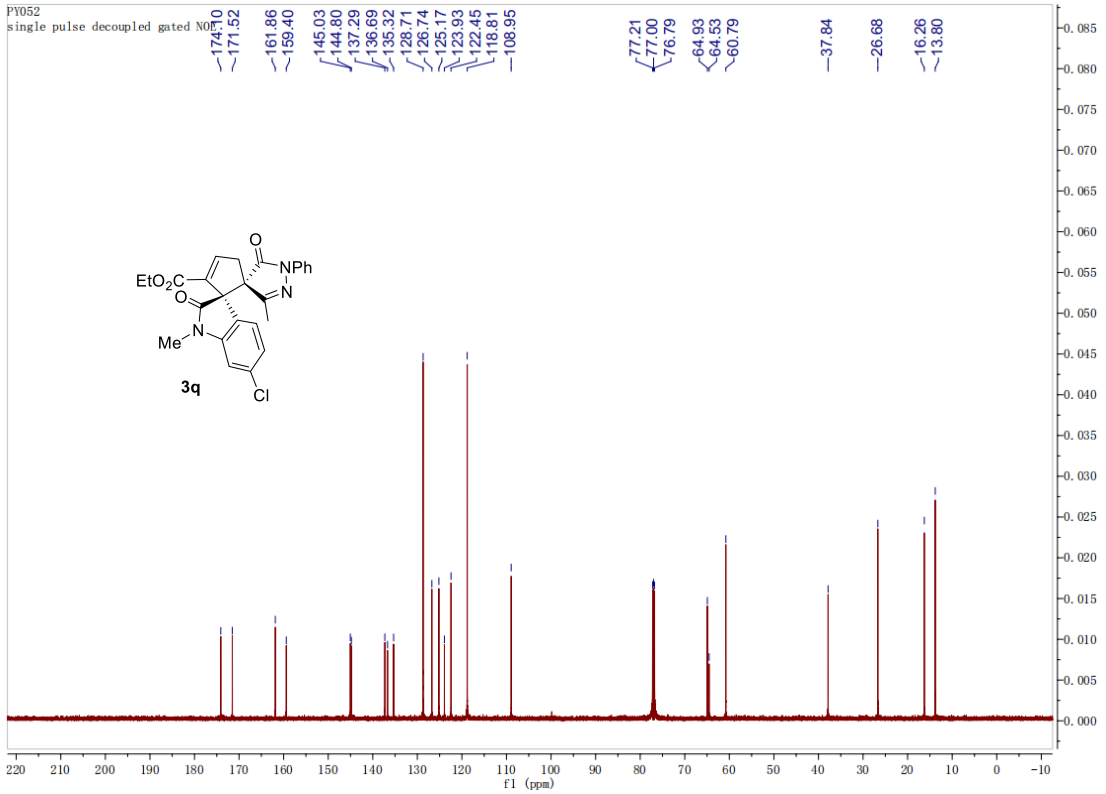
3.961
3.943
3.197
3.159
3.155
3.129
3.125
3.022
3.018
2.992
2.229
1.041
1.030
1.018
0.000
EtO2C
O
NPh
N
Me
3o
2.00
1.03
1.02
2.03
1.00
1.05
1.04
1.02
2.04
3.05
1.02
1.02
3.03
3.02
f1 (ppm)

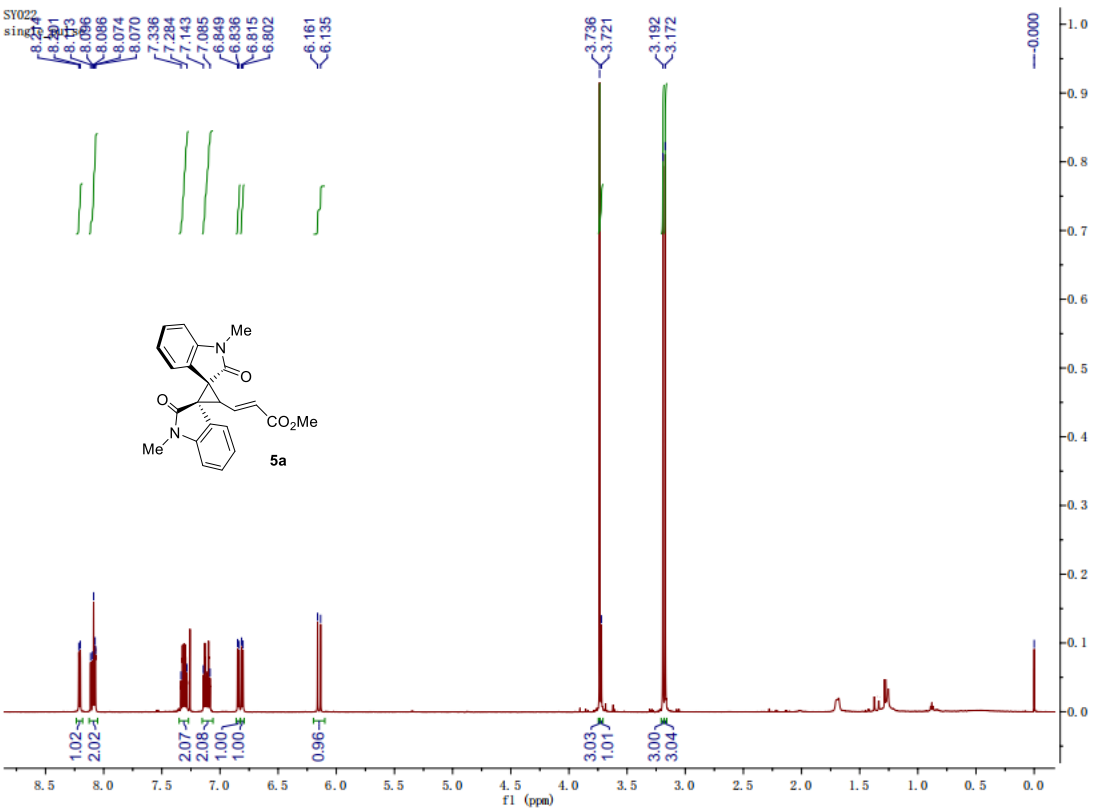

PY076
single pulse decoupled gated NOE
174.15
171.78
162.02
159.57
144.93
143.64
137.41
136.97
129.48
128.64
125.77
125.53
125.03
122.57
118.89
108.11
77.21
77.00
76.79
65.12
64.98
60.62
37.76
26.57
16.29
13.75
EtO2C
O
NPh
N
Me
3o
f1 (ppm)

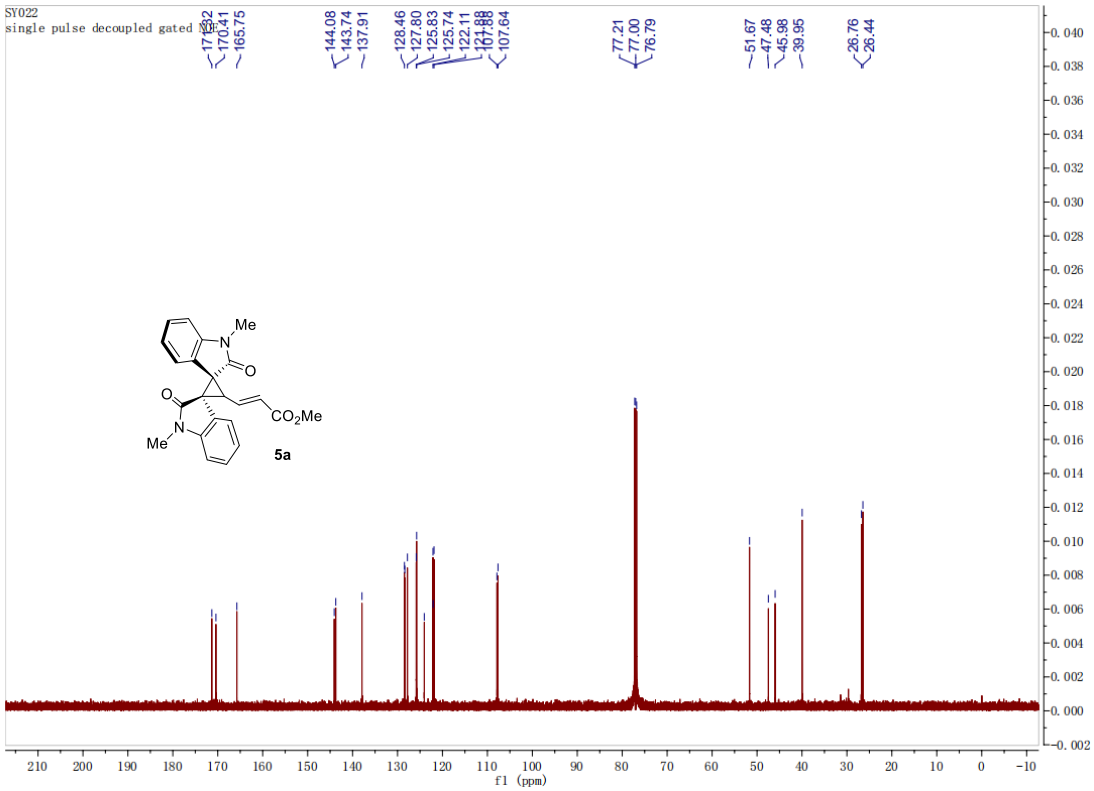

PY051
single
7.622
7.659
7.517
7.514
7.360
7.314
7.149
7.137
7.125
6.632
6.618
4.051
3.982
3.163
3.140
3.136
3.110
3.106
3.013
3.008
2.983
2.979
2.208
1.097
1.085
1.074
0.000
EtO2C
O
NPh
N
Me
N
Br
3p
2.04
1.01
4.11
1.00
1.01
2.03
3.04
1.02
1.02
3.10
3.06
f1 (ppm)

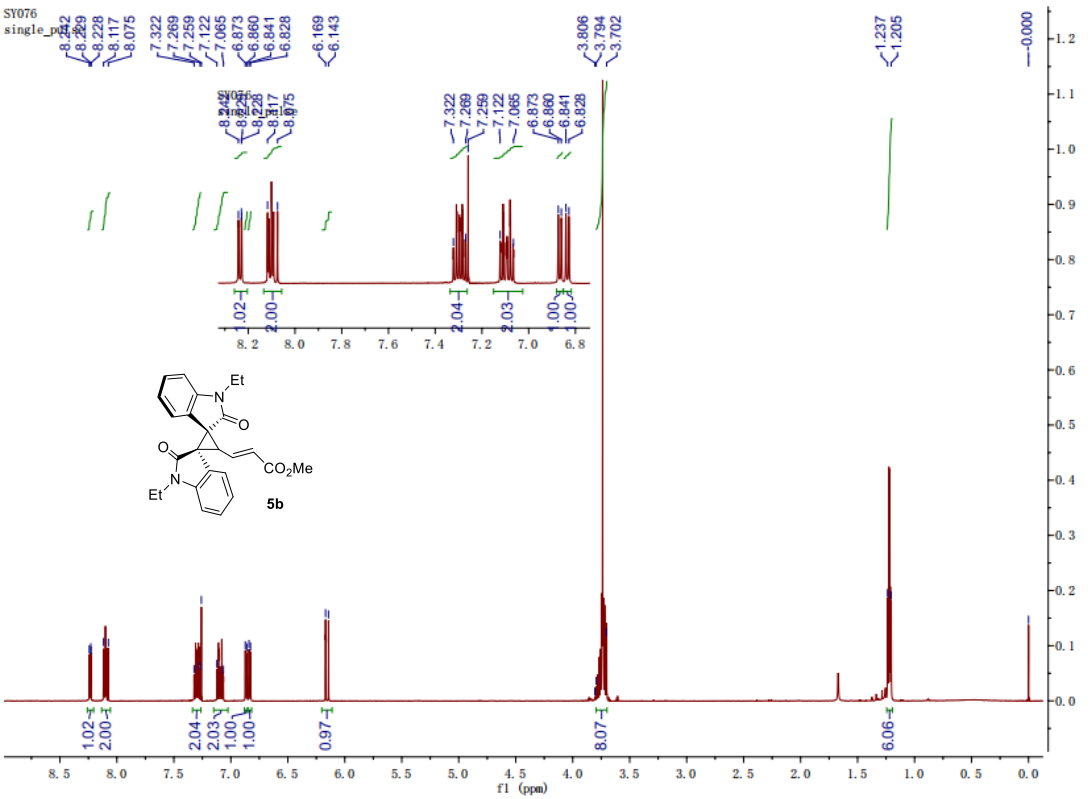

PY051
single pulse decoupled gated C13
173.62
171.60
161.82
159.18
145.48
142.68
137.14
136.35
132.28
128.85
128.73
127.47
125.24
119.01
115.29
109.48
77.21
77.00
76.79
64.89
60.81
37.60
26.64
16.22
13.79
EtO2C
O
NPh
N
Me
N
Br
3p
f1 (ppm)

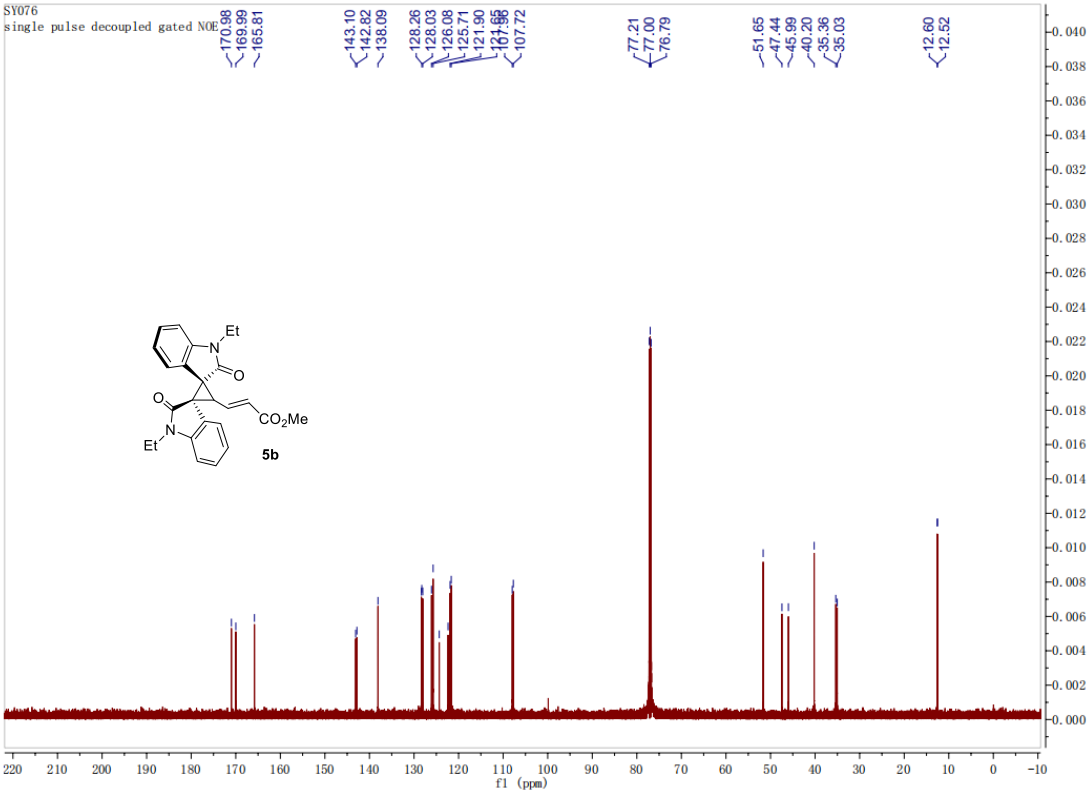

PY052
single_pulse
7.691
7.678
7.331
7.276
7.145
7.133
7.121
6.949
6.945
6.935
6.932
6.784
6.781
4.035
3.976
3.179
3.144
3.140
3.114
3.110
3.018
3.013
2.988
2.983
2.216
1.093
1.081
1.069
0.000
EtO2C
O
NPh
N
Me
N
Cl
3q
2.00
4.07
1.01
1.00
1.00
2.09
3.03
1.00
1.00
3.04
3.05
f1 (ppm)

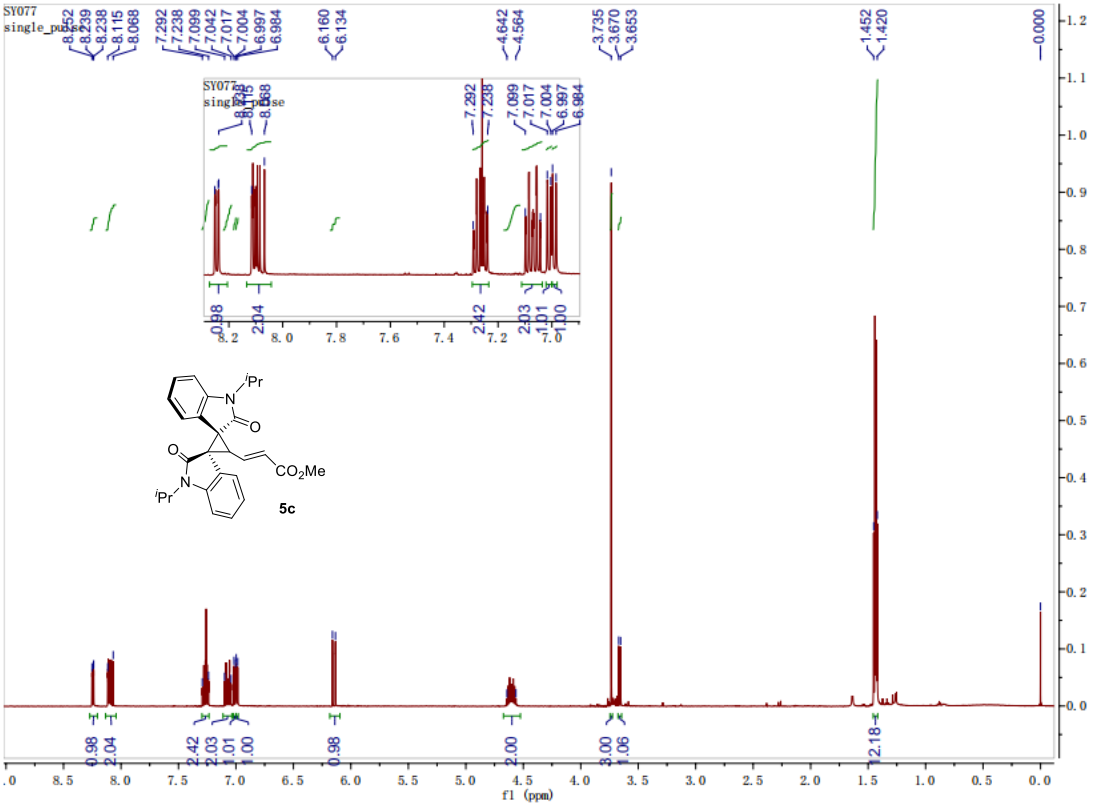

PY052
single pulse decoupled gated NOE
174.10
171.52
161.86
159.40
145.03
144.80
137.29
136.69
135.32
128.71
126.74
125.17
123.93
122.45
118.81
108.95
77.21
77.00
76.79
64.93
64.53
60.79
37.84
26.68
16.26
13.80
EtO2C
O
NPh
N
Me
N
Cl
3q
f1 (ppm)

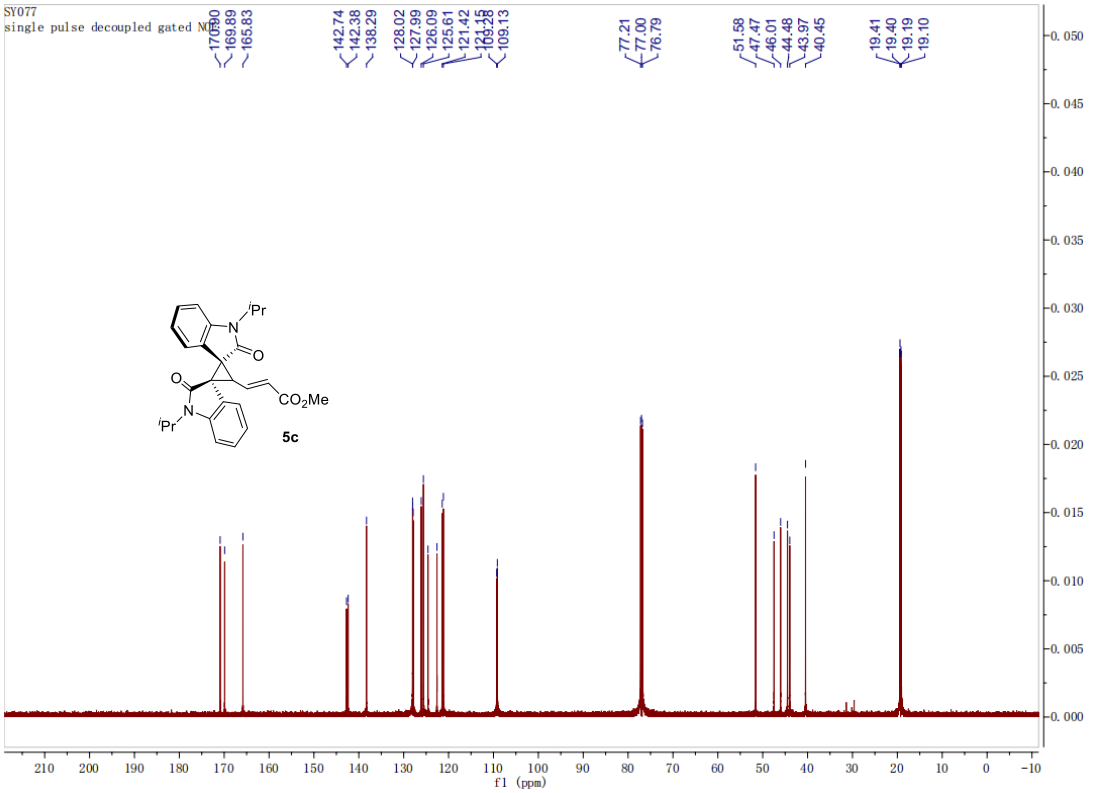

SY022
8.244
8.241
8.093
8.086
8.074
8.070
7.336
7.284
7.143
7.085
6.849
6.836
6.815
6.802
6.161
6.135
3.736
3.721
3.192
3.172
0.000
Me
N
O
O
N
Me
CO2Me
5a
1.02
2.02
2.07
2.08
1.00
1.00
0.96
3.03
1.01
3.00
3.04
f1 (ppm)

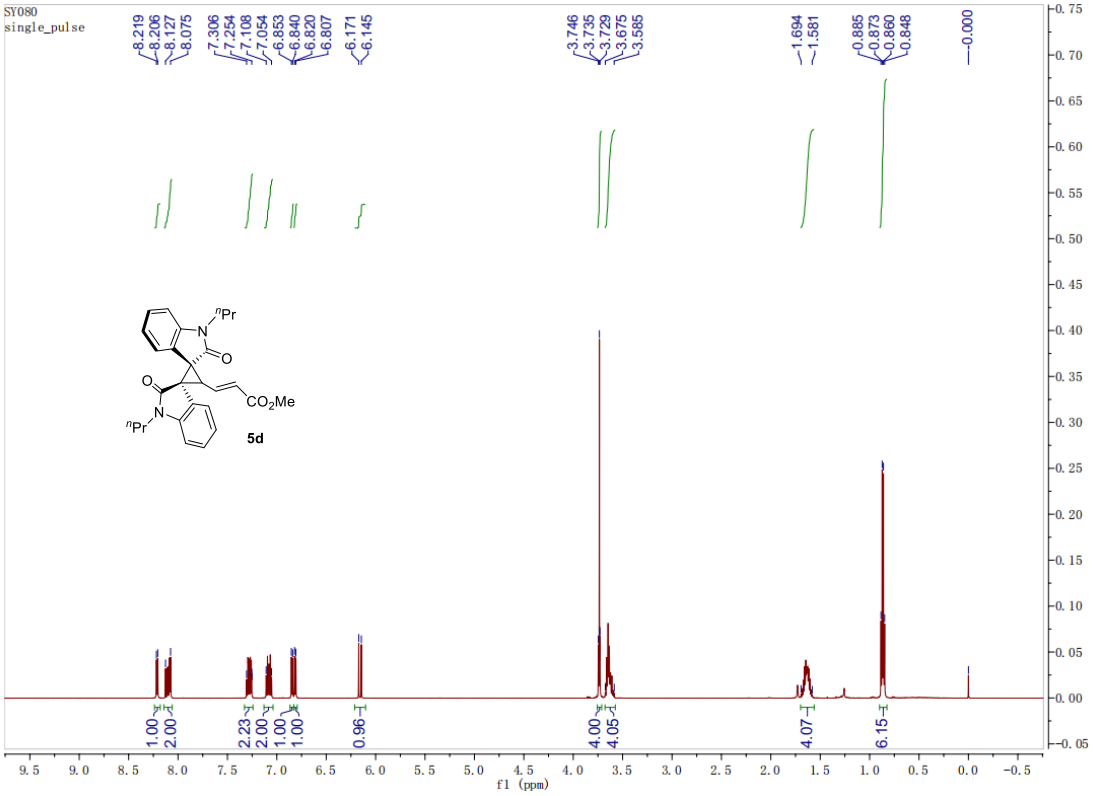

SY022
single pulse decoupled gated
172.22
170.41
165.75
144.08
143.74
137.91
128.46
127.80
125.83
125.74
122.11
107.64
77.21
77.00
76.79
51.67
47.48
45.98
39.95
26.76
26.44
Me
N
O
O
N
Me
CO2Me
5a
f1 (ppm)

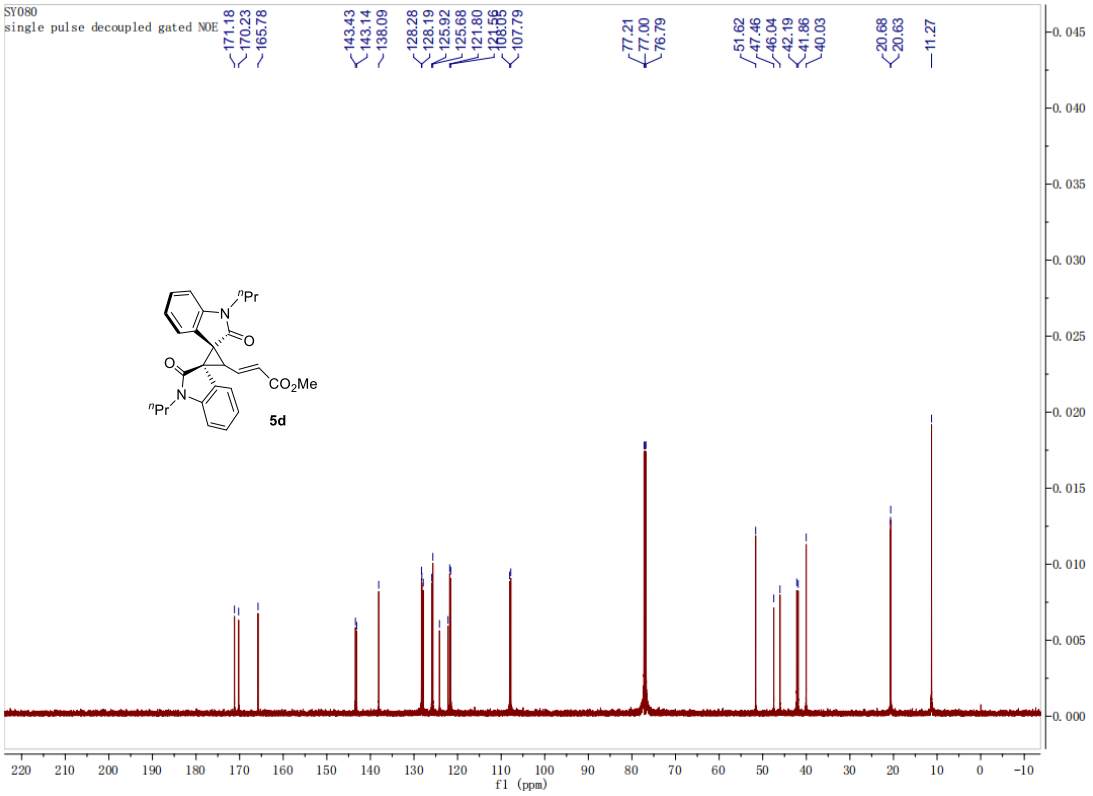

SY076
single_pulse
5b
f1 (ppm)

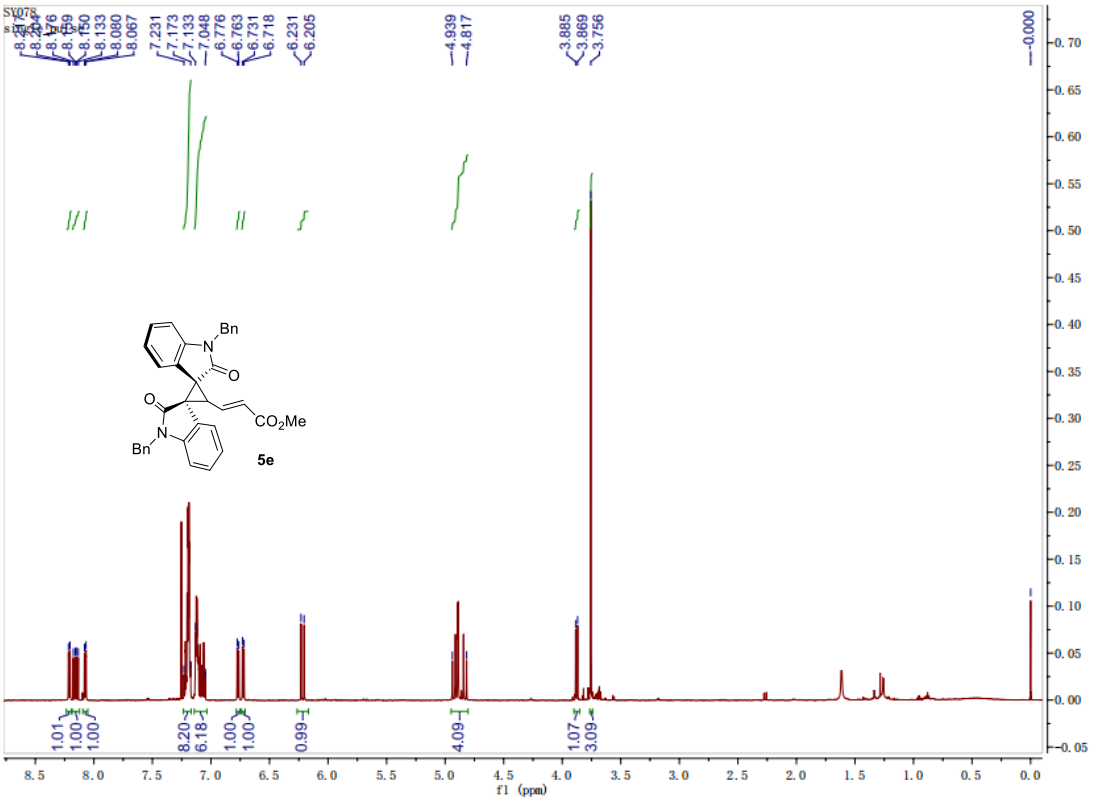

SY076
single pulse decoupled gated NOE
5b
f1 (ppm)

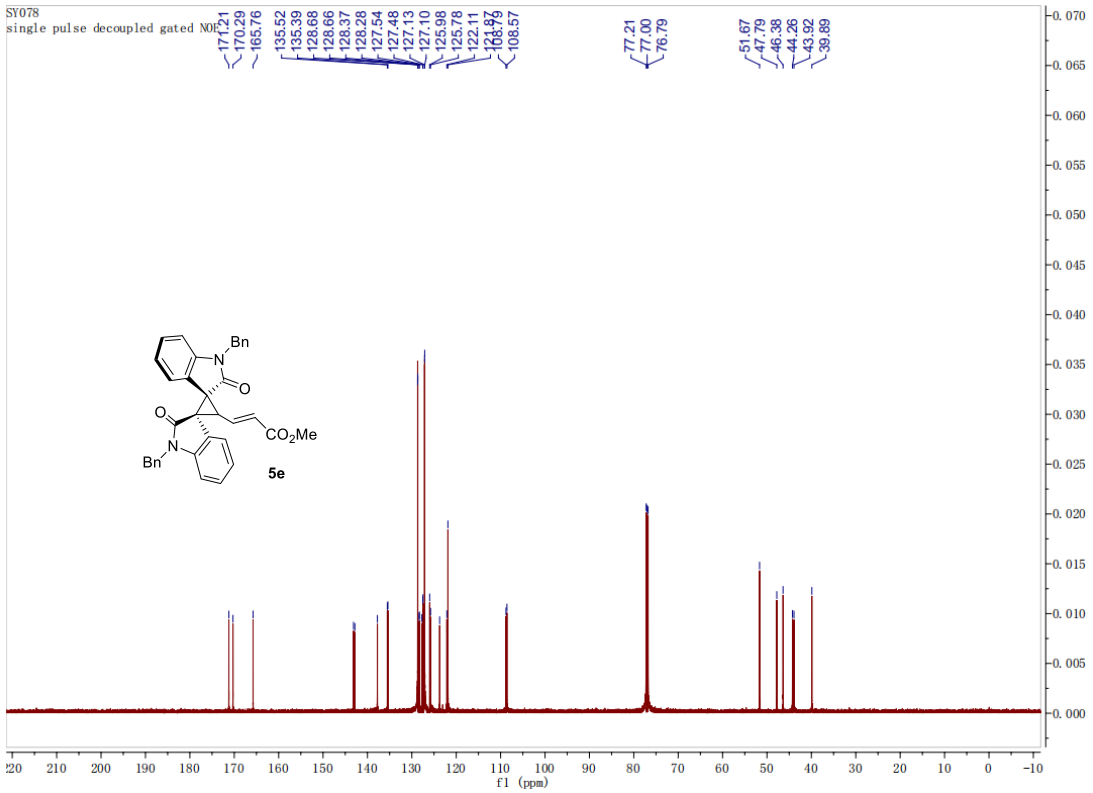

SY077
single_pulse
8.252
8.239
8.238
8.115
8.068
7.292
7.238
7.099
7.042
7.017
7.004
6.997
6.984
6.160
6.134
4.642
4.564
3.735
3.670
3.653
1.452
1.420
0.000
0.98
2.04
2.42
2.03
1.01
1.00
0.98
2.00
3.00
1.06
2.18
f1 (ppm)
5c

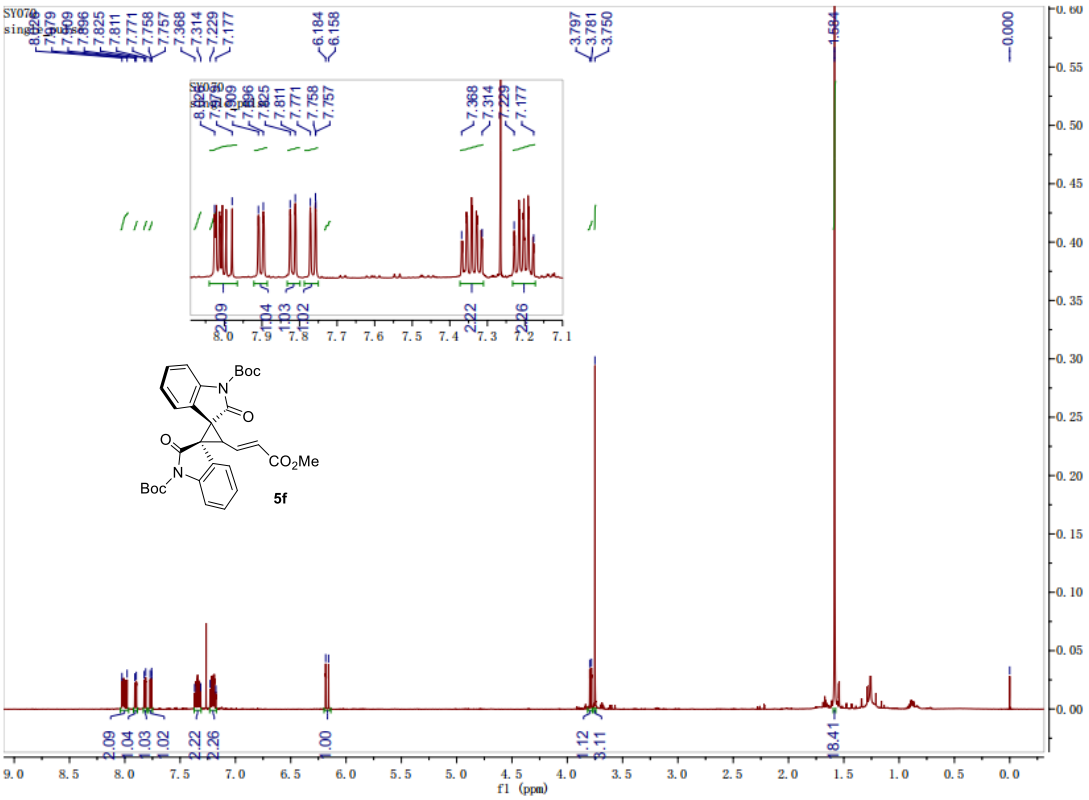

SY077
single pulse decoupled gated NOE
170.80
169.89
165.83
142.74
142.38
138.29
128.02
127.99
126.09
125.61
121.42
121.15
109.28
109.13
77.21
77.00
76.79
51.58
47.47
46.01
44.48
43.97
40.45
19.41
19.40
19.19
19.10
f1 (ppm)
5c

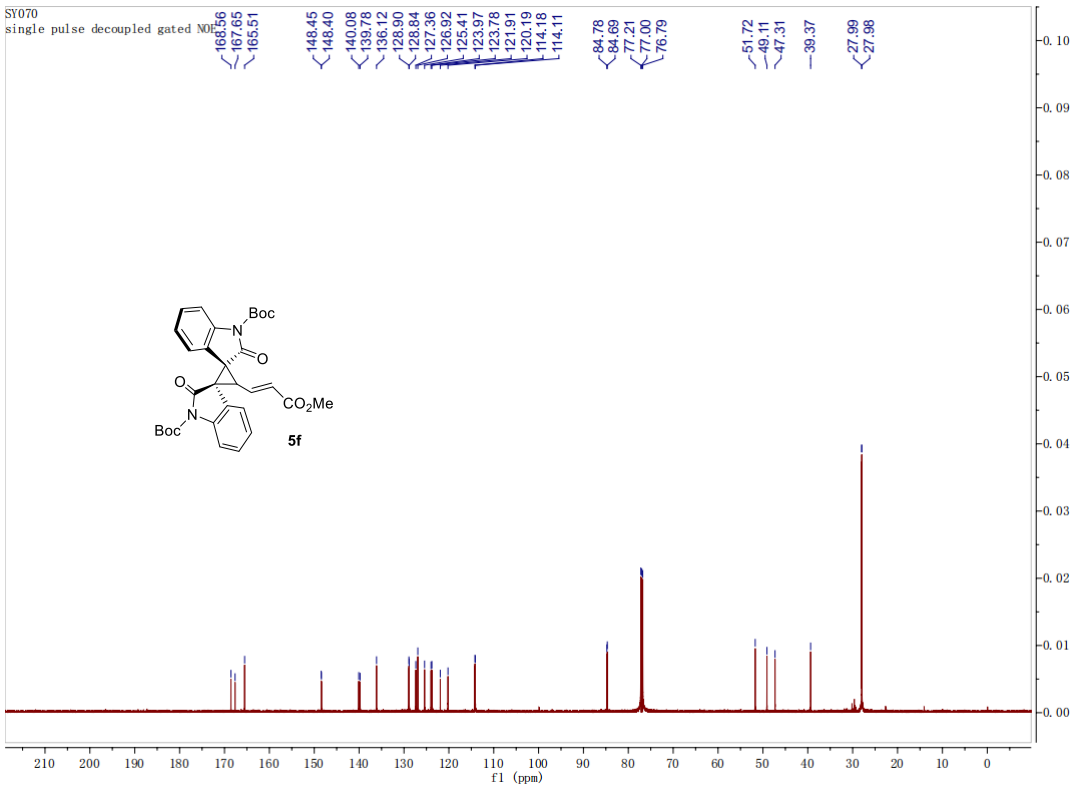

SY080
single_pulse
8.219
8.206
8.127
8.075
7.306
7.254
7.108
7.054
6.853
6.840
6.820
6.807
6.171
6.145
3.746
3.735
3.729
3.675
3.585
1.694
1.581
0.885
0.873
0.860
0.848
0.000
nPr
N
O
O
CO2Me
nPr
N
5d
1.00
2.00
2.23
2.00
1.00
1.00
0.96
4.00
4.05
4.07
6.15
f1 (ppm)

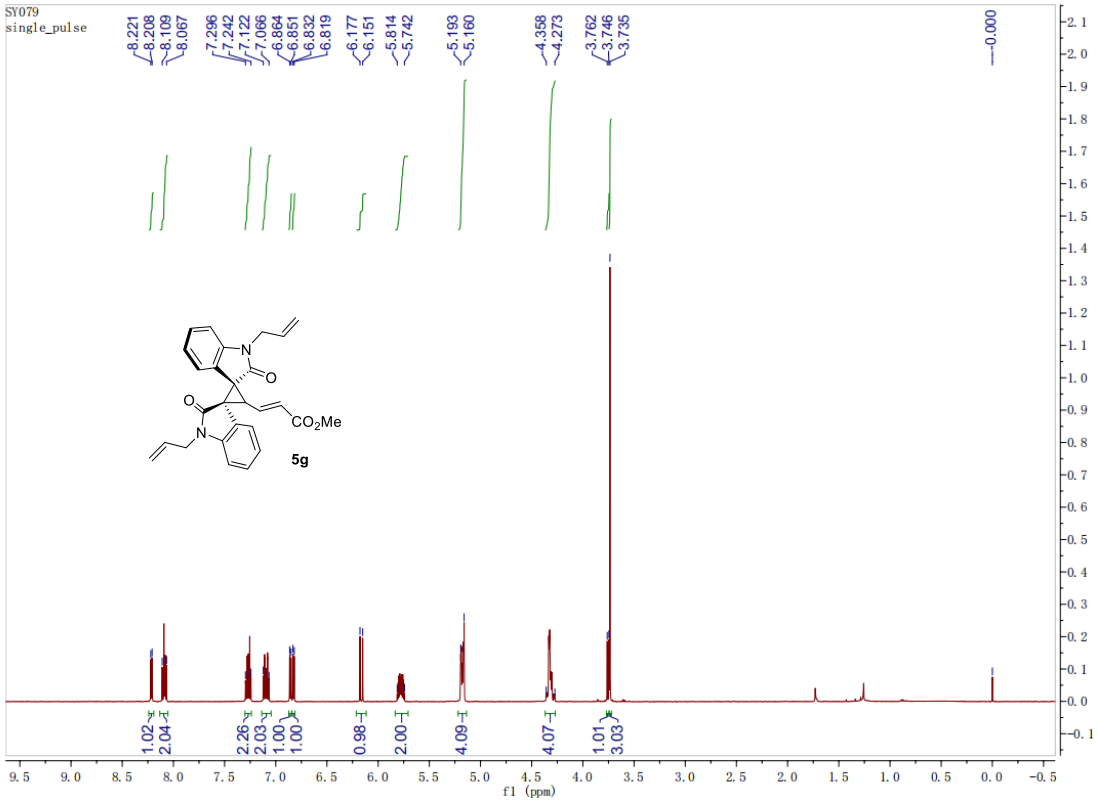

SY080
single pulse decoupled gated NOE
171.18
170.23
165.78
143.43
143.14
138.09
128.28
128.19
125.92
125.68
121.80
121.56
108.05
107.79
77.21
77.00
76.79
51.62
47.46
46.04
42.19
41.86
40.03
20.68
20.63
11.27
nPr
N
O
O
CO2Me
nPr
N
5d
f1 (ppm)

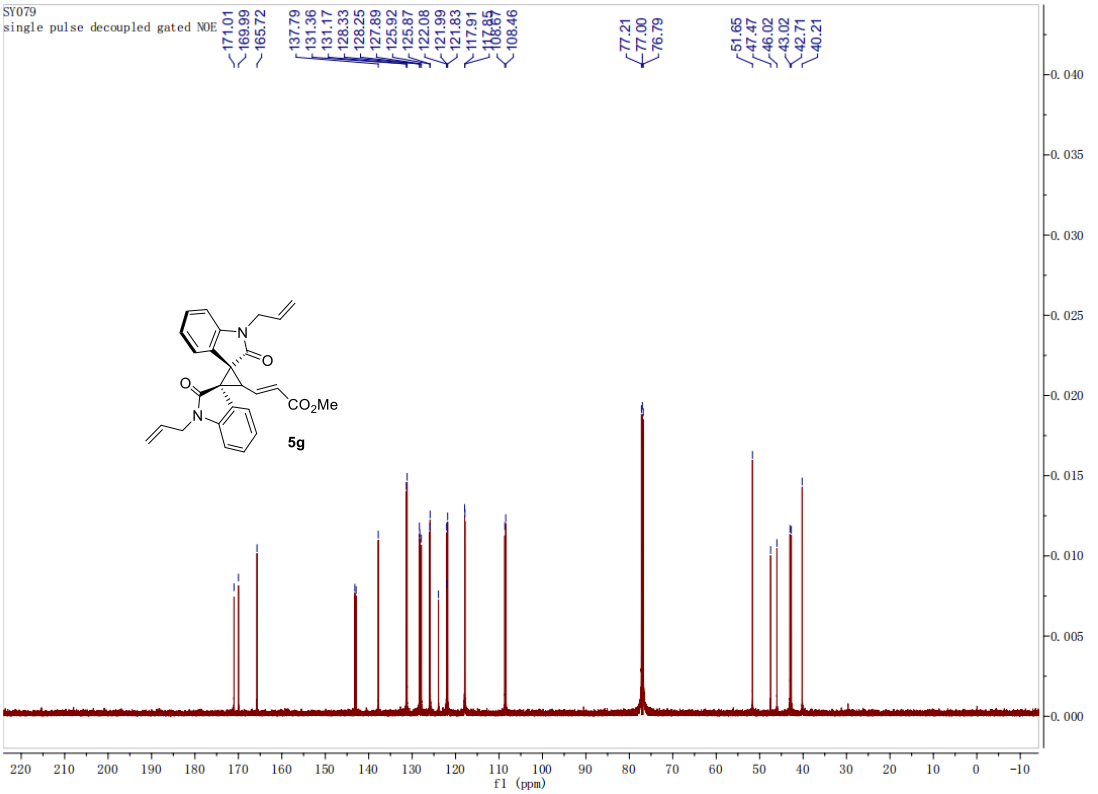

SY078
8.251
8.245
8.176
8.159
8.150
8.133
8.080
8.067
7.231
7.173
7.133
7.048
6.776
6.763
6.731
6.718
6.231
6.205
4.939
4.817
3.885
3.869
3.756
0.000
Bn
N
O
O
N
Bn
CO2Me
5e
1.01
1.00
1.00
8.20
6.18
1.00
1.00
0.99
4.09
1.07
3.09
f1 (ppm)

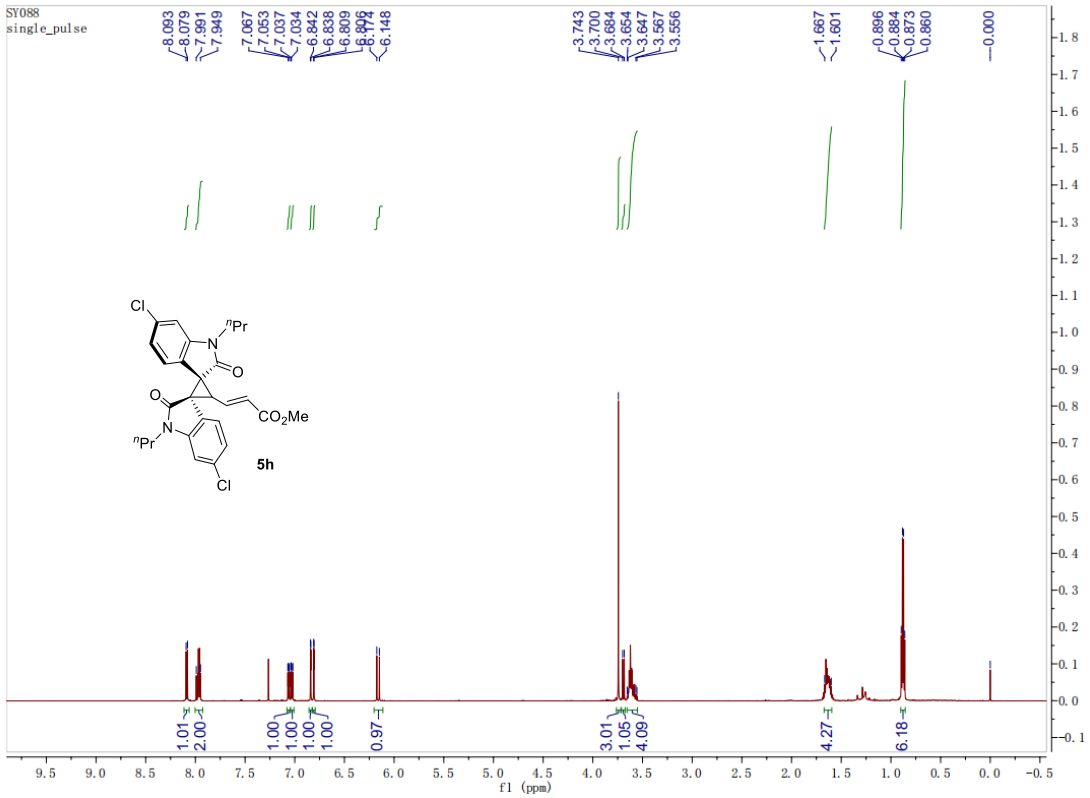

SY078
single pulse decoupled gated NOE
171.21
170.29
165.76
135.52
135.39
128.68
128.66
128.37
128.28
127.54
127.48
127.13
127.10
125.98
125.78
122.11
121.87
108.79
108.57
77.21
77.00
76.79
51.67
47.79
46.38
44.26
43.92
39.89
Bn
N
O
O
N
Bn
CO2Me
5e
f1 (ppm)

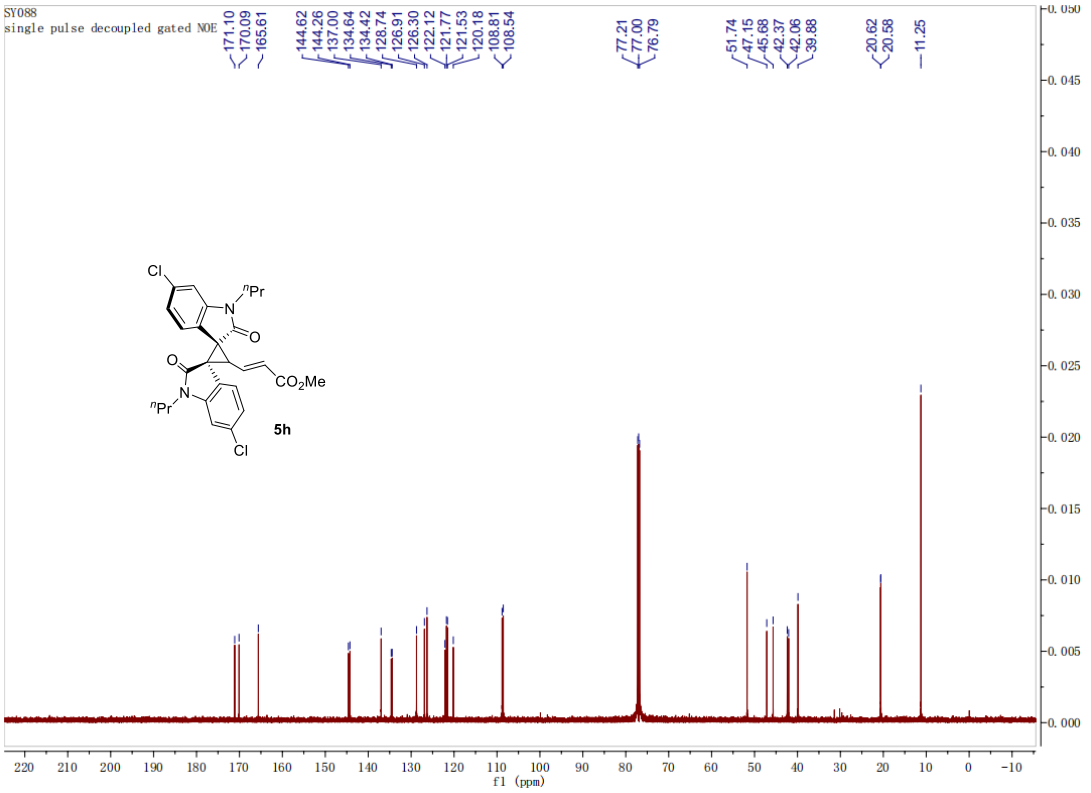

SY070
Boc
CO2Me
5f
f1 (ppm)

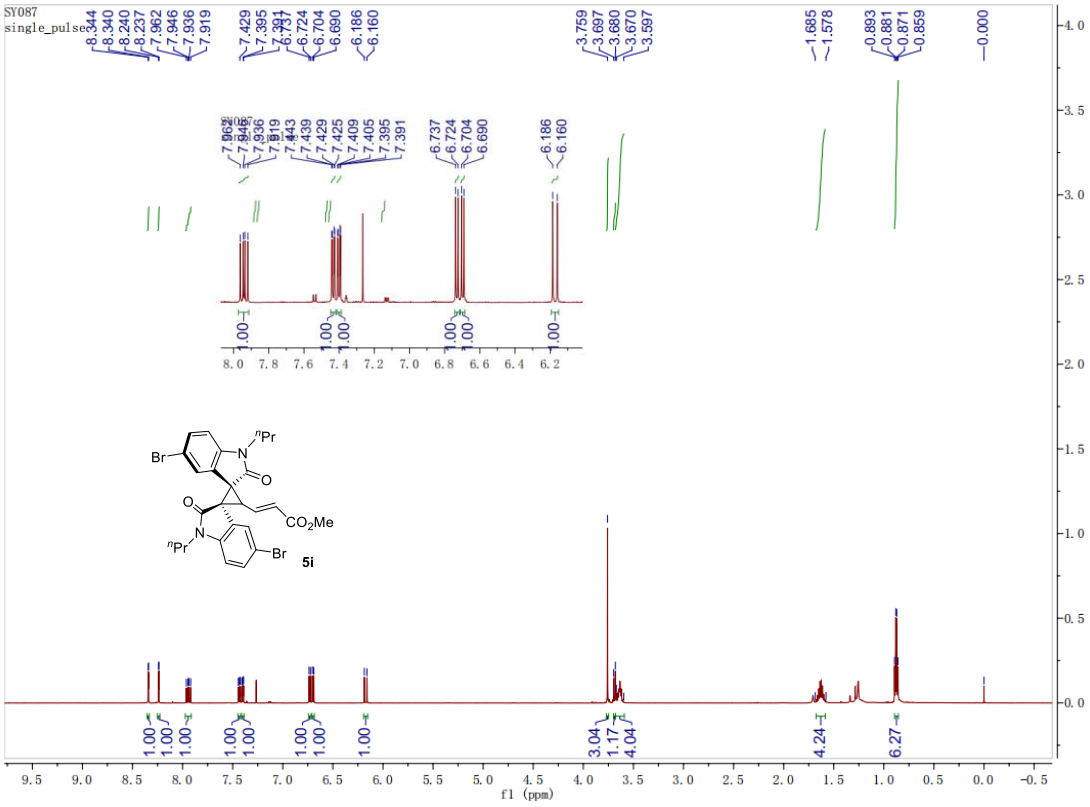

SY070
single pulse decoupled gated NOE
Boc
CO2Me
5f
f1 (ppm)

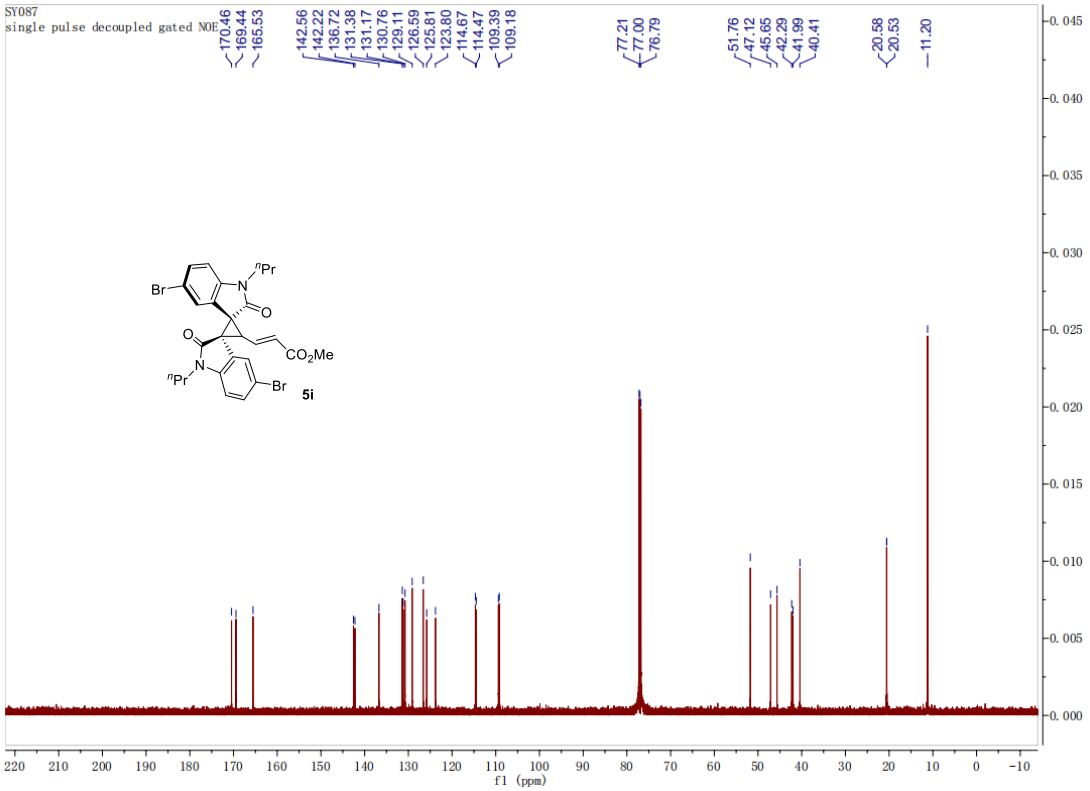

SY079
single_pulse
8.221
8.208
8.109
8.067
7.296
7.242
7.122
7.066
6.864
6.851
6.832
6.819
6.177
6.151
5.814
5.742
5.193
5.160
4.358
4.273
3.762
3.746
3.735
0.000
1.02
2.04
2.26
2.03
1.00
1.00
0.98
2.00
4.09
4.07
1.01
3.03
f1 (ppm)
CO2Me
5g

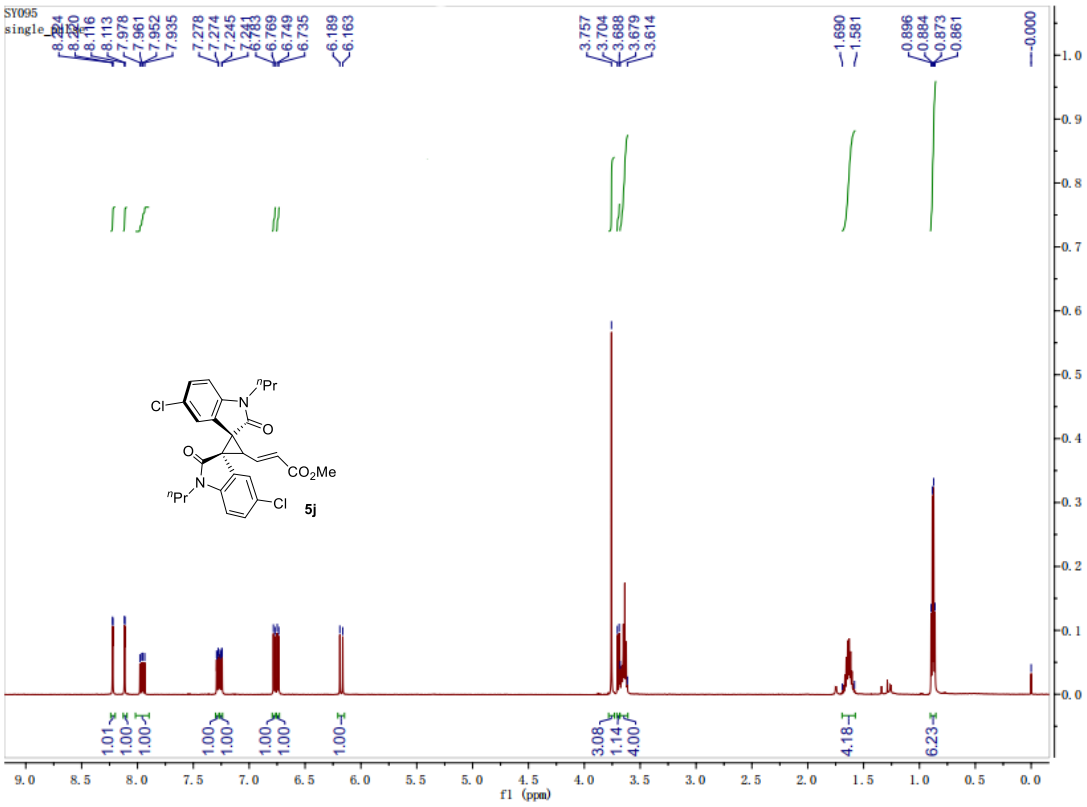

SY079
single pulse decoupled gated NOE
171.01
169.99
165.72
137.79
131.36
131.17
128.33
128.25
127.89
125.92
125.87
122.08
121.99
121.83
117.91
77.21
77.00
76.79
51.65
47.47
46.02
43.02
42.71
40.21
f1 (ppm)
CO2Me
5g

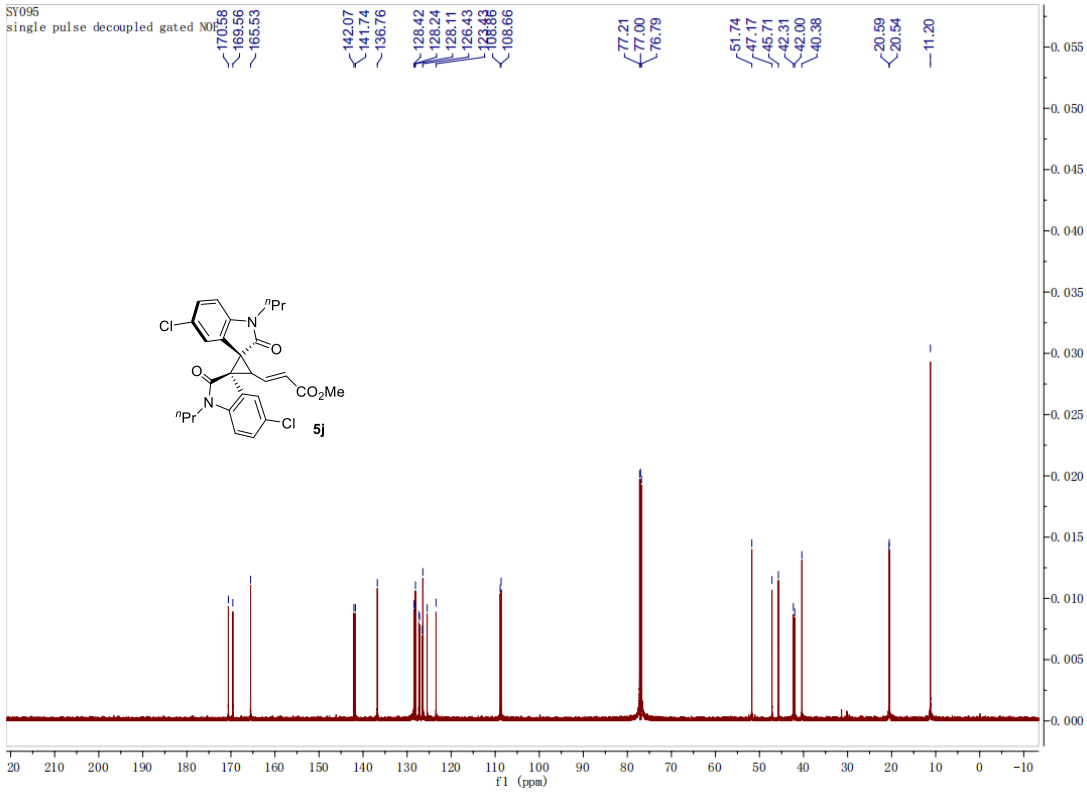

SY088
single_pulse
8.093
8.079
7.991
7.949
7.067
7.053
7.037
7.034
6.842
6.838
6.809
6.806
6.174
6.148
3.743
3.700
3.684
3.654
3.647
3.567
3.556
1.667
1.601
0.896
0.884
0.873
0.860
0.000
1.01
2.00
1.00
1.00
1.00
1.00
0.97
3.01
1.05
4.09
4.27
6.18
f1 (ppm)
5h

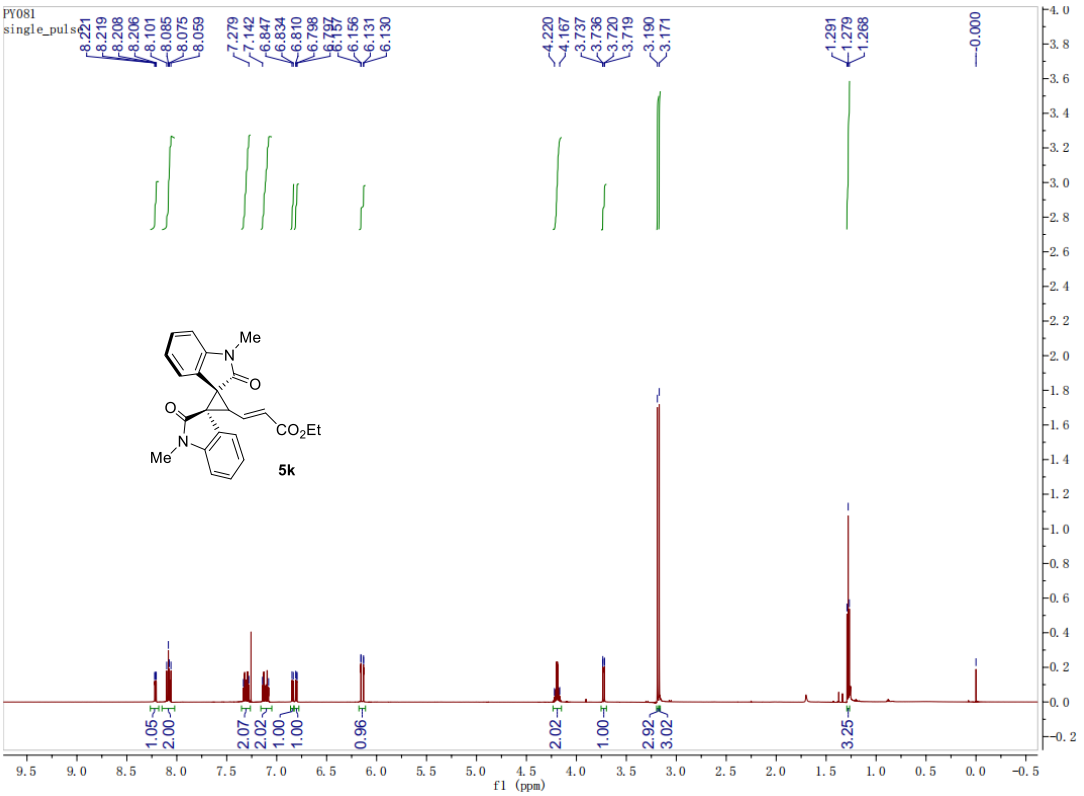

SY088
single pulse decoupled gated NOE
171.10
170.09
165.61
144.62
144.26
137.00
134.64
134.42
128.74
126.91
126.30
122.12
121.77
121.53
120.18
108.81
108.54
77.21
77.00
76.79
51.74
47.15
45.68
42.37
42.06
39.88
20.62
20.58
11.25
f1 (ppm)
5h

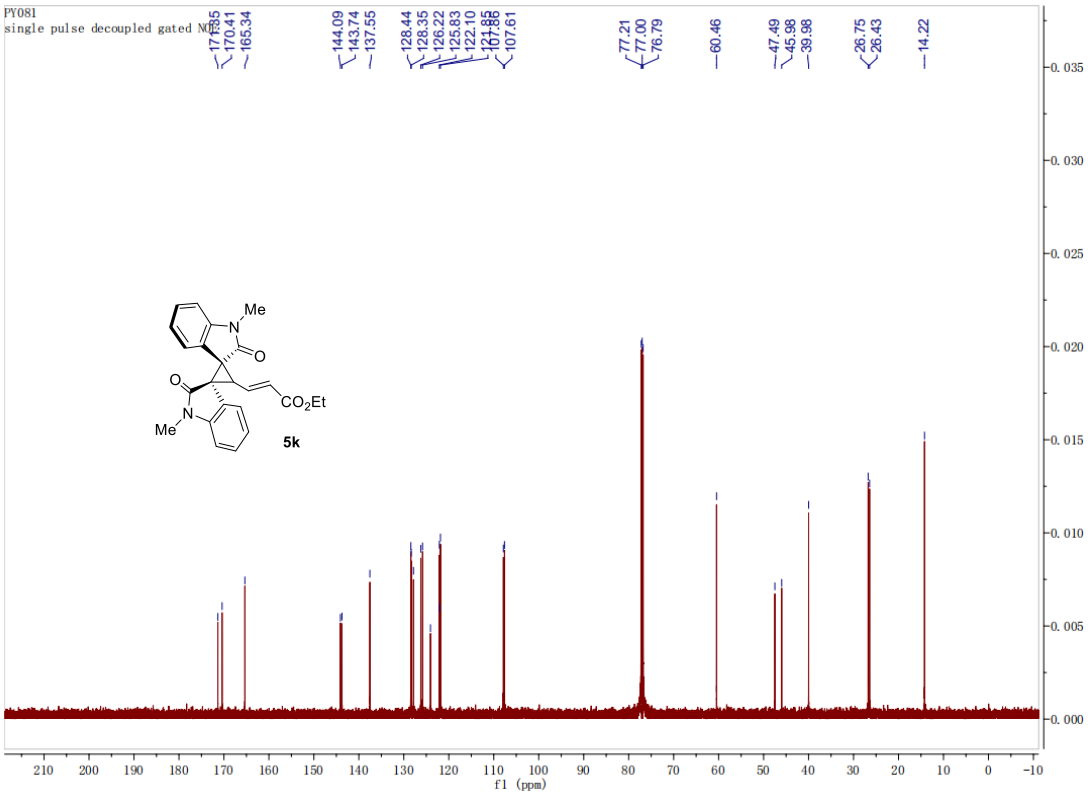

SY087
single_pulse
8.344
8.340
8.240
8.237
7.962
7.946
7.936
7.919
7.429
7.395
7.391
6.737
6.724
6.704
6.690
6.186
6.160
3.759
3.697
3.680
3.670
3.597
1.685
1.578
0.893
0.881
0.871
0.859
0.000
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.04
1.17
4.04
4.24
6.27
f1 (ppm)
Br
nPr
O
N
CO2Me
5i

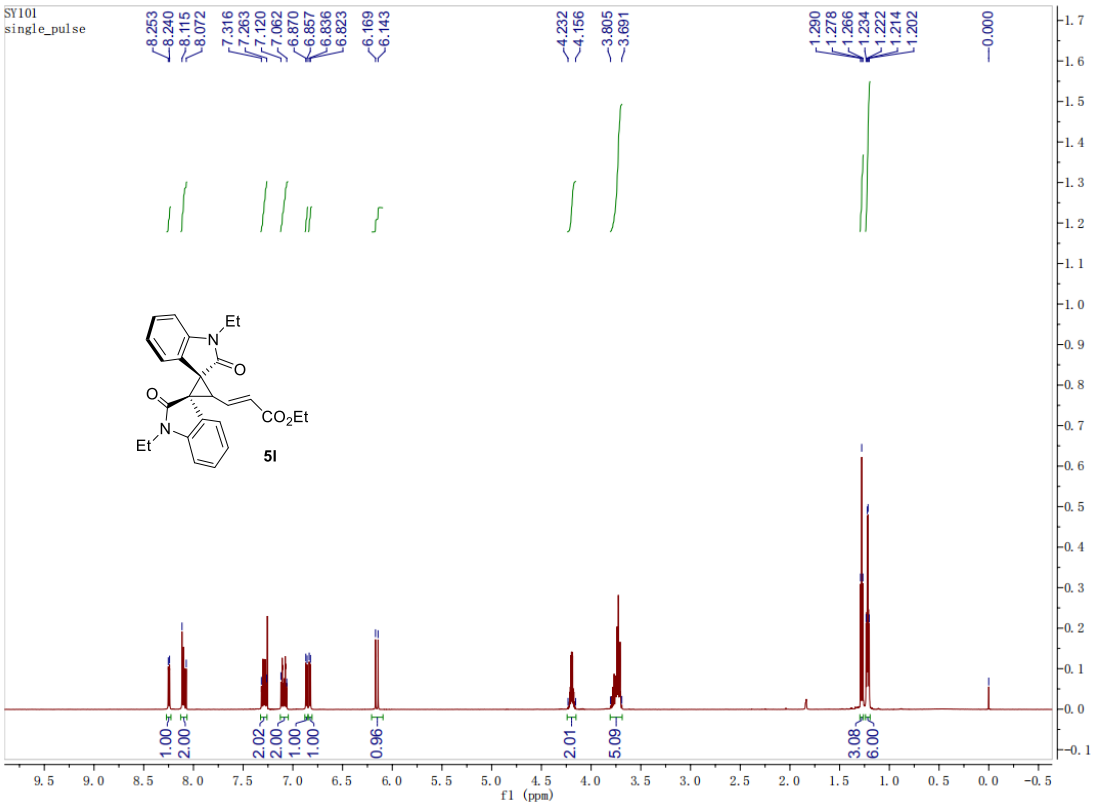

SY087
single pulse decoupled gated NOE
170.46
169.44
165.53
142.56
142.22
136.72
131.38
131.17
130.76
129.11
126.59
125.81
123.80
114.67
114.47
109.39
109.18
77.21
77.00
76.79
51.76
47.12
45.65
42.29
41.99
40.41
20.58
20.53
11.20
f1 (ppm)
Br
nPr
O
N
CO2Me
5i

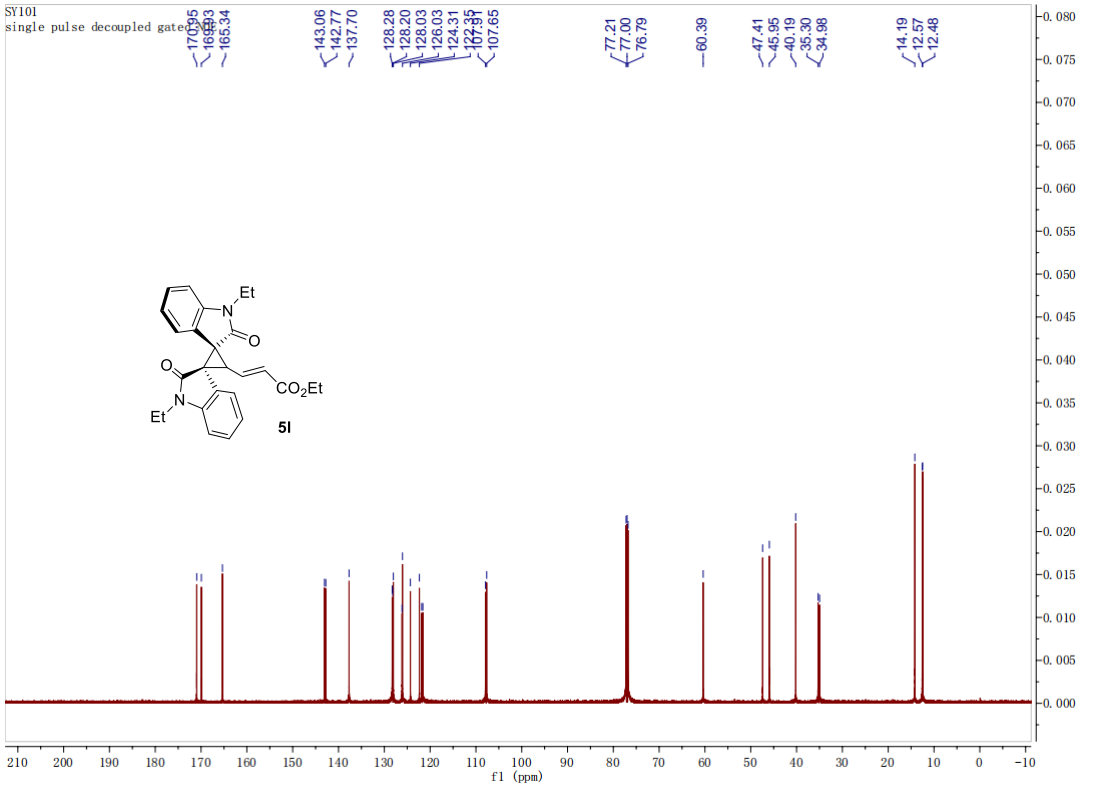

SY095
single_pulse
8.124
8.120
8.116
8.113
7.978
7.961
7.952
7.935
7.278
7.274
7.245
6.783
6.769
6.749
6.735
6.189
6.163
3.757
3.704
3.688
3.679
3.614
1.690
1.581
0.896
0.884
0.873
0.861
0.000
1.01
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.08
1.14
4.00
4.18
6.23
f1 (ppm)
Cl
nPr
O
N
O
CO2Me
nPr
N
Cl
5j

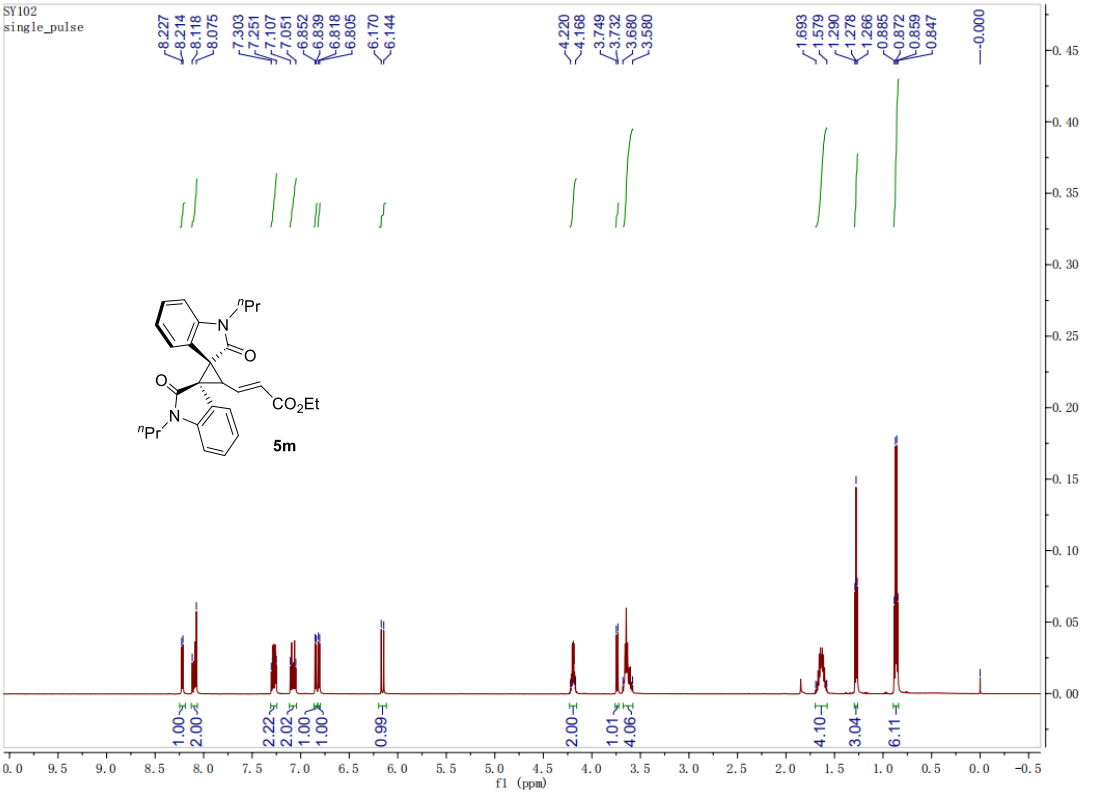

SY095
single pulse decoupled gated NOE
170.58
169.56
165.53
142.07
141.74
136.76
128.42
128.24
128.11
126.43
108.66
77.21
77.00
76.79
51.74
47.17
45.71
42.31
42.00
40.38
20.59
20.54
11.20
f1 (ppm)
Cl
nPr
O
N
O
CO2Me
nPr
N
Cl
5j

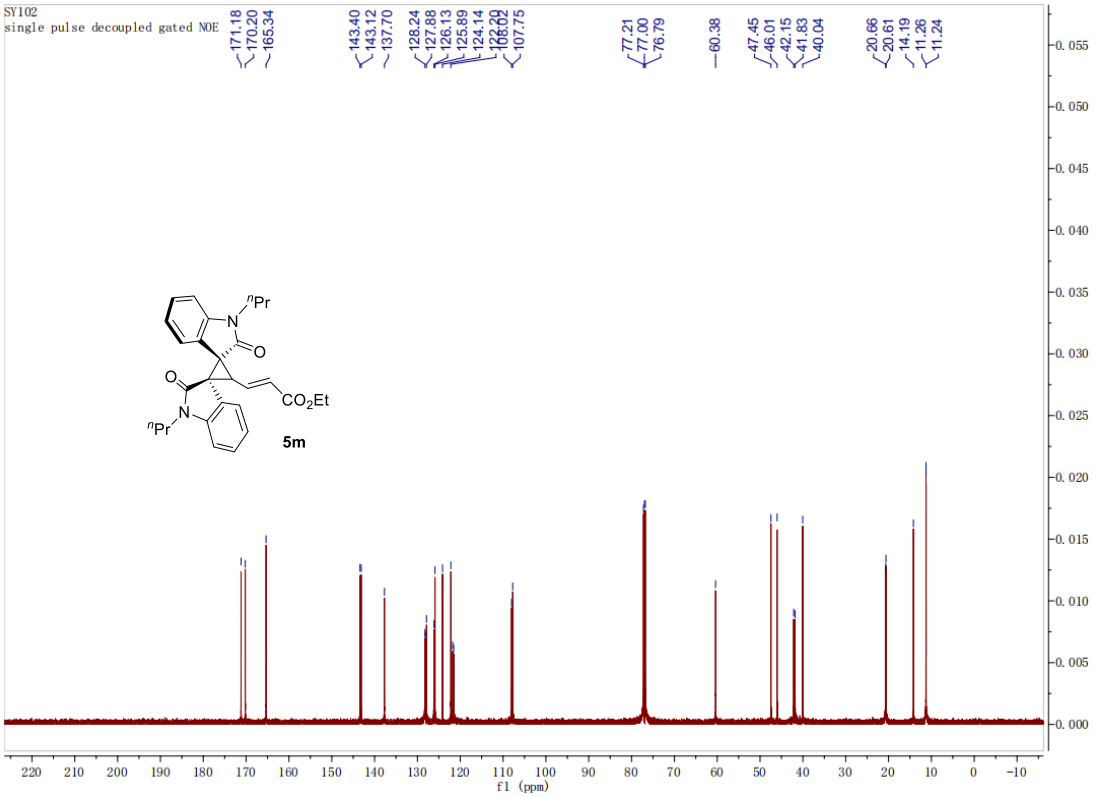

PY081
single_pulse
8.221
8.219
8.208
8.206
8.101
8.085
8.075
8.059
7.279
7.142
6.847
6.834
6.810
6.798
6.156
6.131
6.130
4.220
4.167
3.737
3.736
3.720
3.719
3.190
3.171
1.291
1.279
1.268
0.000
Me
N
O
O
N
Me
CO2Et
5k
1.05
2.00
2.07
2.02
1.00
1.00
0.96
2.02
1.00
2.92
3.02
3.25
f1 (ppm)

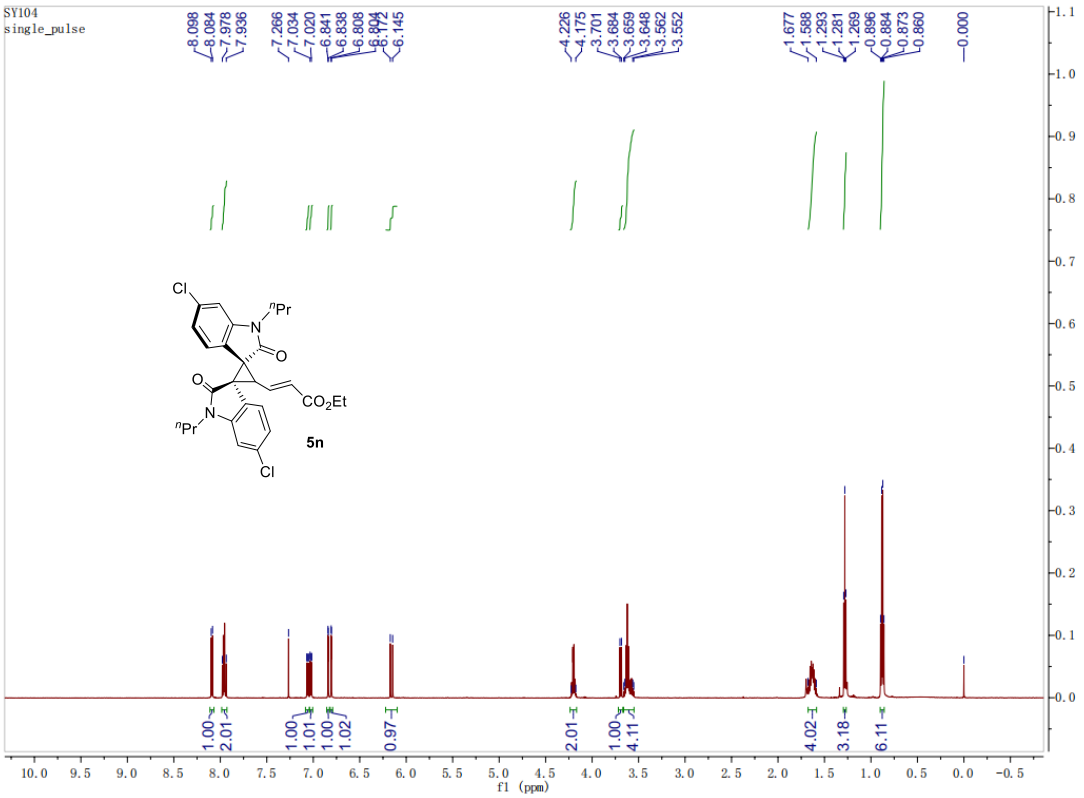

PY081
single pulse decoupled gated NOE
171.35
170.41
165.34
144.09
143.74
137.55
128.44
128.35
126.22
125.83
122.10
121.85
107.86
107.61
77.21
77.00
76.79
60.46
47.49
45.98
39.98
26.75
26.43
14.22
Me
N
O
O
N
Me
CO2Et
5k
f1 (ppm)

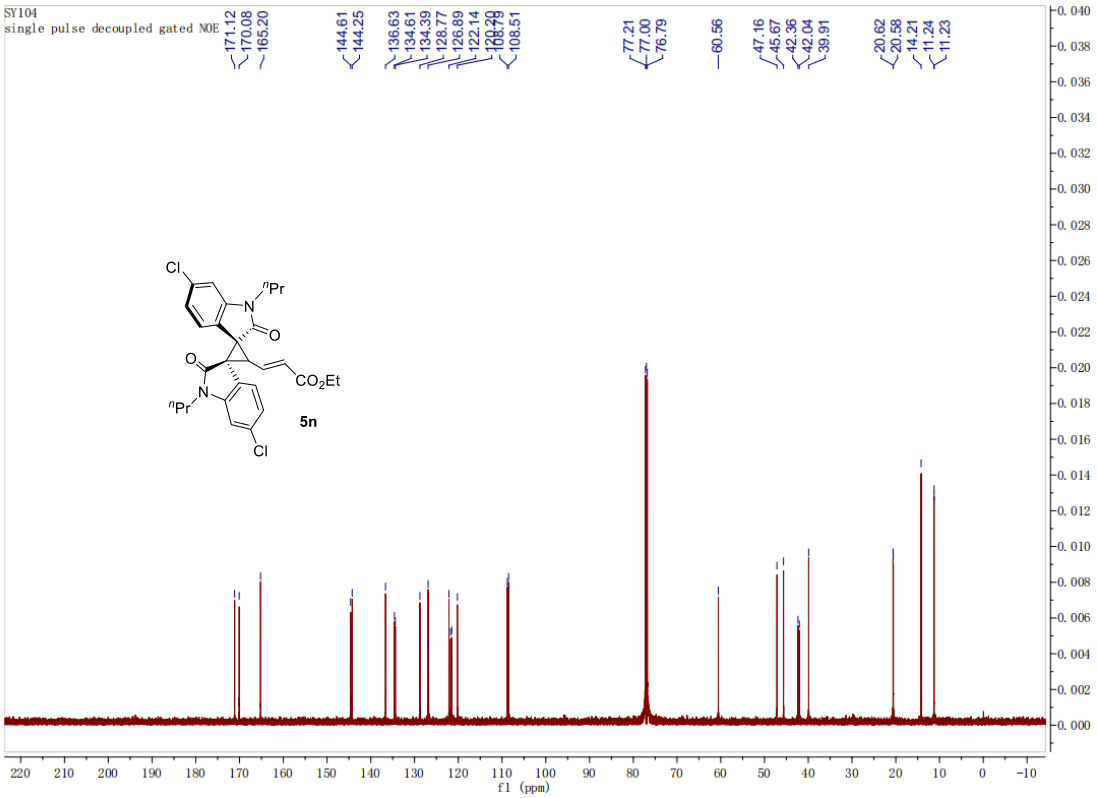

SY101
single_pulse
8.253
8.240
8.115
8.072
7.316
7.263
7.120
7.062
6.870
6.857
6.836
6.823
6.169
6.143
4.232
4.156
3.805
3.691
1.290
1.278
1.266
1.234
1.222
1.214
1.202
0.000
Et
N
O
O
N
Et
CO2Et
5l
1.00
2.00
2.02
2.00
1.00
1.00
0.96
2.01
5.09
3.08
6.00
f1 (ppm)

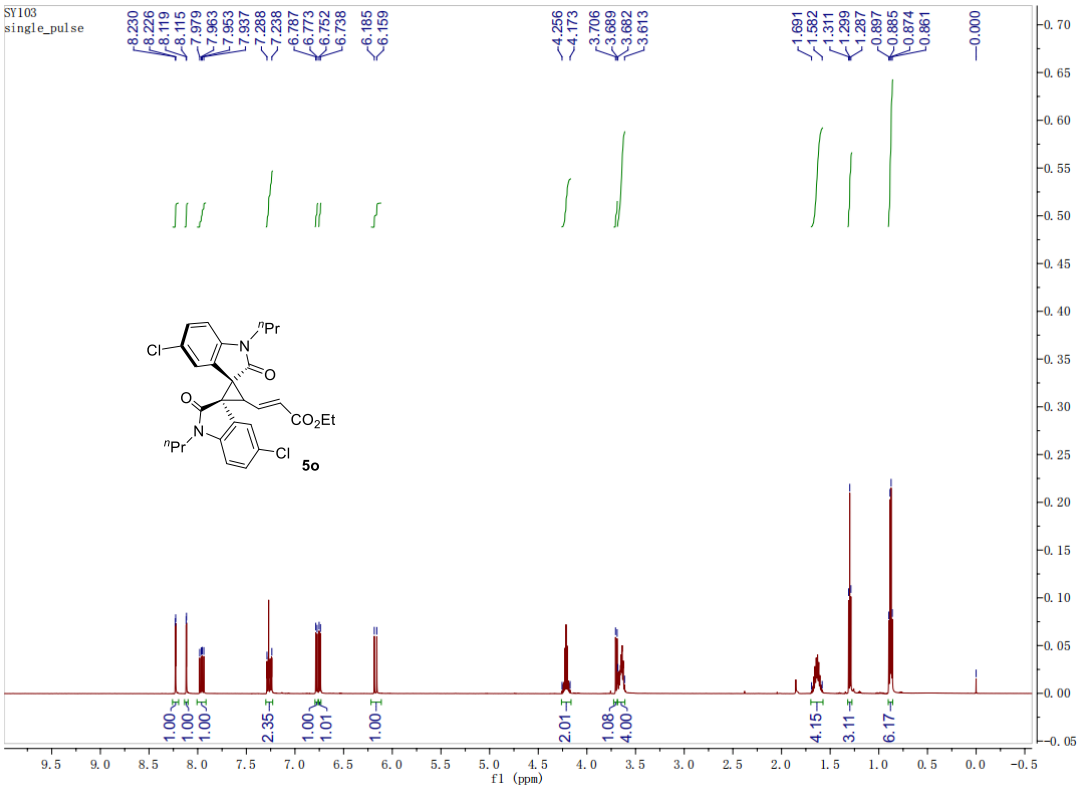

SY101
single pulse decoupled gated
170.95
169.93
165.34
143.06
142.77
137.70
128.28
128.20
128.03
126.03
124.31
107.65
77.21
77.00
76.79
60.39
47.41
45.95
40.19
35.30
34.98
14.19
12.57
12.48
Et
N
O
O
N
Et
CO2Et
5l
f1 (ppm)

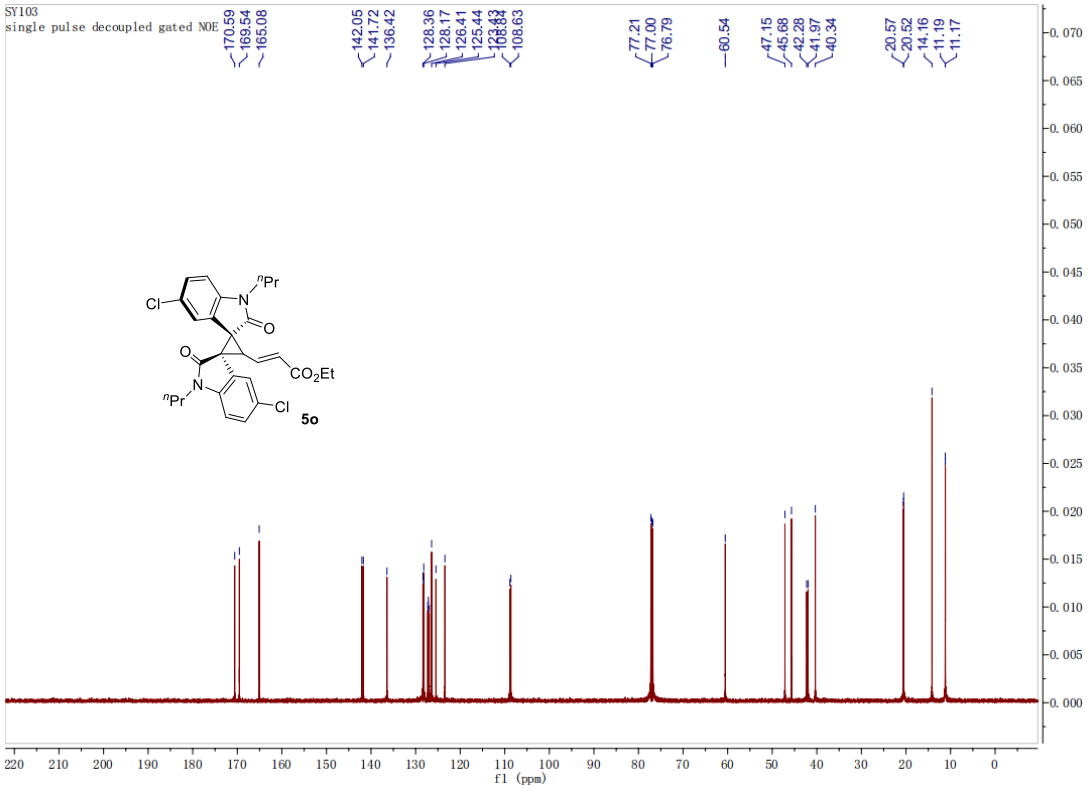

SY102
single_pulse
8.227
8.214
8.118
8.075
7.303
7.251
7.107
7.051
6.852
6.839
6.818
6.805
6.170
6.144
4.220
4.168
3.749
3.732
3.680
3.580
1.693
1.579
1.290
1.278
1.266
0.885
0.872
0.859
0.847
0.000
nPr
N
O
O
CO2Et
nPr
N
5m
1.00
2.00
2.22
2.02
1.00
1.00
0.99
2.00
1.01
4.06
4.10
3.04
6.11
f1 (ppm)

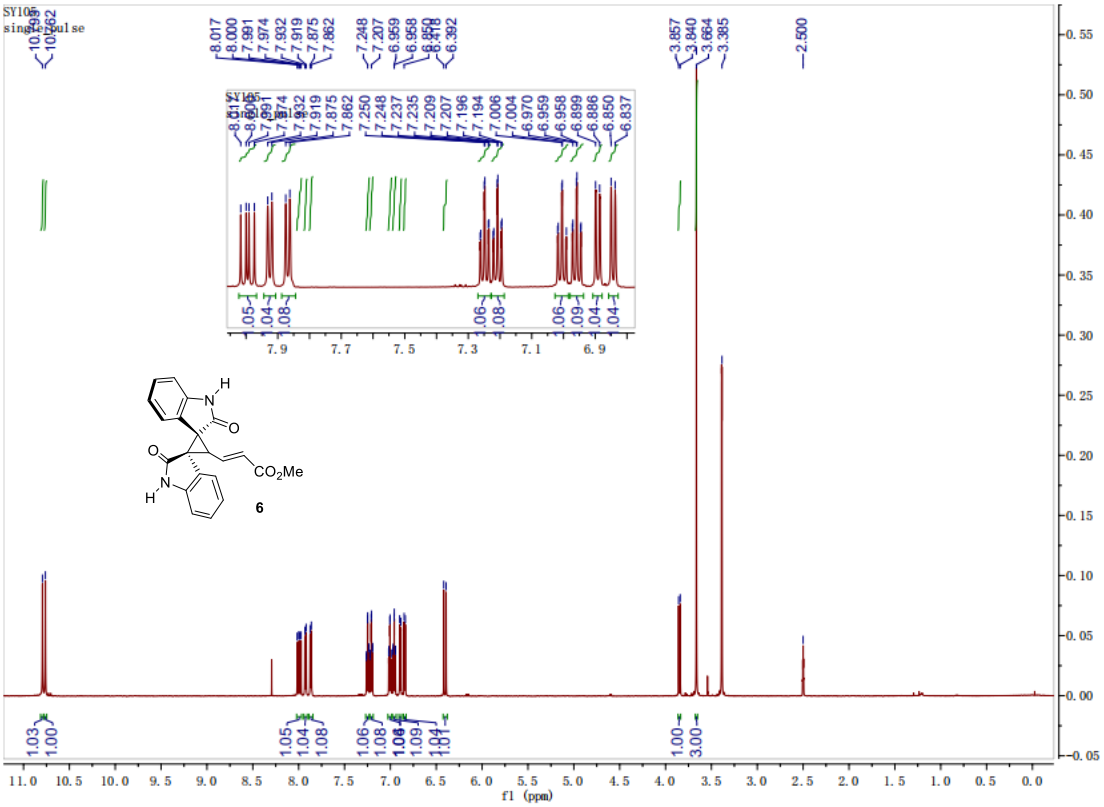

SY102
single pulse decoupled gated NOE
171.18
170.20
165.34
143.40
143.12
137.70
128.24
127.88
126.13
125.89
124.14
122.20
108.02
107.75
77.21
77.00
76.79
60.38
47.45
46.01
42.15
41.83
40.04
20.66
20.61
14.19
11.26
11.24
nPr
N
O
O
CO2Et
nPr
N
5m
f1 (ppm)

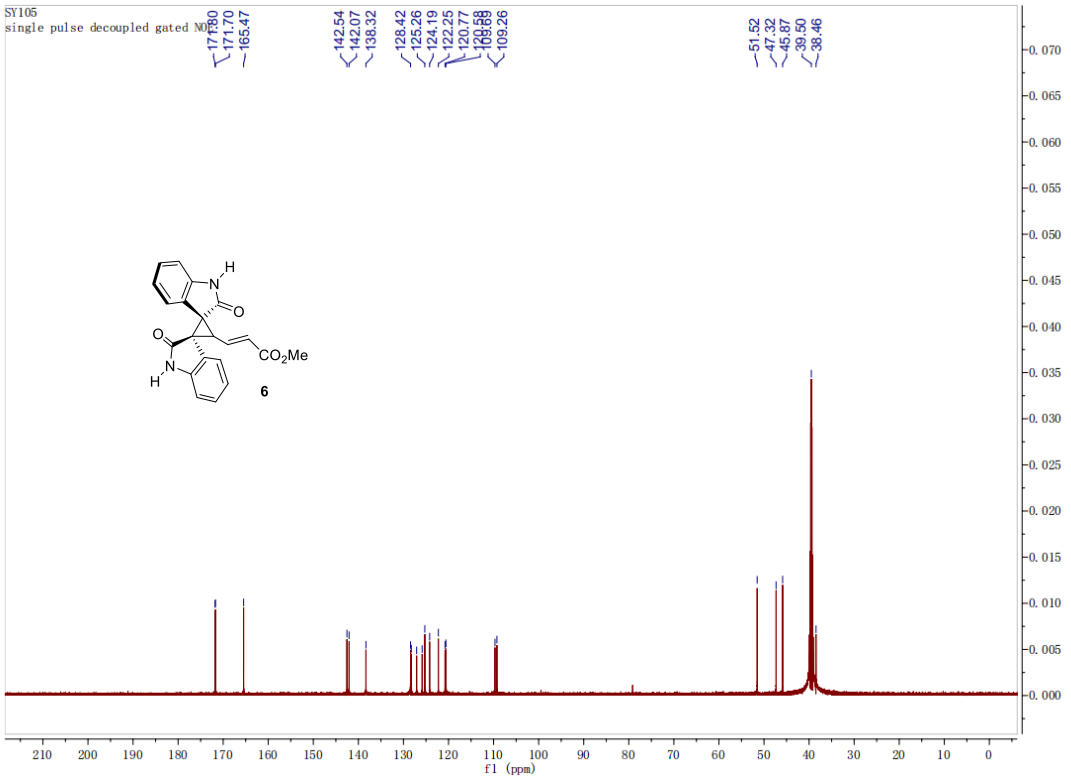

SY104
single_pulse
8.098
8.084
7.978
7.936
7.266
7.034
7.020
6.841
6.838
6.808
6.804
6.172
6.145
4.226
4.175
3.701
3.684
3.659
3.648
3.562
3.552
1.677
1.588
1.293
1.281
1.269
0.896
0.884
0.873
0.860
0.000
Cl
nPr
N
O
O
CO2Et
nPr
N
Cl
5n
1.00
2.01
1.00
1.01
1.00
1.02
0.97
2.01
1.00
4.11
4.02
3.18
6.11
f1 (ppm)


SY104
single pulse decoupled gated NOE
171.12
170.08
165.20
144.61
144.25
136.63
134.61
134.39
128.77
126.89
122.14
120.29
108.78
108.51
77.21
77.00
76.79
60.56
47.16
45.67
42.36
42.04
39.91
20.62
20.58
14.21
11.24
11.23
Cl
nPr
N
O
O
CO2Et
nPr
N
Cl
5n
f1 (ppm)


SY103
single_pulse
8.230
8.226
8.119
8.115
7.979
7.963
7.953
7.937
7.288
7.238
6.787
6.773
6.752
6.738
6.185
6.159
4.256
4.173
3.706
3.689
3.682
3.613
1.691
1.582
1.311
1.299
1.287
0.897
0.885
0.874
0.861
0.000
1.00
1.00
1.00
2.35
1.00
1.01
1.00
2.01
1.08
4.00
4.15
3.11
6.17
f1 (ppm)
5o


SY103
single pulse decoupled gated NOE
170.59
169.54
165.08
142.05
141.72
136.42
128.36
128.17
126.41
125.44
108.63
77.21
77.00
76.79
60.54
47.15
45.68
42.28
41.97
40.34
20.57
20.52
14.16
11.19
11.17
f1 (ppm)
5o


SY105
single pulse
10.339
10.062
8.017
8.000
7.991
7.974
7.932
7.919
7.875
7.862
7.248
7.207
6.959
6.958
6.392
3.857
3.840
3.664
3.385
2.500
CO2Me
6
f1 (ppm)


SY105
single pulse decoupled gated NO
177.80
171.70
165.47
142.54
142.07
138.32
128.42
125.26
124.19
122.25
120.77
109.26
51.52
47.32
45.87
39.50
38.46
CO2Me
6
f1 (ppm)