Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Electronically-Controlled Diastereoselective Synthesis of Spirocycles via [4+2] Cycloaddition of 2-arylidene-1-Indenones with Benzyne

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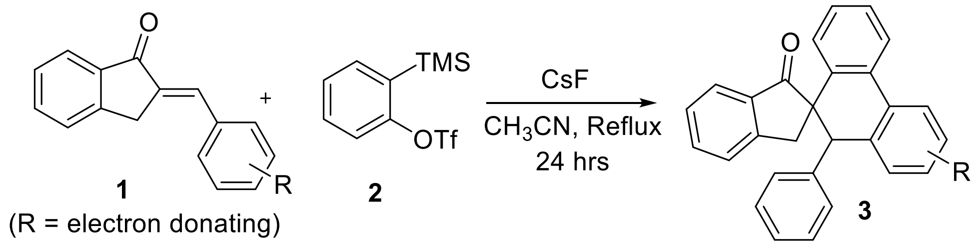
1. General Information

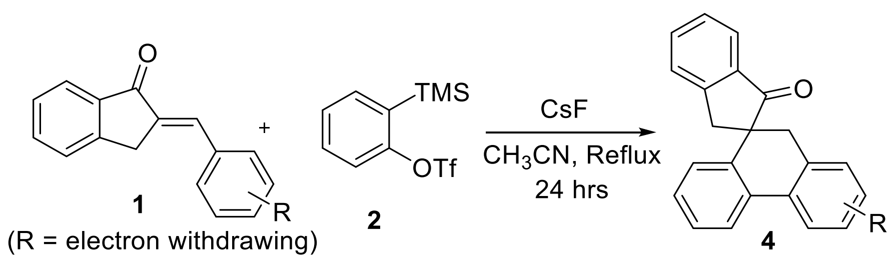
Commercially available chemicals in this manuscript were used without further purification and were purchased from TCI, Sigma-Aldrich, and Avra chemicals. All the 2-arylidene-1-indenones were synthesized by the reported procedure.[1] Solvents used for reactions were p.A. grade, and solvents for column chromatography were technical grade and were distilled before use; solvent mixtures are understood as volume/volume. All the reactions were carried out in a flame or oven-dried glass wares. All the reactions were monitored by analytical thin-layer chromatography (TLC) using Merck pre-coated aluminium sheets and visualized by the UV lamp. Column chromatography using silica gel (100-200 mesh) was performed to purify the products. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on the JEOL 500 FT-NMR spectrometer operating at 500 and 125 MHz, respectively. Chemical shifts (δ) for ^{1}H and $^{13}C\{^{1}H\}$ NMR are given in parts per million (ppm) using the residual solvent peaks as a reference relative to tetramethylsilane (TMS). Coupling constant (J) values are reported in Hz. Mass spectra were recorded on Sciex X500R Q-TOF instruments. Melting points are uncorrected.

2. Procedure for the Synthesis of Compounds 3



In an oven-dried 50 mL bi-neck RB equipped with a magnetic stir bar, **1** (0.25 mmol, 1.0 equiv) and CsF (2.25 mmol, 9.0 equiv) were added and flushed with N_2 gas 3-4 times via a balloon chamber connected to a reflux condenser. Then 5 mL of dry acetonitrile was added and stirred for 5 min. After dissolving the solid, benzyene precursor **2** (0.75 mmol, 3.0 equiv) was added. Next, the whole setup was refluxed in a preheated oil bath for 24 hrs. After the completion of the reaction monitored by TLC, water was added to quench the reaction, then extracted with ethyl acetate twice, dried over Na_2SO_4, and purified by column chromatography by varying the ratio of ethyl acetate/hexane (v/v) as eluent to afford the pure final products (**3a**-**3h**).

3. Procedure for the Synthesis of Compounds 4



In an oven-dried 50 mL bi-neck RB equipped with a magnetic stir bar, **1** (0.25 mmol, 1.0 equiv) and CsF (2.25 mmol, 9.0 equiv) were added and flushed with N_2 gas 3-4 times via a balloon chamber connected to a reflux condenser. Then 5 mL of dry acetonitrile was added and stirred for 5 min. After dissolving the solid, benzyene precursor **2** (0.75 mmol, 3.0 equiv) was added. Next, the whole setup was refluxed in a preheated oil bath for 24 hrs. After the completion of the reaction monitored by TLC, water was added to quench the reaction, then extracted with ethyl acetate twice, dried over Na_2SO_4, and purified by column chromatography by varying the ratio of ethyl acetate/hexane (v/v) as eluent to afford the pure final products (**4a-4j**).

Reference

(1) Kadayat, T. M.; Banskota, S.; Gurung, P.; Bist, G.; Thapa Magar, T. B.; Shrestha, A.; Kim, J.-A.; Lee, E.-S. Discovery and structure-activity relationship studies of 2-benzylidene-2,3-dihydro-1H-inden-1-one and benzofuran-3(2H)-one derivatives as a novel class of potential therapeutics for inflammatory bowel disease. *Eur. J. Med. Chem.* **2017**, *137*, 575-597.

4. Crystallization details and ORTEP diagram of compound 3a (CCDC 2237440) and 4j (CCDC 2237438)

The compounds **3a** & **4j** after collecting from the column were dried under vacuum and dissolved in 3 mL of distilled ethanol in separate vials. Then the vials were kept at room temperature for slow evaporation. After one week, needle shaped crystals of both the compounds were formed in the vials, which were picked up and subjected to single crystal XRD study.

Crystal data & ORTEP diagram of compound 3a (CCDC No. 2237440)

Bond precision: C-C = 0.0018 A   Wavelength=1.54184

Cell:	a=12.38262(19)	b=11.76838(19)	c=14.2059(2)
	alpha=90	beta=94.2755(14)	gamma=90
Temperature:	298 K		

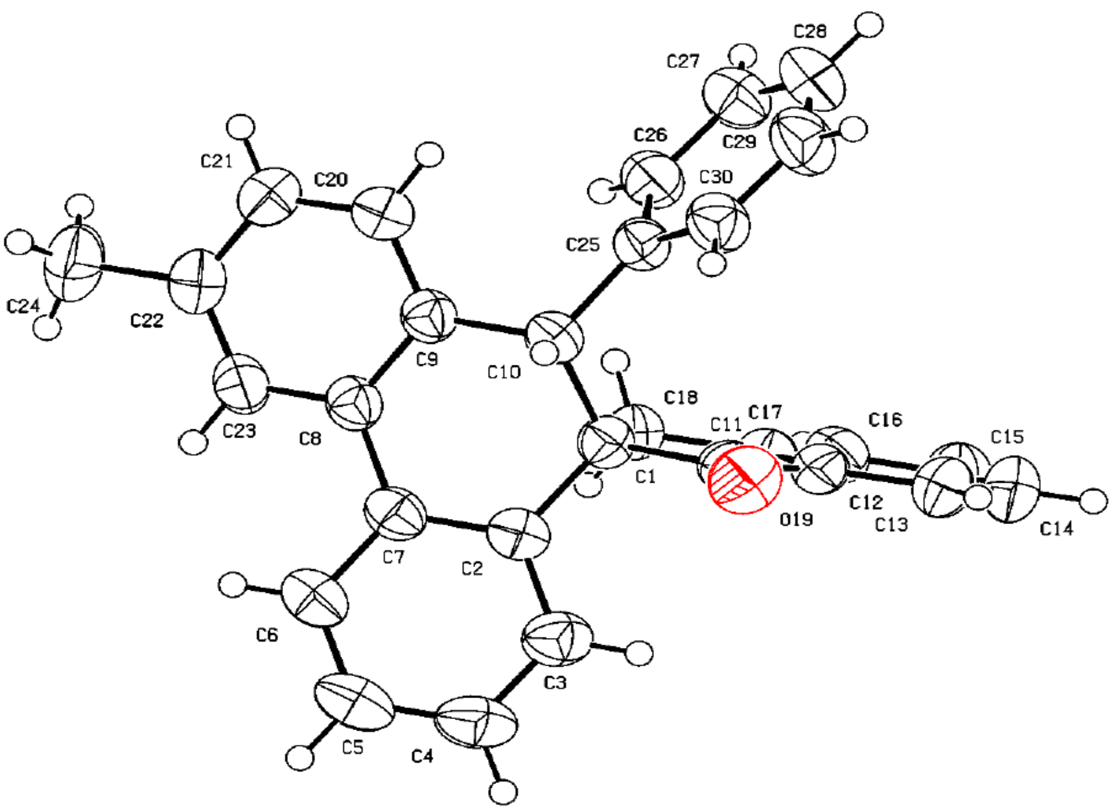
	Calculated	Reported
Volume	2064.37(5)	2064.37(6)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2ybc (x-
Moiety formula	C29 H22 O	C29 H22 O
Sum formula	C29 H22 O	C29 H22 O
Mr	386.47	386.50
Dx,g cm-3	1.243	1.244
Z	4	4
Mu (mm-1)	0.567	0.567
F000	816.0	818.4
F000’	818.20	
h,k,lmax	14,14,17	14,14,16
Nref	3763	3685
Tmin,Tmax	0.893,0.893	2.300,
Tmin’	0.893	

Correction method= # Reported T Limits: Tmin=2.300 Tmax=*****
AbsCorr = MULTI-SCAN

Data completeness= 0.979   Theta(max)= 68.130

R(reflections)= 0.0362(3092)   wR2(reflections)= 0.0970(3685)

S = 1.032   Npar= 280



Crystal data & ORTEP diagram of compound 4j (CCDC No. 2237438)

Bond precision: C-C = 0.0020 A Wavelength=1.54184

Cell:	a=8.03311(10)	b=24.9979(3)	c=8.69995(10)
	alpha=90	beta=99.4412(12)	gamma=90
Temperature:	293 K		

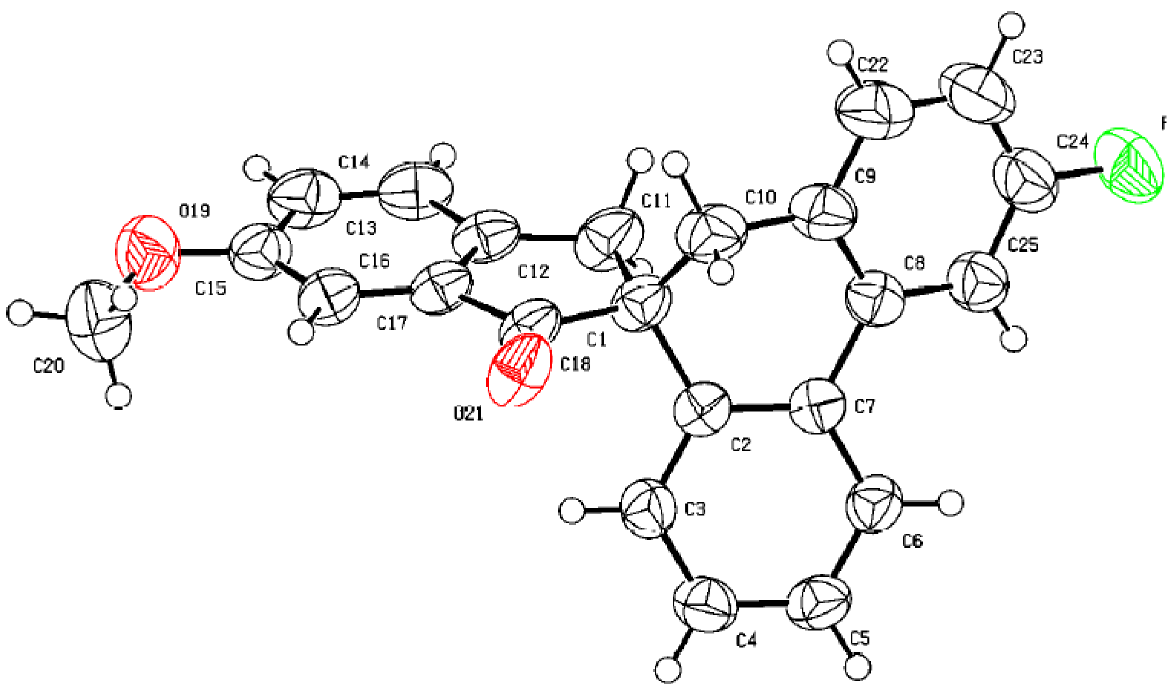
	Calculated	Reported
Volume	1723.38(4)	1723.38(4)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C23 H17 F O2	C23 H17 F O2
Sum formula	C23 H17 F O2	C23 H16 F O2
Mr	344.37	343.36
Dx,g cm-3	1.327	1.323
Z	4	4
Mu (mm-1)	0.739	0.739
F000	720.0	716.0
F000’	722.27	
h,k,lmax	9,30,10	9,30,10
Nref	3156	3126
Tmin,Tmax	0.863,0.863	2.300,
Tmin’	0.863	

Correction method= # Reported T Limits: Tmin=2.300 Tmax=*****
AbsCorr = MULTI-SCAN

Data completeness= 0.990 Theta(max)= 68.095

R(reflections)= 0.0462(2758) wR2(reflections)= 0.1221(3126)

S = 1.090 Npar= 244



5. Characterization Data:

3'-methyl-10'-phenyl-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (3a): (16:1 dr), Isolated yield (62 mg, 65%); Yellow solid; mp: 128-130 ºC. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 10.0 Hz, 1H), 7.71 (s, 1H), 7.59 (d, *J* = 5.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.28 (d, *J* = 5.0 Hz, 1H), 7.17 – 7.13 (m, 3H), 7.11 – 7.09 (m, 3H), 7.04 (d, *J* = 10.0 Hz, 1H), 7.00 (d, *J* = 5.0 Hz, 1H), 6.93 (d, *J* = 10.0 Hz, 1H), 4.54 (s, 1H), 3.65 (d, *J* = 20.0 Hz, 1H), 3.15 (d, *J* = 15.0 Hz, 1H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 207.1, 152.3, 139.9, 138.6, 136.9, 136.4, 135.2, 134.8, 134.7, 133.6, 129.6, 128.9, 128.6, 128.4, 128.2, 127.9, 127.6, 127.2, 126.0, 125.8, 124.7, 58.5, 51.9, 38.4, 21.6; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{29}H_{23}O$, 387.1743, found 387.1761.

3'-methoxy-10'-phenyl-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (3b): (4.6:1 dr), Isolated yield (62 mg, 62%); Pale yellow solid; mp: 158 ºC. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, *J* = 10.0 Hz, 1H), 7.59 (d, *J* = 10.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.44 (s, 1H), 7.37 – 7.26 (m, 4H), 7.18 (t, *J* = 7.5 Hz, H) 7.13 – 7.10 (m, 4H), 7.03 (d, *J* = 5.0 Hz, 1H), 6.94 (d, *J* = 10.0 Hz, 1H), 6.78 (dd, *J* = 5.0 Hz, *J* = 4.33 Hz, 1H), 4.54 (s, 1H), 3.89 (s, 3H), 3.67 (d, *J* = 15.0 Hz, 1H), 3.15 (d, *J* = 15.0 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 207.1, 159.1, 152.3, 139.9, 138.9, 136.4, 135.2, 135.0, 134.5, 130.0, 129.7, 129.6, 128.5, 128.4, 127.9, 127.6, 127.2, 126.0, 125.8, 124.8, 124.6, 113.2, 109.7, 58.6, 55.5, 51.6, 38.3; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{29}H_{23}O_2$, 403.1693, found 403.1695.

3'-ethyl-10'-phenyl-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (3c): (3:1 dr), Isolated yield (60 mg, 60%); Pale yellow sticky solid. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 10.0 Hz, 1H), 7.73 (s, 1H), 7.59 (d, *J* = 5.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 5.0 Hz, 1H), 7.28 (d, *J* = 5.0 Hz, 1H), 7.18 – 7.15 (m, 3H), 7.12 – 7.09 (m, 3H), 7.07 (d, J = 5.0 Hz, 1H), 7.02 (d, J = 10.0 Hz, 1H), 6.93 (d, J = 10.0 Hz, 1H), 4.57 (s, 1H), 3.67 (d, J = 20.0 Hz, 1H), 3.15 (d, J = 15.0 Hz, 1H), 2.73 (q, J = 8.3 Hz, 2H), 1.32 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 207.3, 152.3, 143.2, 139.7, 138.7, 136.4, 135.2, 134.9, 134.7, 133.6, 133.6, 129.7, 128.5, 128.4, 128.2, 127.8, 127.6, 127.1, 125.9, 125.7, 124.6, 124.5, 123.4, 58.5, 51.9, 38.3, 28.9, 15.6; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{30}H_{25}O$, 401.1900, found 401.1887.

1'-hydroxy-10'-phenyl-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (3d): (9:1 dr), Isolated yield (57 mg, 59%); Yellow oil. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^1H NMR (500 MHz, $CDCl_3$): δ 7.97 (d, J = 10.0 Hz, 1H), 7.72 (d, J = 10.0 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.44 (d, J = 10.0 Hz, 1H), 7.35 (t, J = 7.5 Hz, 3H), 7.21 (t, J = 7.5 Hz, 3H), 7.05 (s, 2H), 6.95 (d, J = 5.0 Hz, 1H), 6.84 (d, J = 10.0 Hz, 2H), 6.78 (d, J = 10.0 Hz, 1H), 4.60 (s, 1H), 3.37 (d, J = 20.0 Hz, 1H), 3.24 (d, J = 20.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 203.6, 158.1, 151.8, 141.7, 135.1, 134.3, 133.6, 129.7, 128.9, 128.4, 128.2, 128.1, 126.9, 126.3, 125.6, 125.1, 122.6, 119.6, 119.4, 118.2, 56.9, 44.8, 39.1; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{28}H_{21}O_2$, 389.1536, found 389.1553.

3'-isopropyl-10'-phenyl-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (3e): (3:1 dr), Isolated yield (60 mg, 58%); Yellow oil. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^1H NMR (500 MHz, $CDCl_3$): δ 7.92 (d, J = 10.0 Hz, 1H), 7.74 (s, 1H), 7.58 (d, J = 10.0 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.31 (d, J = 10.0 Hz, 1H), 7.28 – 7.25 (m, 1H, embedded with $CDCl_3$), 7.18 – 7.15 (m, 3H), 7.11 – 7.08 (m, 4H), 7.02 (d, J = 10.0 Hz, 1H), 6.93 (d, J = 5.0 Hz, 1H), 4.58 (s, 1H), 3.69 (d, J = 15.0 Hz, 1H), 3.14 (d, J = 15.0 Hz, 1H), 3.03 – 2.94 (m, 1H), 1.33 (d, J = 5.0 Hz, 3H) ; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 207.5, 152.4, 147.8, 139.6, 138.9, 136.5, 135.2, 134.8, 133.6, 129.7, 128.5, 128.3, 128.1, 127.8, 127.5, 127.2, 126.1, 126.0, 125.7, 124.6, 124.5, 122.1, 58.5, 51.9, 38.3, 34.1, 24.2, 24.1; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{31}H_{27}O$, 415.2056, found 415.2057.

3'-ethyl-6-methoxy-10'-phenyl-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (3f): (11:1 dr), Isolated yield (69 mg, 65%); Yellow oil. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^1H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, J = 10.0 Hz, 1H), 7.72 (s, 1H), 7.35 (t, J = 10.0 Hz, 1H), 7.20 (d, J = 10.0 Hz, 1H), 7.16 (d, J = 5.0 Hz, 3H), 7.13 – 7.11 (m, 4H), 7.06 (d, J = 10.0 Hz, 1H), 7.02 – 7.00 (m, 2H), 6.93 (d, J = 5.0 Hz, 1H), 4.59 (s, 1H), 3.76 (s, 3H), 3.61 (d, J = 20.0 Hz, 1H), 3.05 (d, J = 20.0 Hz, 1H), 2.73 (q, J = 6.6 Hz, 2H), 1.31 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 207.4, 159.5, 145.2, 143.2, 139.6, 139.2, 137.7, 135.0, 134.6, 133.7, 129.7, 128.5, 128.4, 128.1, 127.8, 127.5, 127.2, 126.7, 125.6, 124.6, 123.4, 105.6, 59.4, 55.6, 51.8, 37.6, 28.9, 15.6; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{31}H_{27}O_2$, 431.2006, found 431.2002.

3',6-dimethoxy-10'-phenyl-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (3g): (4.1:1 dr), Isolated yield (68 mg, 63%); Yellow sticky solid. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^1H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, J = 10.0 Hz, 1H), 7.43 (s, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.20 (t, J = 7.5 Hz, 2H), 7.16 – 7.11 (m, 6H), 7.02 – 7.00 (m, 2H), 6.94 (d, J = 5.0 Hz, 1H), 6.78 (d, J = 3.5 Hz, 1H), 4.56 (s, 1H), 3.88 (s, 3H), 3.76 (s, 3H), 3.60 (d, J = 20.0 Hz, 1H), 3.05 (d, J = 20.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 207.3, 159.5, 159.0, 145.1, 139.7, 139.2, 137.6, 135.0, 134.4, 130.1, 129.6, 129.6, 128.4, 128.4, 127.9, 127.2, 126.7, 125.7, 124.7, 124.6, 113.1, 109.7, 105.6, 59.4, 55.6, 55.5, 51.5, 37.5; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{30}H_{25}O_3$, 433.1798, found 433.1794.

6-methoxy-3'-methyl-10'-phenyl-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (3h): (8.6:1 dr), Isolated yield (63 mg, 61%); Brownish yellow sticky solid. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, J = 5.0 Hz, 1H), 7.70 (s, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.19 (t, J = 7.5 Hz, 2H), 7.16 – 7.11 (m, 7H), 7.04 – 7.03 (m, 2H), 6.98 (d, J = 10.0 Hz, 1H), 6.93 (d, J = 5.0 Hz, 1H), 4.57 (s, 1H), 3.76 (s, 3H), 3.59 (d, J = 20.0 Hz, 1H), 3.05 (d, J = 20.0 Hz, 1H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 207.3, 159.5, 145.1, 139.7, 139.0, 137.6, 136.8, 134.8, 134.6, 133.6, 129.6, 128.8, 128.5, 128.4, 128.2, 127.8, 127.2, 126.7, 125.6, 124.6, 124.6, 105.6, 59.3, 55.6, 51.8, 37.6, 21.5; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{30}H_{25}O_2$, 417.1849, found 417.1846.

10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (4a): Isolated yield (44 mg, 60%); Yellow oil. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, J = 10.0 Hz, 1H), 7.85 – 7.81 (m, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.39 – 7.32 (m, 3H), 7.21 – 7.17 (m, 2H), 6.93 (d, J = 5.0 Hz, 1H), 3.51 (d, J = 15.0 Hz, 1H), 3.34 (d, J = 20.0 Hz, 1H), 3.03 (d, J = 20.0 Hz, 1H), 2.68 (d, J = 15.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 210.2, 152.3, 140.3, 136.7, 135.6, 134.2, 134.0, 128.9, 128.3, 127.7, 127.6, 127.0, 125.6, 124.4, 124.3, 123.9, 54.2, 40.9, 38.9; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{22}H_{17}O$, 297.1274, found 297.1263.

2'-bromo-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (4b): (1:1 Regio isomers) Isolated yield (59 mg, 64%); Brownish yellow sticky solid. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46 (d, J = 5.0 Hz, 1H), 7.94 (d, J = 5.0 Hz, 1H), 7.66 – 7.62 (m, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.23 – 7.18 (m, 2H), 7.09 (t, J = 7.5 Hz, 1H), 6.94 (d, J = 10.0 Hz, 1H), 3.43 (d, J = 15.0 Hz, 1H), 3.19 (d, J = 15.0 Hz, 1H), 3.08 (d, J = 20.0 Hz, 1H), 2.65 (d, J = 15.0 Hz, 1H) ; $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 209.4, 152.4, 152.2, 142.3, 138.7, 138.3, 136.8, 135.9, 135.8, 134.5, 134.3, 133.6, 132.8, 131.8, 130.8, 130.4, 129.0, 128.9, 128.8, 128.7, 128.5, 128.3, 127.9, 127.1, 126.4, 125.9, 125.7, 125.6, 125.0, 124.6, 124.5, 124.3, 123.0, 120.6, 118.2, 54.0, 54.0, 41.0, 40.3, 39.8, 38.7; HRMS (ESI-TOF, [M + H]$^+$): Calcd for $C_{22}H_{16}BrO$, 375.0379, found 375.0377.

3'-Bromo-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (4c): Isolated yield (59 mg, 64%); Yellow sticky solid. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (s, 2H), 7.79 (d, J = 5.0 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.21 (t, J = 7.5 Hz, 1H), 7.11 – 7.08 (m, 1H), 6.93 (d, J = 10.0 Hz, 1H), 3.42 (d, J = 15.0 Hz, 1H), 3.31 (d, J = 20.0 Hz, 1H), 3.03 (d, J = 20.0 Hz, 1H), 2.67 (d, J = 15.0, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 209.7, 152.2, 140.4, 136.6, 136.4, 135.8, 133.2, 132.9, 130.6, 130.5, 130.4, 129.1, 128.0, 128.0, 127.1, 127.1, 125.9, 124.6, 124.5, 121.4, 120.6, 54.0, 40.9, 38.4; HRMS (ESI-TOF, [M + H]$^+$): Calcd for $C_{22}H_{16}BrO$, 375.0379, found 375.0391.

2'-Chloro-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (4d): (1:1 Regio isomers) Isolated yield (52 mg, 63%); Brownish yellow sticky solid. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, J = 5.0 Hz, 1H), 7.80 – 7.72 (m, 1H), 7.64 (q, J = 6.6 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.37 – 7.32 (m, 3H), 7.21 – 7.19 (m, 1H), 7.17 – 7.15 (m, 1H), 6.95 – 6.91 (m, 1H), 3.48 – 3.40 (m, 1H), 3.35 – 3.17 (m, 1H), 3.09 – 3.02 (m, 1H), 2.67 – 2.63 (m, 1H) ; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 209.5, 152.4, 152.2, 142.3, 140.2, 138.5, 136.2, 135.9, 135.8, 133.2, 132.9, 132.7, 131.9, 131.6, 130.8, 129.9, 129.0, 128.9, 128.7, 128.6, 128.4, 128.2, 128.0, 127.9, 127.8, 127.6, 127.1, 127.1, 126.6, 125.9, 125.3, 125.1, 124.6, 124.5, 124.3, 119.0, 117.5, 54.0, 54.0, 41.0, 40.1, 39.8, 38.7; HRMS (ESI-TOF, [M + Na]$^+$): Calcd for $C_{22}H_{16}ClO$, 353.0704, found 353.0690.

3'-Chloro-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (4e): Isolated yield (55 mg, 67%); Yellow sticky solid. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, J = 5.0 Hz, 1H), 7.79 (s, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.24 – 7.20 (m, 2H), 7.15 – 7.11 (m, 2H), 6.94 (d, J = 5.0 Hz, 1H), 3.44 (d, J = 15.0 Hz, 1H), 3.32 (d, J = 15.0 Hz, 1H), 3.04 (d, J = 15.0 Hz, 1H), 2.68 (d, J = 15.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 209.7, 152.2, 140.5, 136.7, 136.1, 135.8, 133.4, 133.0, 132.7, 130.2, 129.1, 128.0, 128.0, 127.7, 127.1, 125.9, 124.6, 124.5, 124.2, 54.1, 41.0, 38.4; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{22}H_{16}ClO$, 331.0884, found 331.0881.

3'-(Trifluoromethyl)-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (4f): Isolated yield (63 mg, 70%); Yellow solid; mp: 116-118 ºC. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^1H NMR (500 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.95 (d, J = 5.0 Hz, 1H), 7.87 (d, J = 10.0 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.52 (d, J = 10.0 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.38 – 7.36 (m, 2H), 7.33 (d, J = 10.0 Hz, 1H), 7.24 (d, J = 5.0 Hz, 1H), 6.95 (d, J = 5.0 Hz, 1H), 3.53 (d, J = 15.0 Hz, 1H), 3.31 (d, J = 15.0 Hz, 1H), 3.06 (d, J = 15.0 Hz, 1H), 2.78 (d, J = 15 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 209.5, 152.1, 140.5, 138.3, 136.6, 135.9, 135.1, 132.9, 129.4 (d, J = 10.0 Hz), 128.1 (d, J = 13.7 Hz), 127.1, 125.9, 124.6 – 124.4 (m), 120.8, 53.8, 41.0, 38.8; ^{19}F NMR (470 MHz, $CDCl_3$): δ -62.33 (s) ; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{23}H_{16}F_3O$, 365.1148, found 365.1122.

3'-Chloro-2'-fluoro-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (4g): (1:1 Regio isomers) Isolated yield (58 mg, 67%); Yellow sticky solid. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^1H NMR (500 MHz, $CDCl_3$): δ 8.12 – 8.08 (m, 2H), 7.94 (d, J = 5.0 Hz, 2H), 7.83–7.73 (m, 2H), 7.65 (t, J = 7.5 Hz, 2H), 7.48 – 7.41 (m, 4H), 7.39 – 7.34 (m, 4H), 7.11 (d, J = 5.0 Hz, 2H), 6.96 (t, J = 7.5 Hz, 2H), 3.45 – 3.40 (m, 2H), 3.33 – 3.24 (m, 2H), 3.06 (d, J = 15.0 Hz, 2H), 2.69 – 2.65 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 209.4, 152.1, 141.1, 138.3, 136.6, 135.9, 133.6, 130.4, 129.1 (d, J = 8.7 Hz), 128.9, 128.8, 128.6, 128.1, 128.0, 127.8, 127.1, 126.3, 125.9, 125.7, 125.6, 124.8, 124.8, 124.6, 124.5, 124.2, 122.9, 120.6, 54.0, 53.8, 41.0, 40.4, 38.9, 38.4; ^{19}F NMR (470 MHz, $CDCl_3$): δ -117.09 (s), -117.5 (s); HRMS (ESI-TOF, $[M + Na]^+$): Calcd for $C_{22}H_{14}ClFNaO$, 371.0609, found 371.0610.

3'-Chloro-6-methoxy-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (4h): Isolated yield (58 mg, 65%); Yellow oil. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, J = 5.0 Hz, 2H), 7.36 – 7.33 (m, 2H), 7.25 – 7.20 (m, 4H), 7.14 (d, J = 10.0 Hz, 1H), 6.92 (d, J = 10.0 Hz, 1H), 3.89 (s, 3H), 3.43 (d, J = 15.0 Hz, 1H), 3.23 (d, J = 20.0 Hz, 1H), 2.94 (d, J = 20.0 Hz, 1H), 2.68 (d, J = 15.0 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 209.8, 159.9, 145.0, 140.6, 137.8, 132.8, 130.2, 129.1, 128.0, 127.8, 127.7, 125.8, 125.4, 124.5, 124.2, 105.5, 55.8, 54.9, 40.3, 38.4; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{23}H_{18}ClO_2$, 361.0990, found 361.0984.

2'-Chloro-6-methoxy-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (4i): Isolated yield (54 mg, 61%); Yellow sticky solid. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, J = 5.0 Hz, 1H), 7.73 (d, J = 10.0 Hz, 1H), 7.36 (s, 1H), 7.34 – 7.32 (m, 2H), 7.25 – 7.18 (m, 4H), 6.91 (d, J = 10.0 Hz, 1H), 3.89 (s, 3H), 3.46 (d, J = 15.0 Hz, 1H), 3.25 (d, J = 20.0 Hz, 1H), 2.95 (d, J = 20.0 Hz, 1H), 2.66 (d, J = 15.0 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 209.6, 159.8, 144.9, 140.1, 137.6, 136.1, 133.4, 133.0, 132.7, 128.7, 128.6, 127.8, 127.7, 127.6, 125.7, 125.3, 125.2, 124.1, 105.4, 55.7, 54.7, 40.2, 38.6; HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{23}H_{18}ClO_2$, 361.0990, found 361.0983.

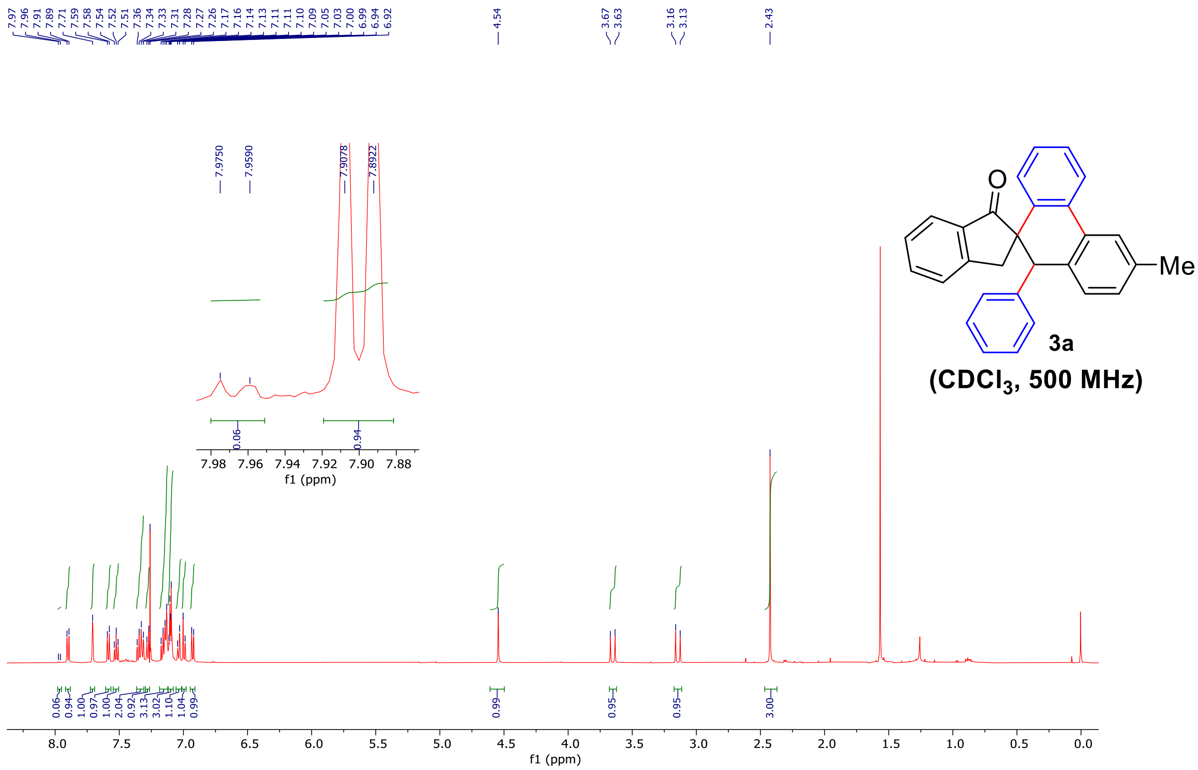
3'-Fluoro-6-methoxy-10'*H*-spiro[indene-2,9'-phenanthren]-1(3*H*)-one (4j): Isolated yield (55 mg, 64%); Yellow solid; mp: 68-70 ºC. Isolation: hexane/ethyl acetate (50/1) as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 10.0 Hz, 1H), 7.49 (d, J = 10.0 Hz, 1H), 7.36 – 7.33 (m, 2H), 7.25 (s, 2H), 7.22 (t, J = 7.5 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 6.97 – 6.92 (m, 2H), 3.89 (s, 3H), 3.43 (d, J = 15.0 Hz, 1H), 3.25 (d, J = 15.0 Hz, 1H), 2.95 (d, J = 15.0 Hz, 1H), 2.67 (d, J =

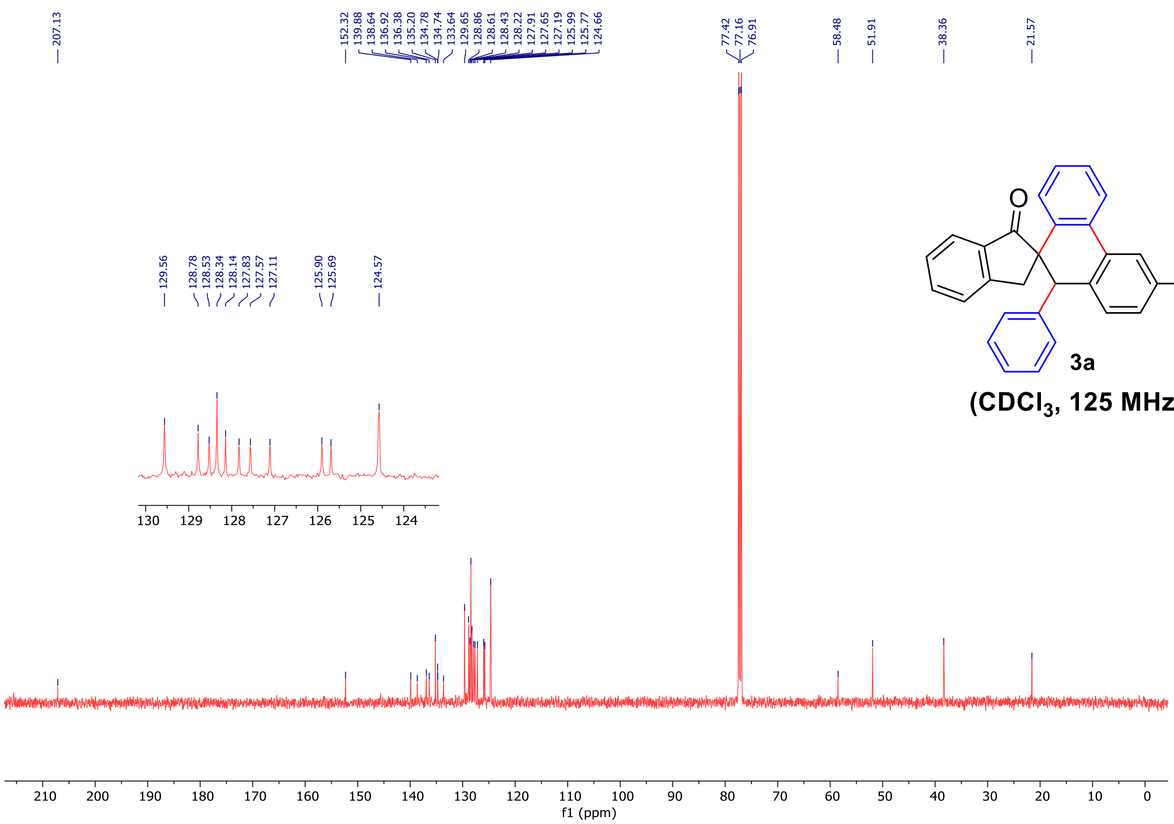
15.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 209.9, 159.9, 145.1, 140.5, 130.2 (d, J = 7.5 Hz), 129.0, 128.0, 127.8, 125.8, 125.4, 124.5, 110.9 (d, J = 21.2 Hz), 105.5, 55.8, 55.1, 40.3, 38.3; ^{19}F NMR (470 MHz, $CDCl_3$): δ -115.11 (s); HRMS (ESI-TOF, $[M + H]^+$): Calcd for $C_{23}H_{18}FO_2$, 345.1285, found 345.1274.

(3-Nitrophenanthren-9-yl)(phenyl)methanone (5a): Isolated yield (42 mg, 51%); Yellow sticky solid; Isolation: hexane/ethyl acetate (50/1) as the eluent. ^1H NMR (500 MHz, $CDCl_3$): δ 9.66 (s, 1H), 8.85 (d, J = 10.0 Hz, 1H), 8.45 – 8.42 (m, 1H), 8.05 – 8.03 (m, 2H), 7.94 (d, J = 10.0 Hz, 2H), 7.88 (s, 1H), 7.83 (t, J = 7.5 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.50 (t, J = 7.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 197.2, 147.1, 139.7, 137.4, 134.1, 134.0, 130.9, 130.8, 130.7, 130.5, 129.7, 128.9, 128.7, 128.6, 127.1, 126.6, 123.4, 121.1, 119.2.

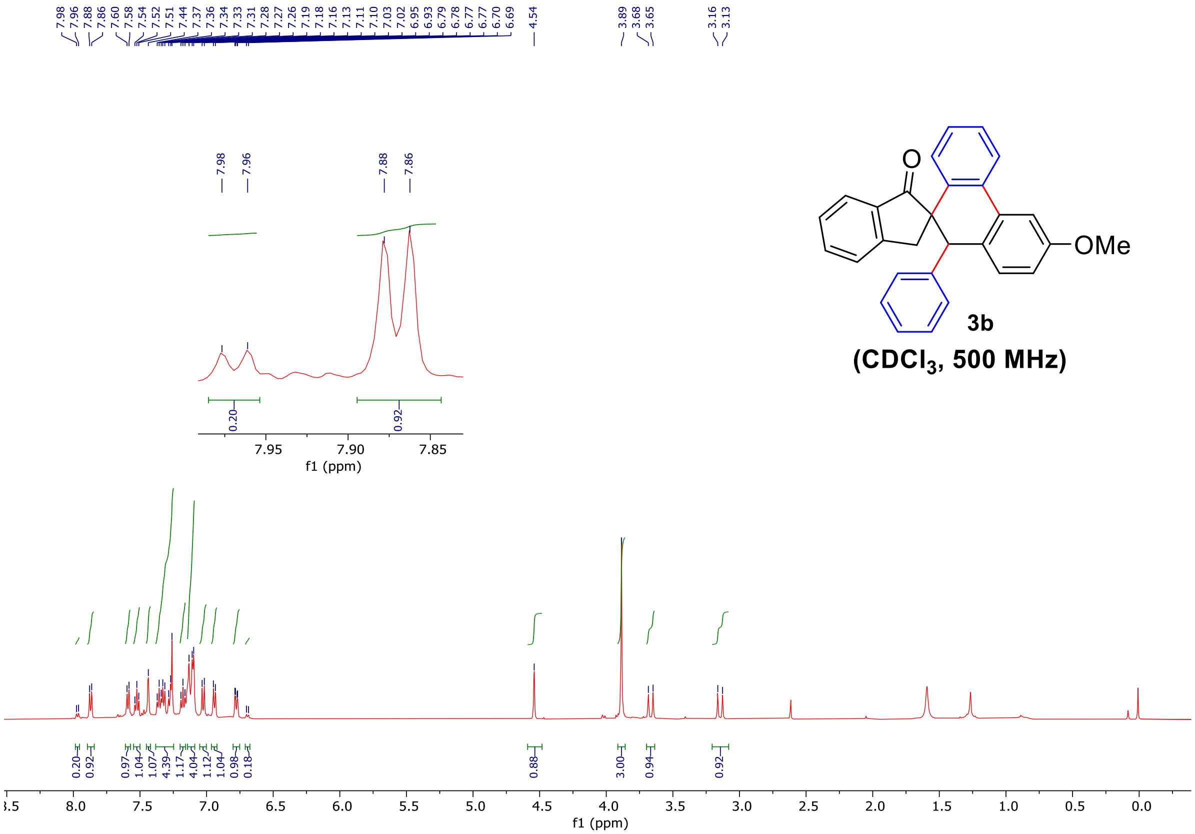
6. NMR Spectra of the compounds 3, 4 and 5

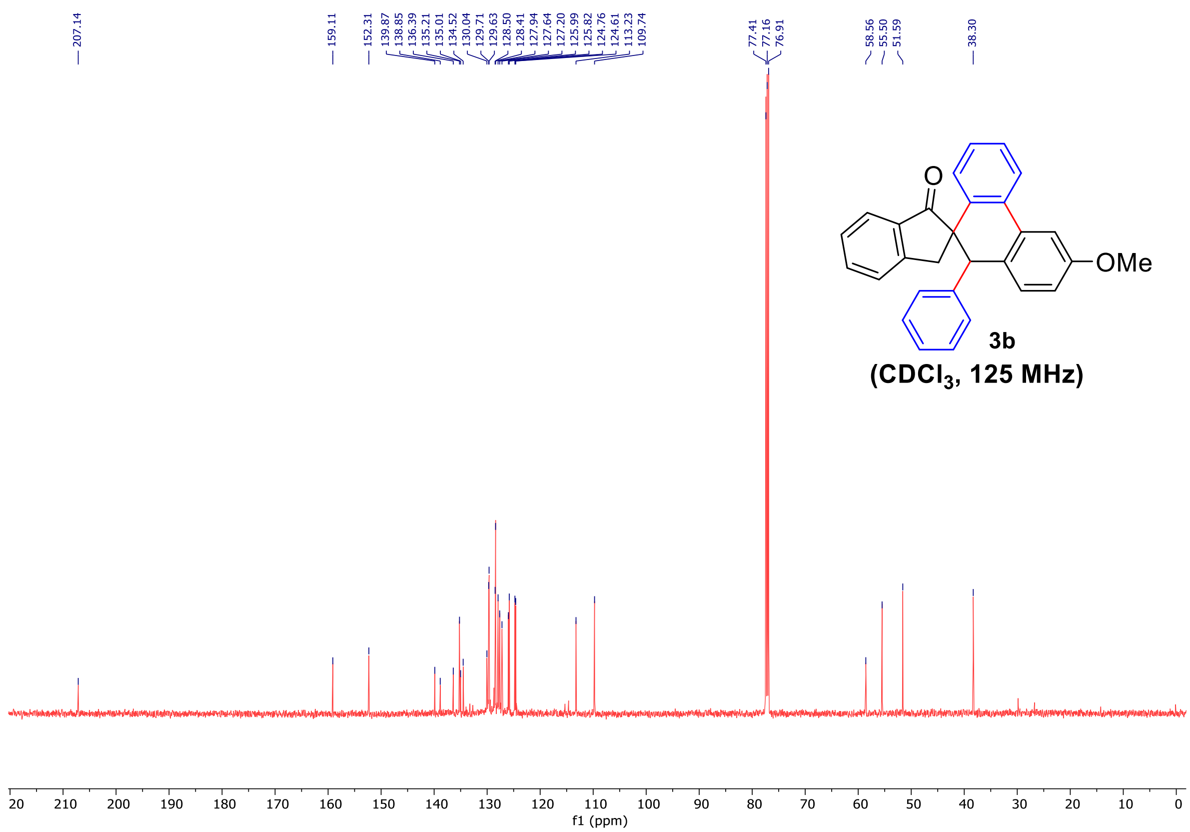
[1]H and [1]H decoupled [13]C NMR spectra of compound **3a**



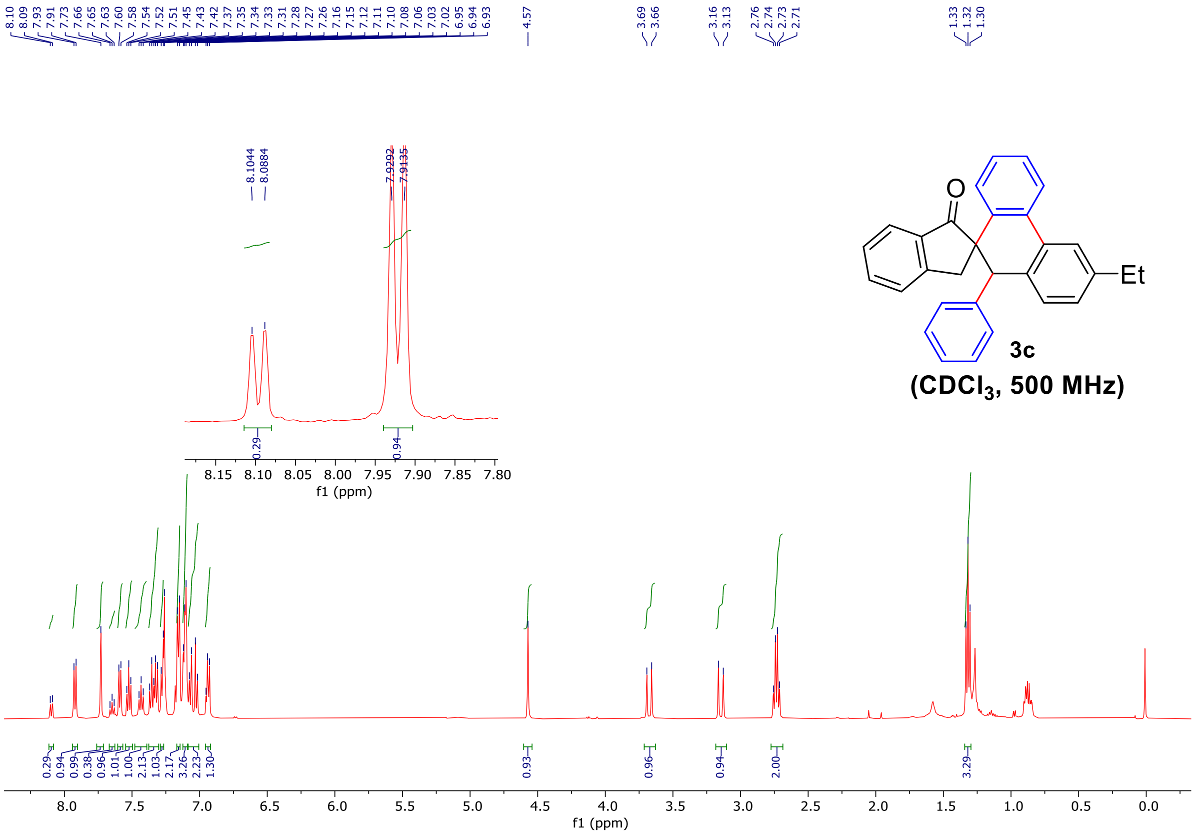


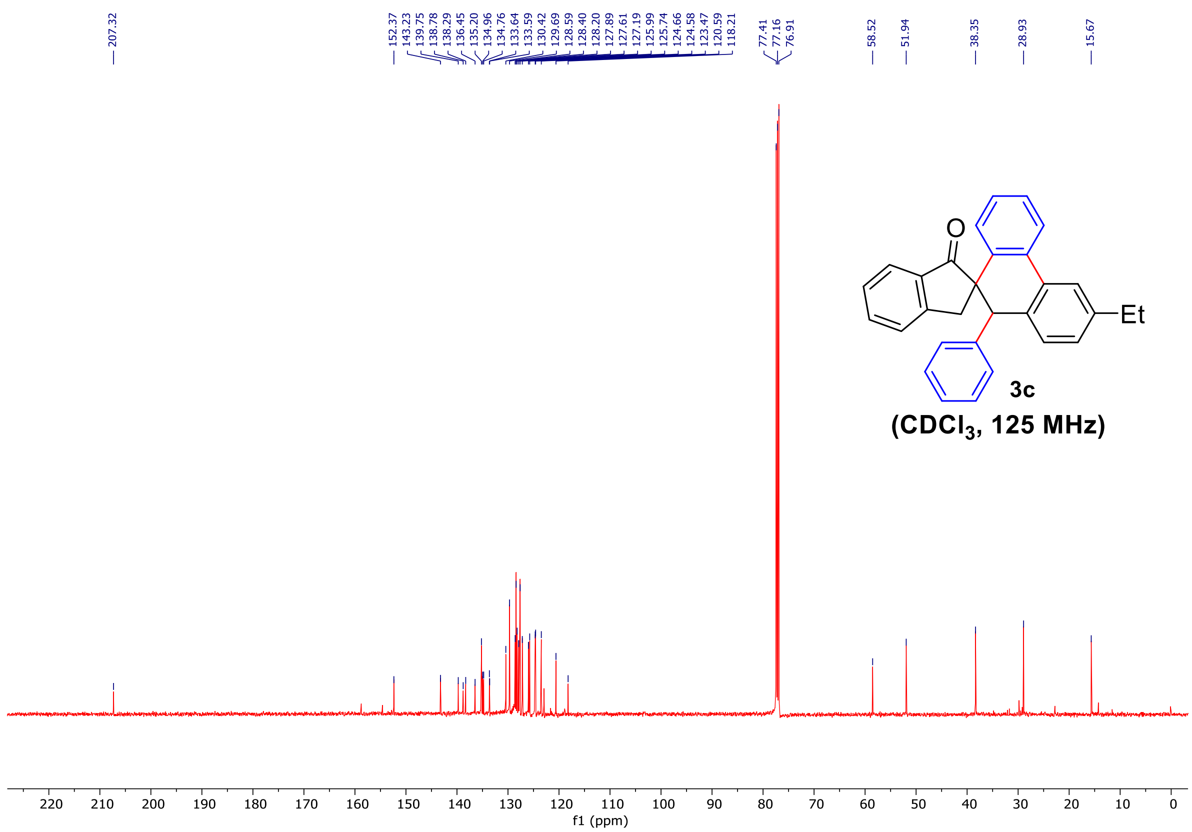
[1]H and [1]H decoupled [13]C NMR spectra of compound 3b



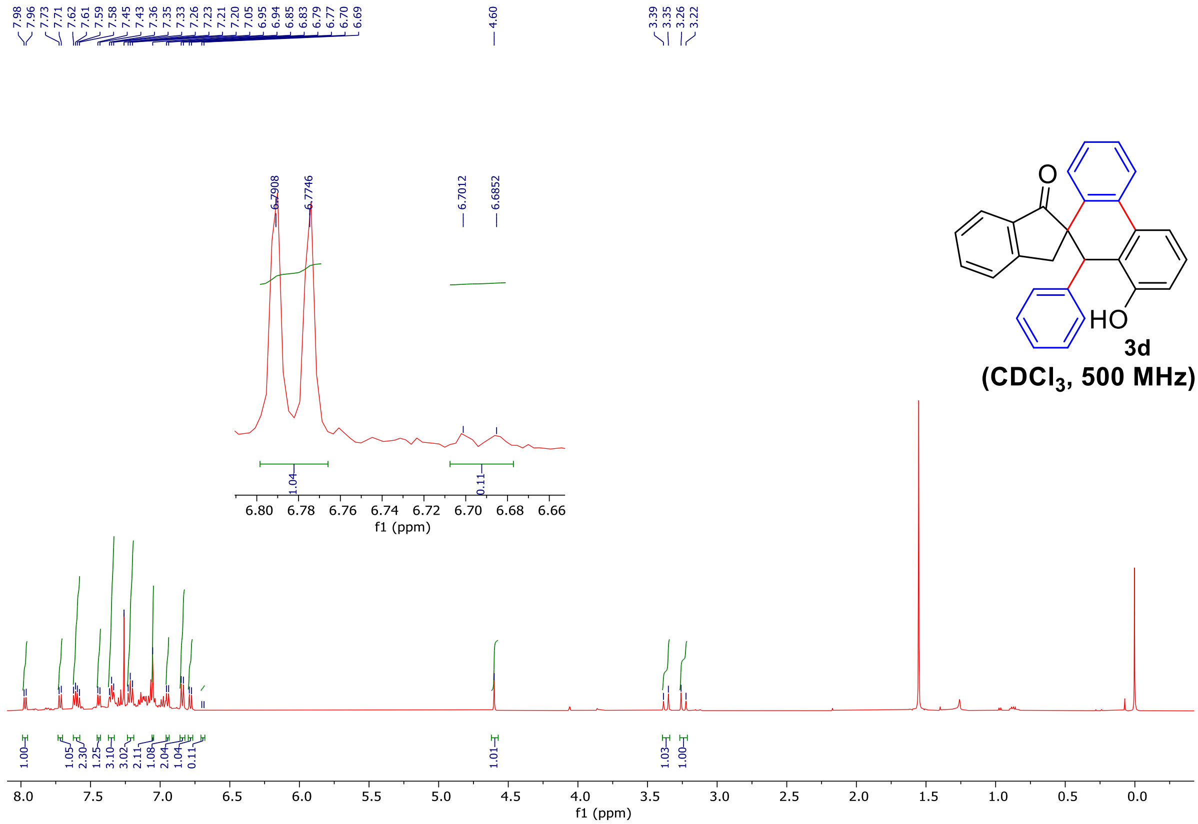


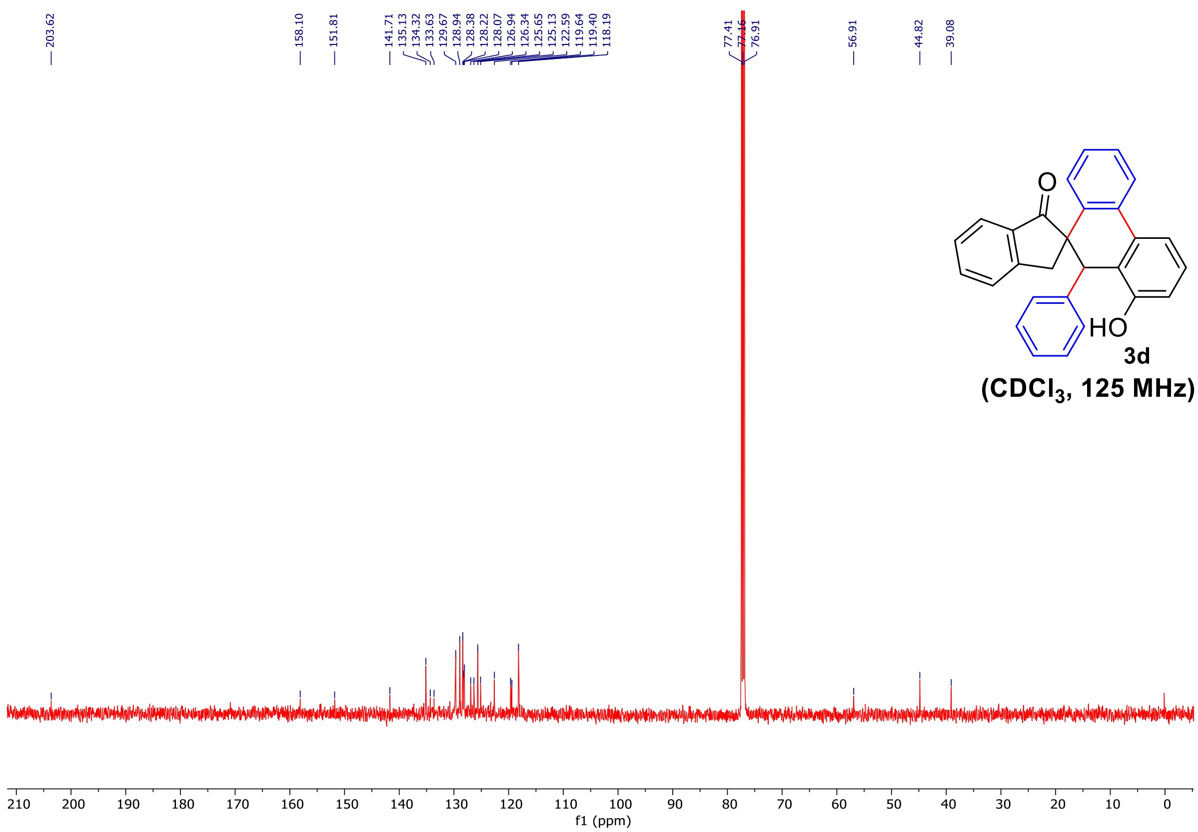
[1]H and [1]H decoupled [13]C NMR spectra of compound 3c



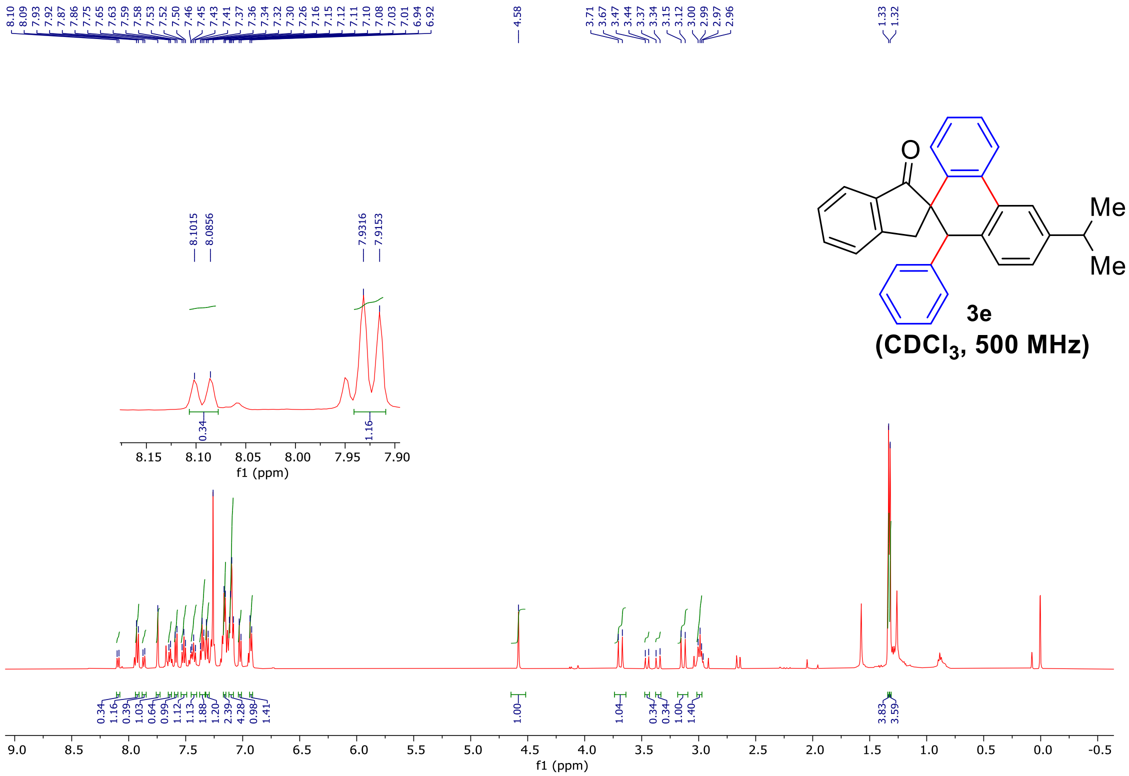


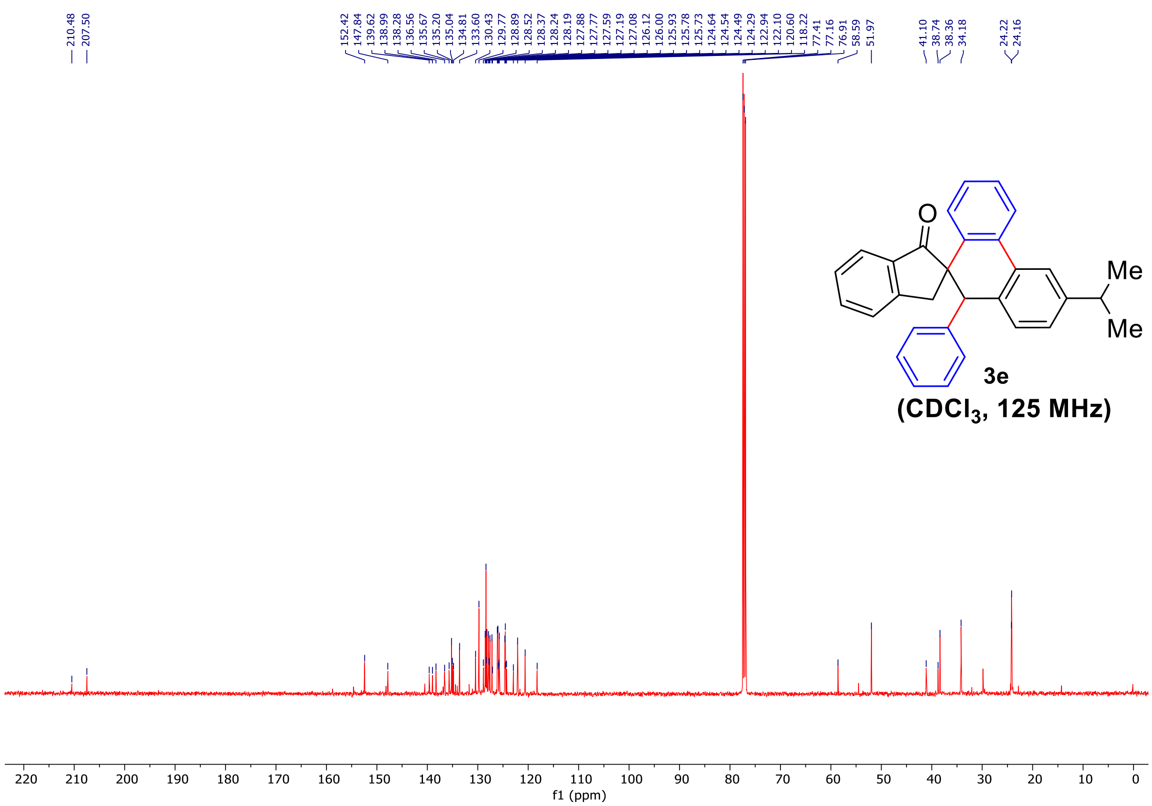
^{1}H and ^{1}H decoupled ^{13}C NMR spectra of compound 3d



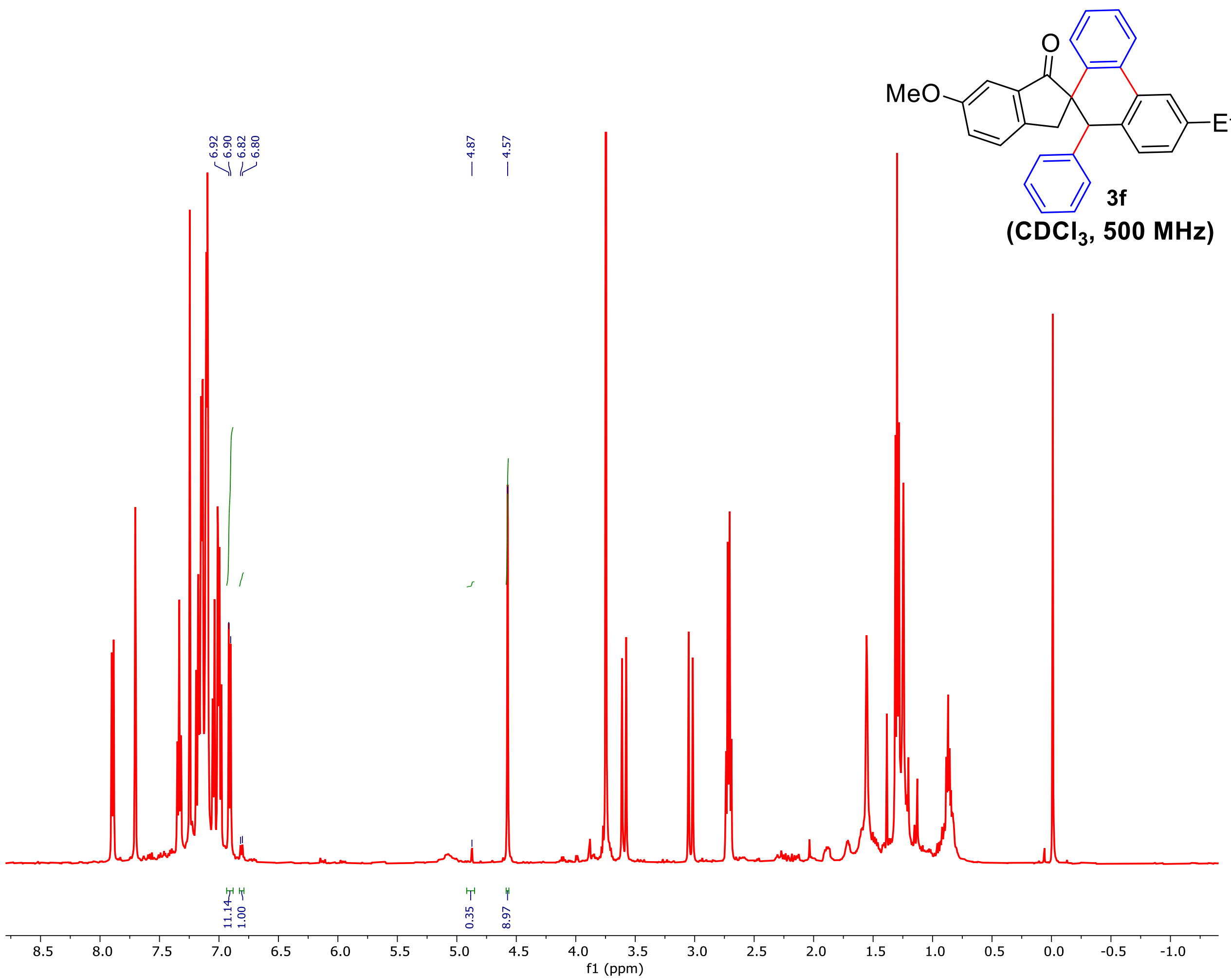


[1]H and [1]H decoupled [13]C NMR spectra of compound 3e

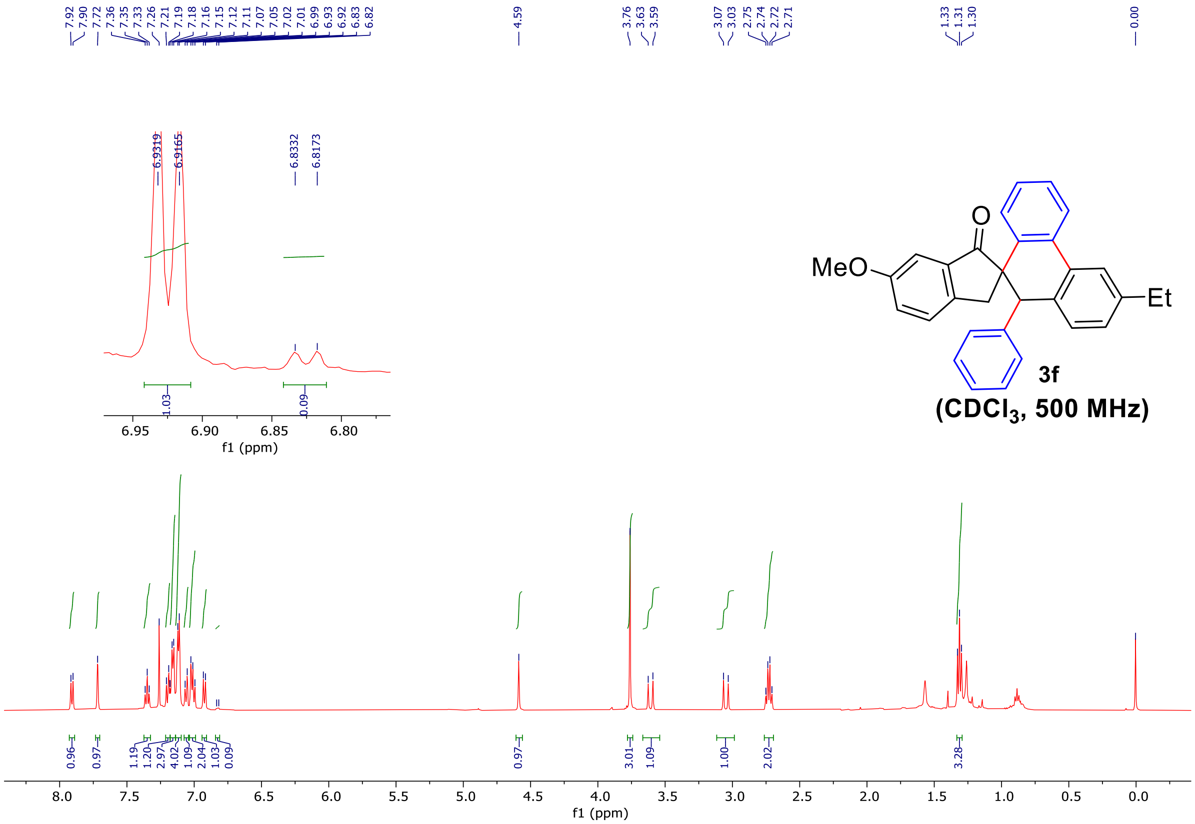


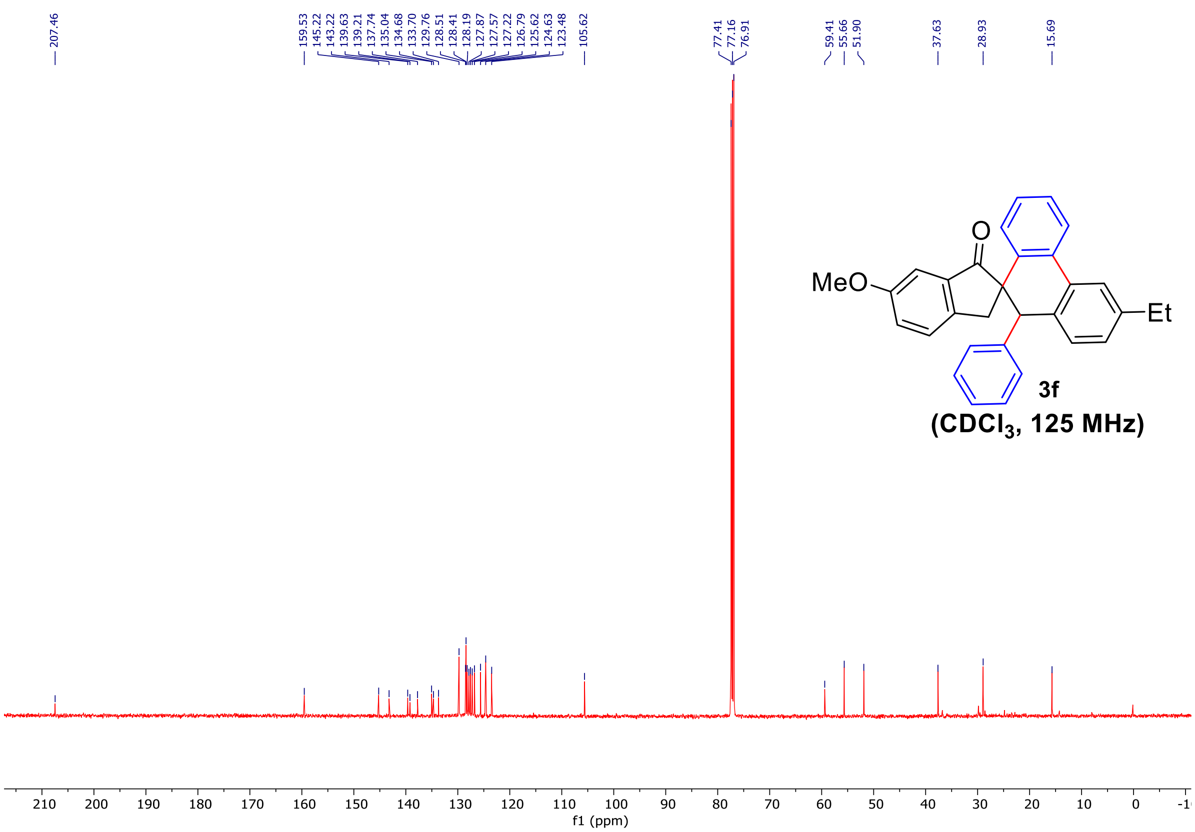


dr from crude reaction mixture of 3f: ^{1}H NMR (500 MHz, $CDCl_3$)

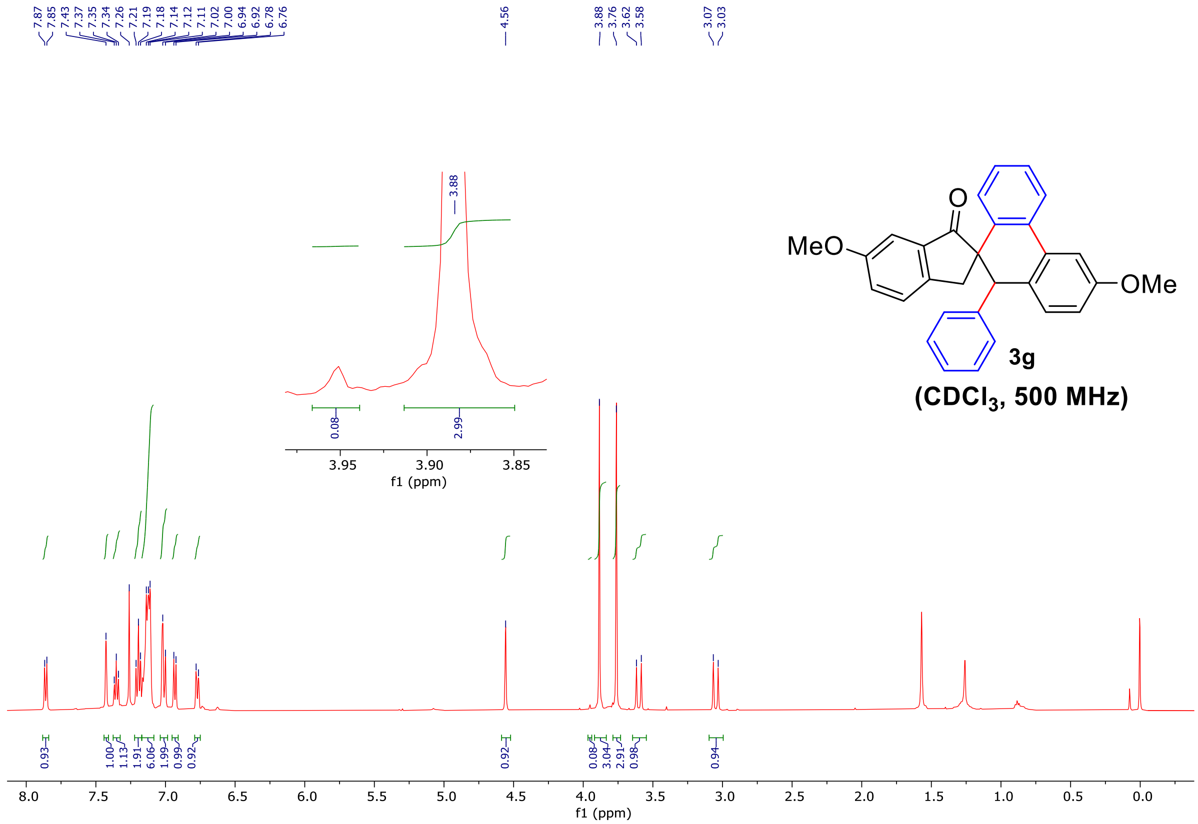


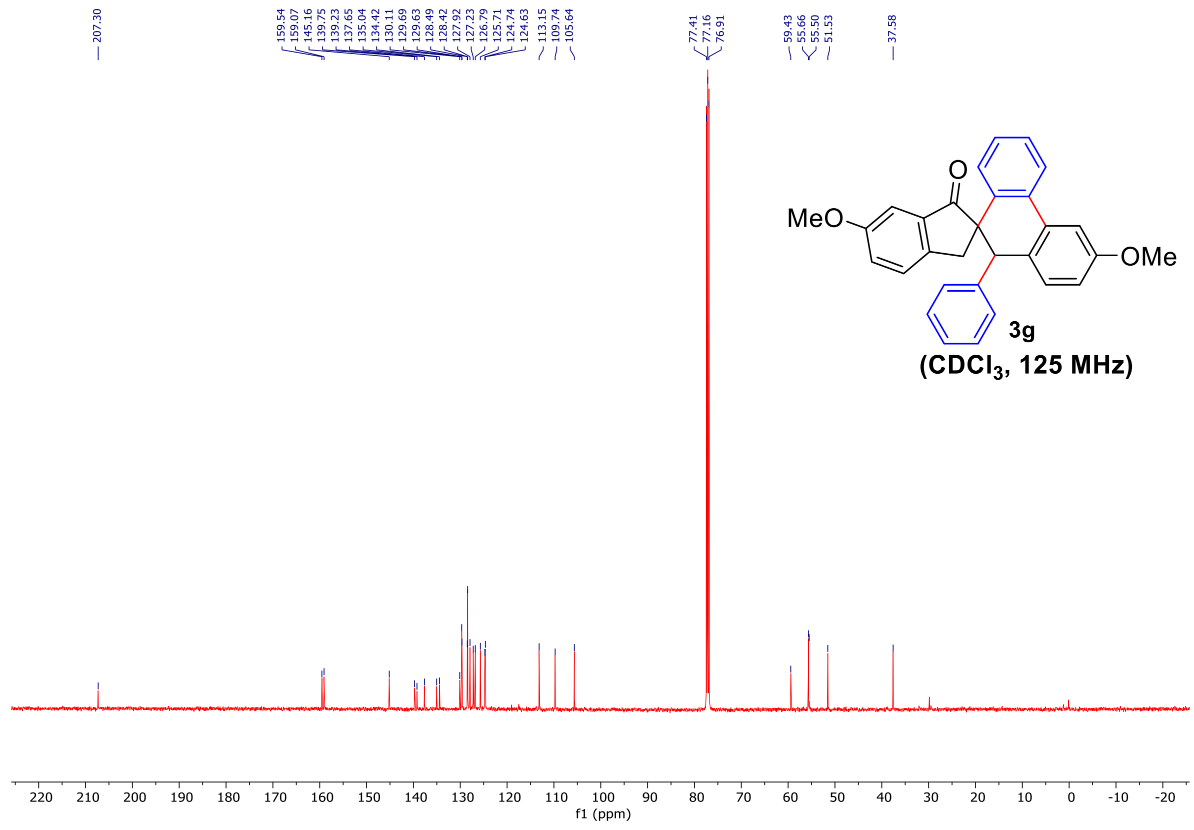
^1H and ^1H decoupled ^{13}C NMR spectra of compound 3f



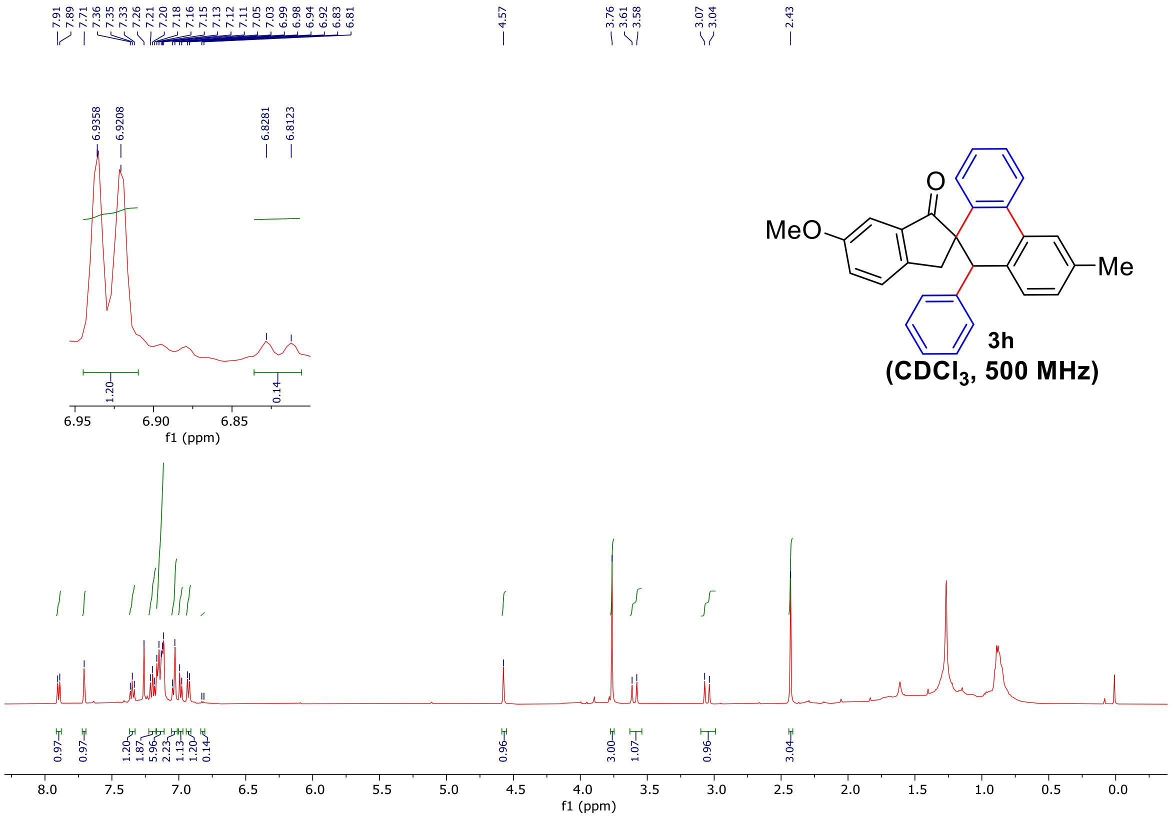


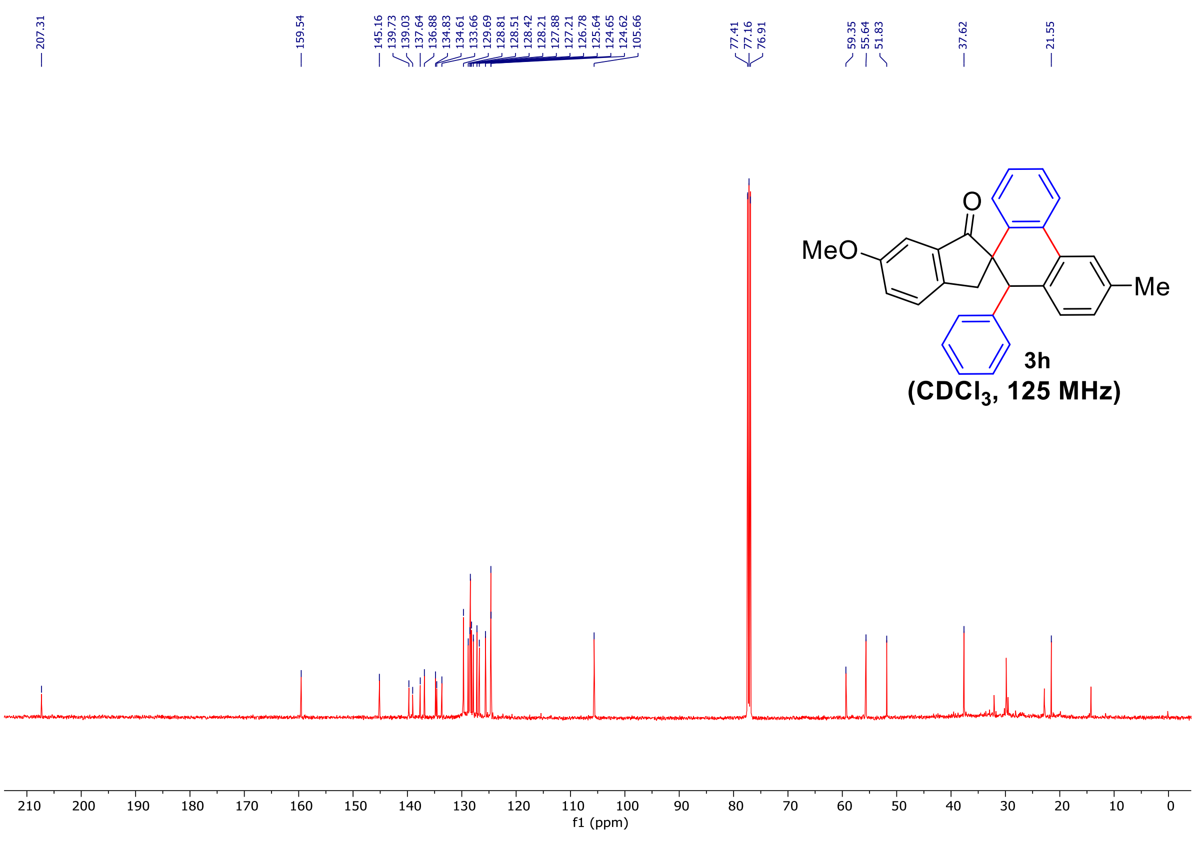
[1]H and [1]H decoupled [13]C NMR spectra of compound 3g



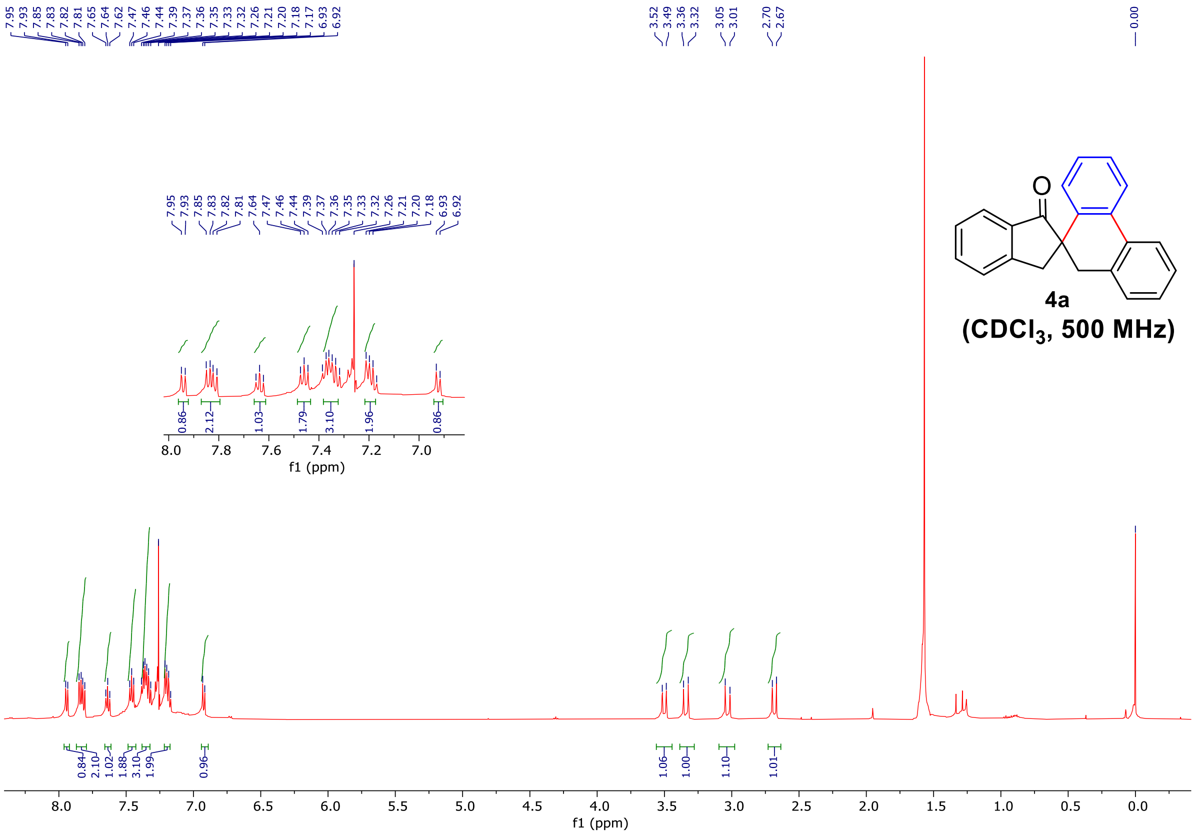


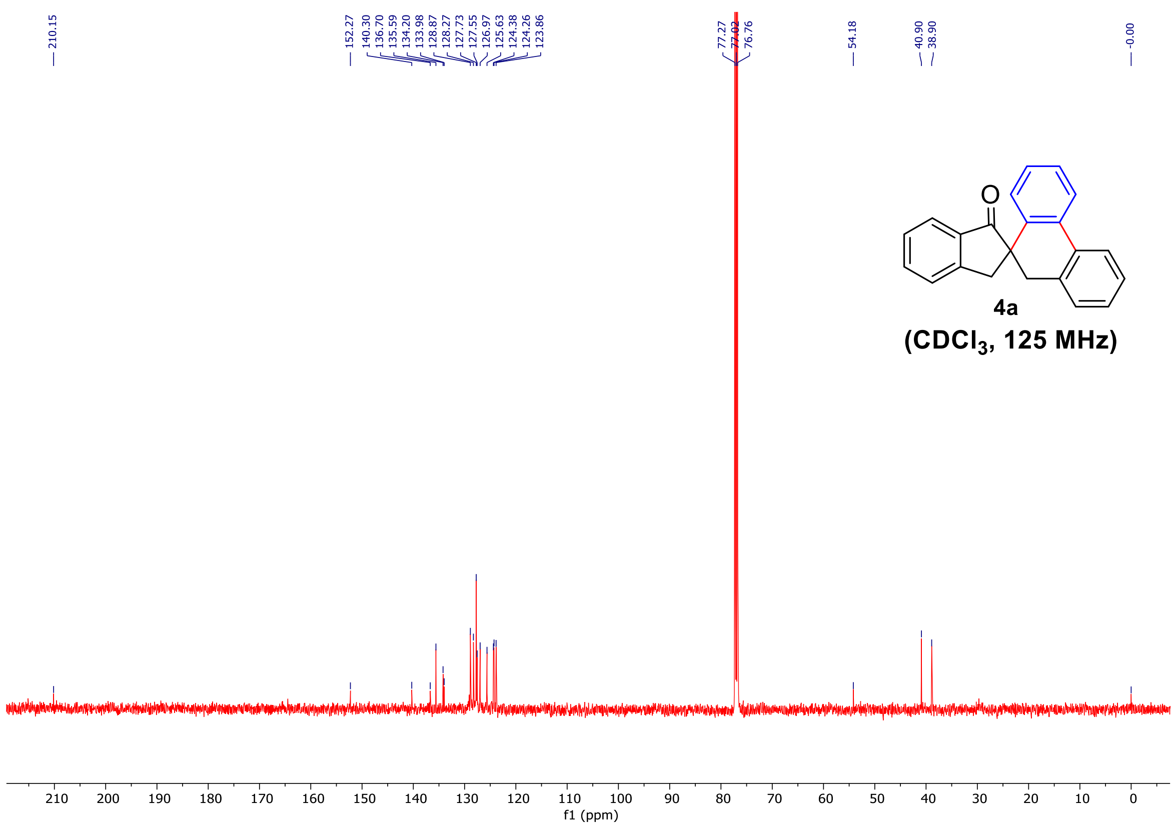
[1]H and [1]H decoupled [13]C NMR spectra of compound 3h



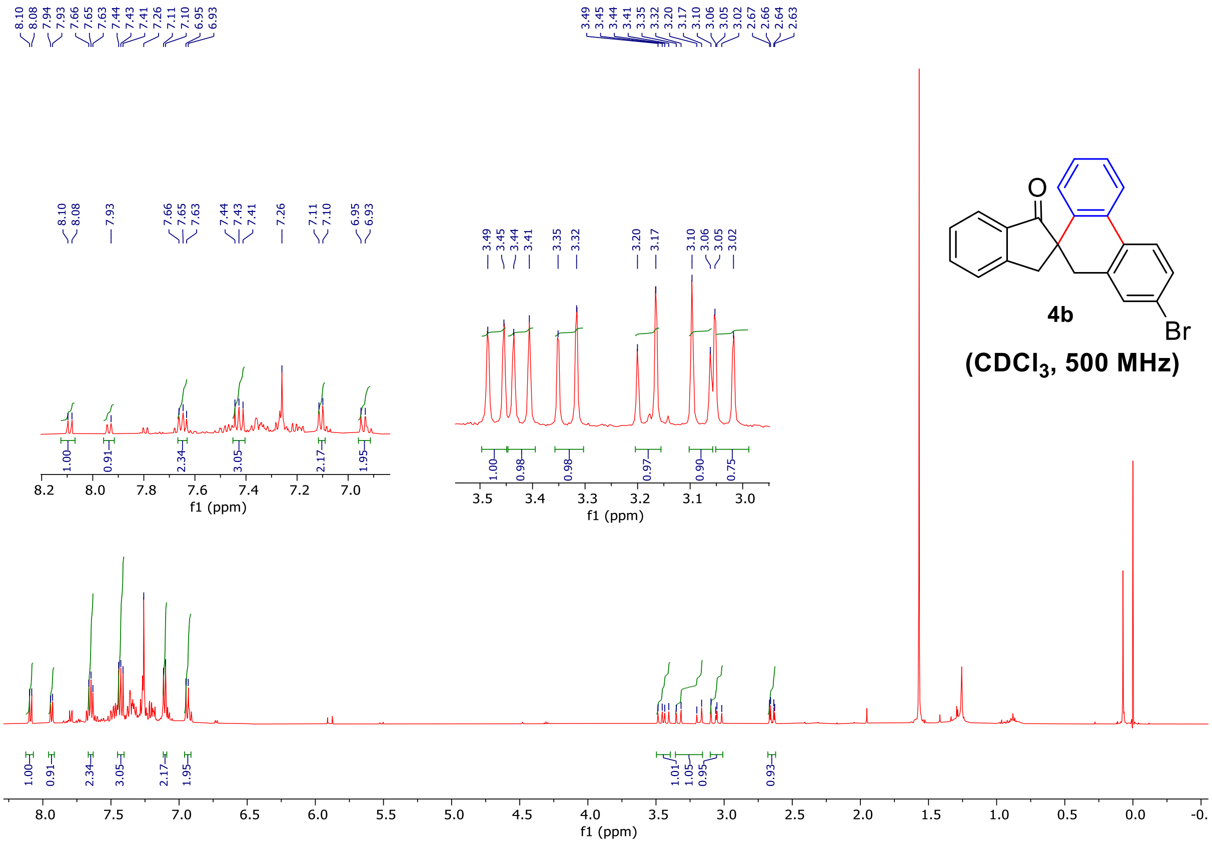


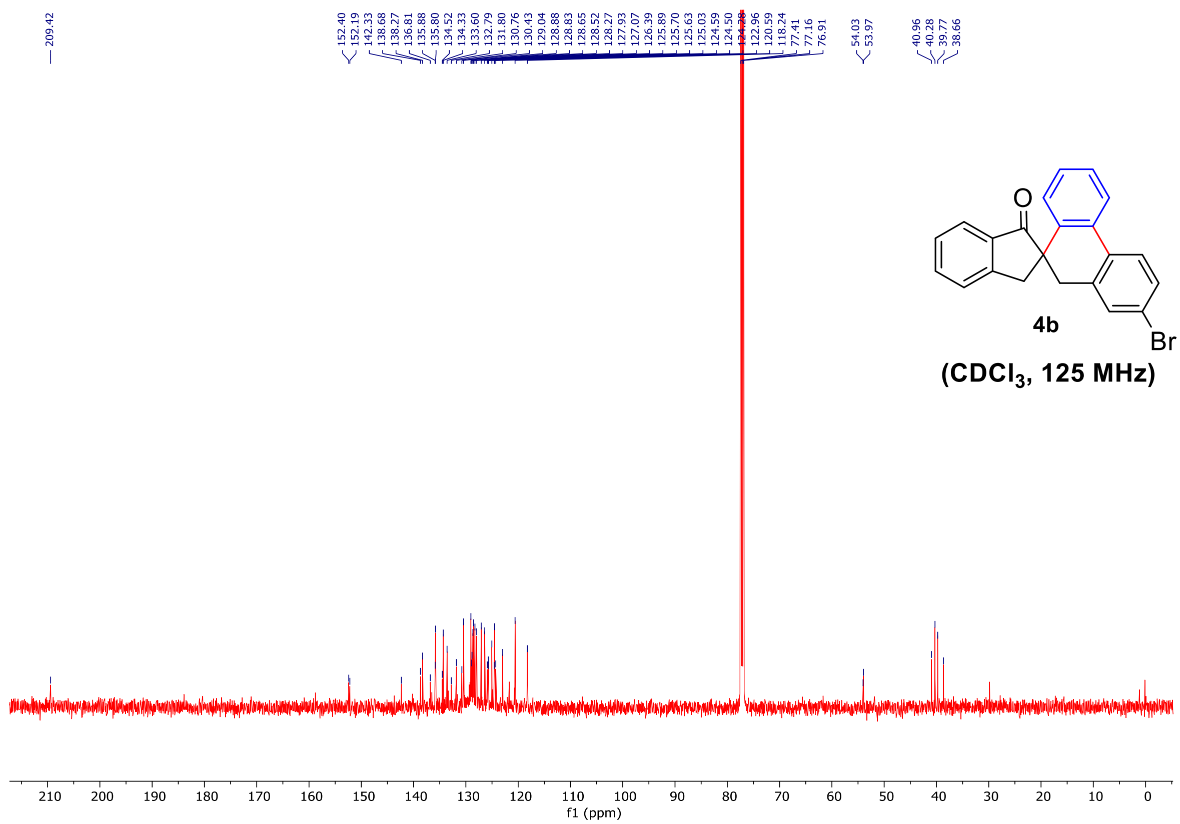
[1]H and [1]H decoupled [13]C NMR spectra of compound 4a



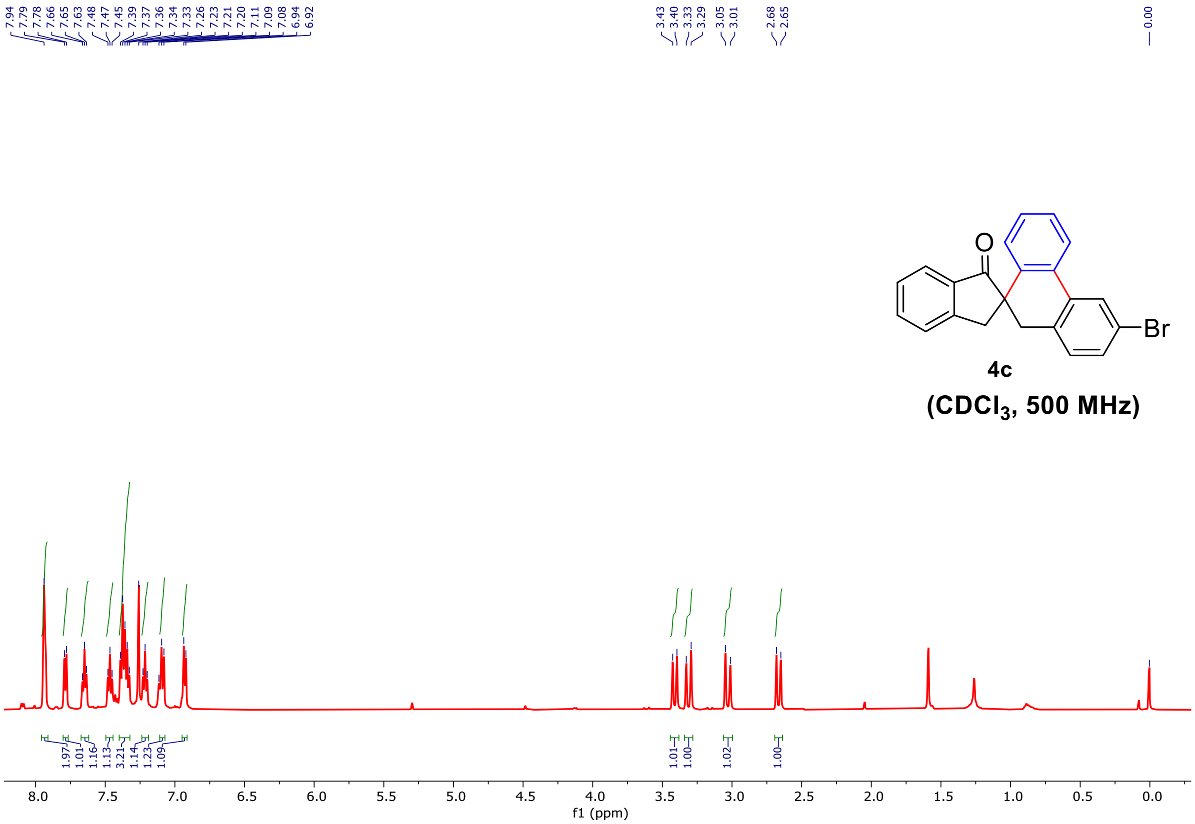


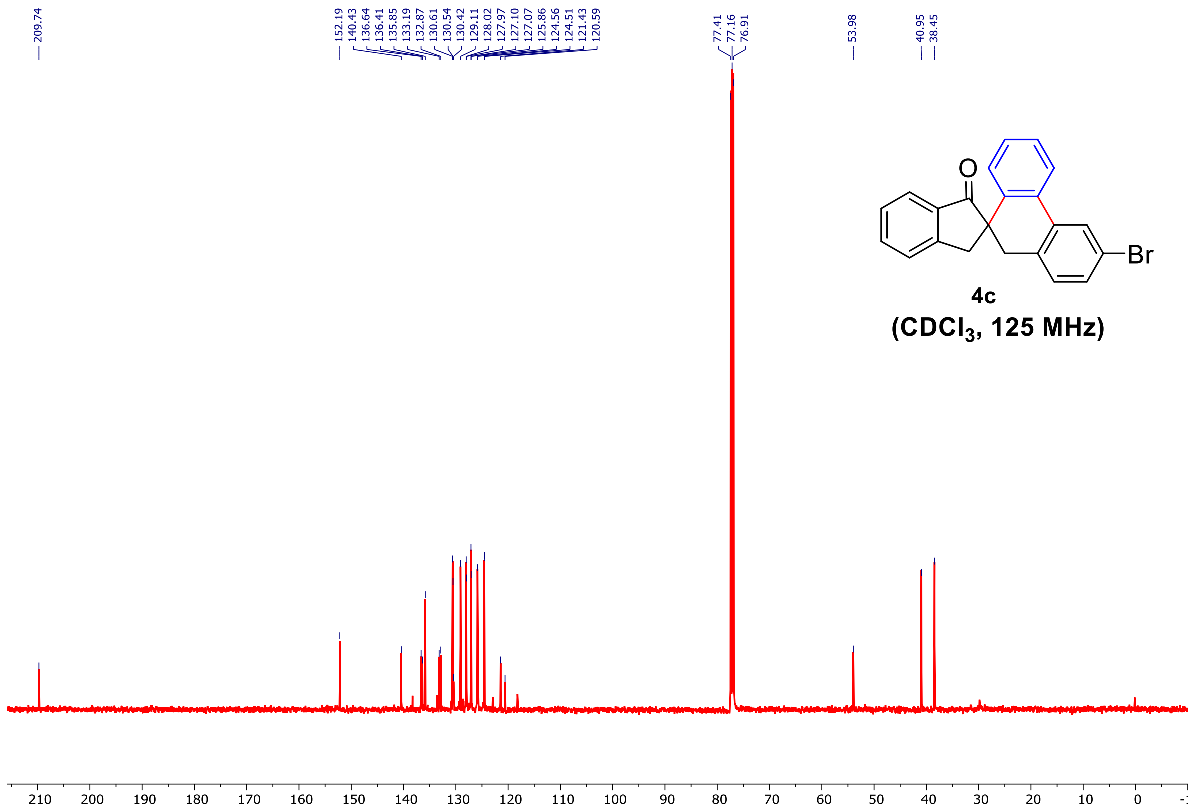
[1]H and [1]H decoupled [13]C NMR spectra of compound 4b



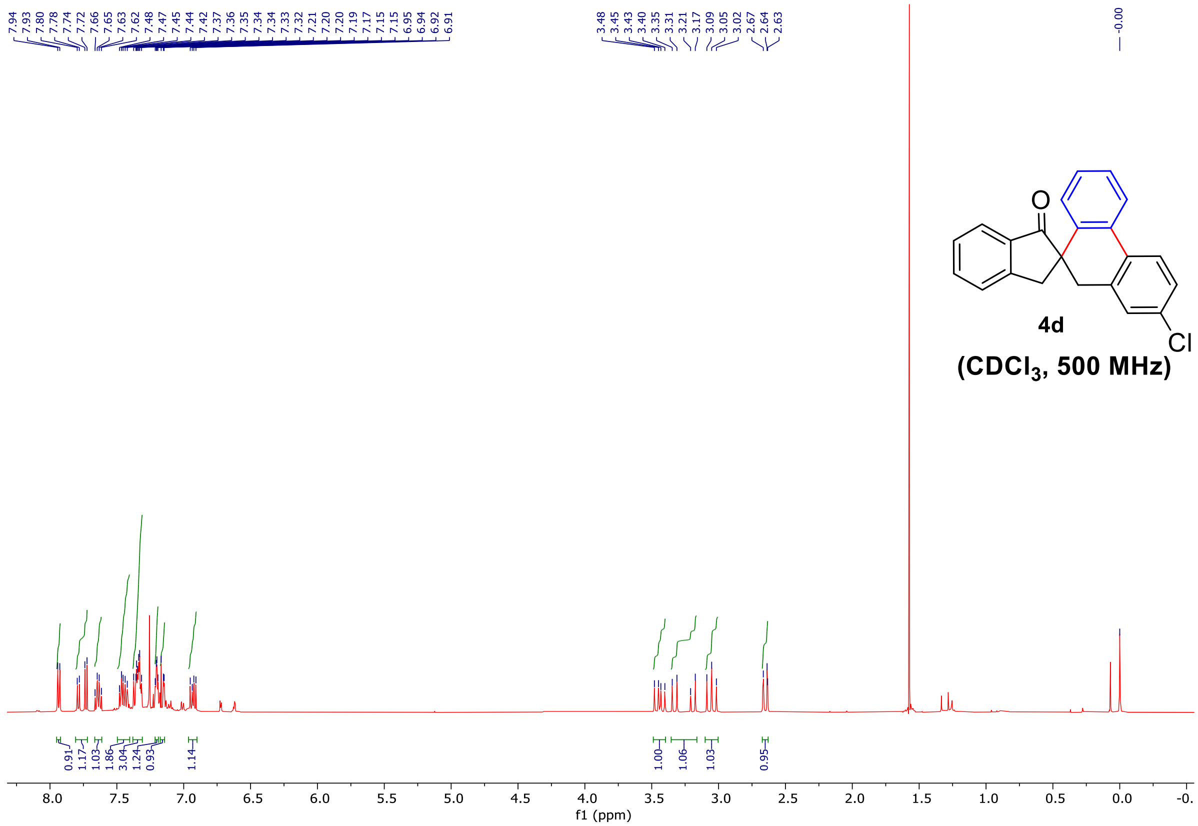


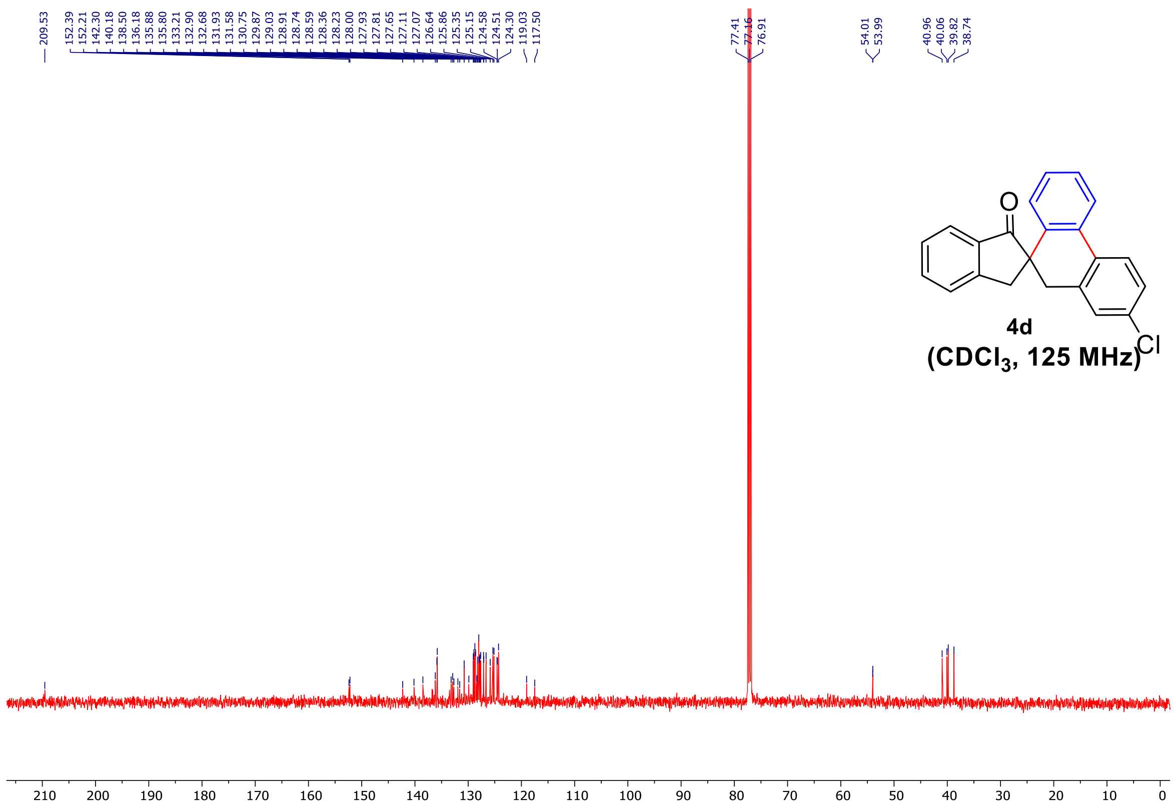
^{1}H and ^{1}H decoupled ^{13}C NMR spectra of compound 4c



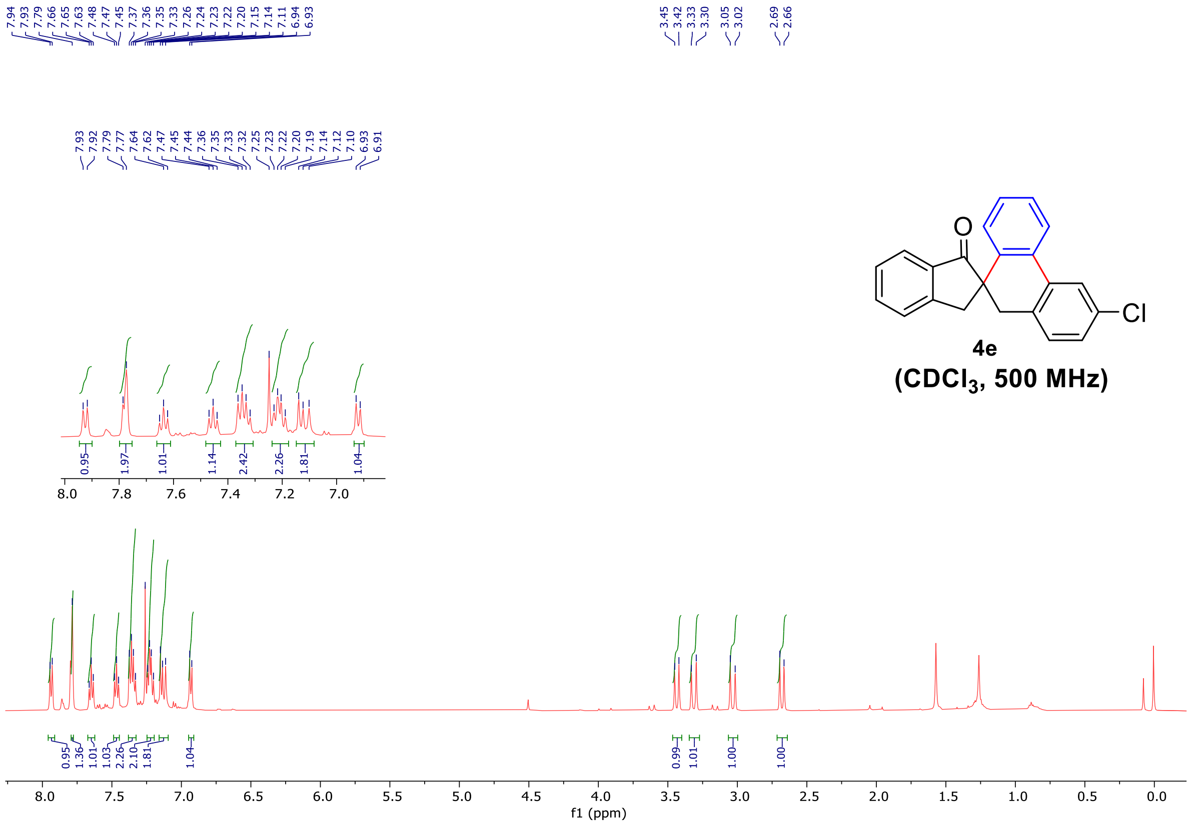


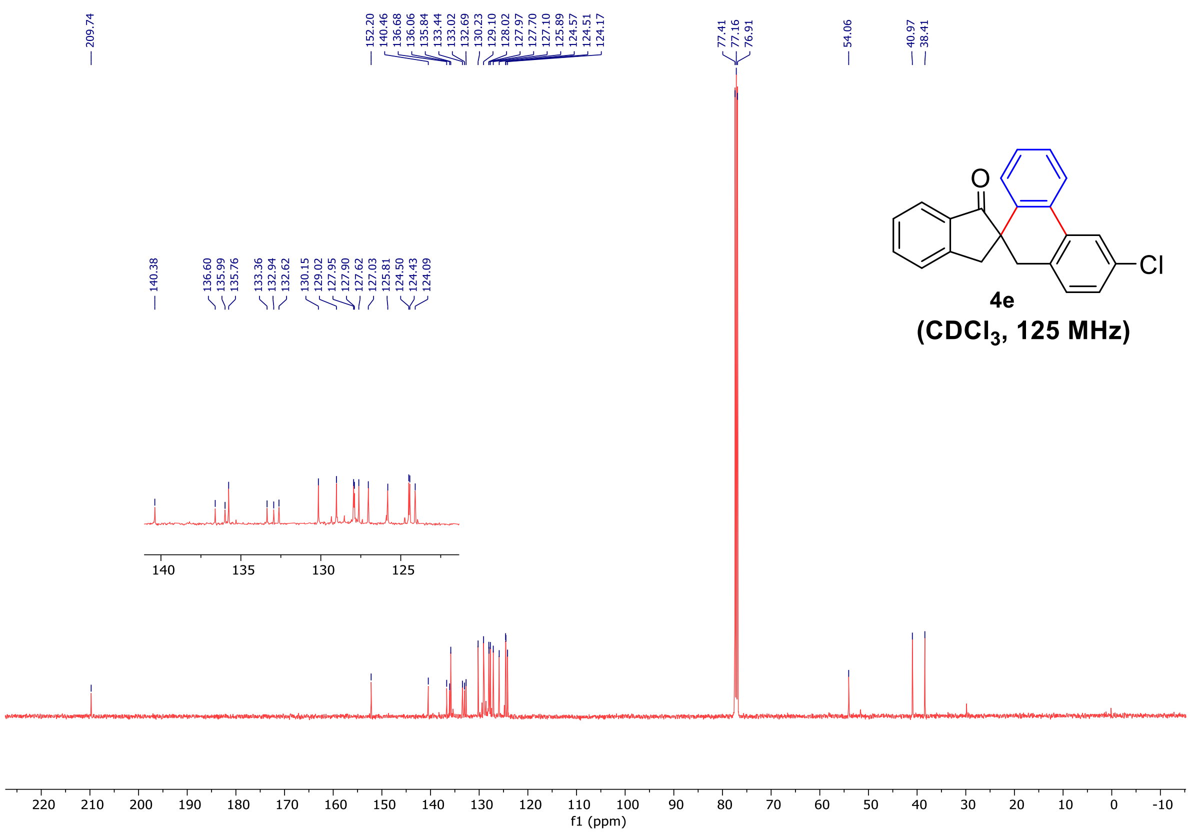
^{1}H and ^{1}H decoupled ^{13}C NMR spectra of compound 4d



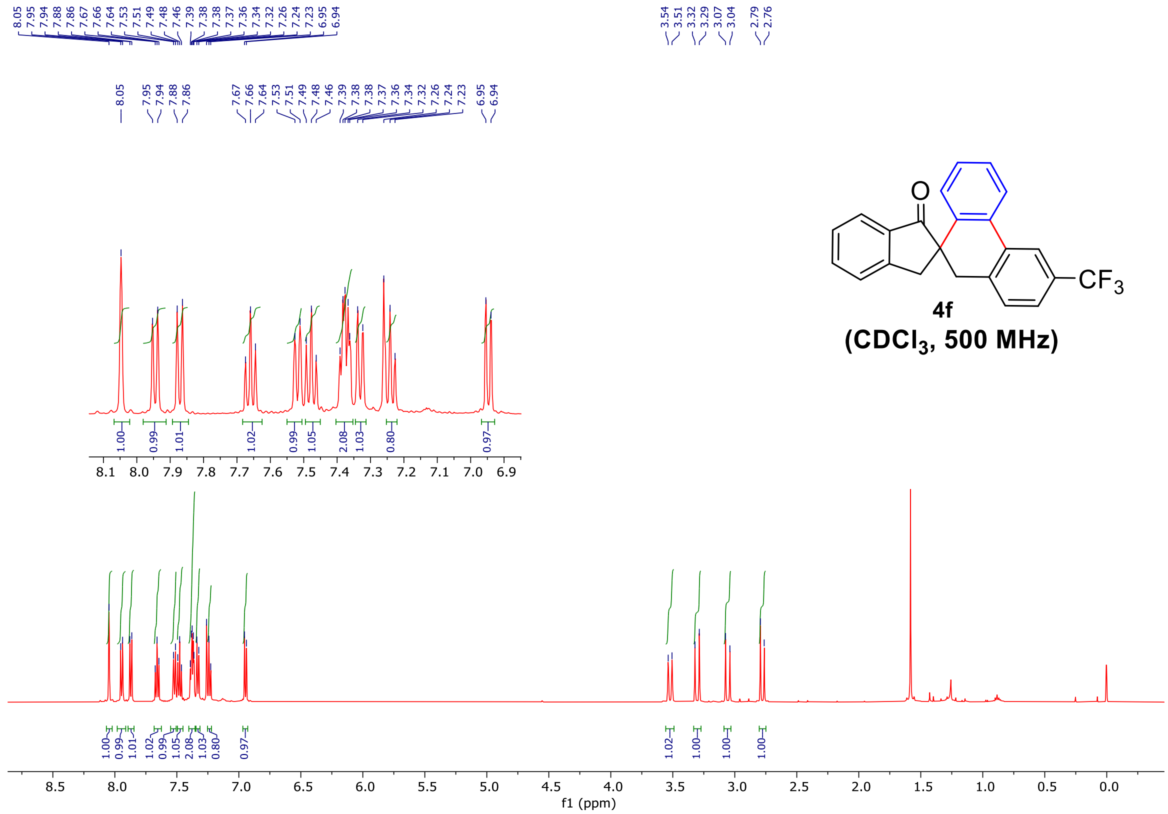


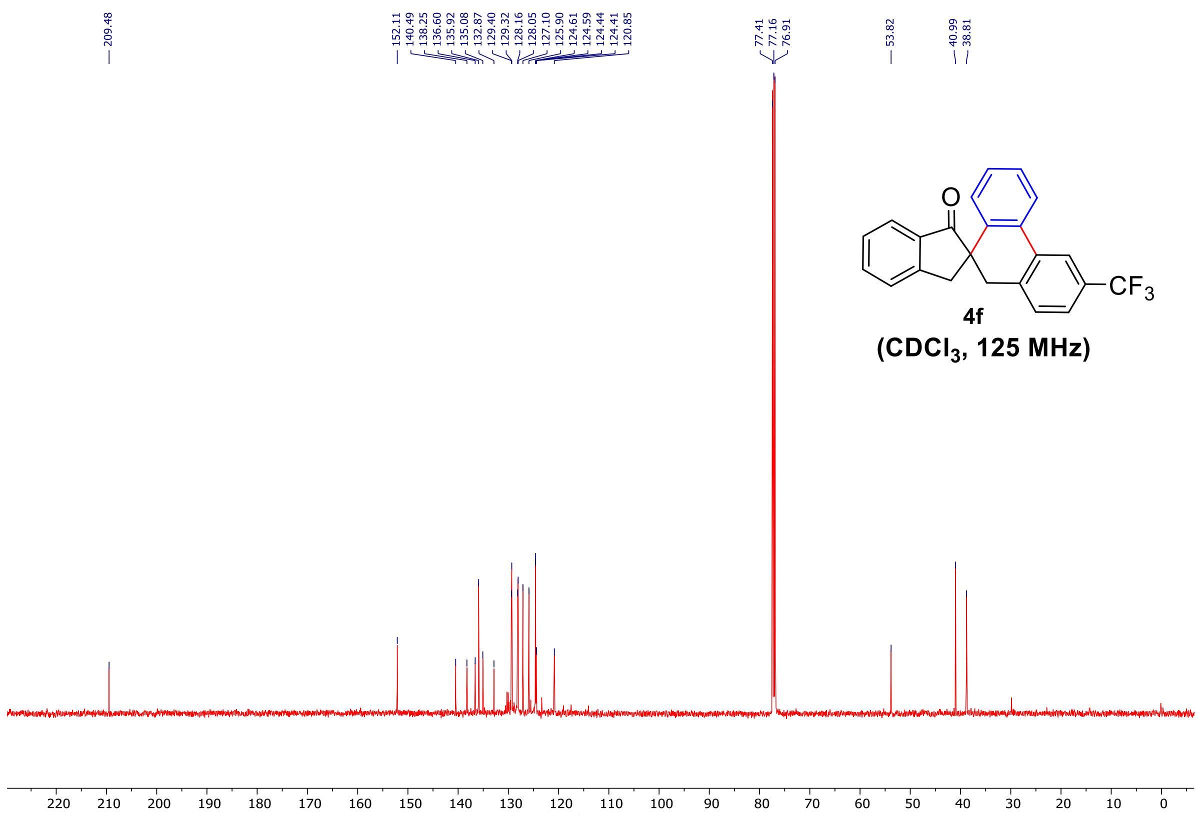
[1]H and [1]H decoupled [13]C NMR spectra of compound 4e



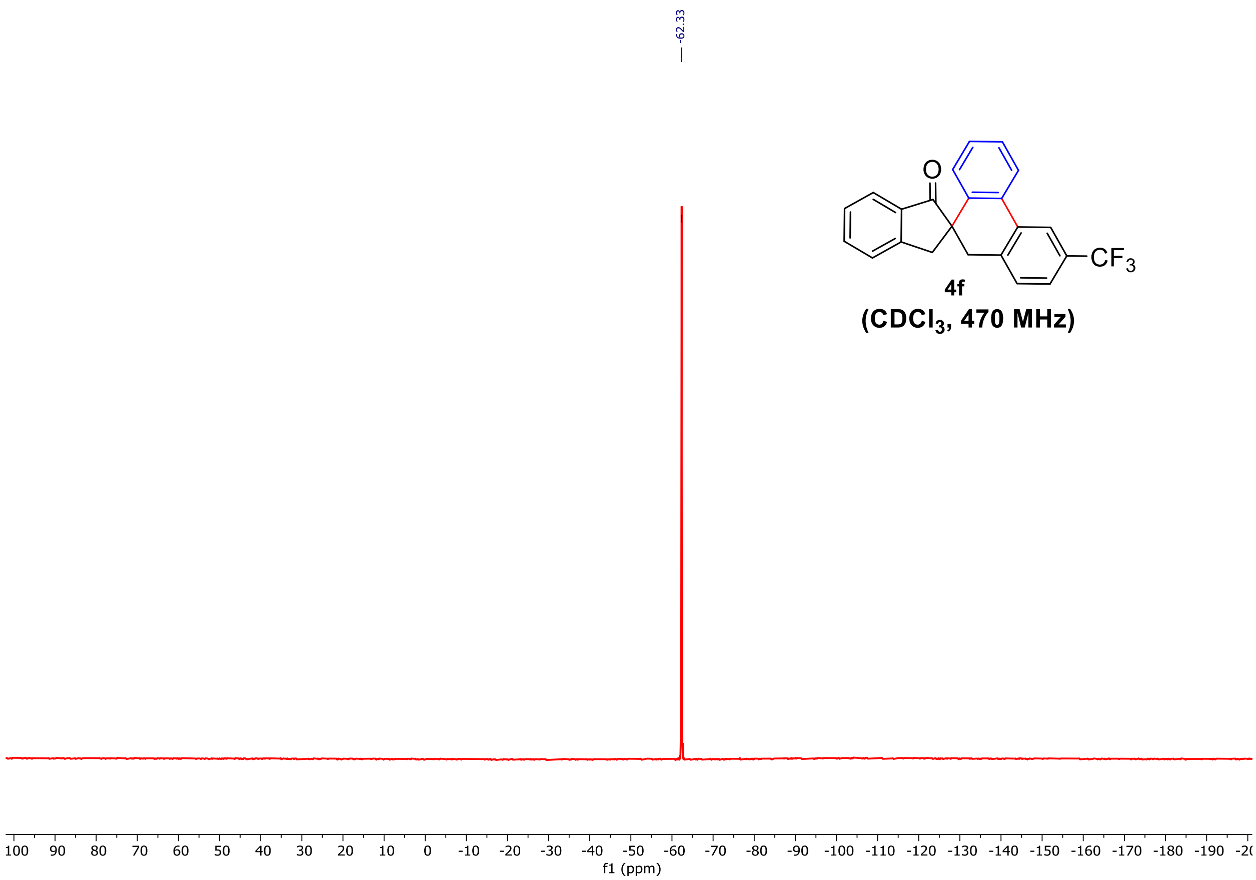


^{1}H and ^{1}H decoupled ^{13}C NMR spectra of compound 4f

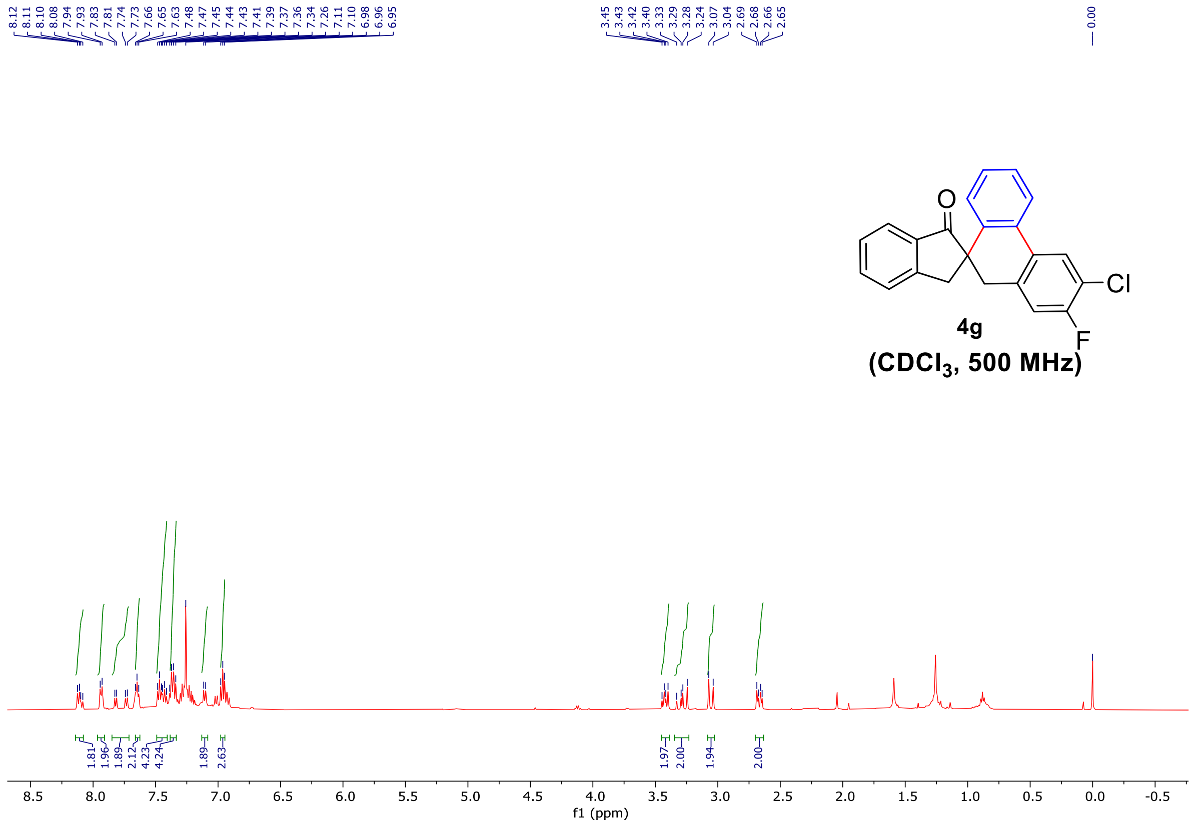


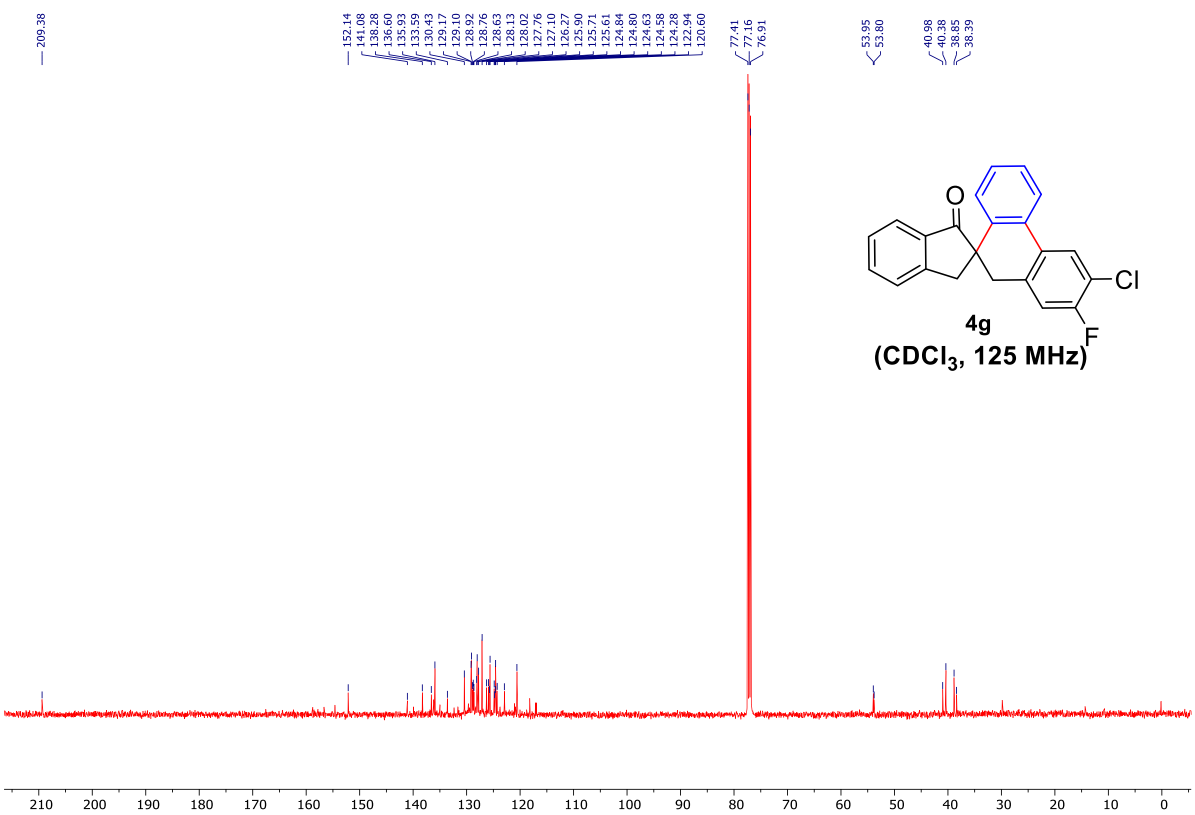


^{19}F NMR spectra of compound 4f

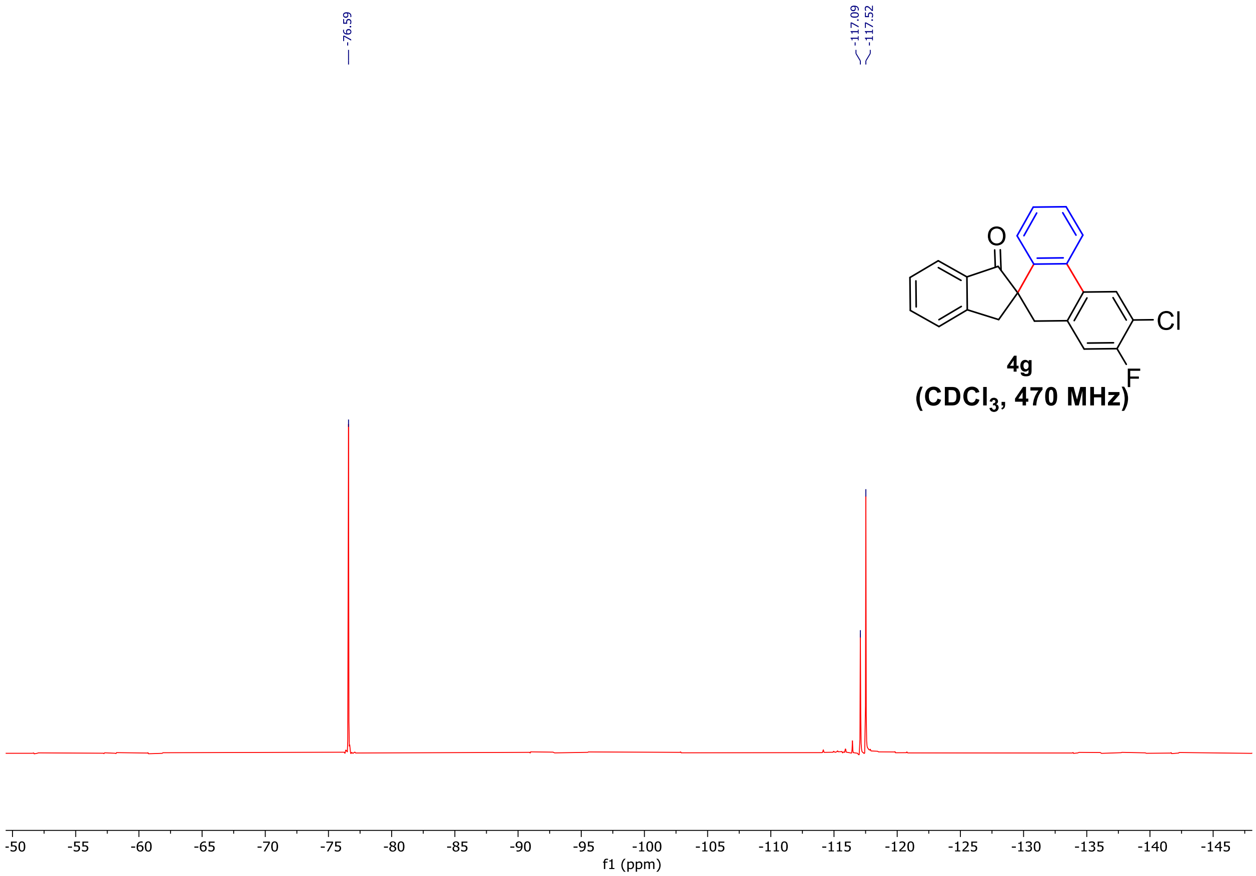


^{1}H and ^{1}H decoupled ^{13}C NMR spectra of compound 4g

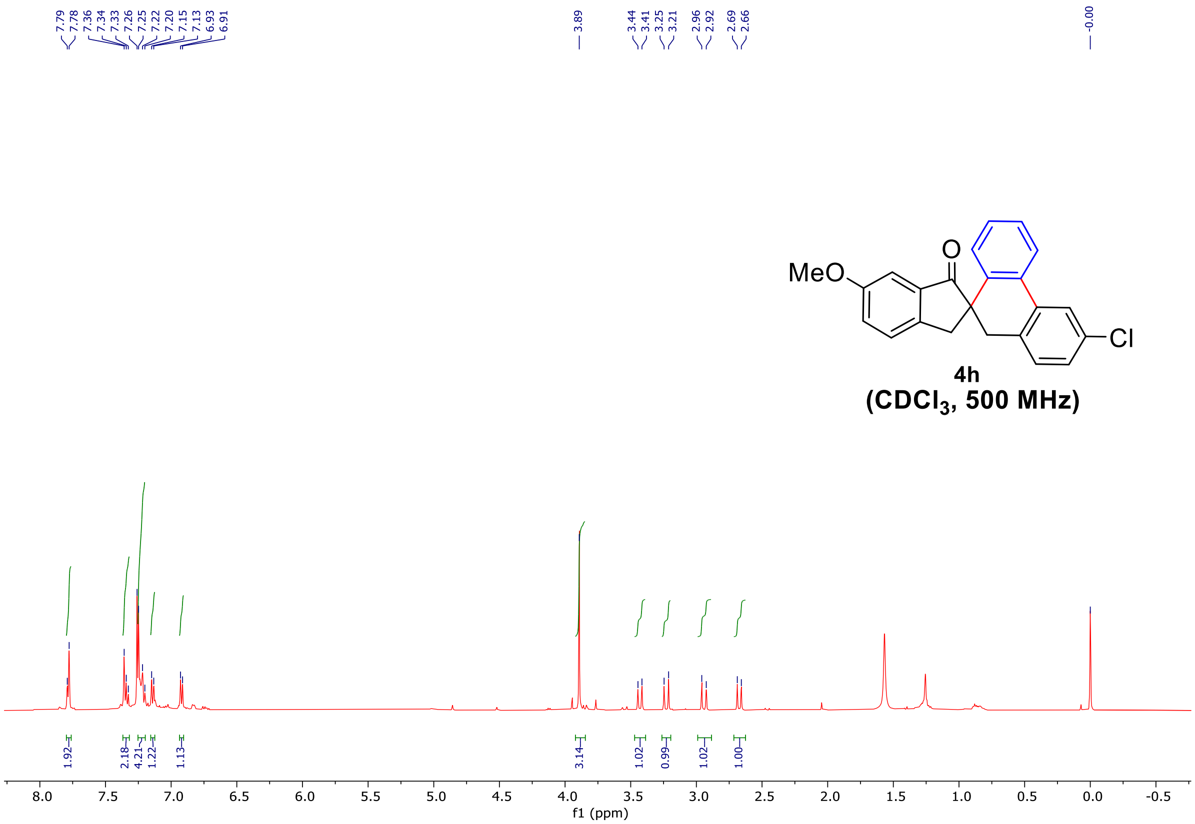


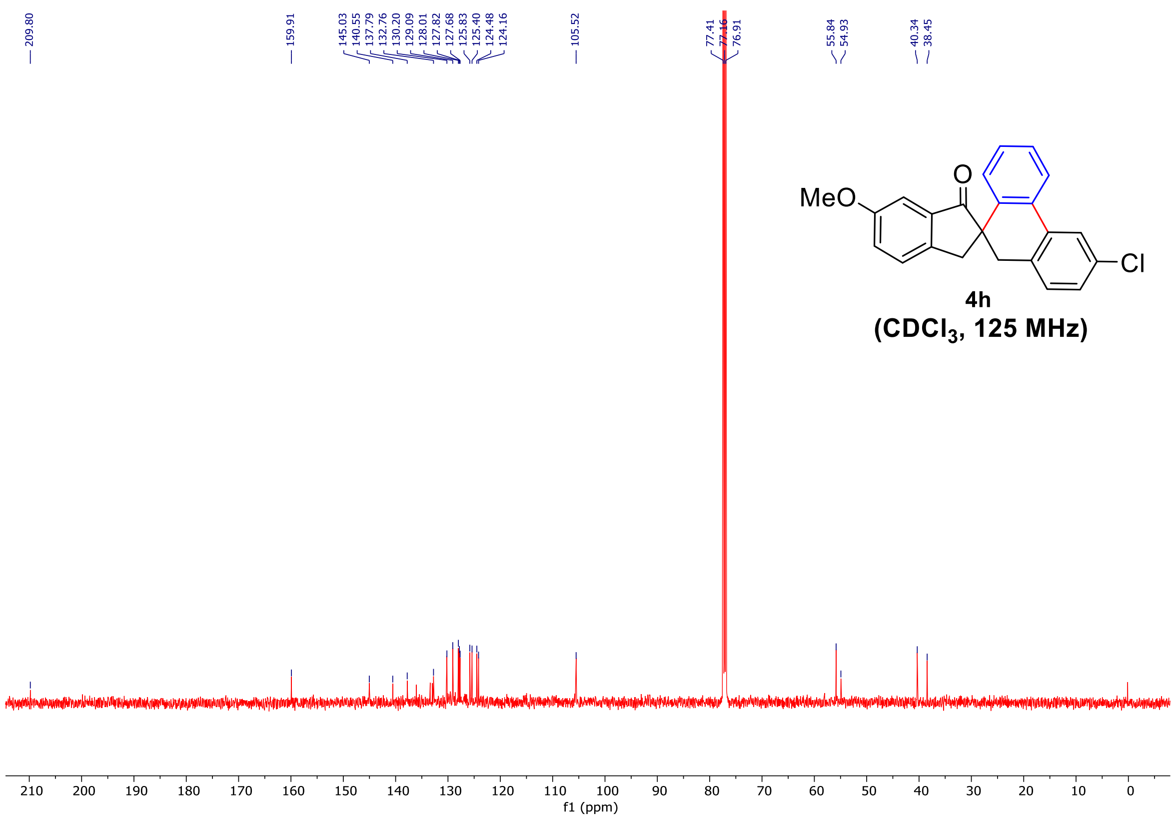


^{19}F NMR spectra of compound 4g

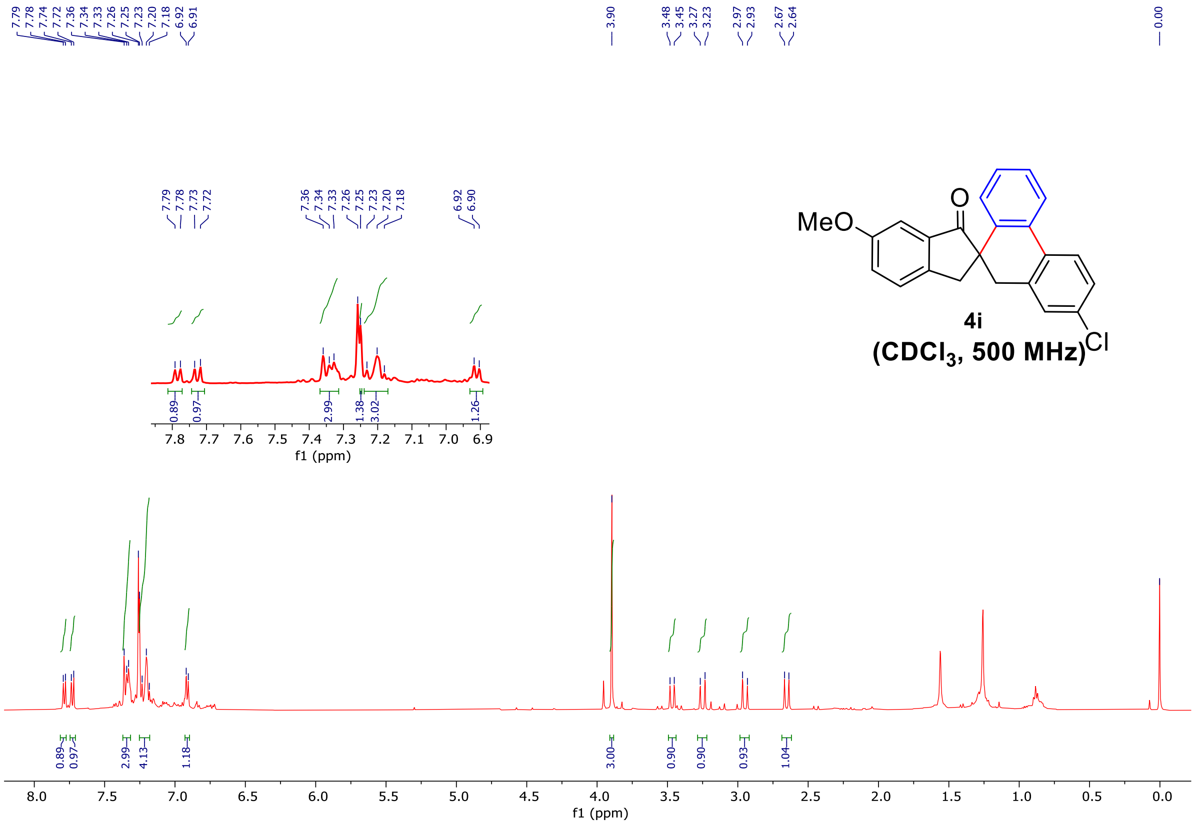


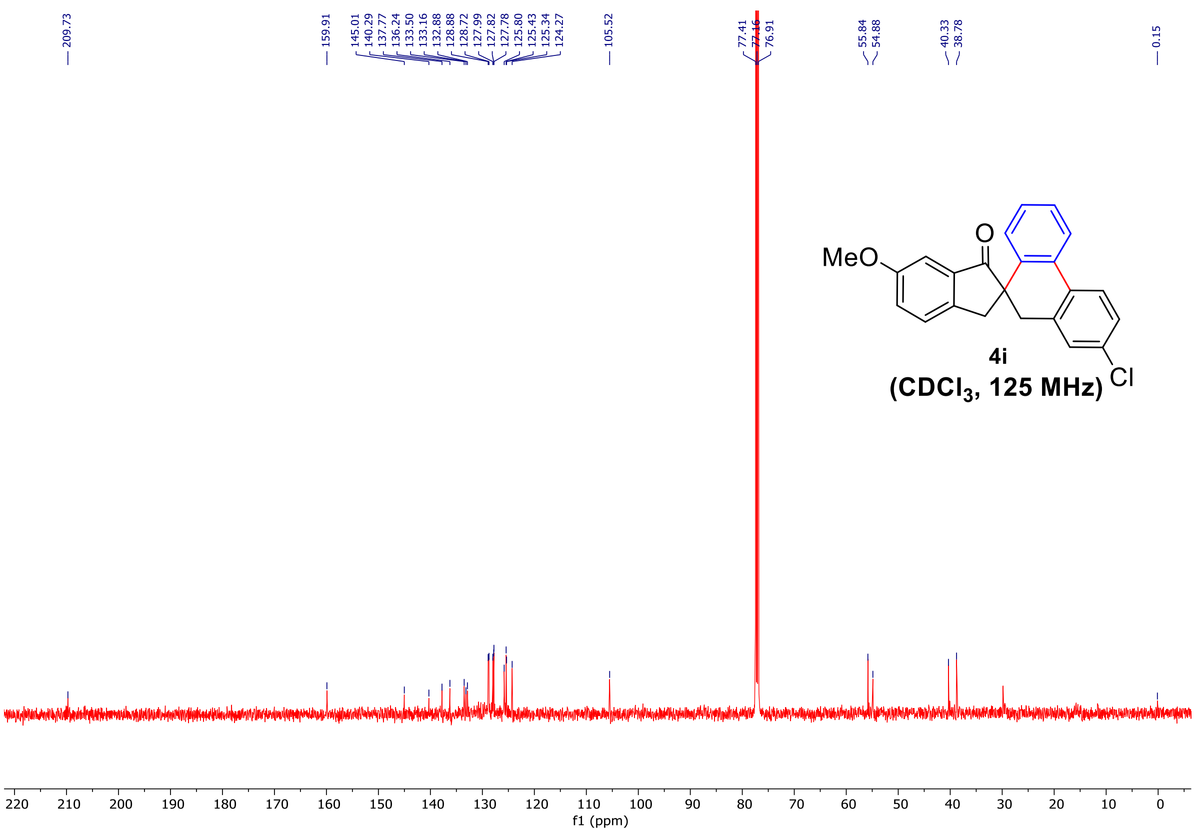
^{1}H and ^{1}H decoupled ^{13}C NMR spectra of compound 4h



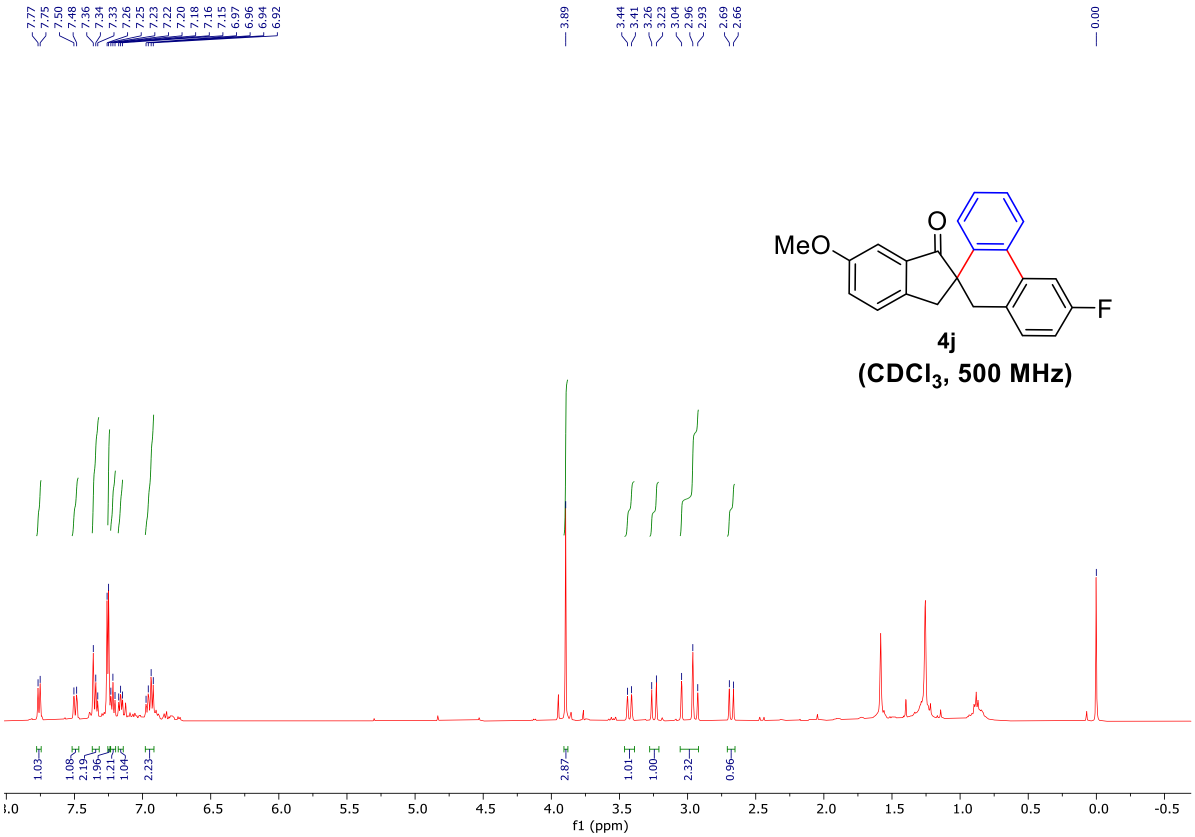


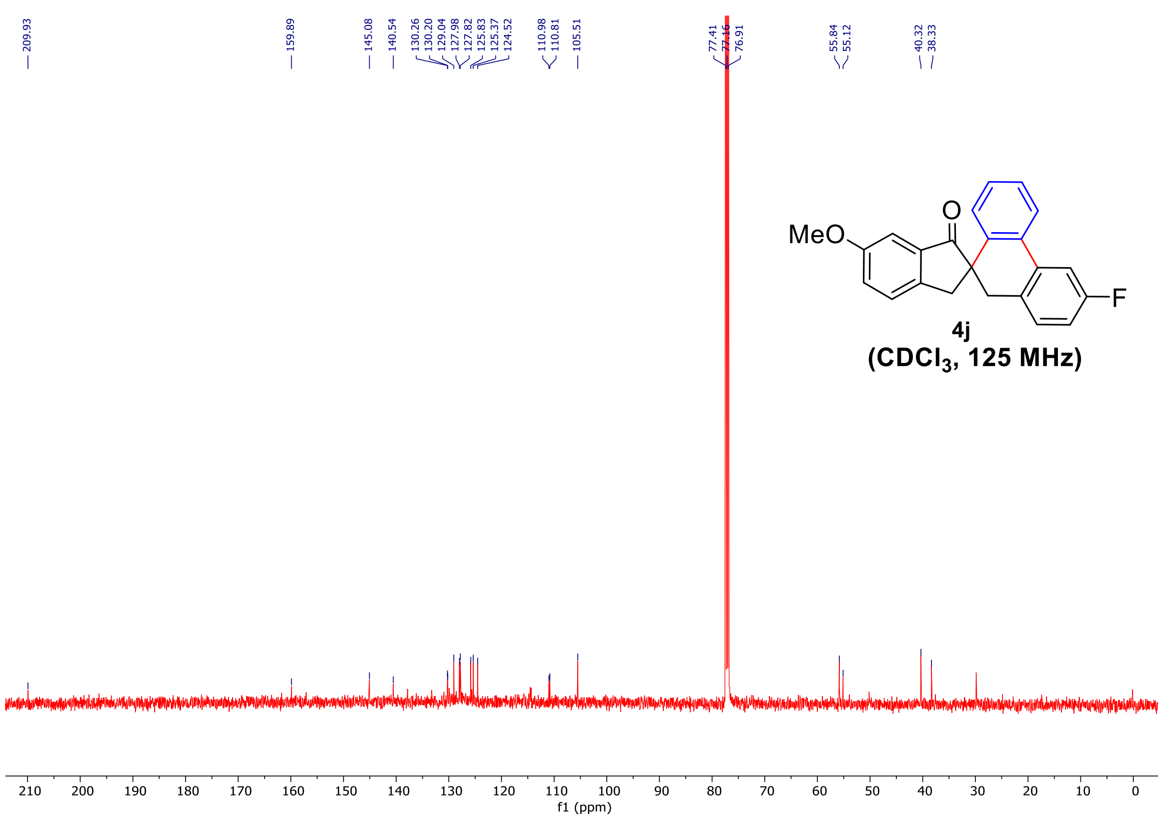
[1]H and [1]H decoupled [13]C NMR spectra of compound 4i



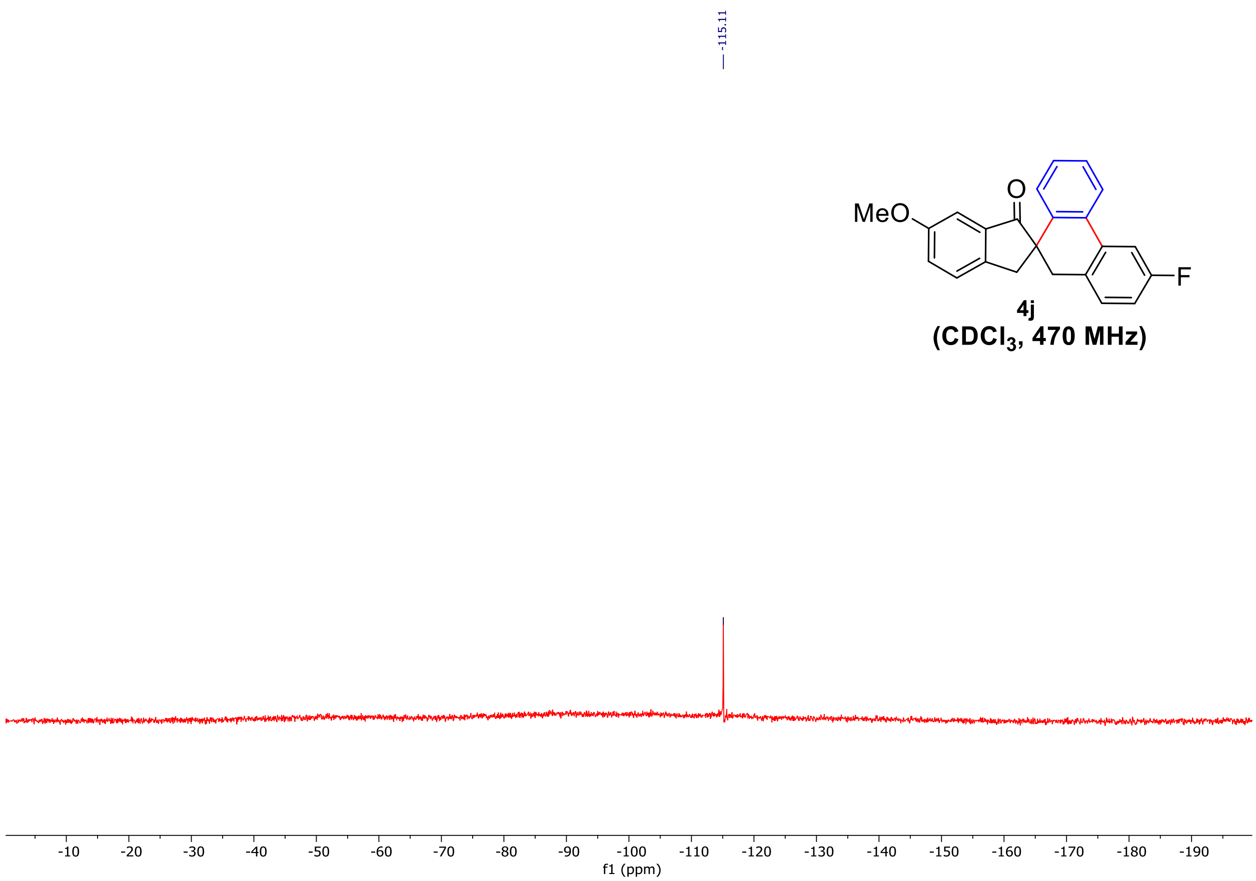


^{1}H and ^{1}H decoupled ^{13}C NMR spectra of compound 4j





^{19}F NMR spectra of compound 4j



^{1}H and ^{1}H decoupled ^{13}C NMR spectra of compound 5a