Supporting Information

for

Pauson-Khand Reaction using Alkynylboronic Esters: Solving a Long-Standing Regioselectivity Issue

Thierry León[a] and Elena Fernández[b]**

[a] Center for Chemical Technology of Catalonia (CTQC), Carrer Marcel·lí Domingo, s/n, Edifici N5, 43007 Tarragona, Spain

[b] Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Carrer Marcel·lí Domingo, s/n, Edifici N4, 43007 Tarragona, Spain

E-mail: mariaelena.fernandez@urv.cat

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General considerations

Solvents and reagents: Solvents and reagents were obtained from commercial suppliers Sigma Aldrich Co., TCI Europe, Apollo Scientific, Alfa Aaesar or FluoroChem.

Flash chromatography: FC was performed on standard silica gel (Merck Kieselgel 60 F_{254} 400-630 mesh).

Thin layer chromatography: TLC was performed on Merck Kieselgel 60 F_{254} which was developed using standard visualizing agents such as UV fluorescence (254 and 366 nm), potassium permanganate/Δ or anisaldehyde solution.

Gas chromatography coupled with Mass Spectrometry: GC-MS spectra were obtained on an Agilent 5973 inert Mass selective Detector equipped with a 6890N Network GC system and an EI source.

Nuclear Magnetic Resonance: NMR spectra were recorded at 300K on a Varian Goku 400 spectrometer. ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts (δ) are reported in ppm with the solvent (or TMS) resonance as the internal standard ($CHCl_3$: 7.26 ppm (^{1}H)) and ($CDCl_3$: 77.16 ppm (^{13}C). ^{11}B{^{1}H} NMR chemical shifts (δ) are reported in ppm relative to $Et_2O{\cdot}BF_3$. Data are reported as follows: chemical shift, multiplicity (d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration.

High Resolution Mass Spectrometry: HRMS were recorded on GC-EI-QTOF-MS. A 7890A gas chromatograph coupled with an electronic impact (EI) source to a 7200 quadrupole time-of-flight mass spectrometer (Agilent Technologies, Santa Clara, USA) was used, equipped with a 7693 autosampler module and a J&W Scientific HP-5MS column (30 m x 0.25 mm, 0.25 mm) (Agilent Technologies, Santa Clara, USA). All these measurements were performed at *Servei de Recursos Científics i Tècnics (Universitat Rovira i Virgili, Tarragona)*.

Known compounds: The following compounds are reported and are not going to be described in this supporting information: **3**[1] and **4**[2].

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[1] Revés, M.; Achard, T.; Solà, J.; Riera, A.; Verdaguer, X. *J. Org. Chem.*, **2008**, *73*, 7080.
[2] Goswami, A.; Maier, C.-J.; Pritzkow, H.; Siebert, W. *Eur. J. Inorg. Chem.*, **2004**, 2635.

General procedures.

General Procedure A: Synthesis of alkynylboronic esters (1a-m).

An oven-dried schlenk flask containing a stirring bar was charged with terminal alkynes (1 equiv.). The schlenk tube was then evacuated and back-filled under argon. THF was added and the mixture was cooled at -78ºC. n-BuLi (1.1 equiv.) was dropwised at this temperature and the mixture left stirring during 1 hour. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1 equiv.) was dropwised at the same temperature and left reacting during 2 hours. Subsequently, the mixture was quenched with hydrogen chloride solution in diethyl ether (1.1 equiv.) and left at room temperature during 30 minutes. The resulting mixture was concentrated until dryness. Freshly distilled diethyl ether was added and the mixture stirred during 30 minutes. LiCl salts were filtered under argon and ethereal fraction was concentrated and distilled with Kugelrohr apparatus.

General Procedure B: Synthesis of alkynylboronic esters (1n and **1o).**

An oven-dried schlenk flask containing a stirring bar was charged with phenylacetylene (1 equiv.). The schlenk tube was then evacuated and back-filled under argon. THF was added and the mixture was cooled at -78ºC. n-BuLi (1.1 equiv.) was dropwised at this temperature and the mixture left stirring during 1 hour. Then, triisopropyl borate (1 equiv.) was dropwised at the same temperature and left reacting during 2 hours. Subsequently, the mixture was quenched with hydrogen chloride solution in diethyl ether (1.1 equiv.) and left at room temperature during 30 minutes. The resulting mixture was concentrated until dryness. Benzopinacol or 1,8-diaminonaphthalene (1 equiv.) were then added at once and dissolved in freshly distilled toluene. The mixture was stirred at 90ºC during 24 hours. Salts were filtered under argon and the resulting liquid fraction was concentrated and purified by flash chromatography (for **1n**) or distilled with Kugelrohr apparatus (for **1o**).

General Procedure C: Pauson-Khand reaction of alkynylboronic esters.

An oven-dried schlenk tube containing a stirring bar was charged with cobalt carbonyl (1 equiv.) and the corresponding alkynylboronic ester (1 equiv.). The schlenk tube was then evacuated and back-filled under argon. Dichloromethane was added and the mixture was left stirring 1 hour at room temperature. Then, norbornadiene (3 equiv.) was added via syringe. The mixture was allowed to stir another 5 minutes. A dissolution of methylmorpholine N-oxide (6 equiv.) in dichloromethane was added and the mixture was stirred overnight at room temperature. The mixture was quenched with charcoal in an open-air flask and stirred during 1 hour and then filtrated through a celite/silica-gel pad.

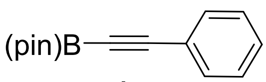
The resulting mixture was concentrated under vacuum and was finally purified by flash chromatography (hexanes/AcOEt).

General Procedure D: Palladium-catalyzed Suzuki-Miyaura cross-coupling of boro-adducts with aryl bromides.

An oven-dried schlenk tube containing a stirring bar was charged with boro-adduct (1 equiv.), Pd(ACN)$_4$OTf, 5 mol%), PPh$_3$ (20 mol%), K$_3$PO$_4$ (3equiv.) and aryl bromide (1.5 equiv.). The schlenk tube was then evacuated and back-filled under argon. The mixture was then dissolved in toluene:EtOH or toluene:MeOH (4:1) (depending the case). The mixture was heated at 90ºC, 24 hours. The mixture was quenched with water and extracted with brine/AcOEt. The combined organic layers were dried over MgSO$_4$ and evaporated. The product was purified by flash chromatography (hexanes/AcOEt).

Spectroscopic data

Alkynylboronic esters 1a-1o.



1a

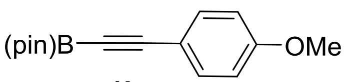
4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (1a).

Following the general procedure A, using phenylacetylene (20 mmol, 2.2 mL) provided 3.42 g (75% yield) of the corresponding alkynylboronic ester **1a** as white solid. The spectroscopic data corresponds to those previously reported in the literature.[3]

B.P. 210ºC/11 mmHg

^{1}H NMR (400 MHz, CDCl$_3$): δ 1.31 (s, 12H), 7.26-7.37 (m, 3H), 7.50-7.54 (m, 2H).

^{11}B NMR (100 MHz, CDCl$_3$): δ 24.3



1b

2-((4-methoxyphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1b).

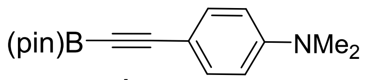
Following the general procedure A, using 1-methoxy-4-ethynylbenzene (20 mmol, 2.6 mL) provided 3.30 g (64% yield) of the corresponding alkynylboronic ester **1b** as white solid. The spectroscopic data corresponds to those previously reported in the literature.[3]

[3] Ho, H. E.; Asao, N.; Yamamoto, Y.; Jin, T. *Org. Lett.*, **2014**, *16*, 4670.

B.P. 235ºC/11 mmHg

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31 (s, 12H), 3.80 (s, 3H), 6.82 (m, 2H), 7.47 (m, 2H).

^{11}B NMR (100 MHz, $CDCl_3$): δ 22.1



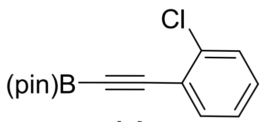
1c

N,N-dimethyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethynyl)aniline (1c). Following the general procedure A, using 1-(dimethylamino)-4-ethynylbenzene (13.8 mmol, 2.0 g) provided 2.27 g (61% yield) of the corresponding alkynylboronic ester **1c** as thick brownish oil. The spectroscopic data corresponds to those previously reported in the literature.[4]

B.P. 265ºC/11 mmHg

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (s, 12H), 2.97 (s, 6H), 6.59 (m, 2H), 7.41 (m, 2H).

^{11}B NMR (100 MHz, $CDCl_3$): δ 23.6.



1d

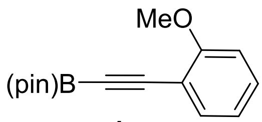
2-((2-chlorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1d).
Following the general procedure A, using 1-chloro-2-ethynylbenzene (14.6 mmol, 2.0 g) provided 2.57 g (67% yield) of the corresponding alkynylboronic ester **1d** as white solid. The spectroscopic data corresponds to those previously reported in the literature.[5]

B.P. 210ºC/11 mmHg

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 12H), 7.20 (m, 1H), 7.28 (m, 1H), 7.38 (m, 1H), 7.55 (m, 1H).

^{11}B NMR (100 MHz, $CDCl_3$): δ 24.4.

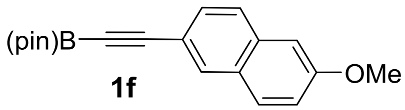
[4] Lee, C.-I.; DeMott, J. C.; Pell, C. J.; Christopher, A.; Zhou, J.; Bhuvanesh, N.; Ozerov, O. V. *Chem. Sci.*, **2015**, *6*, 6572.
[5] Hu, J.-R.; Liu, L.-H.; Ye, H.-D. *Tetrahedron*, **2014**, *70*, 5815.



1e

2-((2-methoxyphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1e).
Following the general procedure A, using 1-methoxy-2-ethynylbenzene (15.0 mmol, 1.94 mL) provided 2.59 g (67% yield) of the corresponding alkynylboronic ester **1e** as yellowish semi-solid.

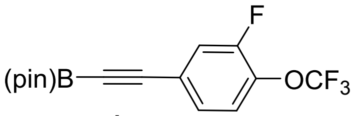
B.P. 240ºC/11 mmHg
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (s, 12H), 3.86 (s, 3H), 6.87 (m, 2H), 7.32 (m, 1H), 7.48 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 24.7, 55.7, 81.1, 84.3, 103.8, 110.5, 111.0, 120.3, 130.9, 134.7, 161.0.
^{11}B NMR (100 MHz, $CDCl_3$): δ 24.1.
HRMS-ESI(+): for [$C_{15}H_{19}BO_3$+Na], calculated: 281.1324; found: 281.1301.



1f

2-((6-methoxynaphthalen-2-yl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1f).
Following the general procedure A, using 2-ethynyl-6-methoxynaphthalene (11 mmol, 2.0 g) provided 2.43 g (72% yield) of the corresponding alkynylboronic ester **1f** as yellowish solid.

B.P. 280ºC/11 mmHg
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 12H), 3.90 (s, 3H), 7.07 (m, 1H), 7.14 (m, 1H), 7.51 (m, 1H), 7.66 (m, 2H), 7.99 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 24.7, 55.4, 83.1, 84.4, 102.6, 105.7, 116.6, 119.6, 126.8, 128.1, 129.2, 129.6, 133.0, 134.7, 158.7.
^{11}B NMR (100 MHz, $CDCl_3$): δ 24.7.
HRMS-ESI(+): for [$C_{19}H_{21}BO_3$], calculated: 309.1662; found: 309.1633.



1g

2-((3-fluoro-4-(trifluoromethoxy)phenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1g).

Following the general procedure A, using 4-ethynyl-2-fluoro-1-(trifluoromethoxy)benzene (9.8 mmol, 2.0 g) provided 2.42 g (75% yield) of the corresponding alkynylboronic ester **1g** as beige solid.

B.P. 210ºC/11 mmHg

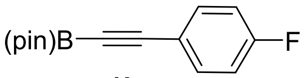
^{1}H NMR (400 MHz, $CDCl_3$): *δ* 1.32 (s, 12H), 7.22-7.28 (m, 1H), 7.29-7.36 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 24.7, 84.3, 84.8, 100.7, 121.0, 121.2, 123.5, 129.0 (d, J = 4 Hz, CF), 135.4, 137.0 (q, J = 240 Hz, CF_3), 137.7, 138.6, 152.6.

^{11}B NMR (100 MHz, $CDCl_3$): *δ* 24.1.

^{19}F NMR (376 MHz, $CDCl_3$): *δ* -127.91 (m, 3F), -58.65 (m, F).

HRMS-EI(+): for [$C_{15}H_{15}BF_4O_3$], calculated: 330.1050; found: 330.1051.



1h

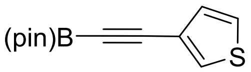
2-((4-fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1h).

Following the general procedure A, using 1-ethynyl-4-fluorobenzene (16.7 mmol, 1.91 mL) provided 3.32 g (81% yield) of the corresponding alkynylboronic ester **1h** as white solid. The spectroscopic data corresponds to those previously reported in the literature.[3]

B.P. 200ºC/11 mmHg

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 1.31 (s, 12H), 7.00 (m, 2H), 7.50 (m, 2H).

^{11}B NMR (100 MHz, $CDCl_3$): *δ* 24.2.



1i

4,4,5,5-tetramethyl-2-(thiophen-3-ylethynyl)-1,3,2-dioxaborolane (1i).

Following the general procedure A, using 3-ethynylthiophene (18.5 mmol, 1.84 mL) provided 2.99 g (69% yield) of the corresponding alkynylboronic ester **1i** as brownish solid.

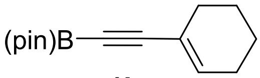
B.P. 210ºC/11 mmHg

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (s, 12H), 7.15 (dd, J = 5 and 1 Hz, 1H), 7.24 (dd, J = 5 and 3 Hz, 1H), 7.59 (dd, J = 3 and 1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 24.7, 83.2, 84.4, 103.4, 121.1, 125.4, 130.2, 131.7.

^{11}B NMR (100 MHz, $CDCl_3$): δ 24.2.

HRMS-EI(+): for [$C_{15}H_{15}BF_4O_3$], calculated: 234.0886; found: 234.0884.



1j

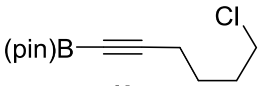
2-(cyclohex-1-en-1-ylethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1j).

Following the general procedure A, using 1-ethynylcyclohex-1-ene (20 mmol, 2.35 mL) provided 3.60 g (78% yield) of the corresponding alkynylboronic ester **1j** as white solid. The spectroscopic data corresponds to those previously reported in the literature.[3]

B.P. 200ºC/11 mmHg

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (s, 12H), 1.53 (m, 4H), 2.06 (m, 4H), 6.25 (tt, J = 4 and 2 Hz, 1H).

^{11}B NMR (100 MHz, $CDCl_3$): δ 24.2.



1k

2-(6-chlorohex-1-yn-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1k).

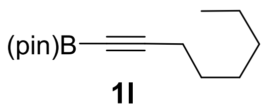
Following the general procedure A, using 6-chlorohex-1-yne (20 mmol, 2.42 mL) provided 3.34 g (69% yield) of the corresponding alkynylboronic ester **1k** as light yellow oil. The spectroscopic data corresponds to those previously reported in the literature.[6]

B.P. 225ºC/11 mmHg

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (s, 12H), 1.62 (m, 2H), 1.83 (m, 2H), 2.25 (t, J = 7 Hz, 2H), 3.48 (t, J = 7 Hz, 2H).

^{11}B NMR (100 MHz, $CDCl_3$): δ 23.4.

[6] Molander, G. A.; Ellis, N. M. *J. Org. Chem.*, **2008**, *73*, 6841.



1l

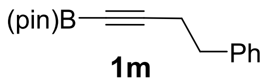
4,4,5,5-tetramethyl-2-(oct-1-yn-1-yl)-1,3,2-dioxaborolane (1l).

Following the general procedure A, using oct-1-yne (20 mmol, 2.95 mL) provided 3.02 g (64% yield) of the corresponding alkynylboronic ester **1l** as colorless oil. The spectroscopic data corresponds to those previously reported in the literature.[7]

B.P. 190ºC/11 mmHg

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82 (t, J = 7 Hz, 3H), 1.2-1.28 (m, 16H), 1.21-1.38 (m, 2H), 1.47 (m, 2H), 2.19 (t, J = 7 Hz, 2H).

^{11}B NMR (100 MHz, $CDCl_3$): δ 24.1.



1m

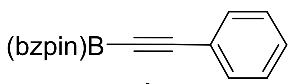
4,4,5,5-tetramethyl-2-(4-phenylbut-1-yn-1-yl)-1,3,2-dioxaborolane (1m).

Following the general procedure A, using but-3-yn-1-ylbenzene (19.2 mmol, 2.7 mL) provided 4.38 g (89% yield) of the corresponding alkynylboronic ester **1m** as colorless oil. The spectroscopic data corresponds to those previously reported in the literature.[8]

B.P. 210ºC/11 mmHg

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 12H), 2.54 (t, J = 8 Hz, 2H), 2.87 (t, J = 8 Hz, 2H), 7.20 (m, 3H), 7.26-7.31 (m, 2H).

^{11}B NMR (100 MHz, $CDCl_3$): δ 23.4.



1n

4,4,5,5-tetraphenyl-2-(phenylethynyl)-1,3,2-dioxaborolane (1n).

Following the general procedure B, using phenylacetylene (4.26 mmol, 0.47 mL) provided 1.30 g (64% yield) of the corresponding alkynylboronic ester **1n** as white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08-7.12 (m, 12H), 7.20-7.24 (m, 7H), 7.29-7.32 (m, 1H), 7.36-7.43 (m, 3H), 7.65 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 82.9, 96.4, 114.4, 127.2, 127.3, 128.4, 128.5, 129.8, 131.6, 132.8, 141.9.

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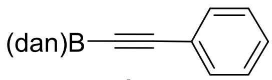
[7] Janetzko, J.; Batey, R. A. *J. Org. Chem.*, **2014**, *79*, 7415.

[8] Lee, C.-I.; Zhou, J.; Ozerov, O. V. *J. Am. Chem. Soc.*, **2013**, *135*, 3560.

^{11}B NMR (100 MHz, $CDCl_3$): δ 25.5.

HRMS-ESI(+): for [$C_{68}H_{50}B2O_4$+Na], calculated: 975.3793; found: 975.3796.



1o

2-(phenylethynyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (1o).

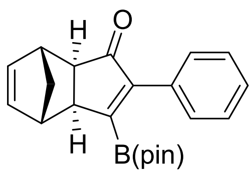
Following the general procedure B, using phenylacetylene (18 mmol, 1.98 mL) provided 2.56 g (53% yield) of the corresponding alkynyldiazaborinine **1o** as dark orange solid. The spectroscopic data corresponds to those previously reported in the literature.[9]

B.P. 305ºC/11 mmHg

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.92 (bs, 2H), 6.32 (dd, J = 7 and 1 Hz, 2H), 7.04 (dd, J = 8 and 1 Hz, 2H), 7.11 (m, 2H), 7.37 (m, 3H), 7.51-7.55 (m, 2H).

^{11}B NMR (100 MHz, $CDCl_3$): δ 21.9.

Boro-adducts resulting of PKR 2a-2o.



2a

(3aS,4S,7R,7aR)-2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (2a).

Following the general procedure C, using 4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (**1a**, 0.6 mmol, 137 mg) provided 157 mg (75% yield) of the corresponding adduct of PKR **2a** as yellowish oil. **2a** could also be purified by Kugelrohr distillation at the temperature indicated below.

B.P. 305ºC/11 mmHg

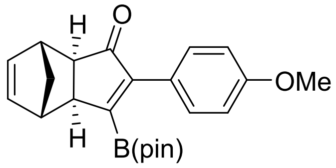
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 12H), 1.34 (m, 1H), 1.42 (m, 1H), 2.41 (dt, J = 5 and 1 Hz, 1H), 2.83 (bs, 1H), 2.95 (m, 1H), 2.99 (bs, 1H), 6.24 (dd, J = 6 and 3 Hz, 1H), 6.36 (dd, J = 6 and 3 Hz, 1H), 7.30-7.37 (m, 3H), 7.40-7.44 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 24.7, 41.6, 43.5, 44.4, 50.7, 52.7, 84.5, 127.8, 128.3, 128.8, 137.2, 138.9, 208.6. The carbon bound to boron was not observed presumably due to low intensity.

[9] Tsuchimoto, T.; Utsugi, H.; Sugiura, T.; Horio, S. *Adv. Synth. Cat.*, **2015**, *357*, 77.

^{11}B NMR (100 MHz, $CDCl_3$): δ 30.9.

HRMS-ESI(+): for [$C_{22}H_{25}BO_3$+Na], calculated: 371.1794; found: 371.1790.



2b

(3aS,4S,7R,7aR)-2-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (2b).

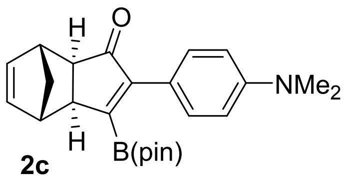
Following the general procedure C, using 2-((4-methoxyphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1b**, 0.6 mmol, 155 mg) provided 120 mg (53% yield) of the corresponding adduct of PKR **2b** as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (s, 12H), 1.31 (m, 1H), 1.39 (m, 1H), 2.38 (dt, J = 5 and 1 Hz, 1H), 2.81 (bs, 1H), 2.92 (m, 1H), 2.97 (bs, 1H), 6.22 (dd, J = 6 and 3 Hz, 1H), 6.35 (dd, J = 6 and 3 Hz, 1H), 6.87 (m, 2H), 7.40 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 24.7, 24.8, 41.6, 43.6, 44.3, 50.5, 52.6, 55.2, 84.4, 113.2, 124.9, 130.1, 137.1, 138.9, 154.4, 159.7, 209.1. The carbon bound to boron was not observed presumably due to low intensity.

^{11}B NMR (100 MHz, $CDCl_3$): δ 30.9.

HRMS-ESI(+): for [$C_{23}H_{27}BO_4$+Na], calculated: 401.1900; found: 401.1897.



2c

(3aS,4S,7R,7aR)-2-(4-(dimethylamino)phenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (2c).

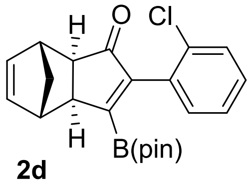
Following the general procedure C, using N,N-dimethyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethynyl)aniline (**1c**, 0.6 mmol, 163 mg) provided 141 mg (60% yield) of the corresponding adduct of PKR **2c** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (m, 13H), 1.38 (m, 1H), 2.36 (dt, J = 5 and 1 Hz, 1H), 2.81 (m, 1H), 2.90 (m, 1H), 2.96 (m, 7H), 6.22 (dd, J = 6 and 3 Hz, 1H), 6.35 (dd, J = 6 and 3 Hz, 1H), 6.69 (m, 2H), 7.40 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 24.7, 24.8, 40.5, 41.6, 43.7, 44.3, 50.4, 52.7, 84.3, 111.7, 129.8, 137.1, 138.9, 150.6, 154.5. The carbon bound to boron was not observed presumably due to low intensity.

^{11}B NMR (100 MHz, $CDCl_3$): δ 31.7.

HRMS-ESI(+): for [$C_{23}H_{30}BNO_3$+H], calculated: 392.2397; found: 392.2400.



2d

(3aS,4S,7R,7aR)-2-(2-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (2d).

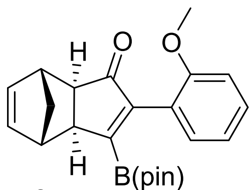
Following the general procedure C, using 2-((2-chlorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1d**, 0.6 mmol, 158 mg) provided 152 mg (66% yield) of the corresponding adduct of PKR **2d** as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (s, 6H), 1.19 (s, 6H), 1.44 (m, 1H), 1.56 (m, 1H), 2.41 (dt, J = 5 and 1 Hz, 1H), 2.90 (bs, 1H), 3.02 (m, 2H), 6.24 (dd, J = 6 and 3 Hz, 1H), 6.39 (dd, J = 6 and 3 Hz, 1H), 7.12-7.16 (m, 1H), 7.21-7.27 (m, 2H), 7.36-7.39 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 24.5, 24.7, 41.7, 43.5, 44.4, 51.1, 52.5, 84.2, 126.1, 129.1, 130.9, 132.1, 132.4, 133.1, 137.1, 139.0, 155.3, 208.1. The carbon bound to boron was not observed presumably due to low intensity.

^{11}B NMR (100 MHz, $CDCl_3$): δ 29.9.

HRMS-ESI(+): for [$C_{21}H_{24}BClO_3$+H], calculated: 383.1585; found: 383.1583.



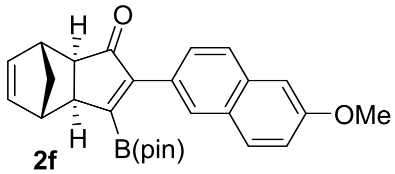
2e

(3aS,4S,7R,7aR)-2-(2-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (2e).

Following the general procedure C, using 2-((2-methoxyphenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1e**, 0.6 mmol, 155 mg) provided 154 mg (68% yield) of the corresponding adduct of PKR **2e** as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (s, 12H), 1.39 (m, 1H), 1.46 (m, 1H), 2.37 (dt, J = 5 and 1 Hz, 1H), 2.84 (bs, 1H), 2.98 (m, 2H), 3.73 (s, 3H), 6.23 (dd, J = 6 and 3 Hz, 1H), 6.36 (dd, J = 6 and 3 Hz, 1H), 6.88 (dd, J = 8 and 1 Hz, 1H), 6.94 (td, J = 8 and 1 Hz,

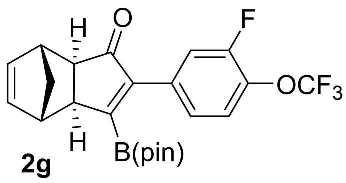
1H), 7.18 (dd, J = 7 and 2 Hz, 1H), 7.27 (ddd, J = 8, 8 and 2 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6, 24.8, 29.7, 41.5, 43.5, 44.4, 51.0, 52.2, 55.8, 84.0, 111.1, 120.2, 122.4, 129.3, 130.5, 137.1, 138.9, 152.8, 156.9, 208.9.
^{11}B NMR (100 MHz, $CDCl_3$): δ 29.8.
HRMS-ESI(+): for [$C_{23}H_{27}BO_4$+Na], calculated: 401.1900; found: 401.1911.



2f

(3aS,4S,7R,7aR)-2-(6-methoxynaphthalen-2-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (2f).
Following the general procedure C, using 2-((6-methoxynaphthalen-2-yl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1f**, 0.6 mmol, 185 mg) provided 167 mg (65% yield) of the corresponding adduct of PKR **2f** as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 12H), 1.42 (m, 2H), 2.44 (m, 1H), 2.86 (bs, 1H), 2.99 (m, 1H), 3.02 (bs, 1H), 3.92 (s, 3H), 6.26 (dd, J = 6 and 3 Hz, 1H), 6.38 (dd, J = 5 and 3 Hz, 1H), 7.12 (m, 2H), 7.52 (dd, J = 8 and 1 Hz, 1H), 7.71 (m, 2H), 7.90 (bs, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 24.7, 24.8, 41.7, 43.6, 44.4, 50.7, 52.8, 55.3, 84.5, 105.5, 118.8, 126.2, 127.3, 127.8, 127.9, 128.5, 129.8, 134.5, 137.2, 138.9, 139.2, 154.9, 157.9, 208.9.
^{11}B NMR (100 MHz, $CDCl_3$): δ 31.6.
HRMS-ESI(+): for [$C_{27}H_{29}BO_4$+H], calculated: 429.2237; found: 429.2241.



2g

(3aS,4S,7R,7aR)-2-(3-fluoro-4-(trifluoromethoxy)phenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (2g).
Following the general procedure C, using 2-((3-fluoro-4-(trifluoromethoxy)phenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1g**, 0.6 mmol, 198 mg) provided 149 mg (55% yield) of the corresponding adduct of PKR **2g** as brown oil.

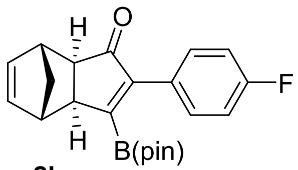
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (m, 13H), 1.43 (m, 1H), 2.42 (m, 1H), 2.84 (m, 1H), 2.98 (m, 2H), 6.25 (dd, J = 6 and 3 Hz, 1H), 6.37 (dd, J = 6 and 3 Hz, 1H), 7.24 (m, 1H), 7.27 (m, 1H), 7.33 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): peaks listed due to complexity: δ 24.6, 24.7, 29.7, 41.5, 43.5, 44.4, 50.9, 52.7, 84.8, 116.6, 117.5, 117.8, 118.0, 118.5, 119.1, 121.7, 122.9, 125.1, 125.2, 132.9, 133.0, 136.2, 137.2, 138.9, 152.6, 152.8, 153.0, 153.3, 155.1, 155.3, 207.9.

^{11}B NMR (100 MHz, $CDCl_3$): δ 30.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.73 (m, 3F), -58.76 (m, F).

HRMS-ESI(+): for [$C_{46}H_{46}BF_8O_8$+Na], calculated: 923.3149; found: 923.3169.



2h

(3aS,4S,7R,7aR)-2-(4-fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (2h).

Following the general procedure C, using 2-((4-fluorophenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1h**, 0.6 mmol, 148 mg) provided 143 mg (65% yield) of the corresponding adduct of PKR **2h** as light red oil.

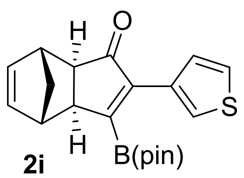
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (s, 12H), 1.30 (m, 1H), 1.40 (m, 1H), 2.38 (dt, J = 5 and 1 Hz, 1H), 2.82 (bs, 1H), 2.94 (m, 1H), 2.97 (bs, 1H), 6.22 (dd, J = 6 and 3 Hz, 1H), 6.35 (dd, J = 6 and 3 Hz, 1H), 7.02 (m, 2H), 7.41 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6, 24.7, 41.5, 43.5, 44.4, 50.7, 52.6, 84.5, 114.7 (d, J = 21 Hz, CF), 128.4 (d, J = 4 Hz, CF), 130.7 (d, J = 9 Hz, CF), 137.1, 138.9, 154.1, 161.6, 164.1, 208.6.

^{11}B NMR (100 MHz, $CDCl_3$): δ 30.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -113.38 (m, F).

HRMS-ESI(+): for [$C_{15}H_{15}BF_4O_3$], calculated: 330.1050; found: 330.1051.



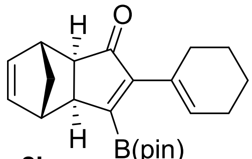
2i

(3aS,4S,7R,7aR)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(thiophen-3-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (2i).

Following the general procedure C, using 4,4,5,5-tetramethyl-2-(thiophen-3-ylethynyl)-

1,3,2-dioxaborolane (**1i**, 0.6 mmol, 140 mg) provided 151 mg (71% yield) of the corresponding adduct of PKR **2i** as yellowish oil.

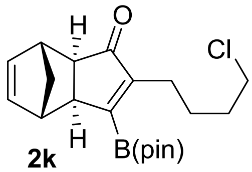
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (m, 14H), 2.36 (m, 1H), 2.81 (bs, 1H), 2.94 (m, 1H), 2.97 (bs, 1H), 6.23 (dd, J = 6 and 3 Hz, 1H), 6.35 (dd, J = 6 and 3 Hz, 1H), 7.27 (m, 1H), 7.43 (dd, J = 5 and 1 Hz, 1H), 7.86 (dd, J = 3 and 1 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 24.8, 24.9, 41.6, 43.7, 44.4, 50.9, 52.4, 84.6, 124.3, 125.5, 128.1, 132.8, 137.1, 138.9, 148.9, 209.0.
^{11}B NMR (100 MHz, $CDCl_3$): δ 30.3.
HRMS-ESI(+): for [$C_{20}H_{23}BO_3$+Na], calculated: 377.1359; found: 377.1362.



2j

(3aS,4S,7R,7aR)-2-(cyclohex-1-en-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (2j).
Following the general procedure C, using 2-(cyclohex-1-en-1-ylethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1j**, 0.6 mmol, 139 mg) provided 124 mg (59% yield) of the corresponding adduct of PKR **2j** as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (m, 14H), 1.60 (m, 2H), 1.66 (m, 2H), 2.10 (m, 2H), 2.18 (m, 2H), 2.23 (m, 1H), 2.72 (bs, 1H), 2.78 (m, 1H), 2.88 (bs, 1H), 5.92 (m, 1H), 6.17 (dd, J = 6 and 3 Hz, 1H), 6.29 (dd, J = 6 and 3 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 22.5, 24.7, 24.8, 25.4, 28.0, 41.4, 43.4, 44.2, 50.1, 52.7, 84.2, 128.1, 131.4, 137.1, 138.7, 157.6, 209.8. The carbon bound to boron was not observed presumably due to low intensity.
^{11}B NMR (100 MHz, $CDCl_3$): δ 30.4.
HRMS-ESI(+): for [$C_{44}H_{58}B_2O_6$+Na], calculated: 727.4317; found: 727.4338.

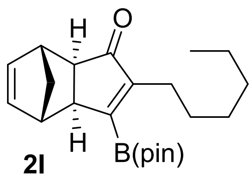


2k

(3aS,4S,7R,7aR)-2-(4-chlorobutyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (2k).
Following the general procedure C, using 2-(6-chlorohex-1-yn-1-yl)-4,4,5,5-tetramethyl-

1,3,2-dioxaborolane (**1k**, 0.6 mmol, 146 mg) provided 140 mg (64% yield) of the corresponding adduct of PKR **2k** as yellowish oil.

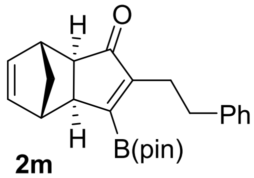
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (m, 1H), 1.31, (m, 13H), 1.55 (m, 2H), 1.76 (m, 2H), 2.21 (m, 1H), 2.42 (m, 2H), 2.74 (bs, 1H), 2.81 (m, 1H), 2.87 (bs, 1H), 3.54 (m, 2H), 6.17 (dd, J = 6 and 3 Hz, 1H), 6.34 (dd, J = 5 and 3 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 24.5, 24.9, 25.3, 26.8, 29.9, 32.6, 41.5, 43.6, 44.3, 45.0, 50.6, 52.3, 84.2, 137.0, 139.3, 160.0, 211.7. The carbon bound to boron was not observed presumably due to low intensity.
^{11}B NMR (100 MHz, $CDCl_3$): δ 29.8.
HRMS-ESI(+): for [$C_{20}H_{28}BClO_3$+Na], calculated: 385.1718; found: 385.1719.



2l

(3aS,4S,7R,7aR)-2-hexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (2l).
Following the general procedure C, using 4,4,5,5-tetramethyl-2-(oct-1-yn-1-yl)-1,3,2-dioxaborolane (**1l**, 0.6 mmol, 142 mg) provided 154 mg (72% yield) of the corresponding adduct of PKR **2l** as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, J = 7 Hz, 3H), 1.11 (m, 1H), 1.23-1.41 (m, 20H), 2.19 (m, 1H), 2.37 (m, 2H), 2.72 (bs, 1H), 2.80 (m, 1H), 2.86 (bs, 1H), 6.17 (dd, J = 5 and 3 Hz, 1H), 6.33 (dd, J = 6 and 3 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.5, 24.6, 25.0, 25.2, 29.3, 29.5, 31.6, 41.2, 43.4, 44.1, 50.3, 52.1, 83.9, 136.9, 139.0, 160.6, 211,5. The carbon bound to boron was not observed presumably due to low intensity.
^{11}B NMR (100 MHz, $CDCl_3$): δ 30.9.
HRMS-ESI(+): for [$C_{44}H_{66}B_2O_6$+Na], calculated: 735.4943; found: 735.4944.



2m

(3aS,4S,7R,7aR)-2-phenethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (2m).

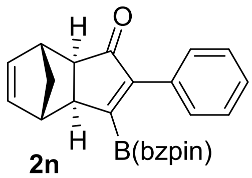
Following the general procedure C, using 4,4,5,5-tetramethyl-2-(4-phenylbut-1-yn-1-yl)-1,3,2-dioxaborolane (**1m**, 0.6 mmol, 154 mg) provided 154 mg (68% yield) of the corresponding adduct of PKR **2m** as dark oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (m, 1H), 1.29 (m, 1H), 1.33 (s, 12H), 2.22 (dt, J = 5 and 1 Hz, 1H), 2.72 (s, 4H), 2.82 (m, 1H), 2.88 (bs, 1H), 6.18 (dd, J = 6 and 3 Hz, 1H), 6.34 (dd, J = 6 and 3 Hz, 1H), 7.14-7.19 (m, 1H), 7.21-7.29 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 24.7, 25.1, 27.6, 35.6, 41.2, 43.3, 44.1, 50.4, 52.2, 84.0, 125.8, 128.2, 128.5, 136.8, 139.1, 142.1, 159.7, 211.2. The carbon bound to boron was not observed presumably due to low intensity.

^{11}B NMR (100 MHz, $CDCl_3$): δ 30.1.

HRMS-ESI(+): for [$C_{24}H_{29}BO_3$+Na], calculated: 399.2106; found: 399.2107.



2n

(3aS,4S,7R,7aR)-2-phenyl-3-(4,4,5,5-tetraphenyl-1,3,2-dioxaborolan-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (2n).

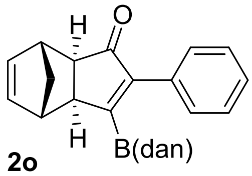
Following the general procedure C, using 4,4,5,5-tetraphenyl-2-(phenylethynyl)-1,3,2-dioxaborolane (**1n**, 0.6 mmol, 286 mg) provided 218 mg (61% yield) of the corresponding adduct of PKR **2n** as light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50 (bs, 2H), 2.55 (m, 1H), 3.02 (bs, 1H), 3.08 (bs, 1H), 3.24 (m, 1H), 6.29 (dd, J = 6 and 3 Hz, 1H), 6.40 (dd, J = 6 and 3 Hz, 1H), 7.02-7.10 (m, 20H), 7.33-7.37 (m, 3H), 7.47-7.52 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): peaks listed due to complexity: δ 41.6, 43.8, 44.5, 50.9, 52.8, 96.6, 127.0, 127.1, 127.2, 127.3, 127.9, 128.4, 128.6, 129.3, 132.4, 137.2, 139.0, 141.8, 142.0, 157.9, 208.9.

^{11}B NMR (100 MHz, $CDCl_3$): δ 33.6.

HRMS-ESI(+): for [$C_{42}H_{33}BO_3$+H], calculated: 595.2546; found: 595.2559.



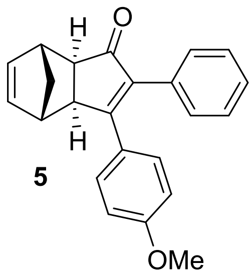
2o

(3aS,4S,7R,7aR)-3-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)-2-phenyl-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (2o).

Following the general procedure C, using 2-(phenylethynyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (**1o**, 0.6 mmol, 161 mg) provided 130 mg (81% yield) of the corresponding adduct of PKR **2o** as orange foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (m, 1H), 1.49 (m, 1H), 2.49 (m, 1H), 2.85 (bs, 1H), 3.00 (m, 1H), 3.07 (bs, 1H), 5.61 (bs, 2H), 6.17 (dd, J = 7 and 1 Hz, 2H), 6.30 (dd, J = 6 and 3 Hz, 1H), 6.41 (dd, J = 6 and 3 Hz, 1H), 7.05 (m, 4H), 7.37-7.43 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 41.6, 43.8, 44.3, 50.6, 52.7, 106.3, 118.3, 120.1, 127.6, 128.5, 128.8, 132.5, 136.2, 137.5, 138.7, 140.2, 154.9, 208.5.
^{11}B NMR (100 MHz, $CDCl_3$): δ 29.9.
HRMS-ESI(+): for [$C_{15}H_{15}BF_4O_3$], calculated: 330.1050; found: 330.1051.

__α,β-disubstituted cyclopentenones resulting of SMC 5-16__

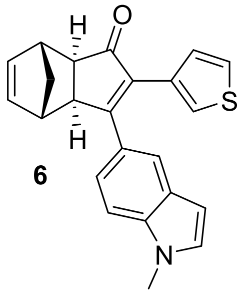


5

(3aS,4S,7R,7aR)-3-(4-methoxyphenyl)-2-phenyl-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (5).

Following the general procedure D, using **2a** (0.14 mmol, 50 mg) provided 35 mg (80% yield) of the corresponding α,β-diaryl cyclopentenone **5** as colorless oil.

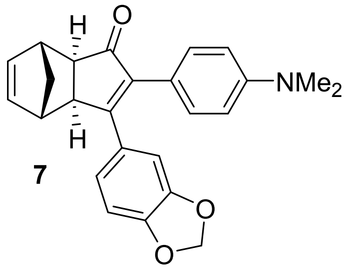
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45 (bs, 2H), 2.61 (m, 1H), 2.65 (bs, 1H), 3.11 (m, 1H), 3.35 (m, 1H), 3.80 (s, 3H), 6.33 (m, 2H), 6.80 (m, 2H), 7.21 (m, 2H), 7.28-7.36 (m, 5H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 42.0, 43.7, 44..4, 49.9, 52.7, 55.3, 113.8, 126.9, 127.7, 128.5, 129.3, 130.4, 132.7, 138.0, 138.2, 142.5, 160.8, 169.1, 207.2.
HRMS-ESI(+): for [$C_{46}H_{40}O_4$], calculated: 656.2927; found: 656.2927.



(3aS,4S,7R,7aR)-3-(1-methyl-1H-indol-5-yl)-2-(thiophen-3-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (6).

Following the general procedure D, using **2i** (0.25 mmol, 95 mg) provided 63 mg (71% yield) of the corresponding α,β-diaryl cyclopentenone **6** as yellow oil.

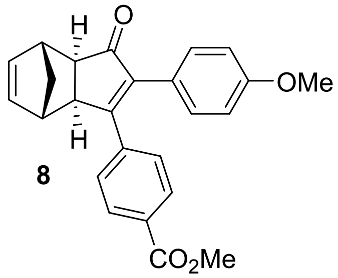
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.44 (m, 2H), 2.60 (m, 2H), 3.11 (m, 1H), 3.37 (m, 1H), 3.81 (s, 3H), 6.31 (m, 2H), 6.51 (m, 1H), 6.85 (m, 1H), 7.10 (m, 1H), 7.14 (m, 1H), 7.21 (m, 1H), 7.27 (m, 1H), 7.63 (m, 1H), 7.73 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 33.0, 42.1, 43.6, 44.1, 51.0, 52.8, 93.5, 102.0, 109.2, 121.1, 122.2, 124.4, 124.9, 126.7, 128.0, 128.3, 129.9, 130.7, 137.8, 138.3, 154.8, 207.3.
HRMS-ESI(+): for [$C_{23}H_{19}NOS$], calculated: 357.1187; found: 357.1213.



(3aS,4S,7R,7aR)-3-(benzo[d][1,3]dioxol-5-yl)-2-(4-(dimethylamino)phenyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (7).

Following the general procedure D, using **2c** (0.14 mmol, 55 mg) provided 39 mg (72% yield) of the corresponding α,β-diaryl cyclopentenone **7** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (m, 2H), 2.55 (m, 1H), 2.61 (m, 1H), 2.95 (s, 6H), 3.08 (bs, 1H), 3.22 (m, 1H), 5.97 (dd, J = 4 and 1 Hz, 2H), 6.30 (m, 2H), 6.67 (m, 2H), 6.76 (m, 1H), 6.86 (m, 1H), 6.96 (m, 1H), 7.11 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 40.4, 42.0, 43.5, 44.0, 50.0, 52.6, 101.3, 108.3, 108.7, 112.3, 119.7, 123.1, 129.5, 129.7, 130.0, 137.9, 138.2, 142.7, 147.6, 148.4, 150.0, 167.0, 207.9.
HRMS-ESI(+): for [$C_{50}H_{46}N_2O_6$], calculated: 770.3352; found: 770.3356.



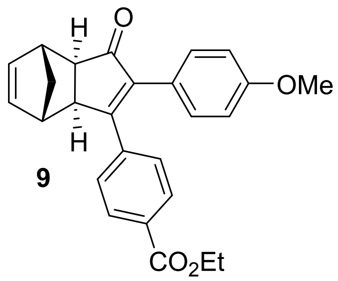
8

Methyl 4-((3aS,4S,7R,7aR)-2-(4-methoxyphenyl)-1-oxo-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-3-yl)benzoate (8).

Following the general procedure D, using **2b** (0.14 mmol, 53 mg) provided 43 mg (81% yield) of the corresponding α,β-diaryl cyclopentenone **8** as yellow oil. The spectroscopic data corresponds to those previously reported in the literature.[10]

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.46 (m, 2H), 2.55 (bs, 1H), 2.62 (m, 1H), 3.12 (bs, 1H), 3.32 (m, 1H), 3.79 (s, 3H), 3.91 (s, 3H), 6.31 (m, 2H), 6.81 (m, 2H), 7.11 (m, 2H), 7.38 (m, 2H), 7.97 (m, 2H).

HRMS-ESI(+): for [$C_{25}H_{22}O_4$+H], calculated: 387.1596; found: 387.1593.



9

Ethyl 4-((3aS,4S,7R,7aR)-2-(4-methoxyphenyl)-1-oxo-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-3-yl)benzoate (9).

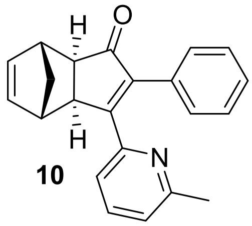
Following the general procedure D, using **2b** (0.14 mmol, 53 mg) provided 39 mg (70% yield) of the corresponding α,β-diaryl cyclopentenone **9** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.38 (t, J = 7 Hz, 3H), 1.45 (bs, 2H), 2.54 (bs, 1H), 2.62 (m, 1H), 3.12 (bs, 1H), 3.32 (m, 1H), 3.79 (s, 3H), 4.37 (q, J = 7 Hz, 2H), 6.31 (m, 2H), 6.82 (m, 2H), 7.12 (m, 2H), 7.39 (m, 2H), 7.98 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 41.8, 43.1, 44.2, 50.3, 52.8, 55.2, 61.2, 114.0, 123.5, 128.2, 129.7, 130.5, 131.0, 137.9, 138.2, 139.9, 144.3, 159.4, 166.0, 167.6, 207.4.

HRMS-ESI(+): for [$C_{26}H_{24}O_4$+Na], calculated: 423.1572; found: 423.1563.

[10] Ji, Y.; Verdaguer, X.; Riera, A. *Chem. Eur. J.* **2011**, *17*, 3942.



10

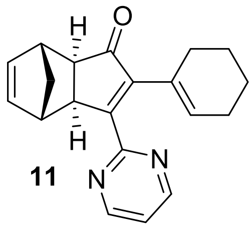
(3aS,4S,7R,7aR)-3-(6-methylpyridin-2-yl)-2-phenyl-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (10).

Following the general procedure D, using **2a** (0.14 mmol, 50 mg) provided 36 mg (82% yield) of the corresponding α,β-diaryl cyclopentenone **10** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.46 (m, 2H), 2.60 (m, 4H), 2.78 (bs, 1H), 3.12 (bs, 1H), 3.60 (m, 1H), 6.29 (dd, J = 5 and 3 Hz, 1H), 6.37 (dd, J = 5 and 3 Hz, 1H), 6.82 (d, J = 8 Hz, 1H), 7.06 (d, J = 7 Hz, 1H), 7.16-7.22 (m, 2H), 7.27-7.37 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 24.7, 41.7, 43.4, 44.5, 49.7, 52.8, 122.0, 123.1, 128.0, 128.4, 129.2, 131.8, 135.9, 137.3, 139.0, 144.8, 153.4, 158.8, 169.5, 208.1.

HRMS-ESI(+): for [$C_{22}H_{19}NO$], calculated: 313.1467; found: 313.1487.



11

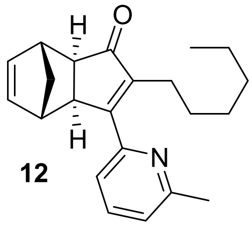
(3aS,4S,7R,7aR)-2-(cyclohex-1-en-1-yl)-3-(pyrimidin-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (11).

Following the general procedure D, using **2j** (0.14 mmol, 49 mg) provided 30 mg (69% yield) of the corresponding α,β-diaryl cyclopentenone **11** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (m, 2H), 1.62 (m, 4H), 1.91 (m, 2H), 2.13 (m, 2H), 2.50 (m, 1H), 2.8 (bs, 1H), 3.04 (bs, 1H), 3.35 (m, 1H), 5.75 (m, 1H), 6.24 (dd, J = 6 and 3 Hz, 1H), 6.33 (dd, J = 5 and 3 Hz, 1H), 7.23 (t, J = 5 Hz, 1H), 8.84 (d, J = 5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 22.6, 25.3, 27.9, 41.6, 43.5, 44.5, 48.9, 52.9, 119.7, 128.5, 129.7, 137.3, 138.8, 150.1, 156.8, 164.2, 208.8.

HRMS-ESI(+): for [$C_{40}H_{40}N_4O_2$], calculated: 608.3151; found: 608.3148.



12

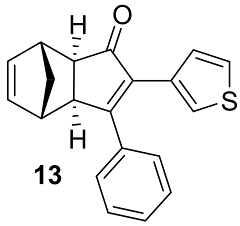
(3aS,4S,7R,7aR)-2-hexyl-3-(6-methylpyridin-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (12).

Following the general procedure D, using **2l** (0.14 mmol, 50 mg) provided 29 mg (65% yield) of the corresponding α,β-diaryl cyclopentenone **12** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 0.84 (t, *J* = 7 Hz, 3H), 1.20-1.32 (m, 7H), 1.37 (m, 1H), 1.45 (m, 2H), 2.42 (m, 1H), 2.51 (m, 2H), 2.60 (s, 3H), 2.65 (bs, 1H), 2.98 (bs, 1H), 3.30 (m, 1H), 6.24 (dd, *J* = 6 and 3 Hz, 1H), 6.30 (dd, *J* = 6 and 3 Hz, 1H), 7.15 (dm *J* = 8 Hz, 1H), 7.30 (d, *J* = 8 Hz, 1H), 7.65 (t, *J* = 8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 14.1, 22.6, 24.3, 24.7, 28.4, 29.7, 31.6, 41.7, 43.3, 43.8, 49.2, 52.2, 120.2, 123.0, 136.4, 137.5, 138.4, 147.6, 153.8, 158.7, 166.2, 210.2.

HRMS-ESI(+): for [$C_{15}H_{15}BF_4O_3$], calculated: 330.1050; found: 330.1051.



13

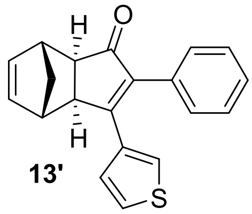
(3aS,4S,7R,7aR)-3-phenyl-2-(thiophen-3-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (13).

Following the general procedure D, using **2i** (0.14 mmol, 50 mg) provided 37 mg (85% yield) of the corresponding α,β-diaryl cyclopentenone **13** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 1.43 (m, 2H), 2.59 (m, 2H), 3.11 (m, 1H), 3.24 (m, 1H), 6.29 (m, 2H), 6.80 (dd, *J* = 5 and 1 Hz, 1H), 7.15 (m, 1H), 7.33-7.41 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): *δ* 41.9, 43.1, 44.2, 51.0, 52.8, 124.6, 125.4, 127.7, 127.8, 128.7, 129.5, 131.5, 135.9, 137.8, 138.3, 169.6, 207.2.

HRMS-ESI(+): for [$C_{20}H_{16}O_3S$], calculated: 304.0922; found: 304.0925.



13'

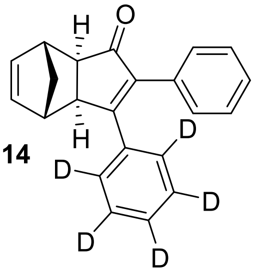
(3aS,4S,7R,7aR)-2-phenyl-3-(thiophen-3-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (13').

Following the general procedure D, using **2a** (0.14 mmol, 50 mg) provided 30 mg (70% yield) of the corresponding α,β-diaryl cyclopentenone **13'** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.49 (m, 2H), 2.61 (m, 1H), 2.88 (bs, 1H), 3.11 (bs, 1H), 3.28 (m, 1H), 6.32 (dd, J = 6 and 3 Hz, 1H), 6.39 (dd, J = 5 and 3 Hz, 1H), 6.92 (dd, J = 5 and 2 HZ, 1H), 7.18-7.25 (m, 3H), 7.34-7.44 (m, 3H), 7.52 (dd, J = 3 and 1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 42.1, 43.9, 44.4, 50.0, 52.6, 125.7, 127.5, 128.0, 128.1, 128.7, 129.2, 132.8, 136.3, 138.0, 138.2, 142.5, 162.7, 207.4.

HRMS-ESI(+): for [$C_{20}H_{16}O_3S$], calculated: 304.0922; found: 304.0926.



14

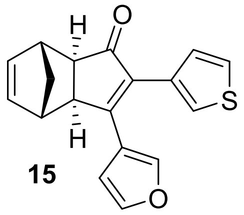
(3aS,4S,7R,7aR)-2-phenyl-3-(phenyl-d$_5$)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (14).

Following the general procedure D, using **2a** (0.25 mmol, 87 mg) provided 65 mg (85% yield) of the corresponding α,β-diaryl cyclopentenone **14** as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.48 (m, 2H), 2.63 (m, 2H), 3.14 (m, 1H), 3.37 (m, 1H), 6.33 (m, 2H), 7.18-7.22 (m, 2H), 7.28-7.34 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 41.9, 43.2, 44.2, 50.3, 52.8, 127.8, 128.4, 129.3, 132.1, 134.7, 137.9, 138.3, 143.7, 169.9, 207.3.

HRMS-ESI(+): for [$C_{22}H_{13}D_5O$+Na], calculated: 326.1569; found: 326.1592.



15

(3aS,4S,7R,7aR)-3-(furan-3-yl)-2-(thiophen-3-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (15).

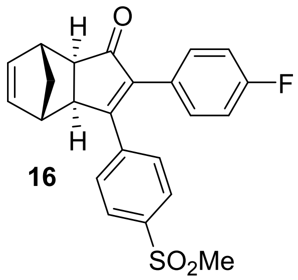
Following the general procedure D, using **2i** (0.14 mmol, 50 mg) provided 30 mg (72% yield) of the corresponding α,β-diaryl cyclopentenone **15** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (m, 1H), 1.49 (m, 1H), 2.56 (m, 1H), 2.89 (m, 1H), 3.08 (m, 2H), 6.30 (dd, J = 6 and 3 Hz, 1H), 6.32 (dd, J = 2 and 1 Hz, 1H), 6.36 (dd, J = 6 and 3 Hz, 1H), 7.04 (dd, J = 5 and 1 Hz, 1H), 7.365 (dd, J = 5 and 3 Hz, 1H), 7.40 (m, 2H), 7.72 (dd, J = 2 and 1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 42.2, 43.7, 44.5, 49.6, 52.4, 109.5, 121.5, 125.0, 125.4, 128.0, 131.9, 137.9, 138.0, 143.6, 143.7, 160.6, 206.7.

HRMS-ESI(+): for [$C_{18}H_{14}O_sS$], calculated: 294.0715; found: 294.0717.

<u>**Key scaffold 16**</u>



16

(3aS,4S,7R,7aR)-2-(4-fluorophenyl)-3-(4-(methylsulfonyl)phenyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoinden-1-one (16).

Following the general procedure D, using **2h** (0.14 mmol, 51 mg) provided 48 mg (88% yield) of the corresponding α,β-diaryl cyclopentenone **16** as yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (m, 1H), 1.50 (m, 1H), 2.54 (bs, 1H), 2.66 (m, 1H), 3.08 (s, 3H), 3.14 (bs, 1H), 3.34 (m, 1H), 6.32 (m, 2H), 7.00 (m, 2H), 7.14 (m, 2H), 7.48 (m, 2H), 7.89 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 41.8, 43.0, 44.3, 50.5, 53.0, 115.8 (d, J = 21 Hz, CF), 126.8 (d, J = 3 Hz, CF), 127.7, 129.1, 131.1 (d, J = 8 Hz, CF), 138.1 (d, J = 18 Hz, CF), 140.7, 141.0, 144.6, 161.4, 163.9, 167.2, 206.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ -112.81 (m, F).

HRMS-ESI(+): for [$C_{23}H_{19}FO_3S$], calculated: 394.1039; found: 394.1034.

X-Ray Crystallography of 2a, 2o and 6

X-Ray Crystallography of 2a

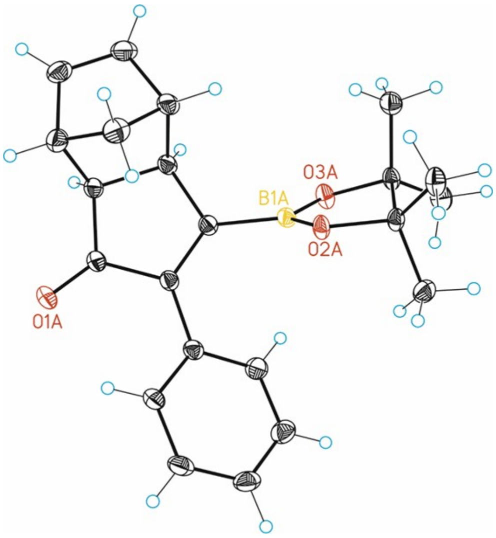


Table 1. Crystal data and structure refinement for **2a**.

Empirical formula	C22 H25 B O3	
Formula weight	348.23	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.7865(5)Å	α= 90.4912(14)°.
	b = 12.5627(6)Å	β = 102.2018(14)°.
	c = 16.1123(7)Å	γ = 93.6195(14)°.
Volume	1931.82(16) $Å^3$	
Z	4	
Density (calculated)	1.197 Mg/m^3	
Absorption coefficient	0.077 mm^{-1}	
F(000)	744	
Crystal size	0.40 x 0.30 x 0.30 mm^3	
Theta range for data collection	2.054 to 31.555°.	
Index ranges	-14<=h<=14,-18<=k<=17,-23<=l<=13	
Reflections collected	28656	
Independent reflections	12256[R(int) = 0.0281]	
Completeness to theta =31.555°	94.8%	
Absorption correction	Empirical	
Max. and min. transmission	0.977 and 0.854	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12256/ 150/ 553
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0484, wR2 = 0.1235
R indices (all data)	R1 = 0.0630, wR2 = 0.1335
Largest diff. peak and hole	0.470 and -0.275 e.Å^{-3}

Table 2. Bond lengths [Å] and angles [°] for **2a**.

Bond lengths----	
B1A-O2A	1.3617(14)
B1A-O3A	1.3658(13)
B1A-C3A	1.5680(15)
O1A-C1A	1.2182(13)
O2A-C17A	1.4747(12)
O3A-C18A	1.4734(12)
C1A-C2A	1.4956(15)
C1A-C9A	1.5156(15)
C2A-C3A	1.3561(14)
C2A-C11A	1.4747(15)
C3A-C4A	1.5137(15)
C4A-C9A	1.5484(14)
C4A-C5A	1.5660(15)
C5A-C6A	1.5222(16)
C5A-C10A	1.5398(17)
C6A-C7A	1.3347(18)
C7A-C8A	1.5191(17)
C8A-C10A	1.5455(16)
C8A-C9A	1.5607(16)
C11A-C12A	1.3996(15)
C11A-C16A	1.4023(16)
C12A-C13A	1.3908(16)
C13A-C14A	1.3876(18)
C14A-C15A	1.3903(18)
C15A-C16A	1.3868(17)
C17A-C19A	1.5181(16)
C17A-C20A	1.5200(15)
C17A-C18A	1.5639(14)
C18A-C21A	1.5202(15)
C18A-C22A	1.5219(16)

B1B-O3B'	1.354(6)
B1B-O2B	1.3633(16)
B1B-O3B	1.3670(16)
B1B-O2B'	1.374(6)
B1B-C3B	1.5682(15)
O1B-C1B	1.2189(13)
C1B-C2B	1.4921(14)
C1B-C9B	1.5137(16)
C2B-C3B	1.3544(15)
C2B-C11B	1.4706(15)
C3B-C4B	1.5137(15)
C4B-C9B	1.5487(14)
C4B-C5B	1.5701(16)
C5B-C6B	1.5274(19)
C5B-C10B	1.539(2)
C6B-C7B	1.3334(19)
C7B-C8B	1.5105(19)
C8B-C10B	1.5400(17)
C8B-C9B	1.5608(15)
C11B-C12B	1.3992(16)
C11B-C16B	1.4015(15)
C12B-C13B	1.3875(17)
C13B-C14B	1.3937(18)
C14B-C15B	1.389(2)
C15B-C16B	1.3863(18)
O2B-C17B	1.4700(14)
O3B-C18B	1.4703(15)
C17B-C19B	1.520(3)
C17B-C20B	1.523(2)
C17B-C18B	1.5587(18)
C18B-C21B	1.518(2)
C18B-C22B	1.528(3)
O2B'-C17'	1.471(7)
O3B'-C18'	1.475(7)
C17'-C20'	1.520(7)
C17'-C19'	1.530(6)
C17'-C18'	1.548(7)
C18'-C21'	1.521(7)
C18'-C22'	1.537(6)

Angles----------

O2A-B1A-O3A	114.45(9)
O2A-B1A-C3A	123.07(9)
O3A-B1A-C3A	122.30(9)
B1A-O2A-C17A	106.89(8)
B1A-O3A-C18A	106.67(8)
O1A-C1A-C2A	126.61(10)
O1A-C1A-C9A	125.02(10)
C2A-C1A-C9A	108.33(9)
C3A-C2A-C11A	126.30(10)
C3A-C2A-C1A	109.31(9)
C11A-C2A-C1A	124.32(9)
C2A-C3A-C4A	112.21(9)
C2A-C3A-B1A	128.73(10)
C4A-C3A-B1A	118.99(9)
C3A-C4A-C9A	105.00(8)
C3A-C4A-C5A	114.57(9)
C9A-C4A-C5A	103.09(9)
C6A-C5A-C10A	100.27(10)
C6A-C5A-C4A	104.75(9)
C10A-C5A-C4A	100.65(8)
C7A-C6A-C5A	107.51(10)
C6A-C7A-C8A	107.67(11)
C7A-C8A-C10A	100.18(9)
C7A-C8A-C9A	104.11(9)
C10A-C8A-C9A	101.33(9)
C1A-C9A-C4A	104.80(9)
C1A-C9A-C8A	114.27(9)
C4A-C9A-C8A	102.97(8)
C5A-C10A-C8A	93.85(9)
C12A-C11A-C16A	118.41(10)
C12A-C11A-C2A	121.38(10)
C16A-C11A-C2A	120.17(9)
C13A-C12A-C11A	120.48(11)
C14A-C13A-C12A	120.41(11)
C13A-C14A-C15A	119.65(11)
C16A-C15A-C14A	120.15(11)
C15A-C16A-C11A	120.80(11)
O2A-C17A-C19A	106.80(8)
O2A-C17A-C20A	108.20(8)

C19A-C17A-C20A	110.85(9)
O2A-C17A-C18A	102.42(8)
C19A-C17A-C18A	113.38(9)
C20A-C17A-C18A	114.43(9)
O3A-C18A-C21A	108.44(9)
O3A-C18A-C22A	106.32(9)
C21A-C18A-C22A	110.73(9)
O3A-C18A-C17A	102.50(7)
C21A-C18A-C17A	115.00(9)
C22A-C18A-C17A	113.05(9)
O2B-B1B-O3B	114.37(10)
O3B'-B1B-O2B'	113.4(3)
O3B'-B1B-C3B	124.6(2)
O2B-B1B-C3B	123.32(10)
O3B-B1B-C3B	122.24(10)
O2B'-B1B-C3B	121.9(2)
O1B-C1B-C2B	126.40(11)
O1B-C1B-C9B	125.23(10)
C2B-C1B-C9B	108.32(9)
C3B-C2B-C11B	126.99(9)
C3B-C2B-C1B	109.51(9)
C11B-C2B-C1B	123.48(9)
C2B-C3B-C4B	112.14(9)
C2B-C3B-B1B	127.01(10)
C4B-C3B-B1B	120.81(9)
C3B-C4B-C9B	104.98(9)
C3B-C4B-C5B	114.44(9)
C9B-C4B-C5B	102.61(8)
C6B-C5B-C10B	100.19(10)
C6B-C5B-C4B	104.50(10)
C10B-C5B-C4B	100.82(9)
C7B-C6B-C5B	107.27(12)
C6B-C7B-C8B	107.86(11)
C7B-C8B-C10B	100.65(10)
C7B-C8B-C9B	105.09(10)
C10B-C8B-C9B	100.41(9)
C1B-C9B-C4B	104.75(8)
C1B-C9B-C8B	113.20(9)
C4B-C9B-C8B	103.28(9)
C5B-C10B-C8B	93.92(10)

C12B-C11B-C16B	118.61(11)
C12B-C11B-C2B	121.06(10)
C16B-C11B-C2B	120.31(10)
C13B-C12B-C11B	120.68(11)
C12B-C13B-C14B	120.05(12)
C15B-C14B-C13B	119.72(12)
C16B-C15B-C14B	120.27(11)
C15B-C16B-C11B	120.57(11)
B1B-O2B-C17B	106.63(9)
B1B-O3B-C18B	106.37(10)
O2B-C17B-C19B	109.19(19)
O2B-C17B-C20B	106.42(11)
C19B-C17B-C20B	110.33(19)
O2B-C17B-C18B	102.30(9)
C19B-C17B-C18B	114.43(19)
C20B-C17B-C18B	113.49(12)
O3B-C18B-C21B	106.25(11)
O3B-C18B-C22B	108.91(19)
C21B-C18B-C22B	110.53(19)
O3B-C18B-C17B	102.57(9)
C21B-C18B-C17B	113.94(13)
C22B-C18B-C17B	113.94(18)
B1B-O2B'-C17'	106.5(4)
B1B-O3B'-C18'	106.6(5)
O2B'-C17'-C20'	106.0(9)
O2B'-C17'-C19'	107.4(6)
C20'-C17'-C19'	112.9(10)
O2B'-C17'-C18'	101.8(5)
C20'-C17'-C18'	113.2(9)
C19'-C17'-C18'	114.2(6)
O3B'-C18'-C21'	104.8(10)
O3B'-C18'-C22'	107.1(6)
C21'-C18'-C22'	113.4(11)
O3B'-C18'-C17'	101.7(5)
C21'-C18'-C17'	114.6(10)
C22'-C18'-C17'	113.7(6)

Table 3. Torsion angles [°] for **2a**.

O3A-B1A-O2A-C17A	-8.29(12)
C3A-B1A-O2A-C17A	176.35(10)
O2A-B1A-O3A-C18A	-9.72(12)
C3A-B1A-O3A-C18A	165.68(10)
O1A-C1A-C2A-C3A	-172.44(12)
C9A-C1A-C2A-C3A	5.47(12)
O1A-C1A-C2A-C11A	4.86(18)
C9A-C1A-C2A-C11A	-177.23(9)
C11A-C2A-C3A-C4A	176.58(10)
C1A-C2A-C3A-C4A	-6.19(12)
C11A-C2A-C3A-B1A	-6.65(18)
C1A-C2A-C3A-B1A	170.58(10)
O2A-B1A-C3A-C2A	-62.67(17)
O3A-B1A-C3A-C2A	122.33(13)
O2A-B1A-C3A-C4A	113.92(12)
O3A-B1A-C3A-C4A	-61.08(14)
C2A-C3A-C4A-C9A	4.43(12)
B1A-C3A-C4A-C9A	-172.69(9)
C2A-C3A-C4A-C5A	116.78(10)
B1A-C3A-C4A-C5A	-60.34(13)
C3A-C4A-C5A-C6A	179.95(9)
C9A-C4A-C5A-C6A	-66.56(11)
C3A-C4A-C5A-C10A	-76.33(11)
C9A-C4A-C5A-C10A	37.16(10)
C10A-C5A-C6A-C7A	-33.34(12)
C4A-C5A-C6A-C7A	70.67(12)
C5A-C6A-C7A-C8A	-0.04(14)
C6A-C7A-C8A-C10A	33.25(13)
C6A-C7A-C8A-C9A	-71.28(12)
O1A-C1A-C9A-C4A	175.39(11)
C2A-C1A-C9A-C4A	-2.56(11)
O1A-C1A-C9A-C8A	63.43(15)
C2A-C1A-C9A-C8A	-114.52(10)
C3A-C4A-C9A-C1A	-0.84(11)
C5A-C4A-C9A-C1A	-121.12(9)
C3A-C4A-C9A-C8A	118.98(9)
C5A-C4A-C9A-C8A	-1.30(10)
C7A-C8A-C9A-C1A	-178.17(9)

C10A-C8A-C9A-C1A	78.17(11)
C7A-C8A-C9A-C4A	68.78(10)
C10A-C8A-C9A-C4A	-34.88(10)
C6A-C5A-C10A-C8A	50.00(10)
C4A-C5A-C10A-C8A	-57.29(9)
C7A-C8A-C10A-C5A	-50.03(10)
C9A-C8A-C10A-C5A	56.74(10)
C3A-C2A-C11A-C12A	146.93(11)
C1A-C2A-C11A-C12A	-29.91(16)
C3A-C2A-C11A-C16A	-30.68(16)
C1A-C2A-C11A-C16A	152.49(11)
C16A-C11A-C12A-C13A	3.07(16)
C2A-C11A-C12A-C13A	-174.58(10)
C11A-C12A-C13A-C14A	-0.40(17)
C12A-C13A-C14A-C15A	-1.63(18)
C13A-C14A-C15A-C16A	0.94(18)
C14A-C15A-C16A-C11A	1.81(18)
C12A-C11A-C16A-C15A	-3.77(16)
C2A-C11A-C16A-C15A	173.90(10)
B1A-O2A-C17A-C19A	-98.16(10)
B1A-O2A-C17A-C20A	142.46(9)
B1A-O2A-C17A-C18A	21.25(10)
B1A-O3A-C18A-C21A	144.07(9)
B1A-O3A-C18A-C22A	-96.82(10)
B1A-O3A-C18A-C17A	22.05(11)
O2A-C17A-C18A-O3A	-26.01(10)
C19A-C17A-C18A-O3A	88.68(10)
C20A-C17A-C18A-O3A	-142.84(9)
O2A-C17A-C18A-C21A	-143.45(9)
C19A-C17A-C18A-C21A	-28.76(13)
C20A-C17A-C18A-C21A	99.72(11)
O2A-C17A-C18A-C22A	88.02(10)
C19A-C17A-C18A-C22A	-157.30(9)
C20A-C17A-C18A-C22A	-28.82(13)
O1B-C1B-C2B-C3B	171.61(11)
C9B-C1B-C2B-C3B	-5.87(12)
O1B-C1B-C2B-C11B	-6.61(17)
C9B-C1B-C2B-C11B	175.91(9)
C11B-C2B-C3B-C4B	-177.35(10)
C1B-C2B-C3B-C4B	4.51(12)

C11B-C2B-C3B-B1B	5.23(18)
C1B-C2B-C3B-B1B	-172.92(10)
O3B'-B1B-C3B-C2B	-96.3(4)
O2B-B1B-C3B-C2B	54.14(17)
O3B-B1B-C3B-C2B	-129.09(13)
O2B'-B1B-C3B-C2B	88.2(4)
O3B'-B1B-C3B-C4B	86.5(4)
O2B-B1B-C3B-C4B	-123.09(12)
O3B-B1B-C3B-C4B	53.69(15)
O2B'-B1B-C3B-C4B	-89.1(4)
C2B-C3B-C4B-C9B	-1.42(12)
B1B-C3B-C4B-C9B	176.19(9)
C2B-C3B-C4B-C5B	-113.13(11)
B1B-C3B-C4B-C5B	64.48(13)
C3B-C4B-C5B-C6B	-178.76(10)
C9B-C4B-C5B-C6B	68.12(12)
C3B-C4B-C5B-C10B	77.62(11)
C9B-C4B-C5B-C10B	-35.50(11)
C10B-C5B-C6B-C7B	33.33(14)
C4B-C5B-C6B-C7B	-70.77(14)
C5B-C6B-C7B-C8B	-0.30(16)
C6B-C7B-C8B-C10B	-32.86(14)
C6B-C7B-C8B-C9B	71.09(14)
O1B-C1B-C9B-C4B	-172.78(11)
C2B-C1B-C9B-C4B	4.73(11)
O1B-C1B-C9B-C8B	-60.98(15)
C2B-C1B-C9B-C8B	116.53(10)
C3B-C4B-C9B-C1B	-2.16(11)
C5B-C4B-C9B-C1B	117.76(10)
C3B-C4B-C9B-C8B	-120.89(9)
C5B-C4B-C9B-C8B	-0.97(11)
C7B-C8B-C9B-C1B	-179.77(9)
C10B-C8B-C9B-C1B	-75.63(11)
C7B-C8B-C9B-C4B	-67.07(11)
C10B-C8B-C9B-C4B	37.07(11)
C6B-C5B-C10B-C8B	-49.65(11)
C4B-C5B-C10B-C8B	57.40(10)
C7B-C8B-C10B-C5B	49.76(10)
C9B-C8B-C10B-C5B	-57.93(10)
C3B-C2B-C11B-C12B	-139.39(12)

C1B-C2B-C11B-C12B	38.51(15)
C3B-C2B-C11B-C16B	38.94(16)
C1B-C2B-C11B-C16B	-143.16(11)
C16B-C11B-C12B-C13B	-3.34(17)
C2B-C11B-C12B-C13B	175.02(10)
C11B-C12B-C13B-C14B	0.97(18)
C12B-C13B-C14B-C15B	1.73(19)
C13B-C14B-C15B-C16B	-1.99(19)
C14B-C15B-C16B-C11B	-0.45(18)
C12B-C11B-C16B-C15B	3.08(17)
C2B-C11B-C16B-C15B	-175.29(10)
O3B-B1B-O2B-C17B	9.67(15)
C3B-B1B-O2B-C17B	-173.33(10)
O2B-B1B-O3B-C18B	9.16(15)
C3B-B1B-O3B-C18B	-167.88(10)
B1B-O2B-C17B-C19B	-144.4(2)
B1B-O2B-C17B-C20B	96.51(13)
B1B-O2B-C17B-C18B	-22.81(13)
B1B-O3B-C18B-C21B	97.32(13)
B1B-O3B-C18B-C22B	-143.60(19)
B1B-O3B-C18B-C17B	-22.55(13)
O2B-C17B-C18B-O3B	27.35(13)
C19B-C17B-C18B-O3B	145.3(2)
C20B-C17B-C18B-O3B	-86.88(13)
O2B-C17B-C18B-C21B	-87.03(13)
C19B-C17B-C18B-C21B	30.9(2)
C20B-C17B-C18B-C21B	158.75(12)
O2B-C17B-C18B-C22B	144.9(2)
C19B-C17B-C18B-C22B	-97.2(3)
C20B-C17B-C18B-C22B	30.7(2)
O3B'-B1B-O2B'-C17'	-8.5(7)
C3B-B1B-O2B'-C17'	167.5(3)
O2B'-B1B-O3B'-C18'	-12.5(7)
C3B-B1B-O3B'-C18'	171.6(3)
B1B-O2B'-C17'-C20'	143.1(10)
B1B-O2B'-C17'-C19'	-95.9(7)
B1B-O2B'-C17'-C18'	24.4(6)
B1B-O3B'-C18'-C21'	146.4(11)
B1B-O3B'-C18'-C22'	-92.9(7)
B1B-O3B'-C18'-C17'	26.7(7)

O2B'-C17'-C18'-O3B'	-30.6(6)
C20'-C17'-C18'-O3B'	-144.0(10)
C19'-C17'-C18'-O3B'	84.8(7)
O2B'-C17'-C18'-C21'	-143.0(11)
C20'-C17'-C18'-C21'	103.6(14)
C19'-C17'-C18'-C21'	-27.6(12)
O2B'-C17'-C18'-C22'	84.3(7)
C20'-C17'-C18'-C22'	-29.1(12)
C19'-C17'-C18'-C22'	-160.3(7)

X-Ray Crystallography of **2o**

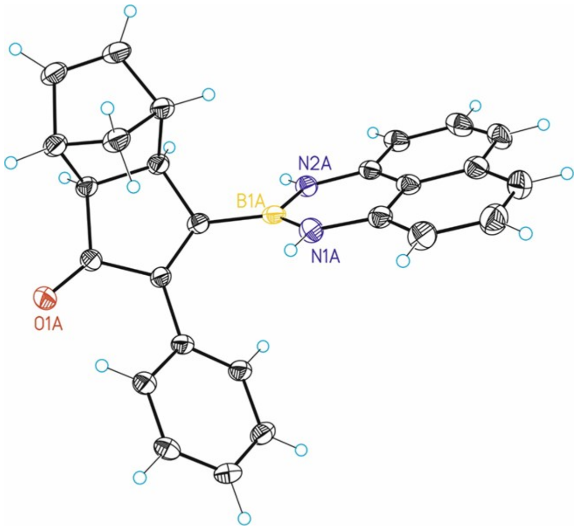


Table 1. Crystal data and structure refinement for **2o**.

Empirical formula	C26 H21 B N2 O	
Formula weight	388.26	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 19.3909(10)Å	α= 90°.
	b = 10.1233(4)Å	β = 95.235(4)°.
	c = 20.4987(7)Å	γ = 90°.
Volume	4007.1(3) Å^3	
Z	8	
Density (calculated)	1.287 Mg/m^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	1632	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	1.995 to 30.535°.	
Index ranges	-25<=h<=27,-14<=k<=9,-28<=l<=29	
Reflections collected	40608	
Independent reflections	10796[R(int) = 0.0503]	
Completeness to theta =30.535°	88.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.998 and 0.768	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10796/ 0/ 541	
Goodness-of-fit on F^2	1.077	

Final R indices [I>2sigma(I)]	R1 = 0.0729, wR2 = 0.1782
R indices (all data)	R1 = 0.1118, wR2 = 0.1958
Largest diff. peak and hole	0.358 and -0.319 e.Å^{-3}

Table 2. Bond lengths [Å] and angles [°] for **2o**.

Bond lengths----	
B1A-N1A	1.411(3)
B1A-N2A	1.426(3)
B1A-C11A	1.566(3)
N1A-C1A	1.394(3)
N2A-C9A	1.391(3)
O1A-C19A	1.221(3)
C1A-C2A	1.379(3)
C1A-C10A	1.435(3)
C2A-C3A	1.394(4)
C3A-C4A	1.374(4)
C4A-C5A	1.414(4)
C5A-C10A	1.423(3)
C5A-C6A	1.426(3)
C6A-C7A	1.364(4)
C7A-C8A	1.404(4)
C8A-C9A	1.387(3)
C9A-C10A	1.425(3)
C11A-C20A	1.355(3)
C11A-C12A	1.510(3)
C12A-C17A	1.549(3)
C12A-C13A	1.575(3)
C13A-C14A	1.521(3)
C13A-C18A	1.543(3)
C14A-C15A	1.329(4)
C15A-C16A	1.522(3)
C16A-C18A	1.537(4)
C16A-C17A	1.567(3)
C17A-C19A	1.517(3)
C19A-C20A	1.483(3)
C20A-C21A	1.479(3)
C21A-C22A	1.394(3)
C21A-C26A	1.396(3)
C22A-C23A	1.394(3)

C23A-C24A	1.387(3)
C24A-C25A	1.388(4)
C25A-C26A	1.386(3)
B1B-N2B	1.408(3)
B1B-N1B	1.419(4)
B1B-C11B	1.575(4)
N1B-C1B	1.403(3)
N2B-C9B	1.401(3)
O1B-C19B	1.213(3)
C1B-C2B	1.380(4)
C1B-C10B	1.424(3)
C2B-C3B	1.411(4)
C3B-C4B	1.362(4)
C4B-C5B	1.420(4)
C5B-C6B	1.421(4)
C5B-C10B	1.425(3)
C6B-C7B	1.366(4)
C7B-C8B	1.418(3)
C8B-C9B	1.374(3)
C9B-C10B	1.428(3)
C11B-C20B	1.350(4)
C11B-C12B	1.517(4)
C12B-C17B	1.551(4)
C12B-C13B	1.558(4)
C13B-C14B	1.523(4)
C13B-C18B	1.543(4)
C14B-C15B	1.313(5)
C15B-C16B	1.522(5)
C16B-C18B	1.542(4)
C16B-C17B	1.564(4)
C17B-C19B	1.519(4)
C19B-C20B	1.485(3)
C20B-C21B	1.480(4)
C21B-C26B	1.399(4)
C21B-C22B	1.400(3)
C22B-C23B	1.390(4)
C23B-C24B	1.390(4)
C24B-C25B	1.392(3)
C25B-C26B	1.380(4)

Angles----------

N1A-B1A-N2A	117.4(2)
N1A-B1A-C11A	122.7(2)
N2A-B1A-C11A	119.7(2)
C1A-N1A-B1A	122.84(19)
C9A-N2A-B1A	122.3(2)
C2A-C1A-N1A	122.4(2)
C2A-C1A-C10A	119.7(2)
N1A-C1A-C10A	117.8(2)
C1A-C2A-C3A	120.5(2)
C4A-C3A-C2A	121.3(2)
C3A-C4A-C5A	120.2(2)
C4A-C5A-C10A	119.1(2)
C4A-C5A-C6A	122.6(2)
C10A-C5A-C6A	118.3(2)
C7A-C6A-C5A	120.3(2)
C6A-C7A-C8A	122.0(2)
C9A-C8A-C7A	119.4(2)
C8A-C9A-N2A	121.5(2)
C8A-C9A-C10A	120.1(2)
N2A-C9A-C10A	118.38(19)
C5A-C10A-C9A	119.8(2)
C5A-C10A-C1A	119.1(2)
C9A-C10A-C1A	121.1(2)
C20A-C11A-C12A	111.96(19)
C20A-C11A-B1A	129.5(2)
C12A-C11A-B1A	118.18(19)
C11A-C12A-C17A	105.23(17)
C11A-C12A-C13A	110.88(19)
C17A-C12A-C13A	103.10(18)
C14A-C13A-C18A	99.86(19)
C14A-C13A-C12A	106.15(19)
C18A-C13A-C12A	99.82(18)
C15A-C14A-C13A	107.7(2)
C14A-C15A-C16A	107.6(2)
C15A-C16A-C18A	99.8(2)
C15A-C16A-C17A	104.80(18)
C18A-C16A-C17A	101.57(18)
C19A-C17A-C12A	104.20(17)
C19A-C17A-C16A	113.02(18)

C12A-C17A-C16A	102.71(19)
C16A-C18A-C13A	93.95(18)
O1A-C19A-C20A	126.7(2)
O1A-C19A-C17A	124.7(2)
C20A-C19A-C17A	108.50(19)
C11A-C20A-C21A	127.4(2)
C11A-C20A-C19A	109.63(19)
C21A-C20A-C19A	122.90(19)
C22A-C21A-C26A	118.9(2)
C22A-C21A-C20A	121.4(2)
C26A-C21A-C20A	119.6(2)
C21A-C22A-C23A	120.5(2)
C24A-C23A-C22A	119.8(2)
C23A-C24A-C25A	120.0(2)
C26A-C25A-C24A	120.1(2)
C25A-C26A-C21A	120.6(2)
N2B-B1B-N1B	116.4(2)
N2B-B1B-C11B	123.4(2)
N1B-B1B-C11B	120.1(2)
C1B-N1B-B1B	123.3(2)
C9B-N2B-B1B	123.5(2)
C2B-C1B-N1B	122.1(2)
C2B-C1B-C10B	120.4(2)
N1B-C1B-C10B	117.5(2)
C1B-C2B-C3B	119.8(3)
C4B-C3B-C2B	121.3(2)
C3B-C4B-C5B	120.5(2)
C4B-C5B-C6B	122.5(2)
C4B-C5B-C10B	118.9(2)
C6B-C5B-C10B	118.6(2)
C7B-C6B-C5B	120.6(2)
C6B-C7B-C8B	121.1(2)
C9B-C8B-C7B	120.0(2)
C8B-C9B-N2B	122.2(2)
C8B-C9B-C10B	120.2(2)
N2B-C9B-C10B	117.6(2)
C1B-C10B-C5B	119.1(2)
C1B-C10B-C9B	121.4(2)
C5B-C10B-C9B	119.5(2)
C20B-C11B-C12B	111.6(2)

C20B-C11B-B1B	126.7(2)
C12B-C11B-B1B	121.7(2)
C11B-C12B-C17B	105.1(2)
C11B-C12B-C13B	113.8(2)
C17B-C12B-C13B	103.0(2)
C14B-C13B-C18B	99.8(3)
C14B-C13B-C12B	105.9(2)
C18B-C13B-C12B	100.6(2)
C15B-C14B-C13B	107.3(3)
C14B-C15B-C16B	108.7(3)
C15B-C16B-C18B	99.4(3)
C15B-C16B-C17B	105.5(3)
C18B-C16B-C17B	100.2(2)
C19B-C17B-C12B	104.7(2)
C19B-C17B-C16B	113.1(2)
C12B-C17B-C16B	103.0(2)
C16B-C18B-C13B	93.9(2)
O1B-C19B-C20B	125.7(3)
O1B-C19B-C17B	126.3(2)
C20B-C19B-C17B	108.0(2)
C11B-C20B-C21B	128.9(2)
C11B-C20B-C19B	110.6(2)
C21B-C20B-C19B	120.5(2)
C26B-C21B-C22B	118.6(2)
C26B-C21B-C20B	121.3(2)
C22B-C21B-C20B	120.1(2)
C23B-C22B-C21B	120.6(2)
C24B-C23B-C22B	120.1(2)
C23B-C24B-C25B	119.6(2)
C26B-C25B-C24B	120.5(2)
C25B-C26B-C21B	120.7(2)

Table 3. Torsion angles [°] for **2o**.

N2A-B1A-N1A-C1A	0.2(3)
C11A-B1A-N1A-C1A	-174.4(2)
N1A-B1A-N2A-C9A	-3.2(3)
C11A-B1A-N2A-C9A	171.6(2)
B1A-N1A-C1A-C2A	-177.4(2)

B1A-N1A-C1A-C10A	2.5(3)
N1A-C1A-C2A-C3A	-178.5(2)
C10A-C1A-C2A-C3A	1.6(4)
C1A-C2A-C3A-C4A	0.7(4)
C2A-C3A-C4A-C5A	-1.4(4)
C3A-C4A-C5A-C10A	-0.2(4)
C3A-C4A-C5A-C6A	-179.1(2)
C4A-C5A-C6A-C7A	178.3(2)
C10A-C5A-C6A-C7A	-0.5(4)
C5A-C6A-C7A-C8A	-0.2(4)
C6A-C7A-C8A-C9A	0.6(4)
C7A-C8A-C9A-N2A	179.0(2)
C7A-C8A-C9A-C10A	-0.2(3)
B1A-N2A-C9A-C8A	-176.1(2)
B1A-N2A-C9A-C10A	3.2(3)
C4A-C5A-C10A-C9A	-178.1(2)
C6A-C5A-C10A-C9A	0.8(3)
C4A-C5A-C10A-C1A	2.4(3)
C6A-C5A-C10A-C1A	-178.7(2)
C8A-C9A-C10A-C5A	-0.5(3)
N2A-C9A-C10A-C5A	-179.7(2)
C8A-C9A-C10A-C1A	179.0(2)
N2A-C9A-C10A-C1A	-0.2(3)
C2A-C1A-C10A-C5A	-3.1(3)
N1A-C1A-C10A-C5A	176.9(2)
C2A-C1A-C10A-C9A	177.4(2)
N1A-C1A-C10A-C9A	-2.5(3)
N1A-B1A-C11A-C20A	-52.7(4)
N2A-B1A-C11A-C20A	132.8(2)
N1A-B1A-C11A-C12A	119.8(2)
N2A-B1A-C11A-C12A	-54.7(3)
C20A-C11A-C12A-C17A	0.9(3)
B1A-C11A-C12A-C17A	-172.84(19)
C20A-C11A-C12A-C13A	111.7(2)
B1A-C11A-C12A-C13A	-62.0(2)
C11A-C12A-C13A-C14A	-177.05(18)
C17A-C12A-C13A-C14A	-64.9(2)
C11A-C12A-C13A-C18A	-73.7(2)
C17A-C12A-C13A-C18A	38.5(2)
C18A-C13A-C14A-C15A	-33.1(3)

C12A-C13A-C14A-C15A	70.2(2)
C13A-C14A-C15A-C16A	-0.4(3)
C14A-C15A-C16A-C18A	33.9(2)
C14A-C15A-C16A-C17A	-71.0(3)
C11A-C12A-C17A-C19A	-4.7(2)
C13A-C12A-C17A-C19A	-120.96(18)
C11A-C12A-C17A-C16A	113.38(19)
C13A-C12A-C17A-C16A	-2.9(2)
C15A-C16A-C17A-C19A	-178.7(2)
C18A-C16A-C17A-C19A	77.7(2)
C15A-C16A-C17A-C12A	69.6(2)
C18A-C16A-C17A-C12A	-33.9(2)
C15A-C16A-C18A-C13A	-50.50(19)
C17A-C16A-C18A-C13A	56.97(19)
C14A-C13A-C18A-C16A	50.3(2)
C12A-C13A-C18A-C16A	-58.15(19)
C12A-C17A-C19A-O1A	-171.6(2)
C16A-C17A-C19A-O1A	77.7(3)
C12A-C17A-C19A-C20A	6.8(2)
C16A-C17A-C19A-C20A	-103.9(2)
C12A-C11A-C20A-C21A	-173.9(2)
B1A-C11A-C20A-C21A	-1.1(4)
C12A-C11A-C20A-C19A	3.5(3)
B1A-C11A-C20A-C19A	176.3(2)
O1A-C19A-C20A-C11A	171.7(2)
C17A-C19A-C20A-C11A	-6.6(3)
O1A-C19A-C20A-C21A	-10.7(4)
C17A-C19A-C20A-C21A	171.0(2)
C11A-C20A-C21A-C22A	-39.4(4)
C19A-C20A-C21A-C22A	143.5(2)
C11A-C20A-C21A-C26A	137.9(3)
C19A-C20A-C21A-C26A	-39.2(3)
C26A-C21A-C22A-C23A	-1.2(4)
C20A-C21A-C22A-C23A	176.1(2)
C21A-C22A-C23A-C24A	-0.1(4)
C22A-C23A-C24A-C25A	1.1(4)
C23A-C24A-C25A-C26A	-0.8(4)
C24A-C25A-C26A-C21A	-0.6(4)
C22A-C21A-C26A-C25A	1.5(4)
C20A-C21A-C26A-C25A	-175.8(2)

N2B-B1B-N1B-C1B	5.2(4)
C11B-B1B-N1B-C1B	-172.4(2)
N1B-B1B-N2B-C9B	-1.5(4)
C11B-B1B-N2B-C9B	175.9(2)
B1B-N1B-C1B-C2B	175.1(2)
B1B-N1B-C1B-C10B	-4.9(4)
N1B-C1B-C2B-C3B	-178.6(2)
C10B-C1B-C2B-C3B	1.4(4)
C1B-C2B-C3B-C4B	-1.6(4)
C2B-C3B-C4B-C5B	0.2(4)
C3B-C4B-C5B-C6B	-179.2(3)
C3B-C4B-C5B-C10B	1.4(4)
C4B-C5B-C6B-C7B	-178.3(3)
C10B-C5B-C6B-C7B	1.1(4)
C5B-C6B-C7B-C8B	-0.2(4)
C6B-C7B-C8B-C9B	0.0(4)
C7B-C8B-C9B-N2B	177.7(2)
C7B-C8B-C9B-C10B	-0.8(4)
B1B-N2B-C9B-C8B	179.5(3)
B1B-N2B-C9B-C10B	-2.1(4)
C2B-C1B-C10B-C5B	0.3(4)
N1B-C1B-C10B-C5B	-179.8(2)
C2B-C1B-C10B-C9B	-179.0(2)
N1B-C1B-C10B-C9B	0.9(4)
C4B-C5B-C10B-C1B	-1.6(4)
C6B-C5B-C10B-C1B	179.0(2)
C4B-C5B-C10B-C9B	177.7(2)
C6B-C5B-C10B-C9B	-1.7(4)
C8B-C9B-C10B-C1B	-179.1(2)
N2B-C9B-C10B-C1B	2.4(4)
C8B-C9B-C10B-C5B	1.6(4)
N2B-C9B-C10B-C5B	-176.9(2)
N2B-B1B-C11B-C20B	-25.5(4)
N1B-B1B-C11B-C20B	151.9(3)
N2B-B1B-C11B-C12B	157.4(2)
N1B-B1B-C11B-C12B	-25.3(4)
C20B-C11B-C12B-C17B	-1.9(3)
B1B-C11B-C12B-C17B	175.6(2)
C20B-C11B-C12B-C13B	110.1(3)
B1B-C11B-C12B-C13B	-72.4(3)

C11B-C12B-C13B-C14B	179.2(2)
C17B-C12B-C13B-C14B	-67.6(3)
C11B-C12B-C13B-C18B	-77.3(3)
C17B-C12B-C13B-C18B	35.9(3)
C18B-C13B-C14B-C15B	-34.1(3)
C12B-C13B-C14B-C15B	70.0(3)
C13B-C14B-C15B-C16B	0.8(4)
C14B-C15B-C16B-C18B	32.8(3)
C14B-C15B-C16B-C17B	-70.6(3)
C11B-C12B-C17B-C19B	1.5(3)
C13B-C12B-C17B-C19B	-117.9(2)
C11B-C12B-C17B-C16B	120.0(2)
C13B-C12B-C17B-C16B	0.6(3)
C15B-C16B-C17B-C19B	178.4(2)
C18B-C16B-C17B-C19B	75.6(3)
C15B-C16B-C17B-C12B	66.0(3)
C18B-C16B-C17B-C12B	-36.8(3)
C15B-C16B-C18B-C13B	-49.8(3)
C17B-C16B-C18B-C13B	57.9(3)
C14B-C13B-C18B-C16B	50.6(3)
C12B-C13B-C18B-C16B	-57.8(2)
C12B-C17B-C19B-O1B	179.9(3)
C16B-C17B-C19B-O1B	68.5(3)
C12B-C17B-C19B-C20B	-0.8(3)
C16B-C17B-C19B-C20B	-112.2(2)
C12B-C11B-C20B-C21B	-178.2(2)
B1B-C11B-C20B-C21B	4.4(4)
C12B-C11B-C20B-C19B	1.5(3)
B1B-C11B-C20B-C19B	-175.9(2)
O1B-C19B-C20B-C11B	178.9(3)
C17B-C19B-C20B-C11B	-0.4(3)
O1B-C19B-C20B-C21B	-1.4(4)
C17B-C19B-C20B-C21B	179.3(2)
C11B-C20B-C21B-C26B	-83.8(3)
C19B-C20B-C21B-C26B	96.6(3)
C11B-C20B-C21B-C22B	98.7(3)
C19B-C20B-C21B-C22B	-81.0(3)
C26B-C21B-C22B-C23B	-0.3(4)
C20B-C21B-C22B-C23B	177.3(2)
C21B-C22B-C23B-C24B	-1.0(4)

C22B-C23B-C24B-C25B	1.6(4)
C23B-C24B-C25B-C26B	-0.8(4)
C24B-C25B-C26B-C21B	-0.6(4)
C22B-C21B-C26B-C25B	1.2(4)
C20B-C21B-C26B-C25B	-176.4(2)

X-Ray Crystallography of **6**

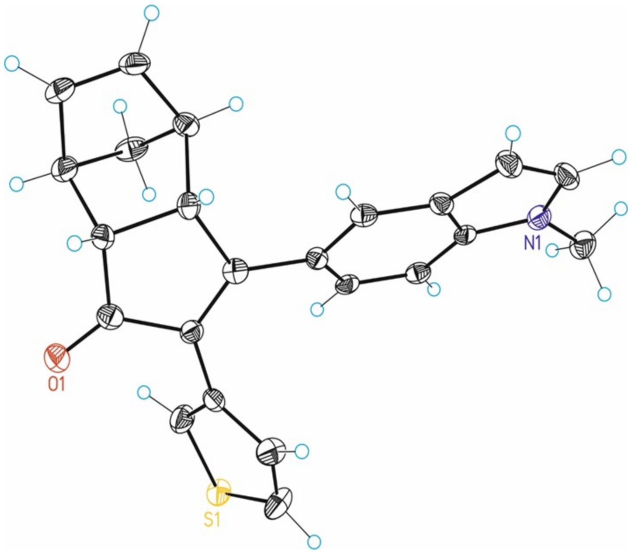


Table 1. Crystal data and structure refinement for **6**.

Empirical formula	C23 H19 N O S	
Formula weight	357.45	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 5.6327(6)Å	α= 90°.
	b = 14.2928(15)Å	β = 90°.
	c = 21.544(3)Å	γ = 90°.
Volume	1734.4(3) $Å^3$	
Z	4	
Density (calculated)	1.369 Mg/m^3	
Absorption coefficient	0.198 mm^{-1}	
F(000)	752	
Crystal size	0.20 x 0.20 x 0.10 mm^3	
Theta range for data collection	1.710 to 26.346°.	
Index ranges	-6<=h<=5,-17<=k<=17,-26<=l<=24	
Reflections collected	11276	
Independent reflections	3394[R(int) = 0.0580]	
Completeness to theta =26.346°	98.299995%	
Absorption correction	Empirical	
Max. and min. transmission	0.980 and 0.892	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3394/ 50/ 254	
Goodness-of-fit on F^2	1.052	

Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.0995
R indices (all data)	R1 = 0.0677, wR2 = 0.1104
Flack parameter	x =0.06(9)
Largest diff. peak and hole	0.228 and -0.263 e.Å^{-3}

Table 2. Bond lengths [Å] and angles [°] for **6**.

Bond lengths----	
S1-C23	1.699(5)
S1-C22	1.723(12)
S1'-C21	1.640(6)
S1'-C22'	1.715(12)
N1-C15	1.373(5)
N1-C16	1.381(4)
N1-C19	1.464(5)
O1-C4	1.218(4)
C1-C2	1.518(5)
C1-C5	1.547(4)
C1-C9	1.559(5)
C2-C3	1.360(5)
C2-C11	1.479(4)
C3-C20	1.466(5)
C3-C4	1.488(5)
C4-C5	1.512(5)
C5-C6	1.568(5)
C6-C7	1.519(5)
C6-C10	1.532(5)
C7-C8	1.330(5)
C8-C9	1.511(5)
C9-C10	1.543(5)
C11-C12	1.385(5)
C11-C18	1.421(5)
C12-C13	1.394(5)
C13-C16	1.416(5)
C13-C14	1.434(5)
C14-C15	1.361(5)
C16-C17	1.393(5)
C17-C18	1.385(5)
C20-C23	1.383(5)
C20-C21	1.395(5)

C21-C22	1.347(11)
C22'-C23	1.381(11)

Angles----------

C23-S1-C22	89.2(5)
C21-S1'-C22'	91.2(6)
C15-N1-C16	108.0(3)
C15-N1-C19	125.4(3)
C16-N1-C19	126.1(3)
C2-C1-C5	104.6(3)
C2-C1-C9	113.3(3)
C5-C1-C9	103.1(3)
C3-C2-C11	127.9(3)
C3-C2-C1	112.4(3)
C11-C2-C1	119.6(3)
C2-C3-C20	129.2(3)
C2-C3-C4	109.2(3)
C20-C3-C4	121.5(3)
O1-C4-C3	125.9(4)
O1-C4-C5	125.3(3)
C3-C4-C5	108.7(3)
C4-C5-C1	105.1(3)
C4-C5-C6	113.1(3)
C1-C5-C6	102.9(3)
C7-C6-C10	100.4(3)
C7-C6-C5	104.5(3)
C10-C6-C5	100.7(3)
C8-C7-C6	107.3(3)
C7-C8-C9	108.0(3)
C8-C9-C10	100.1(3)
C8-C9-C1	105.3(3)
C10-C9-C1	100.4(3)
C6-C10-C9	94.0(3)
C12-C11-C18	118.5(3)
C12-C11-C2	120.1(3)
C18-C11-C2	121.3(3)
C11-C12-C13	121.0(4)
C12-C13-C16	118.5(3)
C12-C13-C14	134.7(4)
C16-C13-C14	106.8(3)

C15-C14-C13	106.4(3)
C14-C15-N1	111.0(3)
N1-C16-C17	130.0(3)
N1-C16-C13	107.8(3)
C17-C16-C13	122.2(3)
C18-C17-C16	117.4(3)
C17-C18-C11	122.3(3)
C23-C20-C21	111.1(4)
C23-C20-C3	124.1(3)
C21-C20-C3	124.8(3)
C22-C21-C20	112.2(7)
C20-C21-S1'	114.0(4)
C21-C22-S1	113.8(9)
C23-C22'-S1'	111.7(10)
C22'-C23-C20	111.7(7)
C20-C23-S1	113.7(3)

Table 3. Torsion angles [°] for **6**.

C5-C1-C2-C3	-1.5(4)
C9-C1-C2-C3	-113.0(4)
C5-C1-C2-C11	174.8(3)
C9-C1-C2-C11	63.3(4)
C11-C2-C3-C20	5.1(7)
C1-C2-C3-C20	-179.0(4)
C11-C2-C3-C4	-174.5(4)
C1-C2-C3-C4	1.4(4)
C2-C3-C4-O1	177.4(4)
C20-C3-C4-O1	-2.2(6)
C2-C3-C4-C5	-0.7(4)
C20-C3-C4-C5	179.6(3)
O1-C4-C5-C1	-178.4(4)
C3-C4-C5-C1	-0.2(4)
O1-C4-C5-C6	-66.9(5)
C3-C4-C5-C6	111.3(3)
C2-C1-C5-C4	0.9(4)
C9-C1-C5-C4	119.6(3)
C2-C1-C5-C6	-117.7(3)
C9-C1-C5-C6	0.9(4)

C4-C5-C6-C7	179.0(3)
C1-C5-C6-C7	-68.2(3)
C4-C5-C6-C10	-77.2(3)
C1-C5-C6-C10	35.6(4)
C10-C6-C7-C8	-33.1(4)
C5-C6-C7-C8	70.9(4)
C6-C7-C8-C9	-0.2(5)
C7-C8-C9-C10	33.1(4)
C7-C8-C9-C1	-70.7(4)
C2-C1-C9-C8	179.2(3)
C5-C1-C9-C8	66.7(4)
C2-C1-C9-C10	75.6(3)
C5-C1-C9-C10	-36.9(3)
C7-C6-C10-C9	49.8(3)
C5-C6-C10-C9	-57.3(3)
C8-C9-C10-C6	-49.8(3)
C1-C9-C10-C6	58.0(3)
C3-C2-C11-C12	-151.9(4)
C1-C2-C11-C12	32.5(5)
C3-C2-C11-C18	30.8(6)
C1-C2-C11-C18	-144.8(4)
C18-C11-C12-C13	-3.3(5)
C2-C11-C12-C13	179.3(3)
C11-C12-C13-C16	2.0(5)
C11-C12-C13-C14	-177.2(4)
C12-C13-C14-C15	178.7(4)
C16-C13-C14-C15	-0.6(4)
C13-C14-C15-N1	0.9(4)
C16-N1-C15-C14	-0.9(4)
C19-N1-C15-C14	-172.9(3)
C15-N1-C16-C17	-179.6(4)
C19-N1-C16-C17	-7.7(6)
C15-N1-C16-C13	0.5(4)
C19-N1-C16-C13	172.4(3)
C12-C13-C16-N1	-179.3(3)
C14-C13-C16-N1	0.1(4)
C12-C13-C16-C17	0.7(5)
C14-C13-C16-C17	-179.9(3)
N1-C16-C17-C18	178.0(3)
C13-C16-C17-C18	-2.0(5)

C16-C17-C18-C11	0.7(5)
C12-C11-C18-C17	1.9(5)
C2-C11-C18-C17	179.3(3)
C2-C3-C20-C23	-129.3(4)
C4-C3-C20-C23	50.3(5)
C2-C3-C20-C21	50.3(6)
C4-C3-C20-C21	-130.1(4)
C23-C20-C21-C22	1.3(12)
C3-C20-C21-C22	-178.4(11)
C23-C20-C21-S1'	-1.1(5)
C3-C20-C21-S1'	179.2(4)
C22'-S1'-C21-C20	3.6(11)
C20-C21-C22-S1	-0.8(18)
C23-S1-C22-C21	0.1(15)
C21-S1'-C22'-C23	-5.1(18)
S1'-C22'-C23-C20	5(2)
C21-C20-C23-C22'	-2.8(14)
C3-C20-C23-C22'	176.8(13)
C21-C20-C23-S1	-1.2(4)
C3-C20-C23-S1	178.4(3)
C22-S1-C23-C20	0.6(9)

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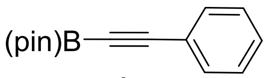
^{1}H NMR and ^{13}C NMR spectra



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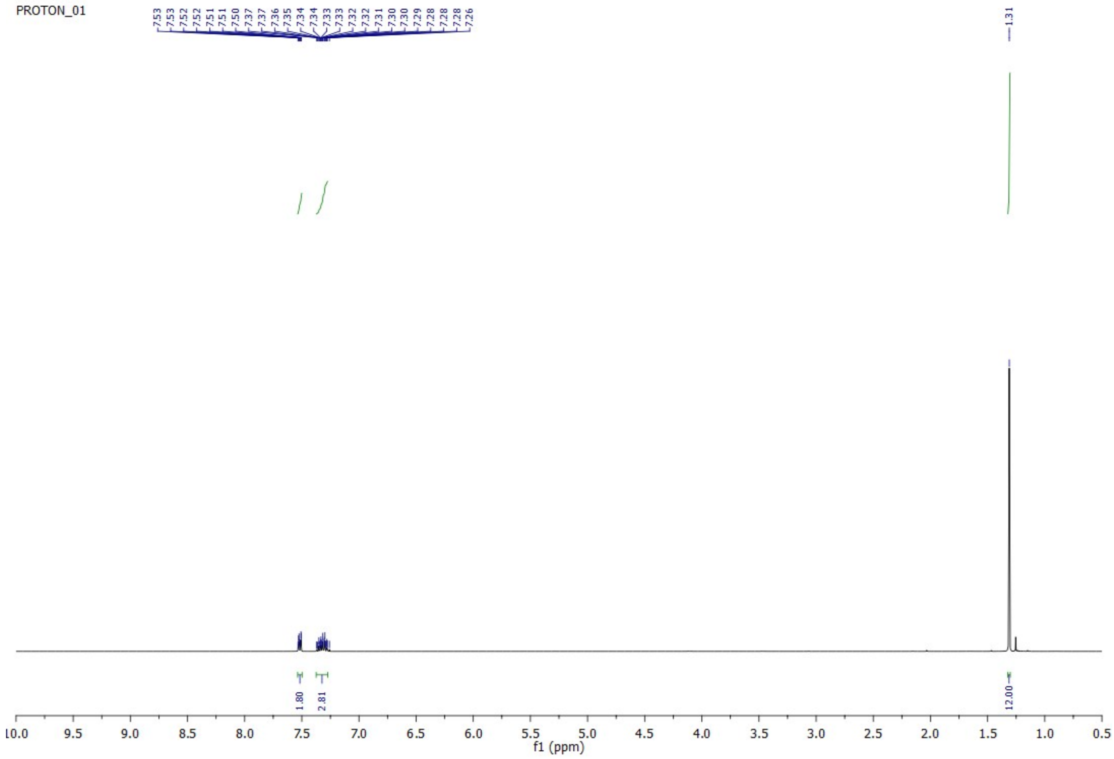
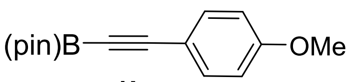
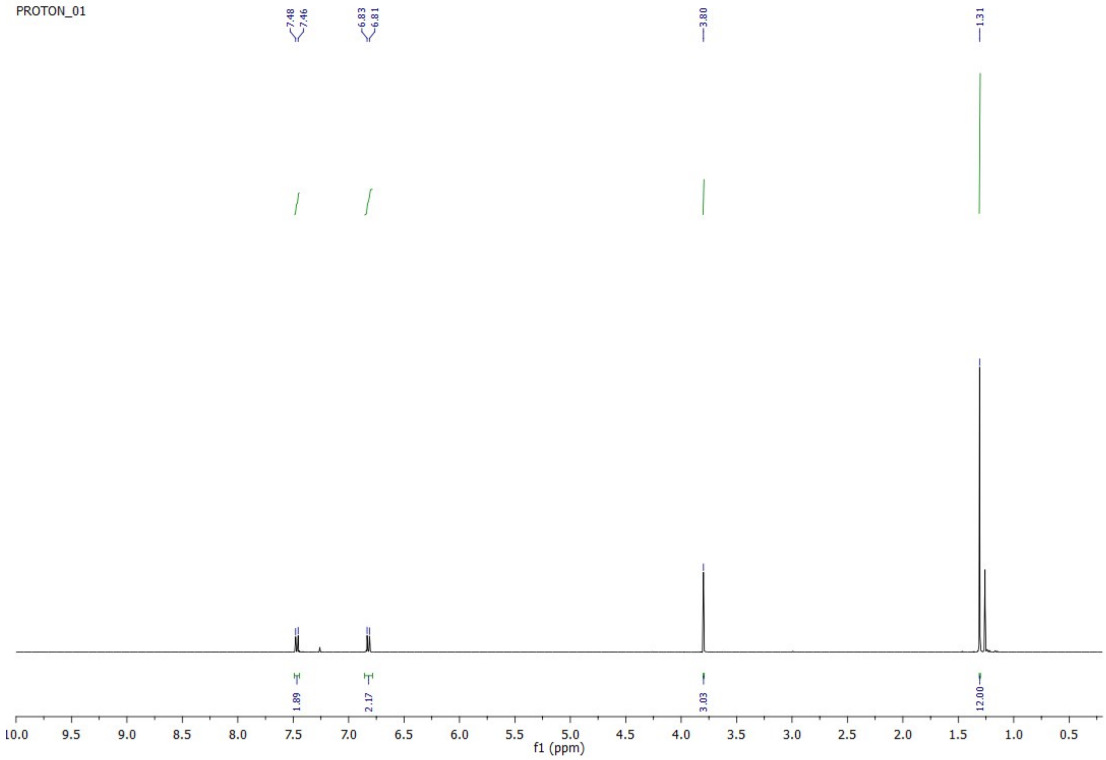




1b



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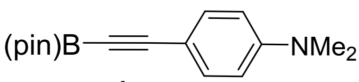
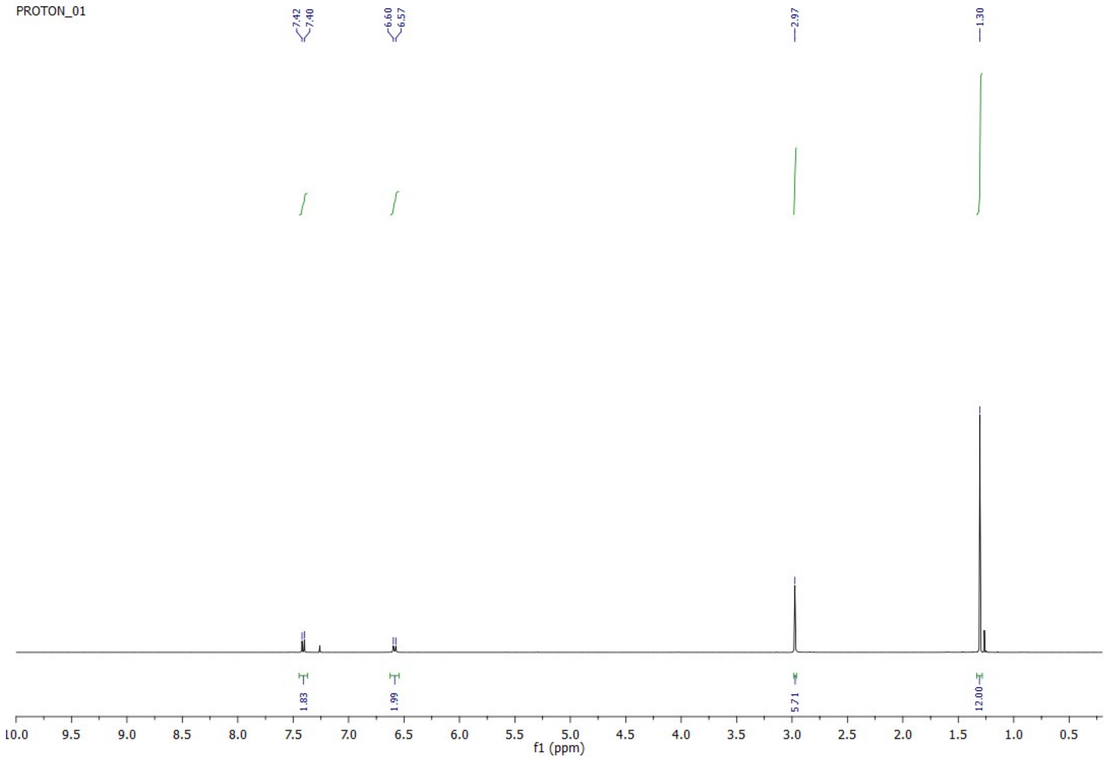
6.83
6.81
3.80
1.31
1.89
2.17
3.03
12.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


(pin)B
NMe2

1c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1.83
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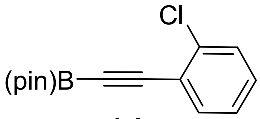
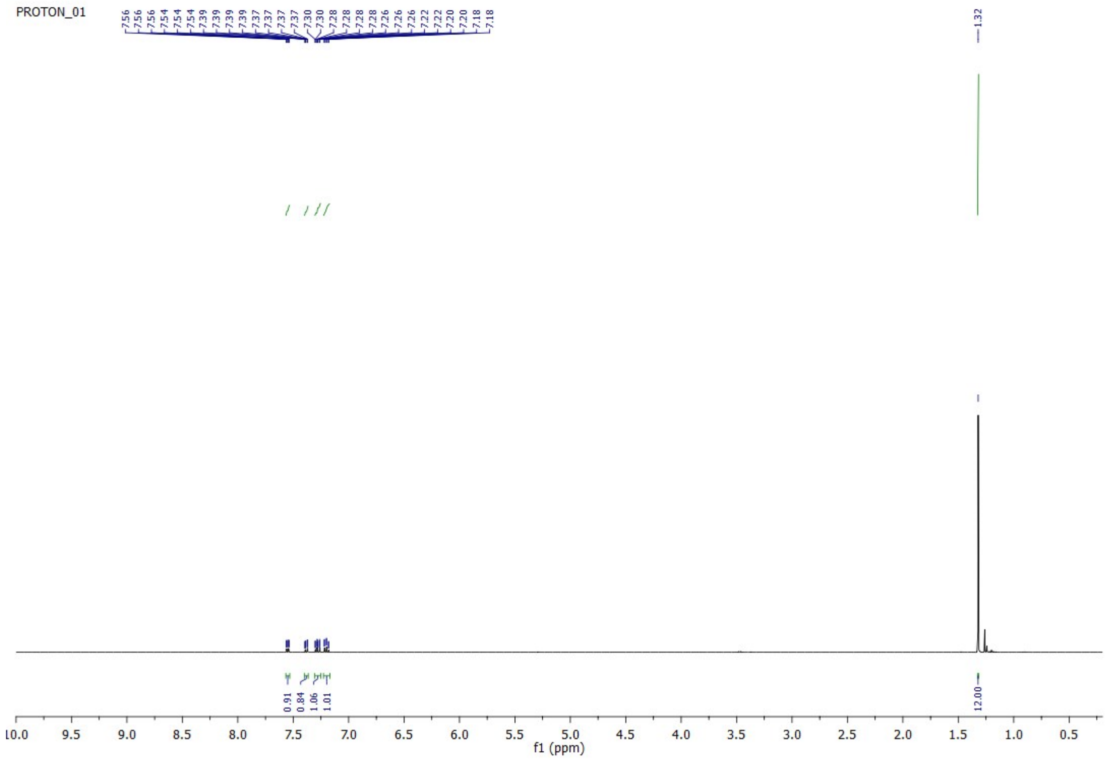
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



Cl
(pin)B

1d



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7.54
7.54
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7.39
7.39
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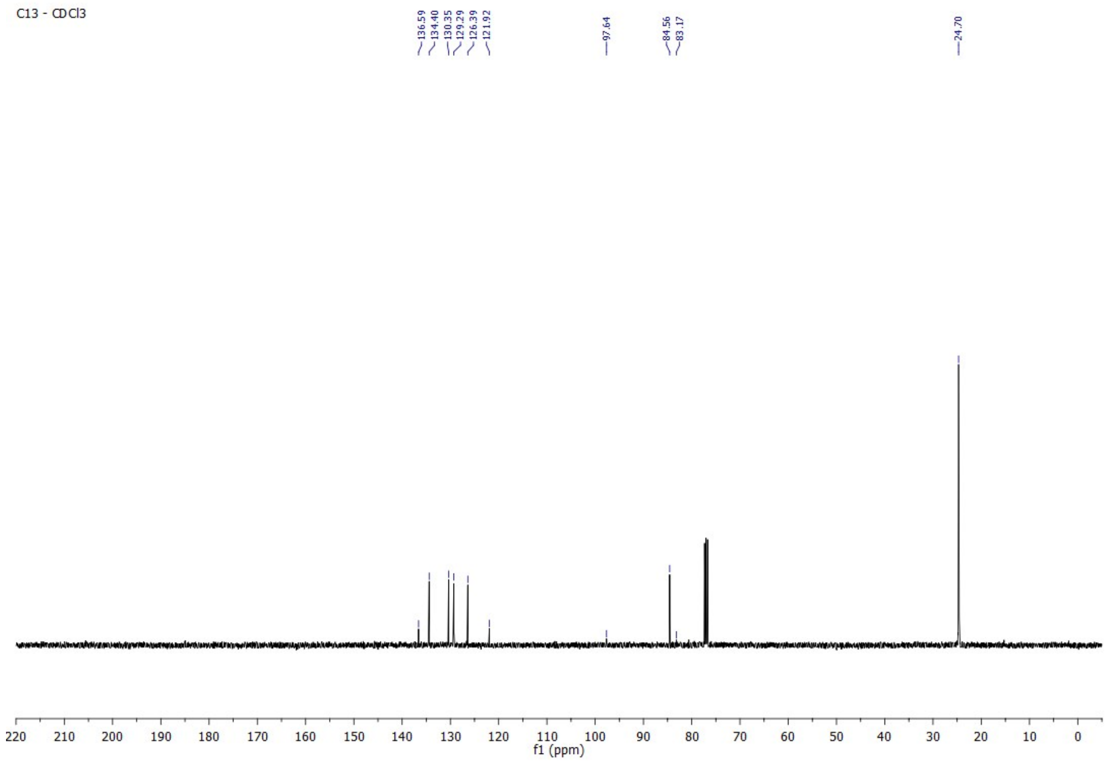
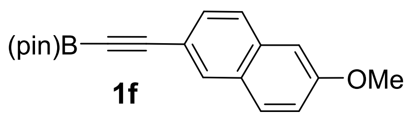
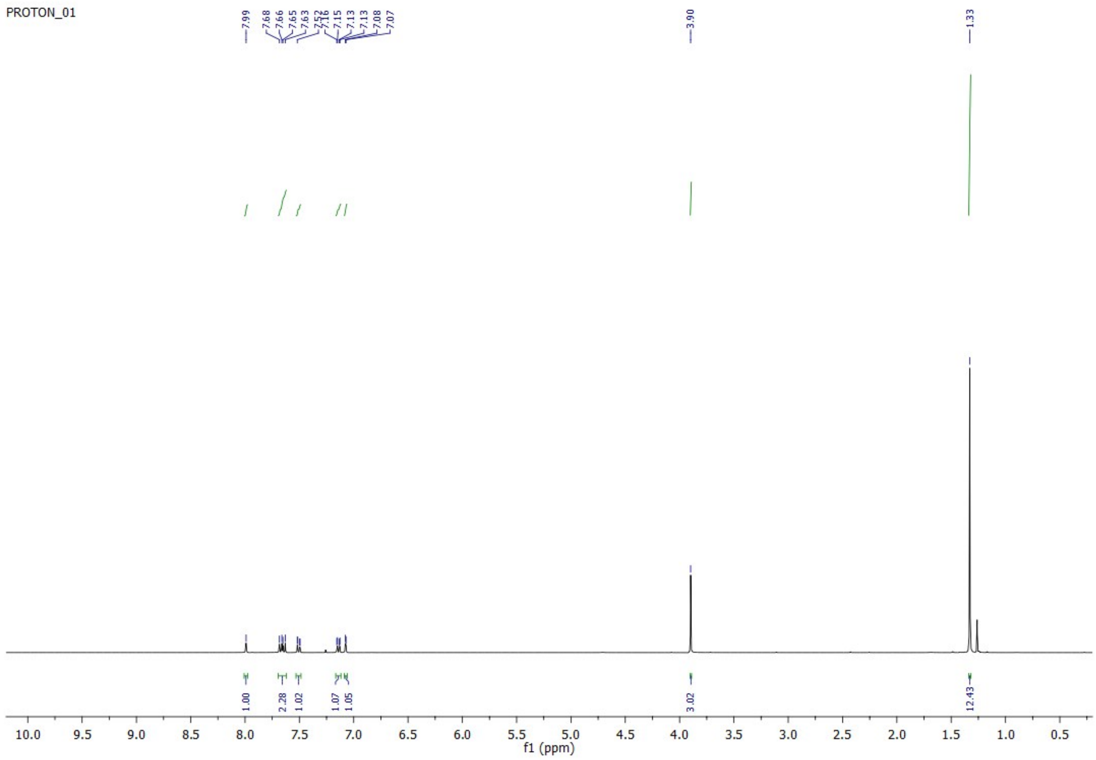
7.37
7.37
7.37
7.30
7.30
7.28
7.28
7.28
7.26
7.26
7.26
7.22
7.22
7.20
7.20
7.18
7.18
1.32
0.91
0.84
1.06
1.01
12.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



C13 - CDCl3
136.59
134.40
130.35
129.29
126.39
121.92
97.64
84.56
83.17
24.70
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


(pin)B
OMe

1f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7.63
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7.15
7.13
7.13
7.08
7.07
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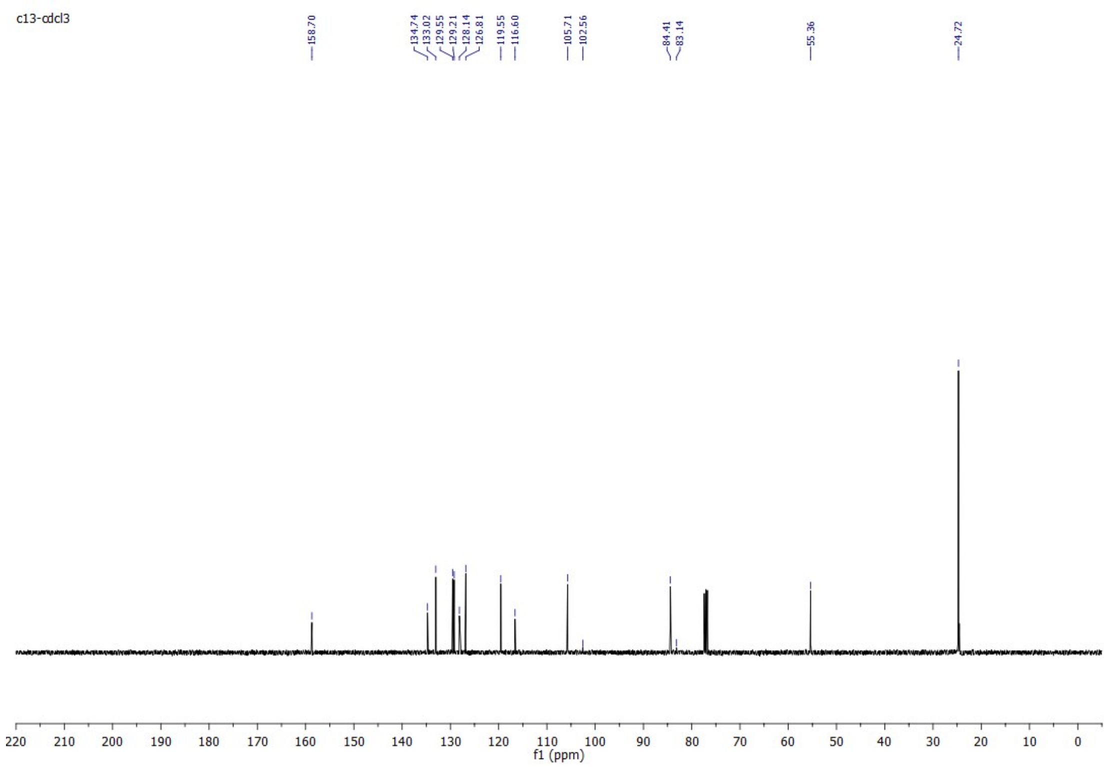
1.33
1.00
2.28
1.02
1.07
1.05
3.02
12.43
f1 (ppm)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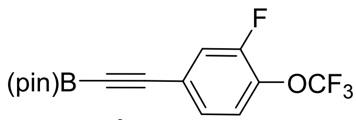
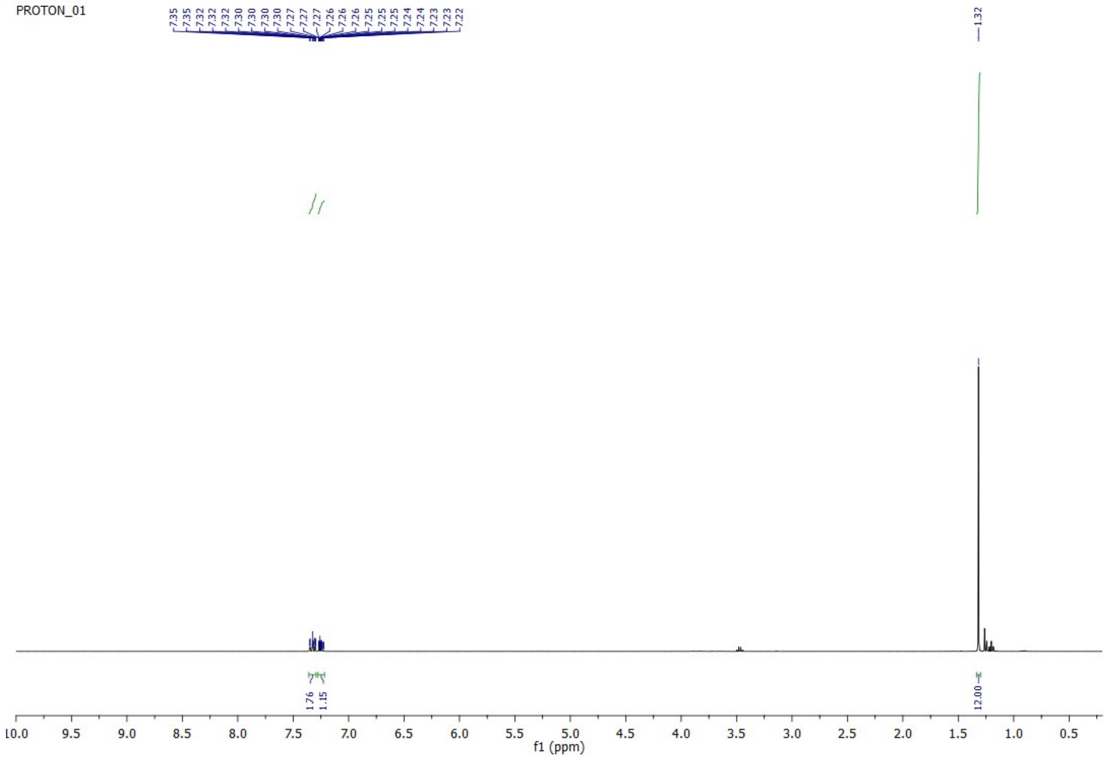
134.74
133.02
129.55
129.21
128.14
126.81
119.55
116.60
105.71
102.56
84.41
83.14
55.36
24.72
f1 (ppm)


F
(pin)B
OCF3

1g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7.35
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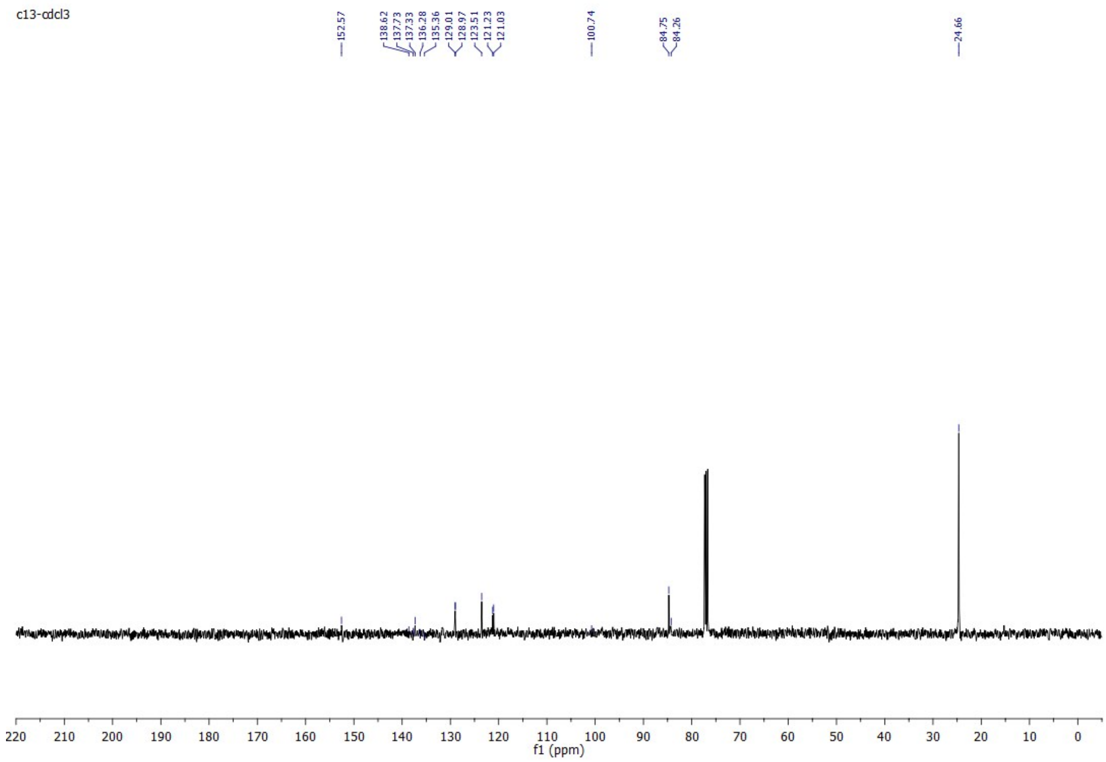
7.32
7.32
7.30
7.30
7.30
7.30
7.27
7.27
7.27
7.26
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
1.32
1.76
1.15
12.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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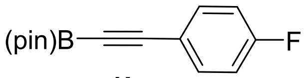
138.62
137.73
137.23
136.28
135.36
129.01
128.97
123.51
121.23
121.03
100.74
84.75
84.26
24.66
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



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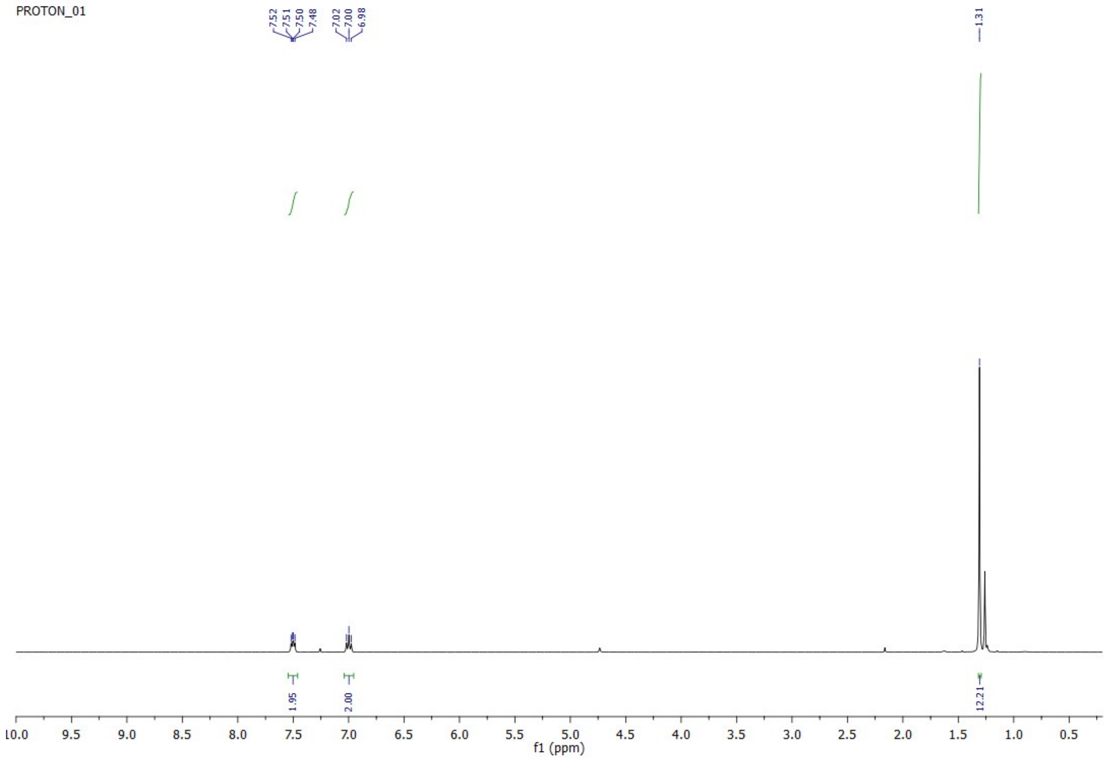
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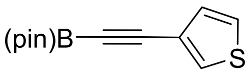
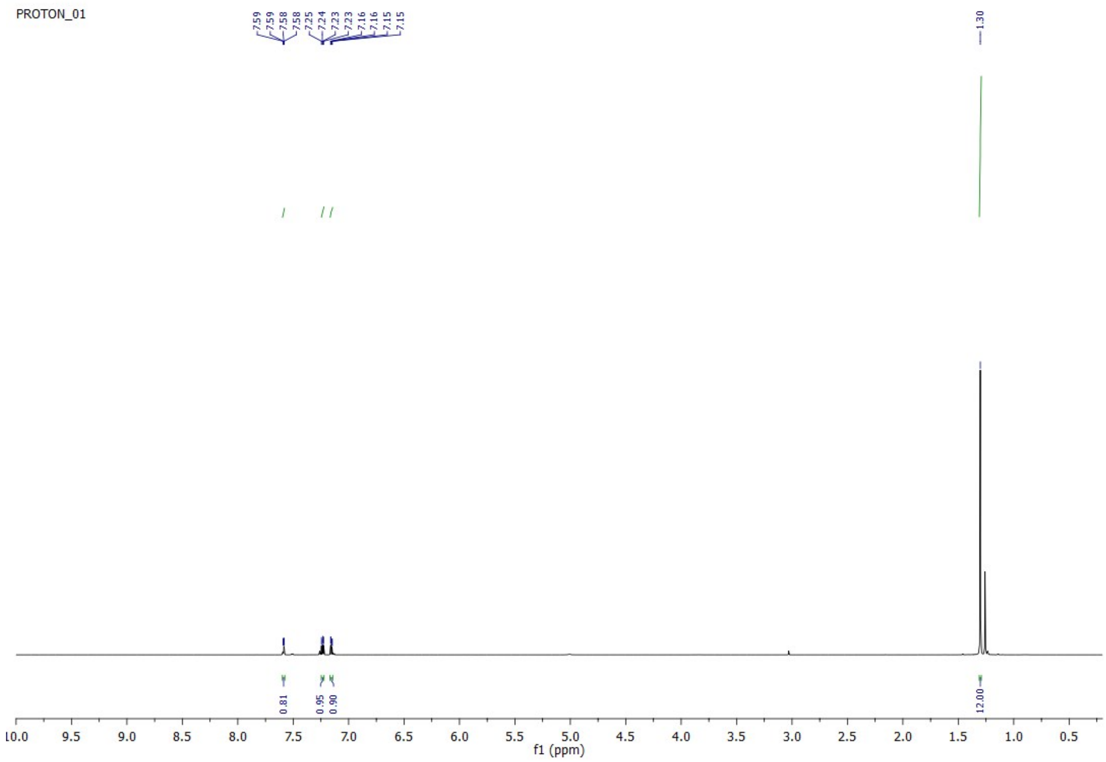
6.98
1.31
1.95
2.00
12.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



1i



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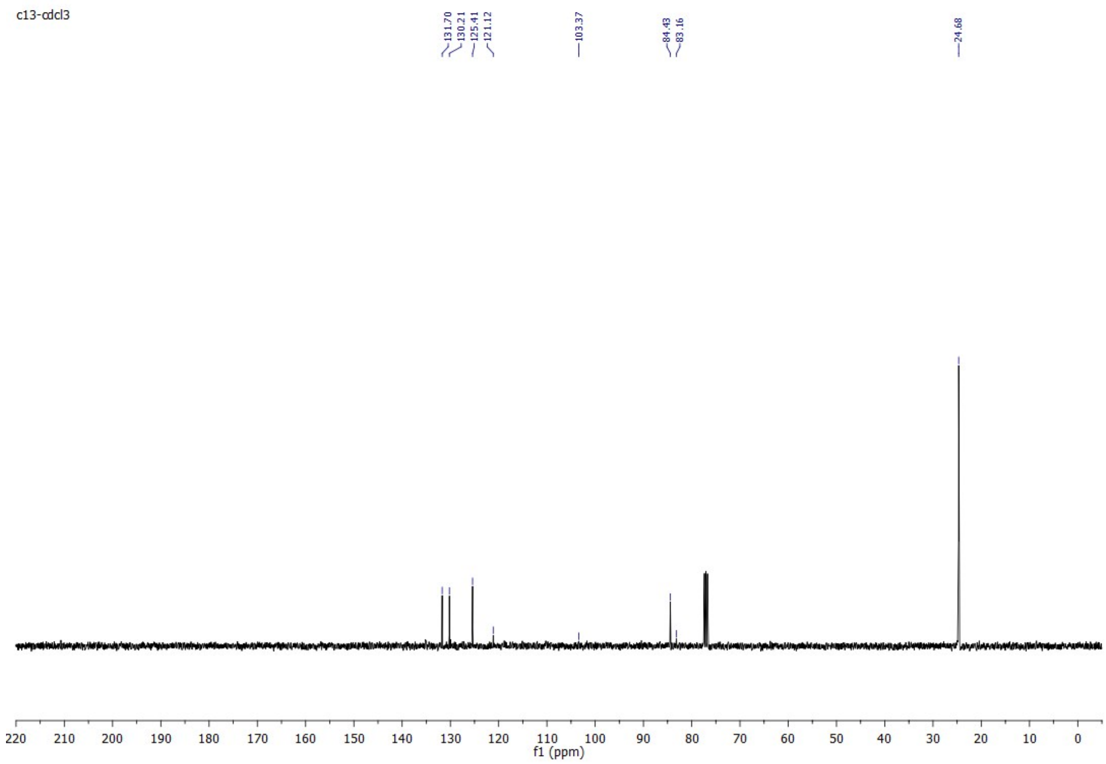
7.58
7.25
7.24
7.23
7.23
7.16
7.16
7.15
7.15
1.30
0.81
0.95
0.90
12.00
f1 (ppm)



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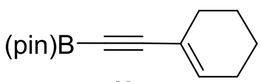
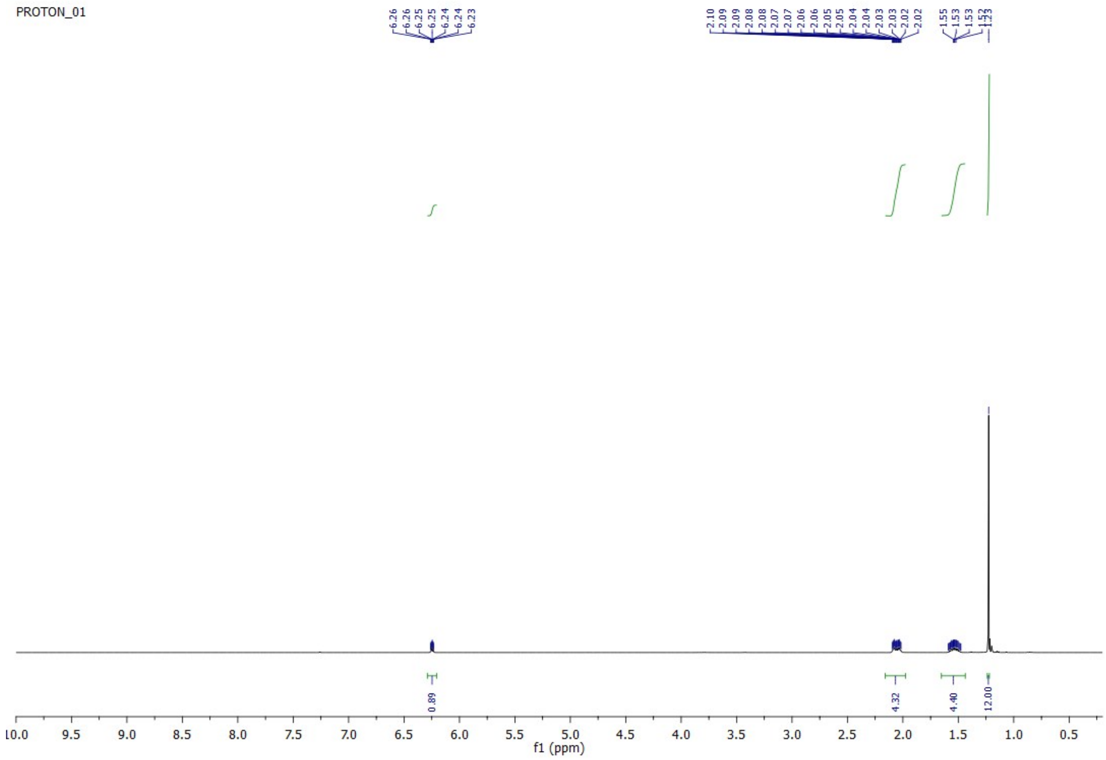
121.12
103.37
84.43
83.16
24.68
f1 (ppm)



1j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6.23
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2.09
2.09
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2.08
2.07
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2.06
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2.05
2.05
2.04
2.04
2.03
2.03
2.02
2.02
1.55
1.53
1.53
1.52
1.23
0.89
4.32
4.40
12.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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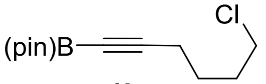
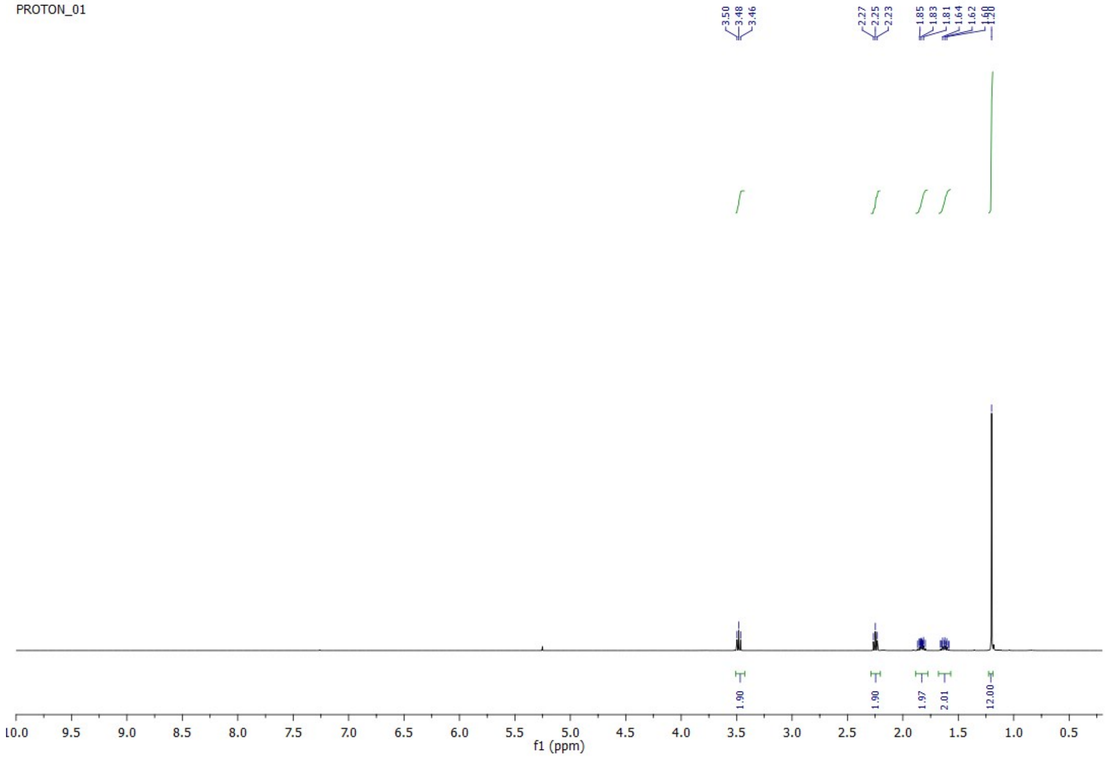
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


(pin)B
Cl

1k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2.23
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1.81
1.64
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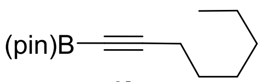
2.01
12.00
f1 (ppm)



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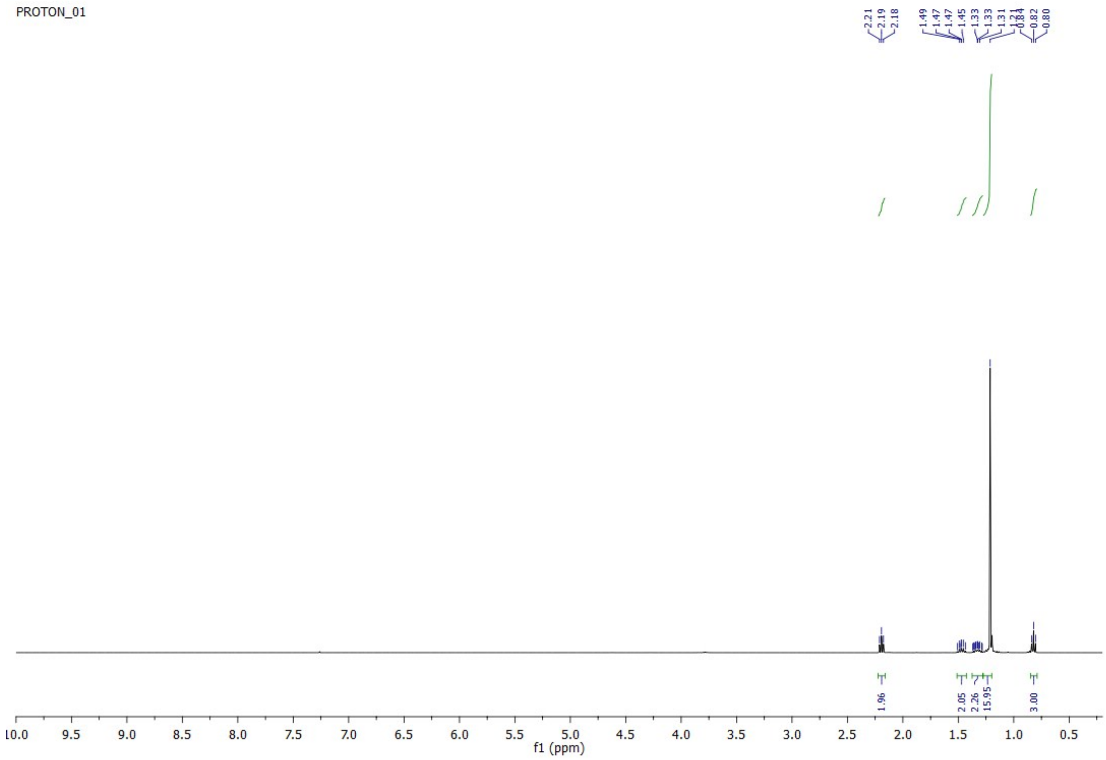
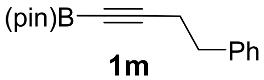
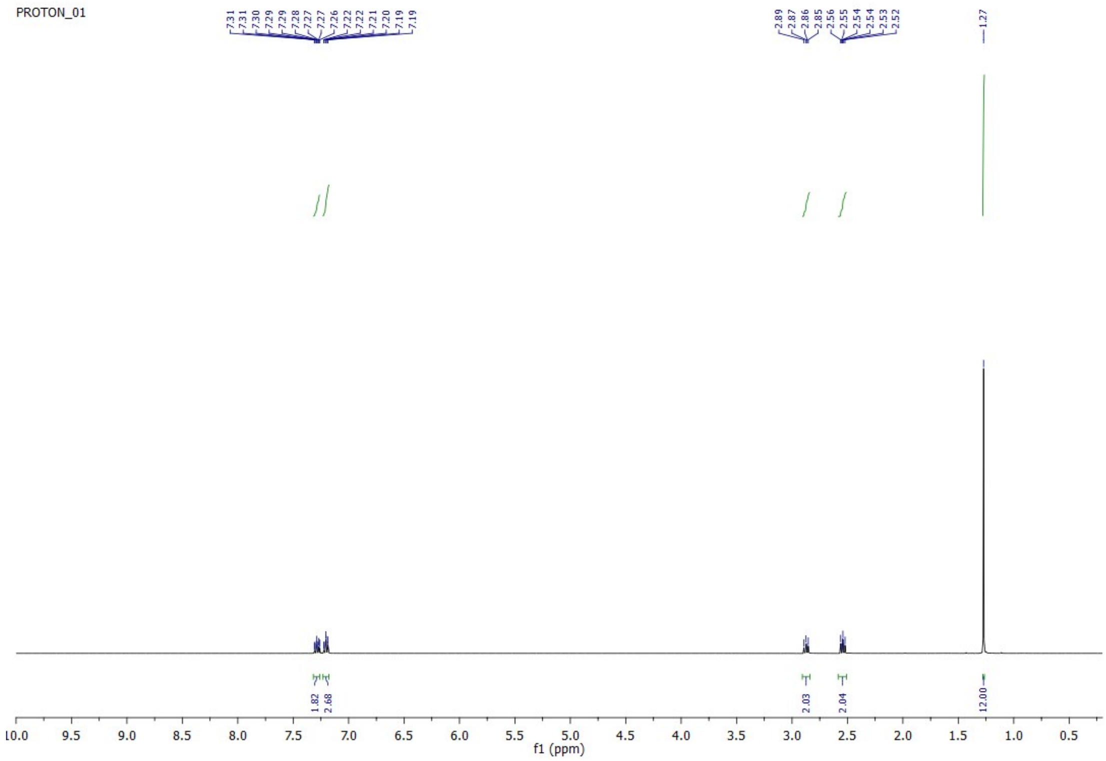



(pin)B
Ph

1m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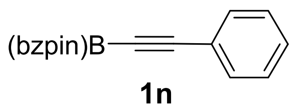
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.26
7.22
7.22
7.21
7.20
7.19
7.19
2.89
2.87
2.86
2.85
2.56
2.55
2.54
2.54
2.53
2.52
1.27
1.82
2.68
2.03
2.04
12.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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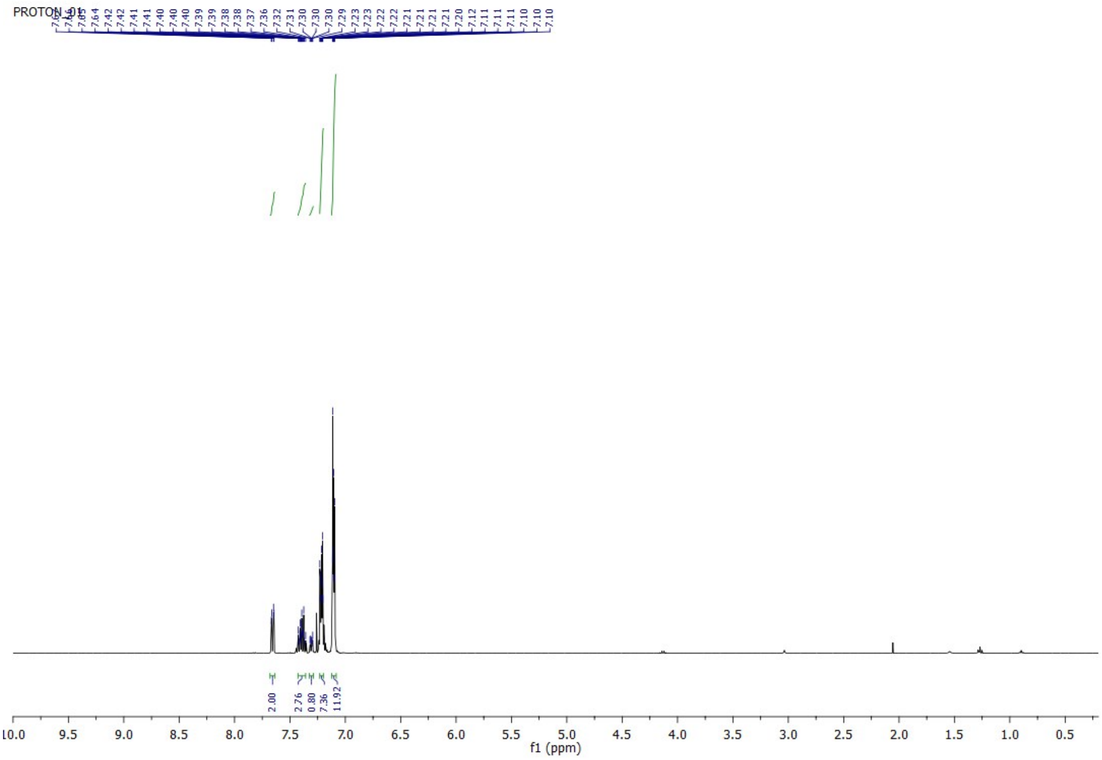
1n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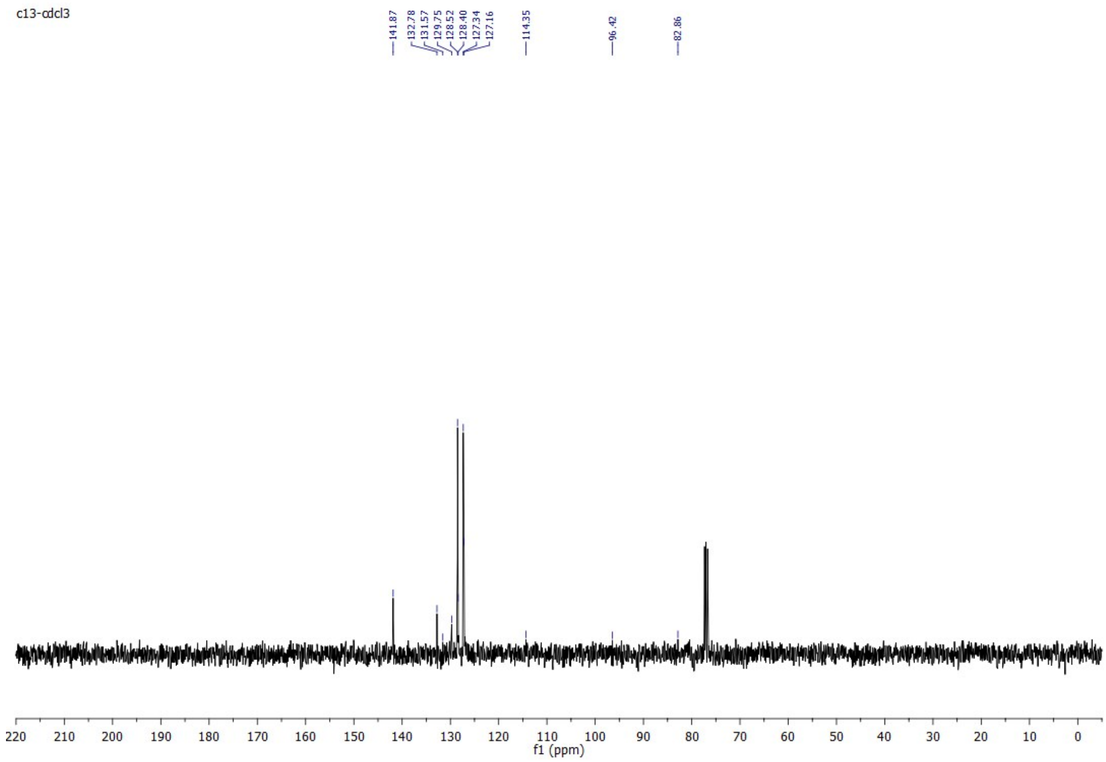
7.36
11.92
f1 (ppm)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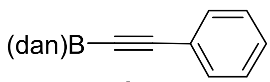
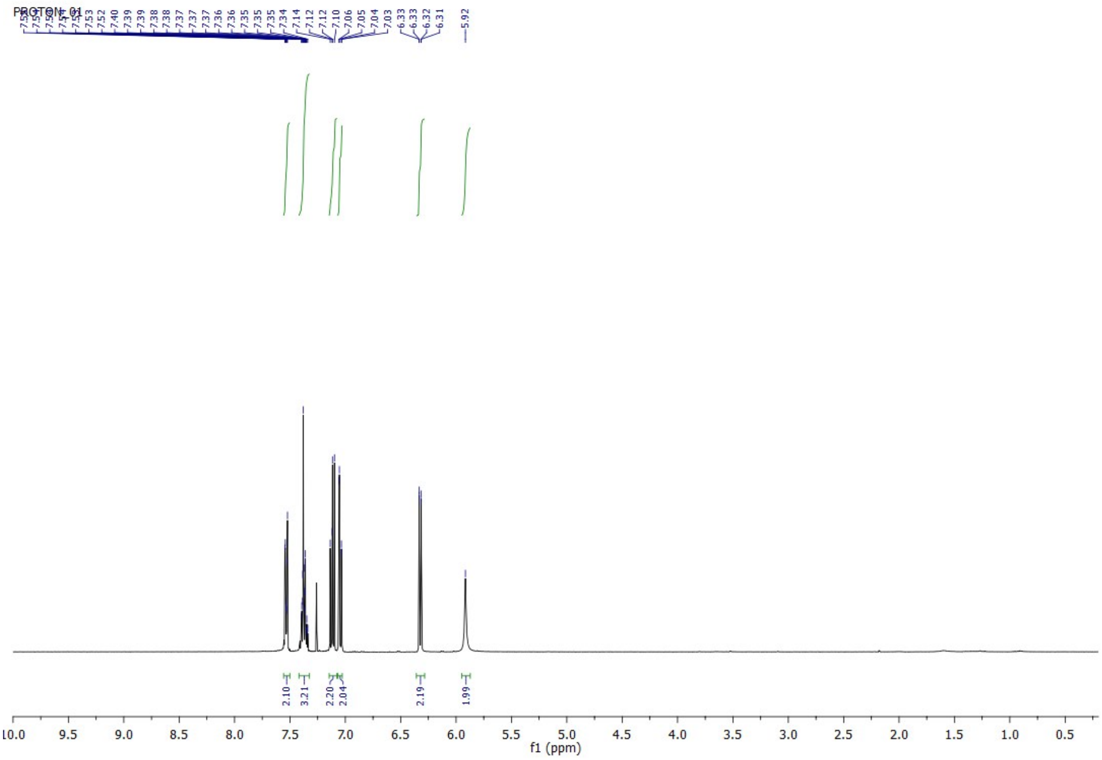
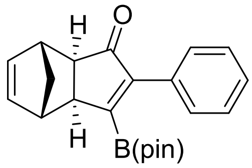
141.87
132.28
131.57
129.75
128.52
128.40
127.34
127.16
114.35
96.42
82.86
f1 (ppm)

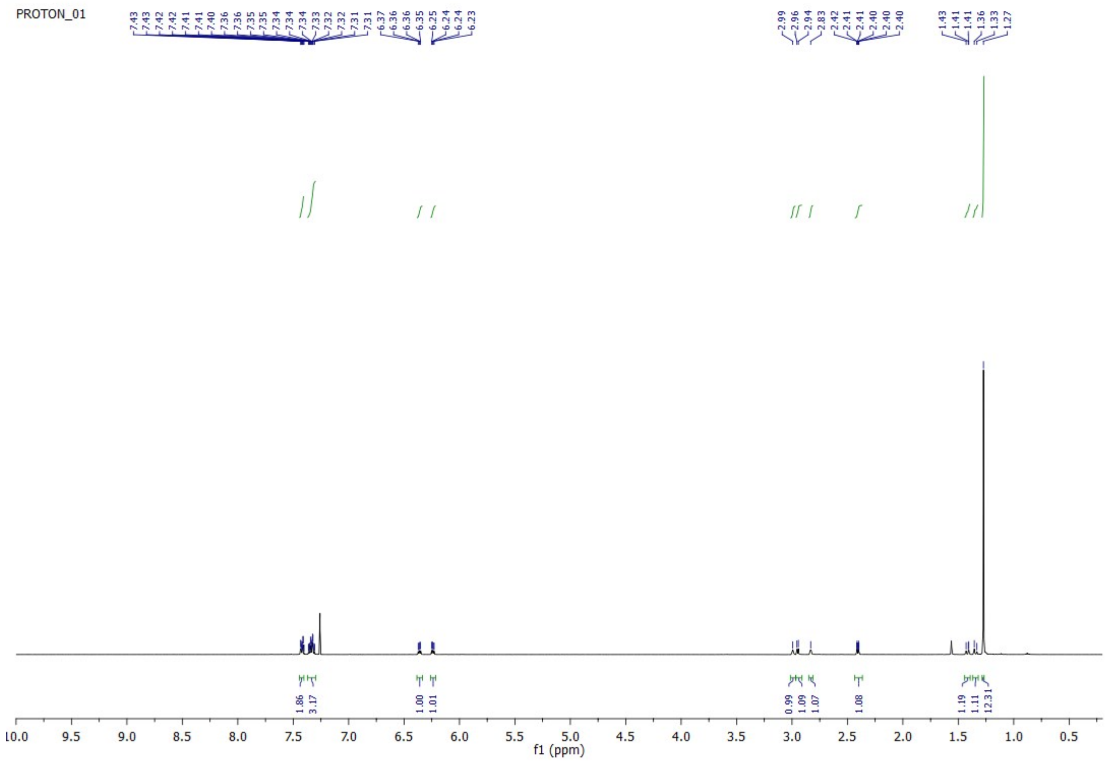


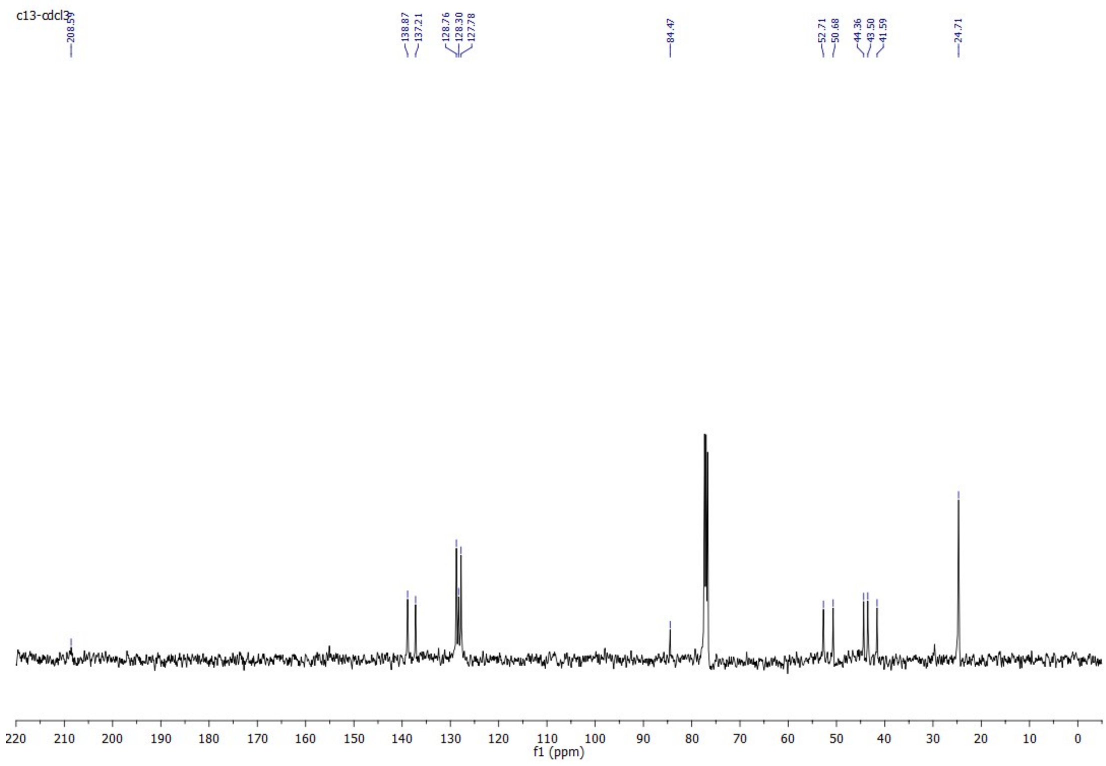
1o

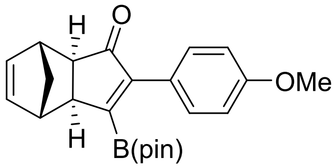




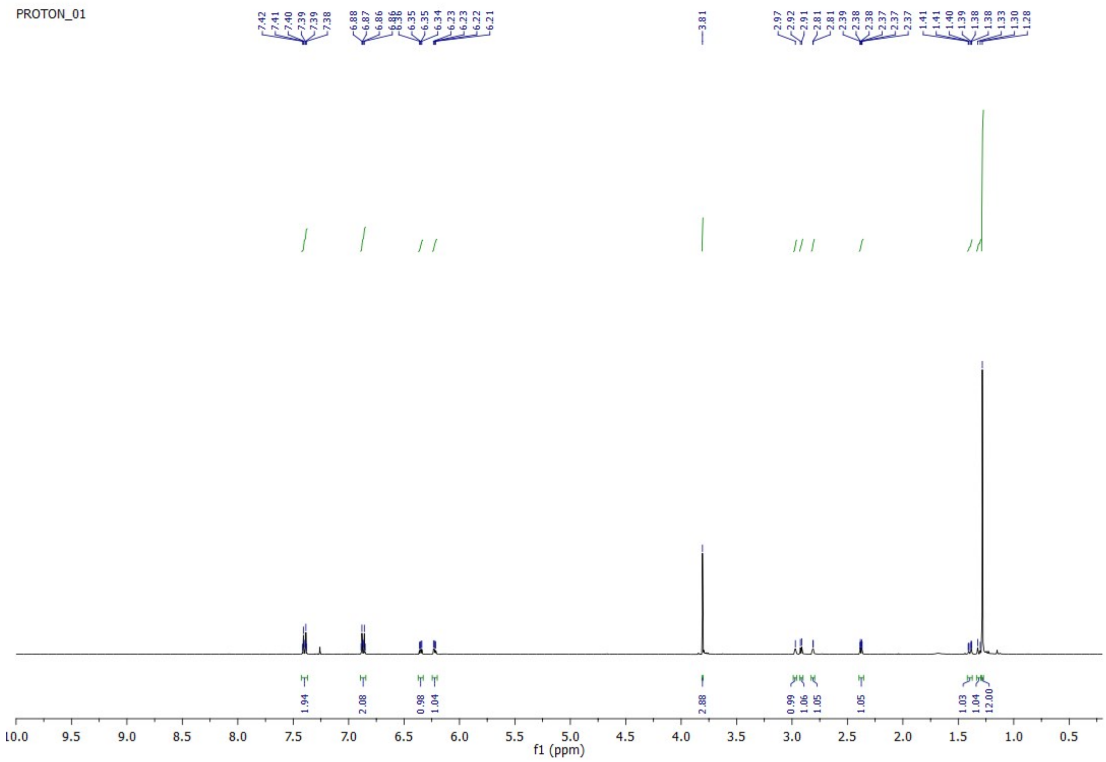
2a

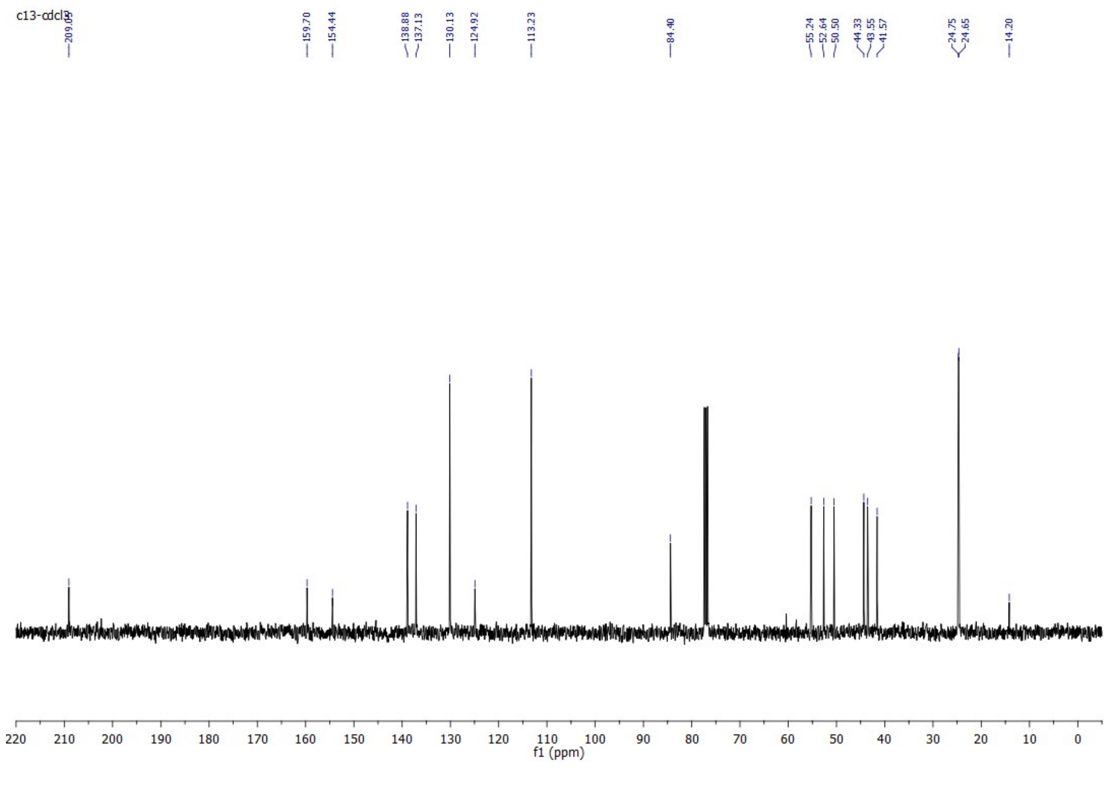

PROTON_01
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.33
7.32
7.32
7.31
7.31
6.37
6.36
6.36
6.35
6.25
6.24
6.24
6.23
2.99
2.96
2.94
2.83
2.42
2.41
2.41
2.40
2.40
2.40
1.43
1.41
1.41
1.36
1.33
1.27
1.86
3.17
1.00
1.01
0.99
1.09
1.07
1.08
1.19
1.11
12.31
f1 (ppm)

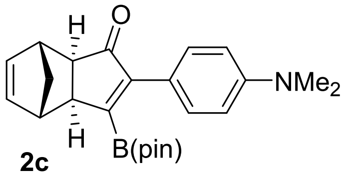

c13-cdcl3
208.59
138.87
137.21
128.76
128.30
127.78
84.47
52.71
50.68
44.36
43.50
41.59
24.71
f1 (ppm)


O
H
H
OMe
B(pin)

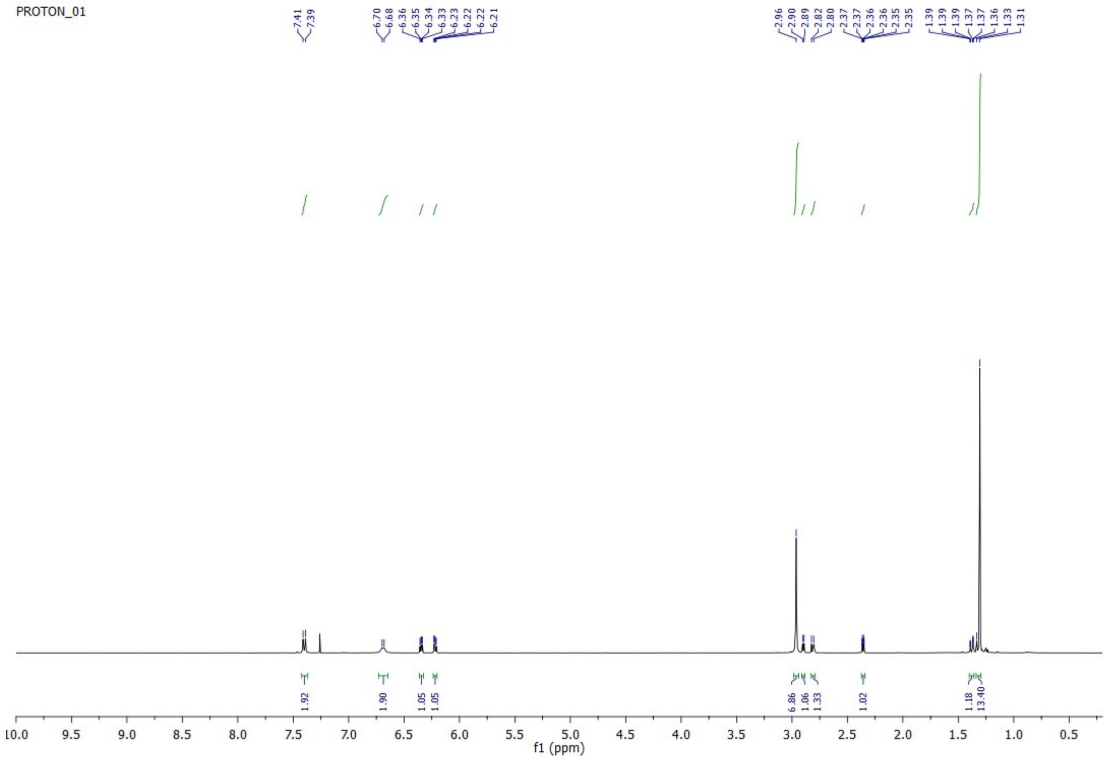
2b

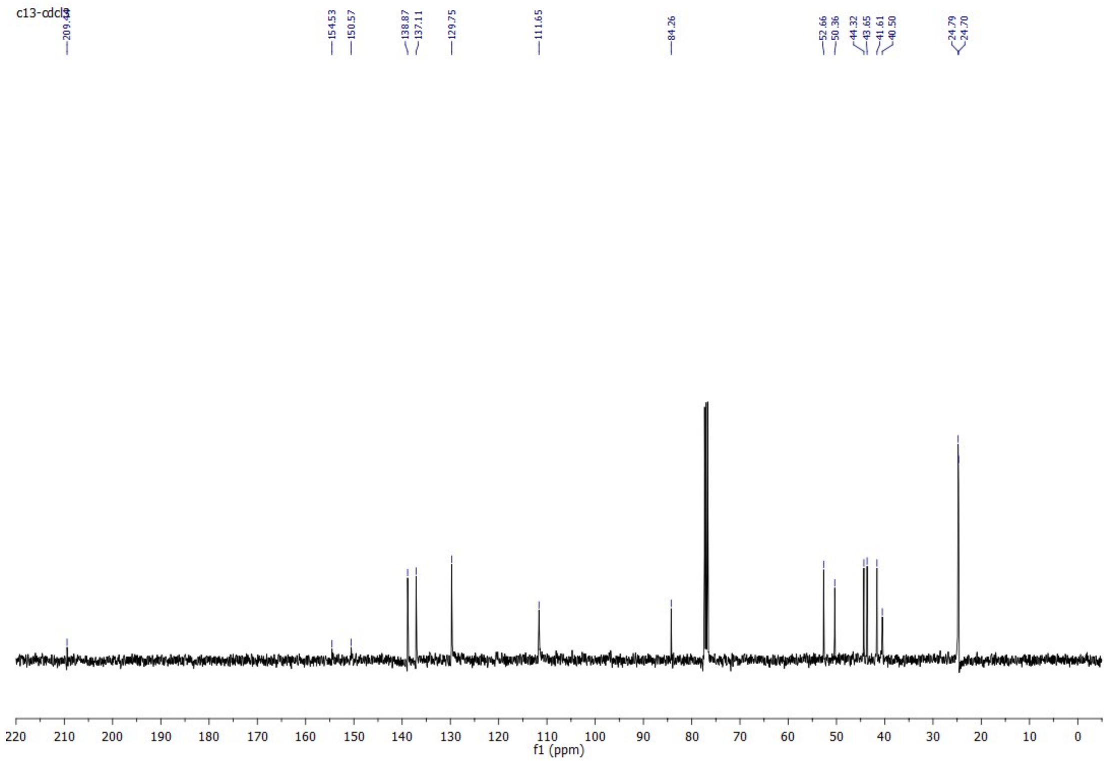

PROTON_01
f1 (ppm)


c13-cdcl3
209.09
159.70
154.44
138.88
137.13
130.13
124.92
113.23
84.40
55.24
52.64
50.50
44.33
43.55
41.57
24.75
24.65
14.20
f1 (ppm)


H
O
NMe2
H
B(pin)

2c


PROTON_01
7.41
7.39
6.70
6.68
6.36
6.35
6.34
6.33
6.23
6.22
6.22
6.21
2.96
2.90
2.89
2.82
2.80
2.37
2.37
2.36
2.36
2.35
2.35
1.39
1.39
1.39
1.37
1.37
1.36
1.33
1.31
1.92
1.90
1.05
1.05
6.86
1.06
1.33
1.02
1.18
13.40
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


c13-cdcl3
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137.11
129.75
111.65
84.26
52.66
50.36
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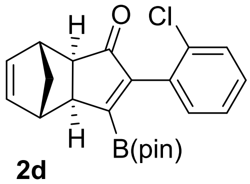
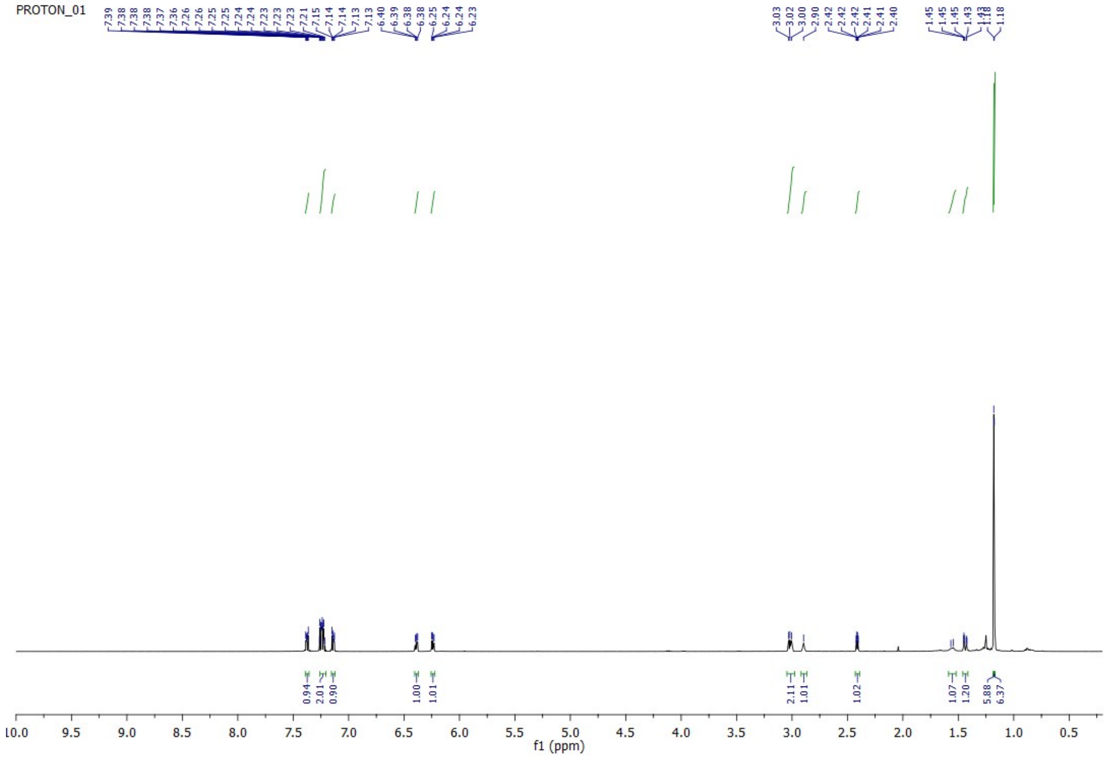
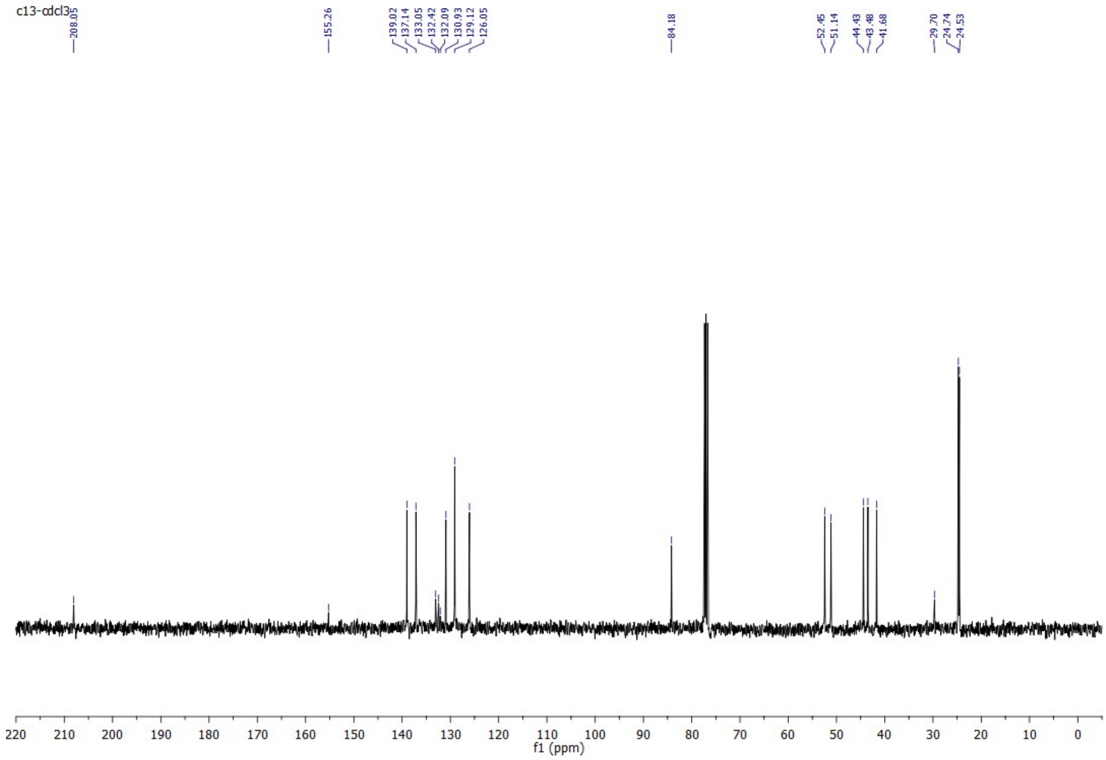
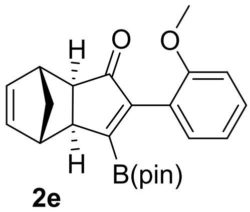
43.65
41.61
40.50
24.79
24.70
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



2d

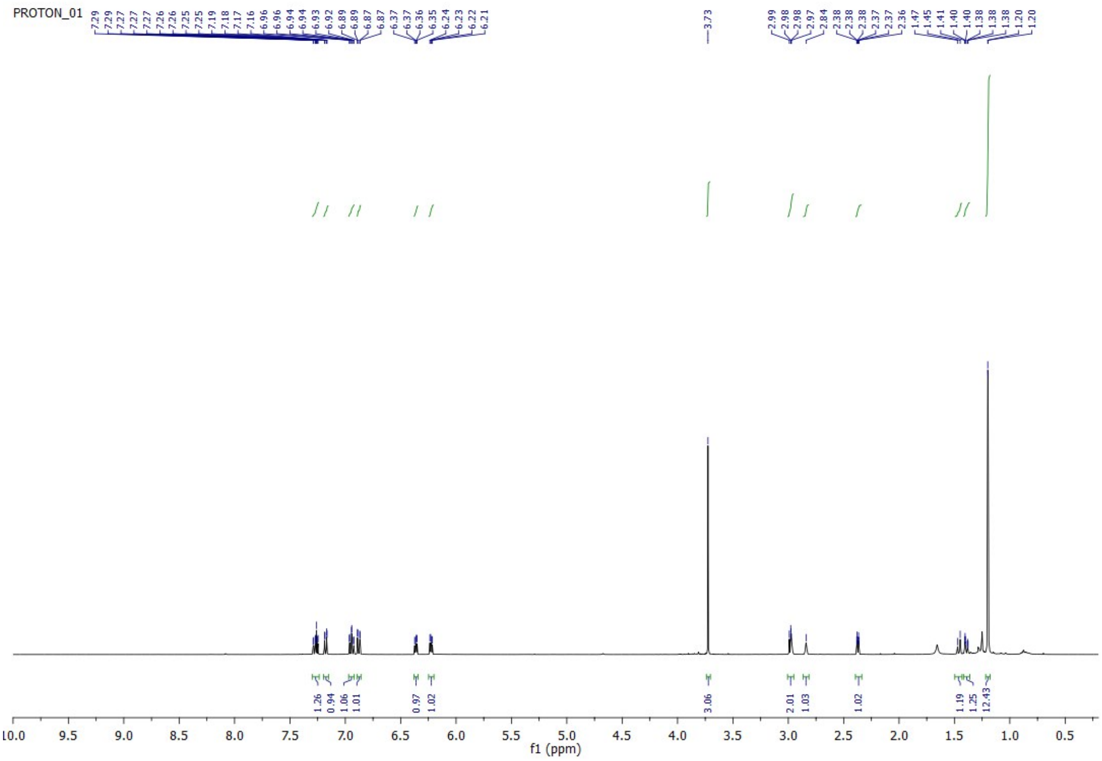




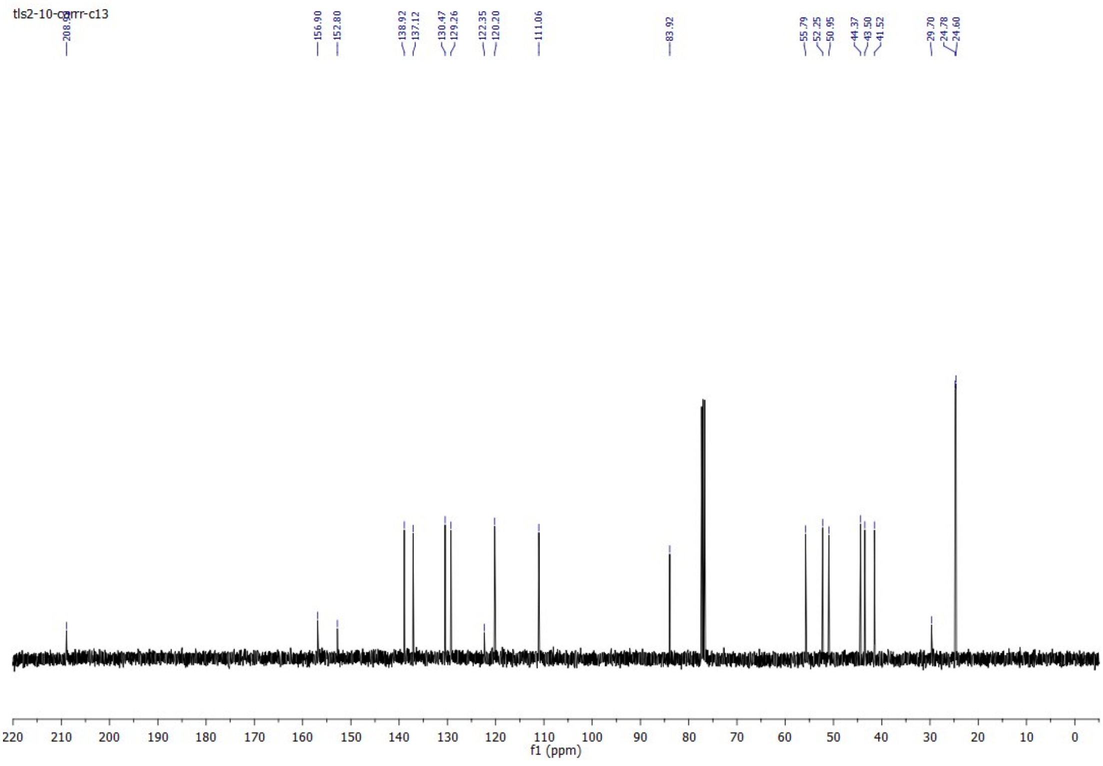


O
O
H
H
B(pin)

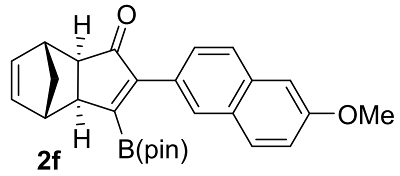
2e

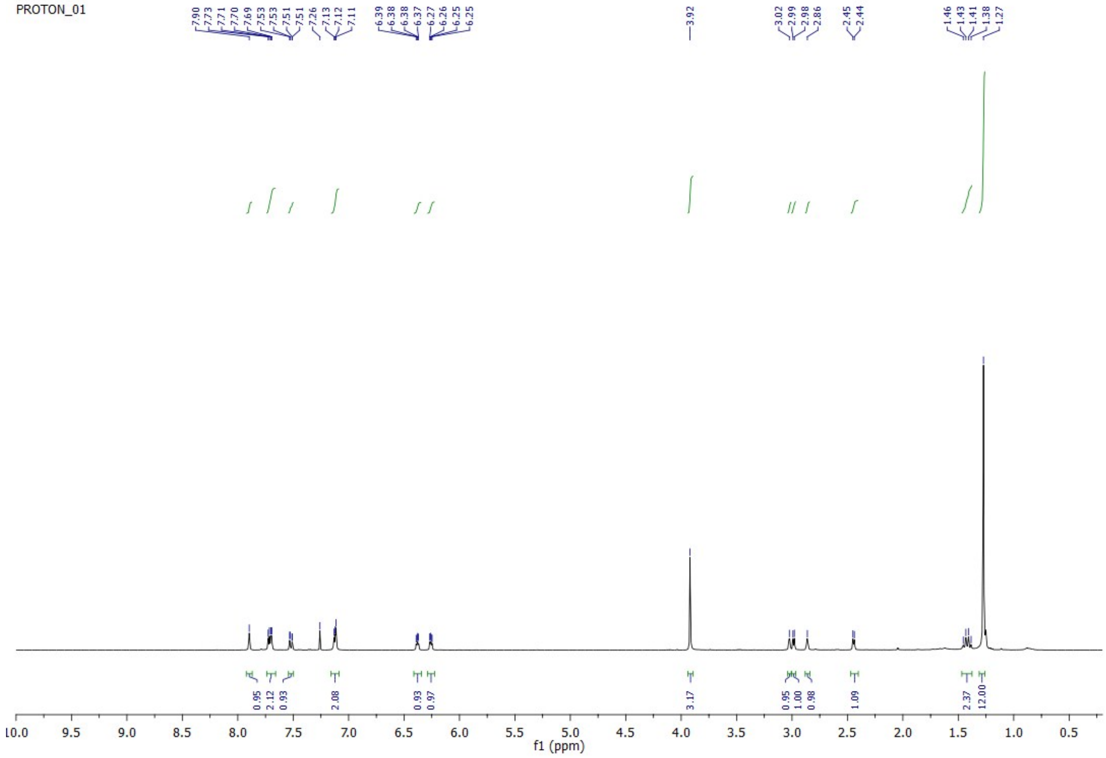


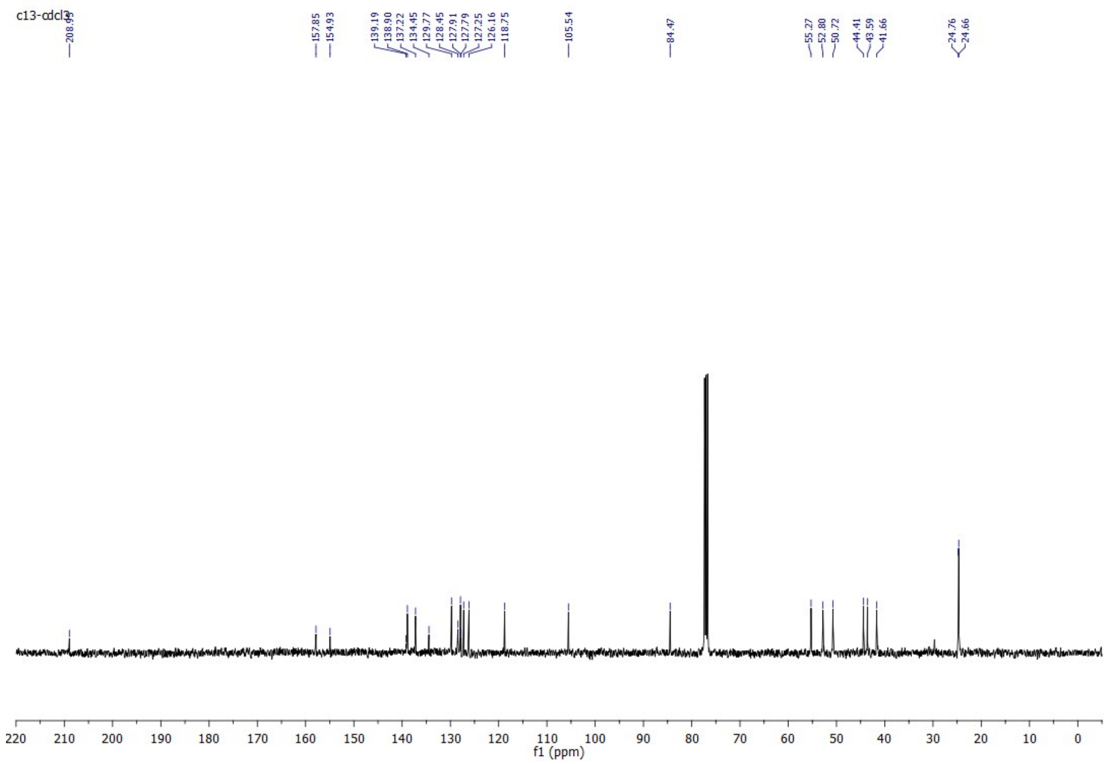
PROTON_01
7.29 7.29 7.27 7.27 7.27 7.26 7.26 7.25 7.25 7.19 7.18 7.17 7.16 6.96 6.96 6.94 6.94 6.93 6.92 6.89 6.89 6.87 6.87 6.37 6.37 6.36 6.35 6.24 6.23 6.22 6.21
3.73
2.99 2.98 2.98 2.97 2.84 2.38 2.38 2.38 2.38 2.37 2.37 2.36 1.47 1.45 1.41 1.40 1.40 1.38 1.38 1.38 1.20
1.26 0.94 1.06 1.01 0.97 1.02 3.06 2.01 1.03 1.02 1.19 1.25 12.43
f1 (ppm)

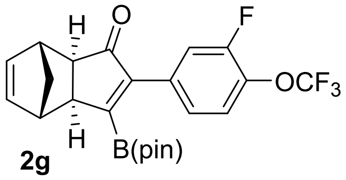


tls2-10-carr-c13
156.90 152.80 138.92 137.12 130.47 129.26 122.35 120.20 111.06 83.92 55.79 52.25 50.95 44.37 43.50 41.52 29.70 24.78 24.60
f1 (ppm)

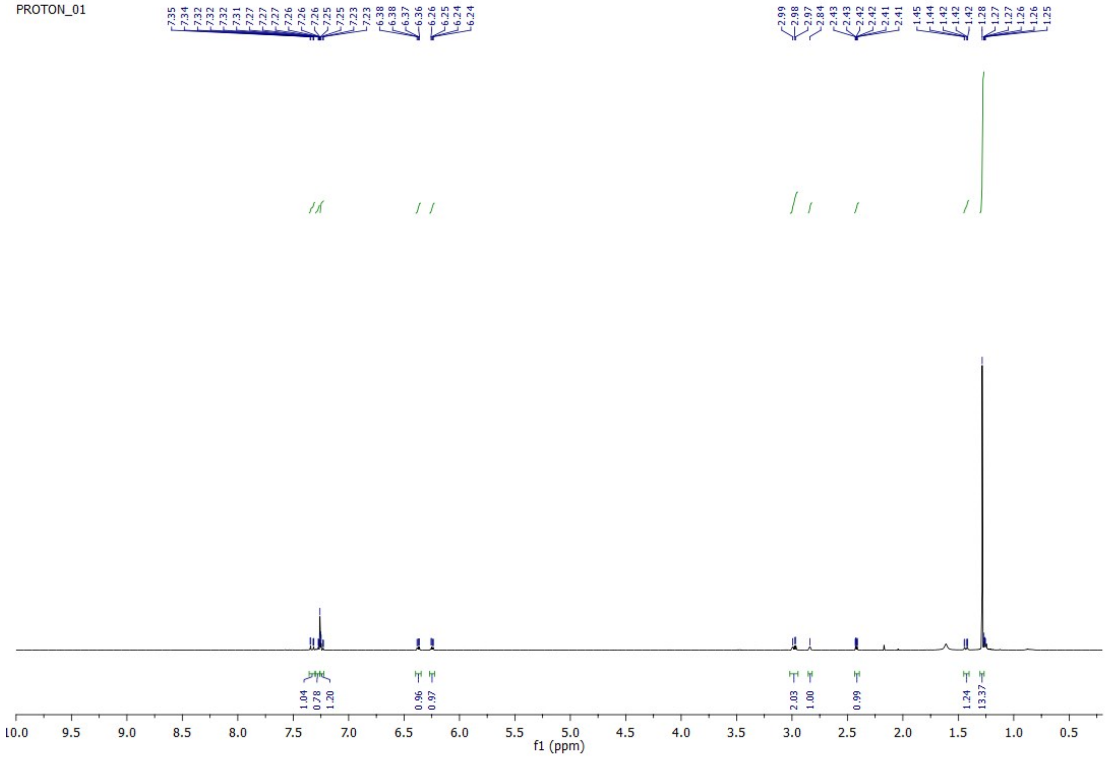


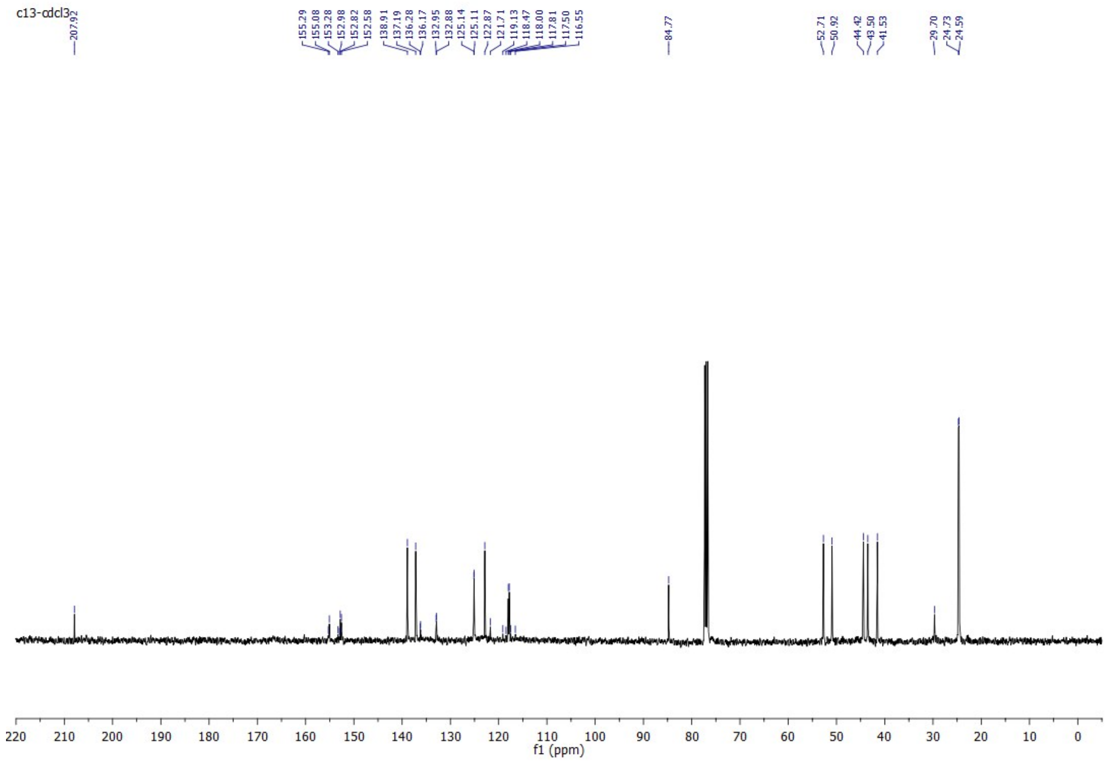


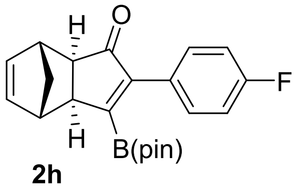



O
H
H
F
OCF3
B(pin)

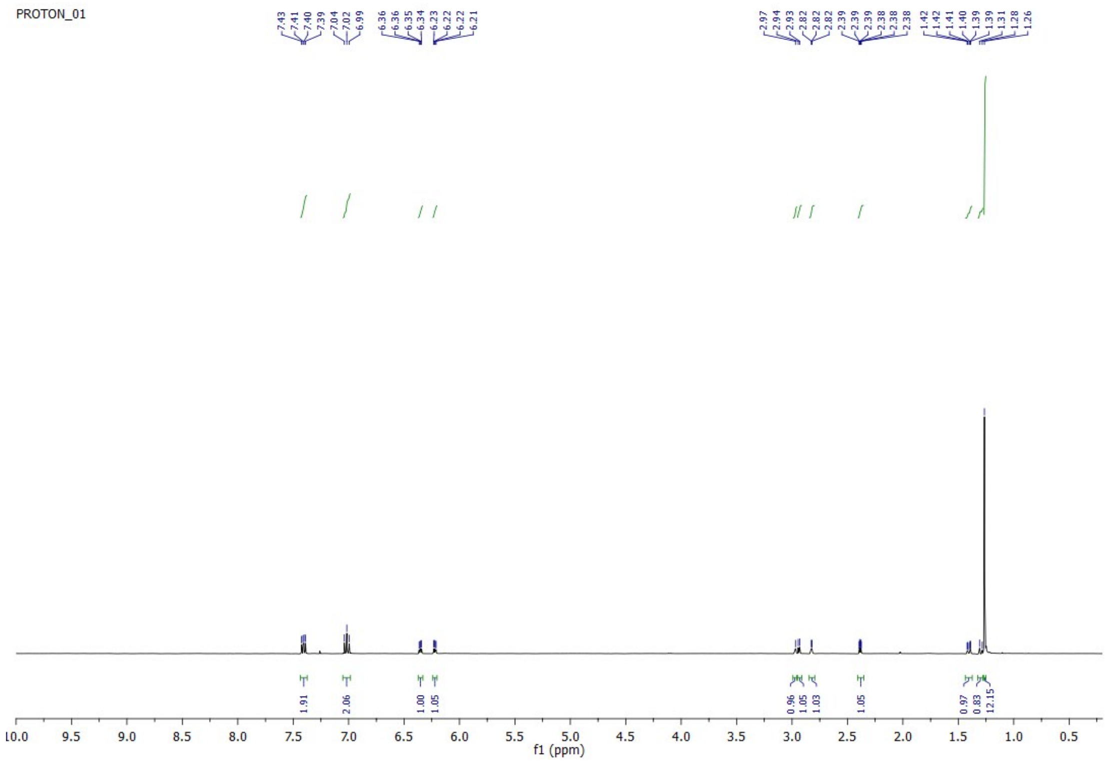
2g

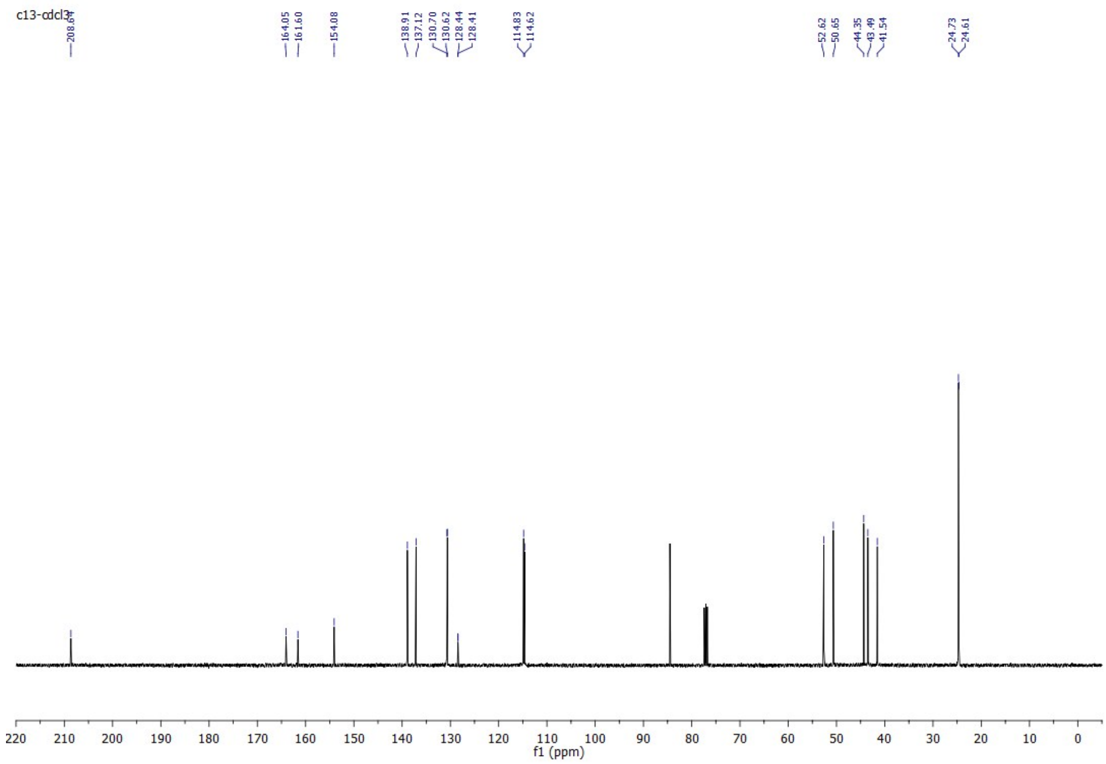

PROTON_01
7.35 7.34 7.32 7.32 7.32 7.31 7.27 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.23 7.23 6.38 6.38 6.37 6.36 6.26 6.25 6.24 6.24
2.99 2.98 2.97 2.84 2.43 2.43 2.42 2.42 2.41 2.41 1.45 1.44 1.42 1.42 1.42 1.28 1.27 1.27 1.26 1.26 1.25
1.04 0.78 1.20 0.96 0.97 2.03 1.00 0.99 1.24 13.37
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


c13-cdcl3
207.92
155.29 155.08 153.28 152.98 152.82 152.58 138.91 137.19 136.28 136.17 132.95 132.88 125.14 125.11 122.87 121.71 119.13 118.47 118.00 117.81 117.50 116.55
84.77
52.71 50.92 44.42 43.50 41.53 29.70 24.73 24.59
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



2h


PROTON_01
7.43
7.41
7.40
7.39
7.04
7.02
6.99
6.36
6.36
6.35
6.34
6.23
6.22
6.22
6.21
2.97
2.94
2.93
2.82
2.82
2.82
2.39
2.39
2.39
2.38
2.38
2.38
1.42
1.42
1.41
1.40
1.39
1.39
1.31
1.28
1.26
1.91
2.06
1.00
1.05
0.96
1.05
1.03
1.05
0.97
0.83
12.15
f1 (ppm)


c13-cdcl3
208.64
164.05
161.60
154.08
138.91
137.12
130.70
130.62
128.44
128.41
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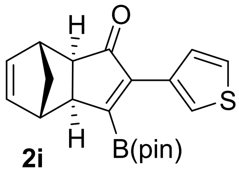
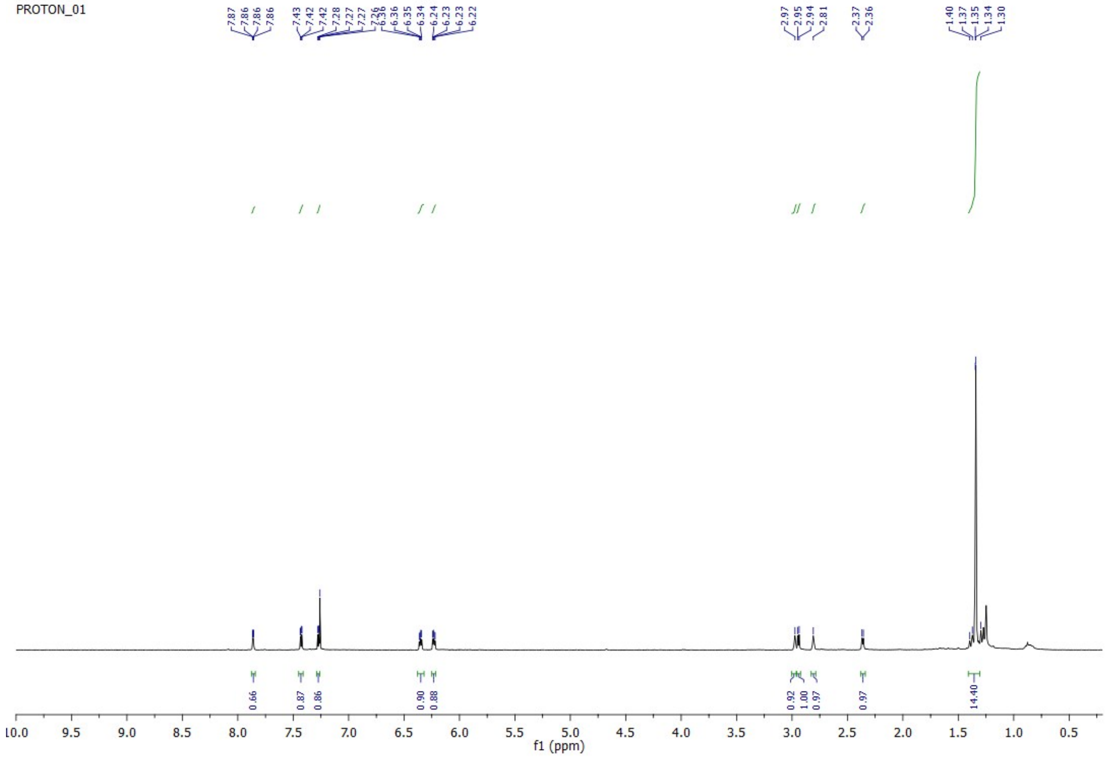
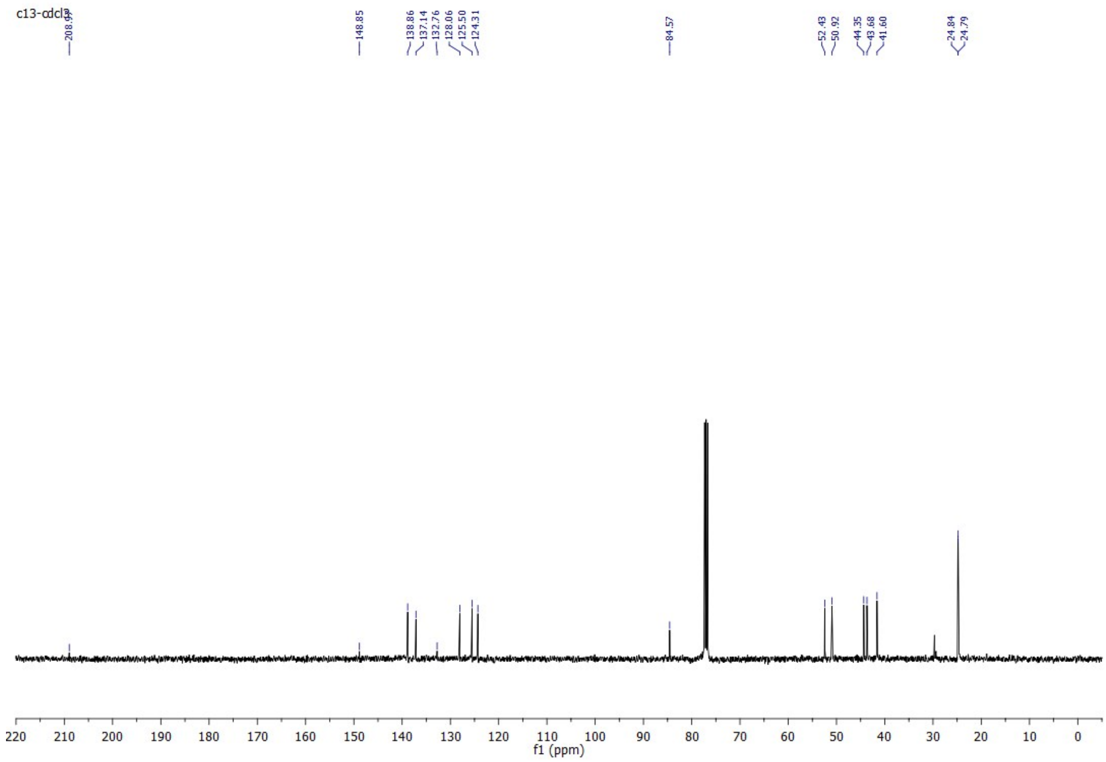
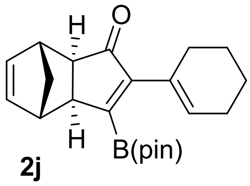
24.73
24.61
f1 (ppm)



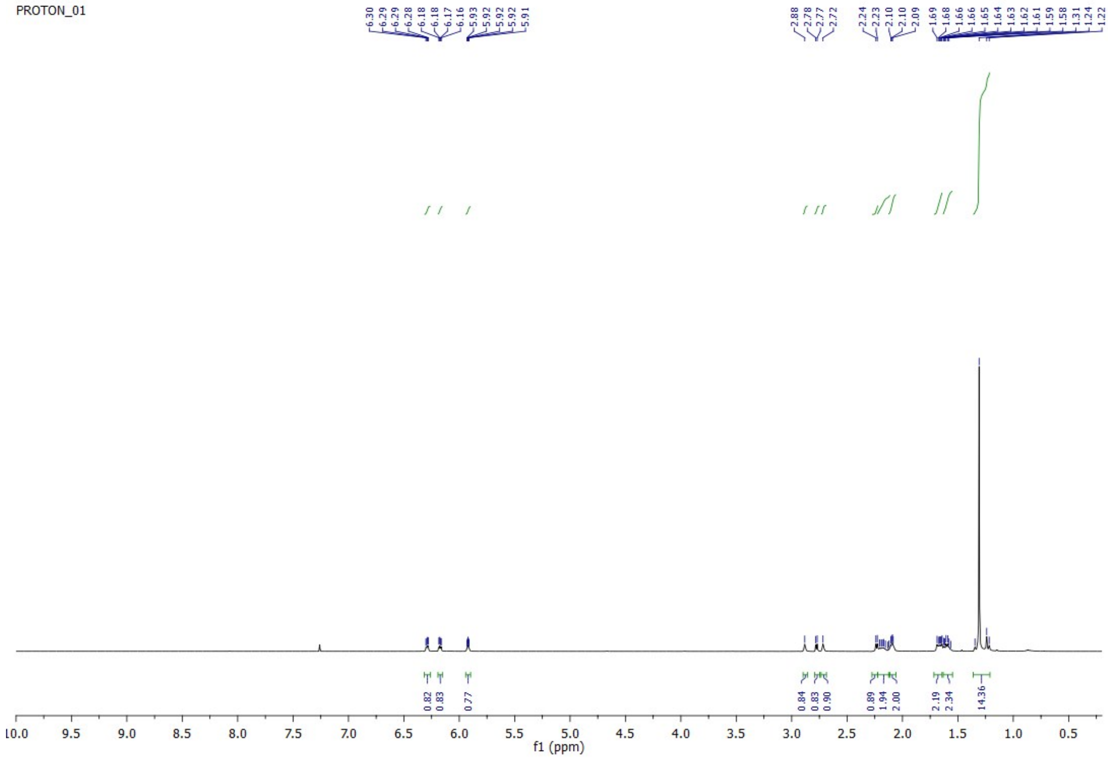
2i






O
H
H
B(pin)

2j


PROTON_01
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6.29
6.28
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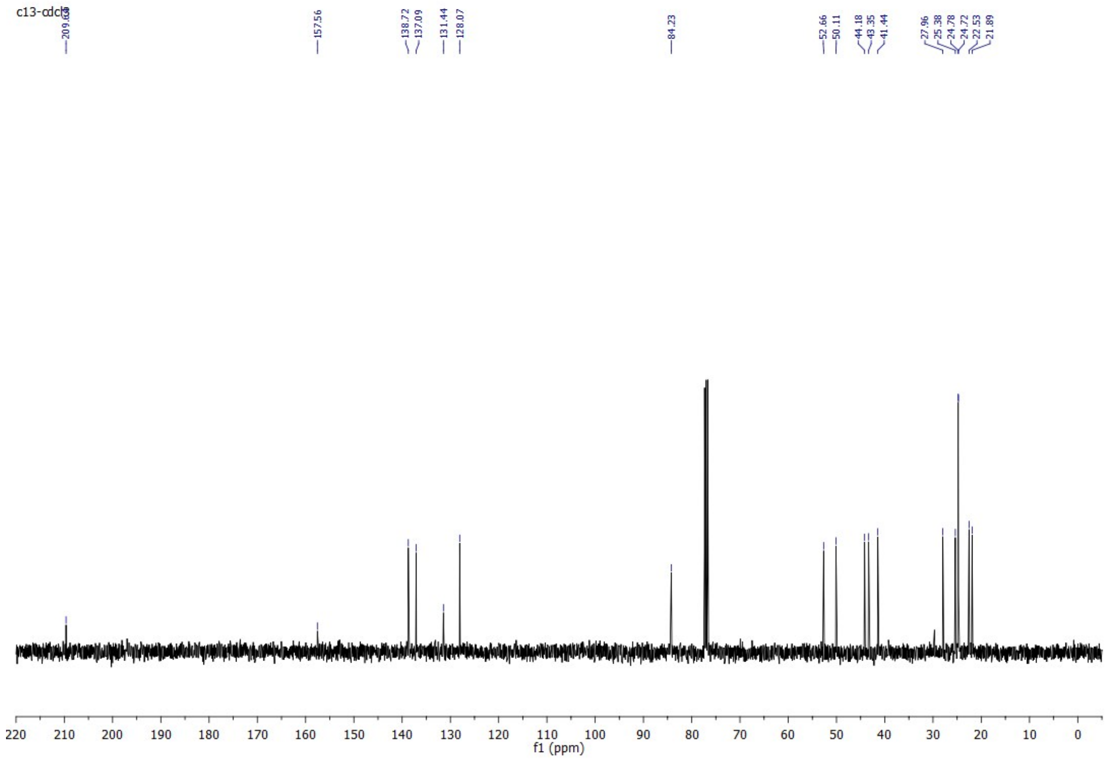
6.17
6.16
5.93
5.92
5.92
5.92
5.91
2.88
2.78
2.77
2.72
2.24
2.23
2.10
2.10
2.09
1.69
1.68
1.66
1.66
1.65
1.64
1.63
1.62
1.61
1.59
1.58
1.31
1.24
1.22
0.82
0.83
0.77
0.84
0.83
0.90
0.89
1.94
2.00
2.19
2.34
14.36
f1 (ppm)


c13-cdcl3
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128.07
84.23
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50.11
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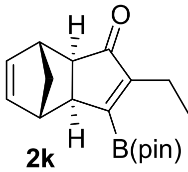
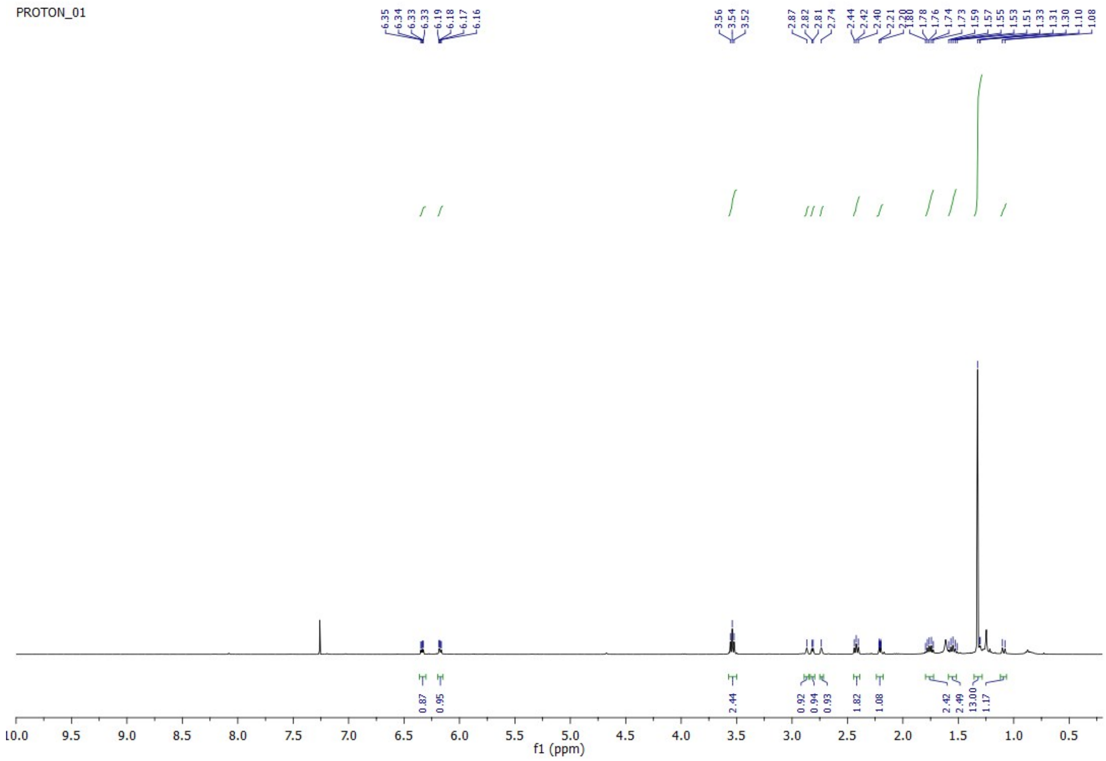
43.35
41.44
27.96
25.38
24.78
24.72
22.53
21.89
f1 (ppm)

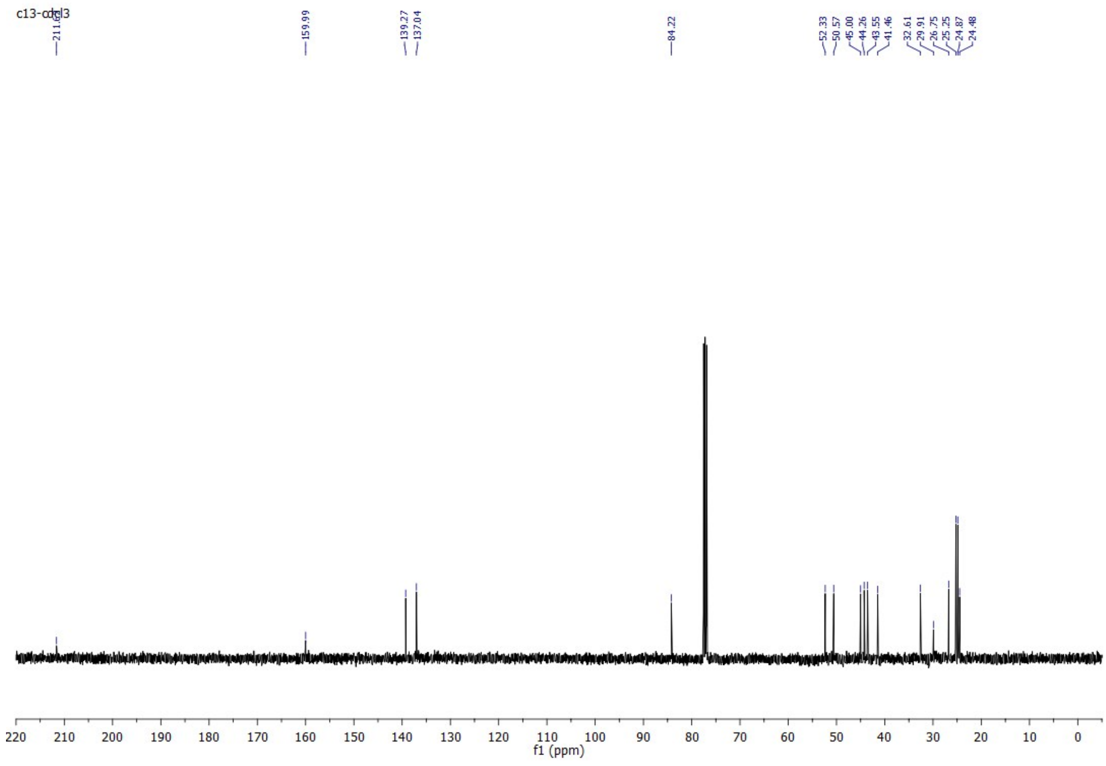


O
H
H
Cl
B(pin)

2k



PROTON_01
6.35 6.34 6.33 6.33 6.19 6.18 6.17 6.16
3.56 3.54 3.52
2.87 2.82 2.81 2.74 2.44 2.42 2.40 2.21 2.20 1.80 1.78 1.76 1.74 1.73 1.59 1.57 1.55 1.53 1.51 1.33 1.31 1.30 1.10 1.08
0.87 0.95 2.44 0.92 0.94 0.93 1.82 1.08 2.42 2.49 13.00 1.17
f1 (ppm)



c13-cdcl3
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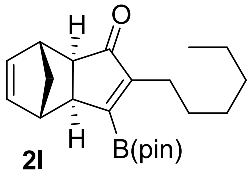
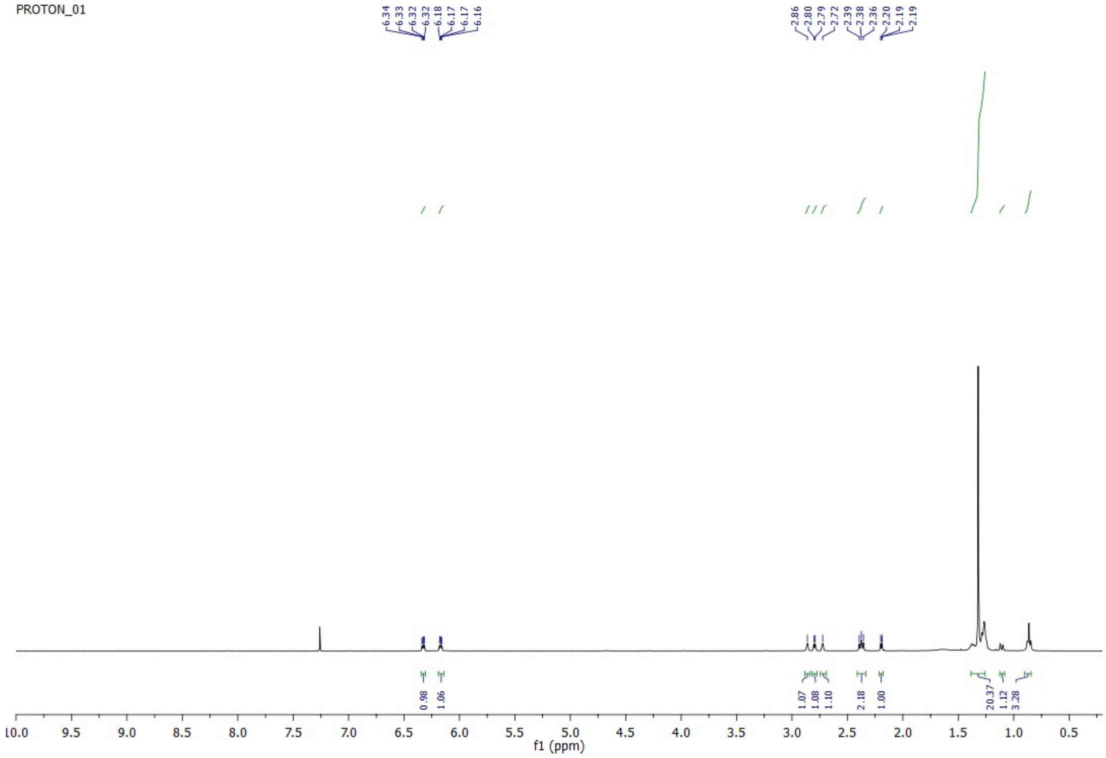
f1 (ppm)

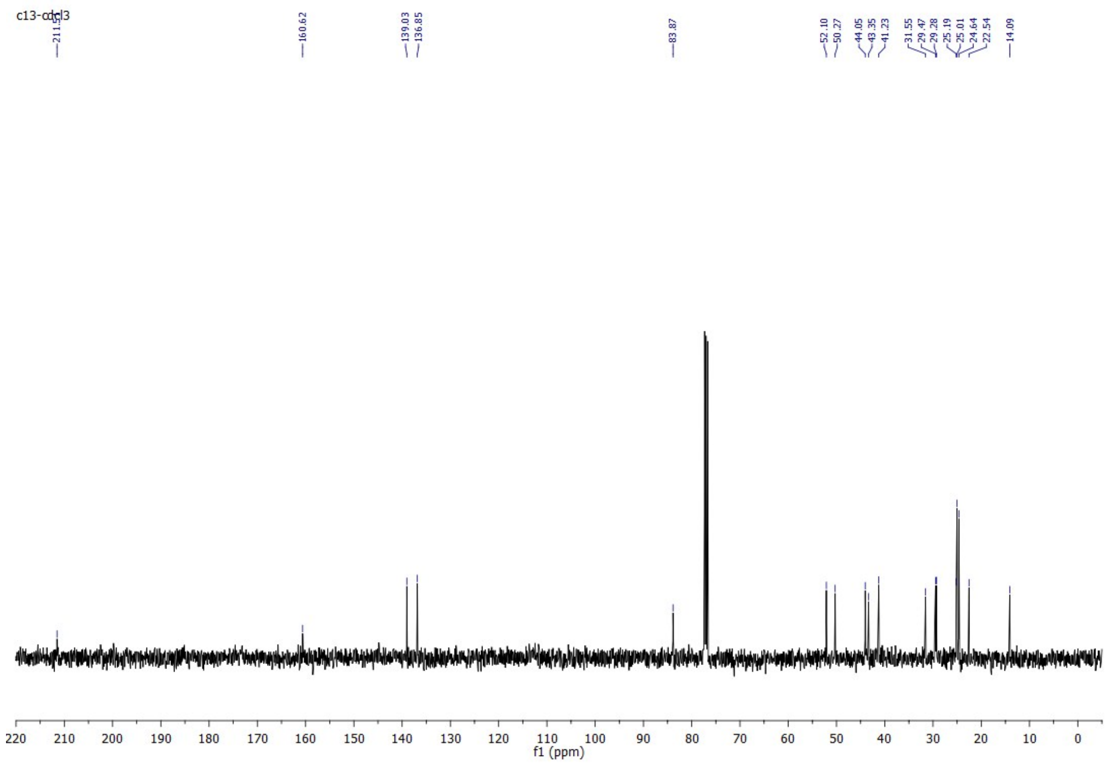


H
O
H
B(pin)

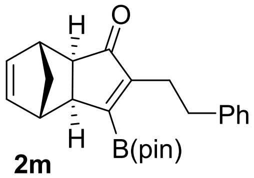
2l



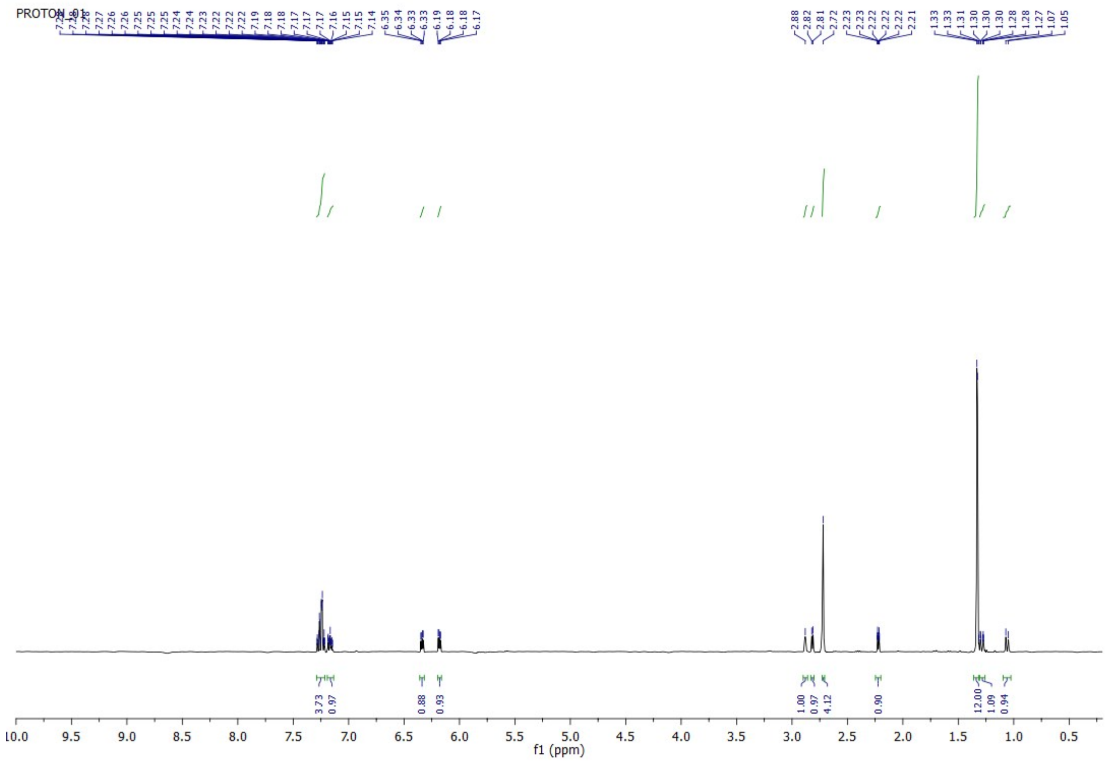
PROTON_01
6.34 6.33 6.32 6.32 6.18 6.17 6.17 6.16
2.86 2.80 2.79 2.72 2.39 2.38 2.36 2.20 2.19 2.19
0.98 1.06 1.07 1.08 1.10 2.18 1.00 20.37 1.12 3.28
f1 (ppm)

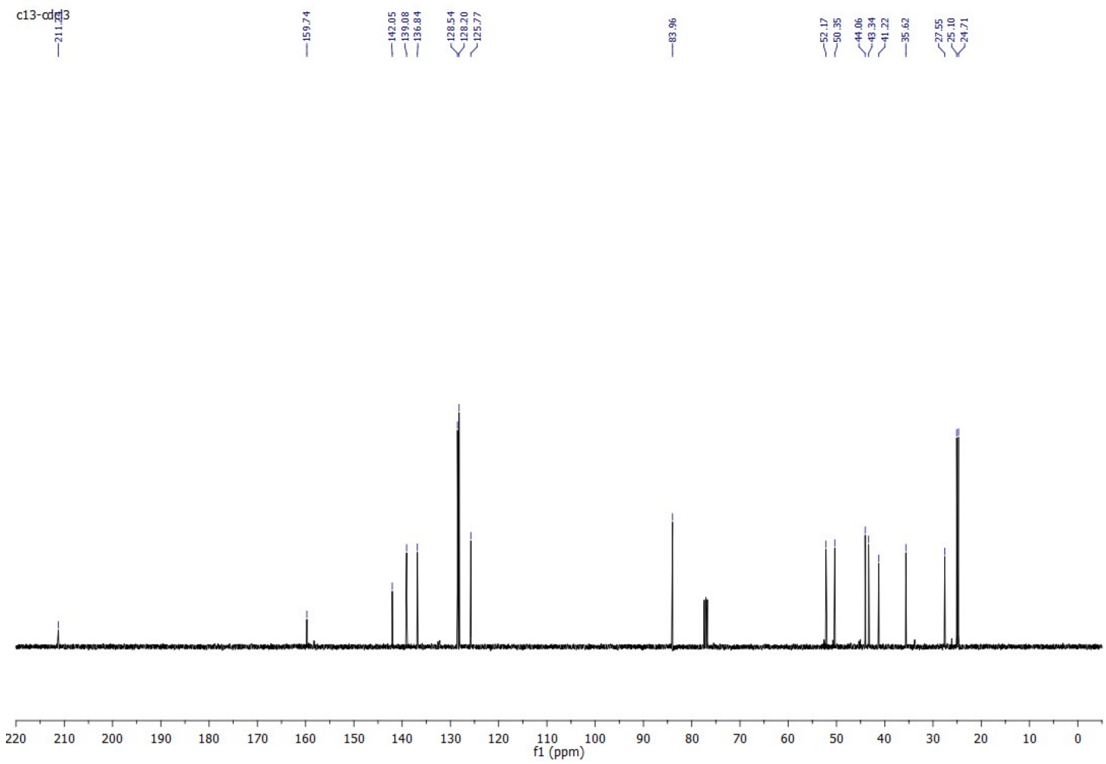


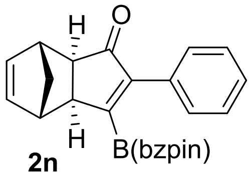
c13-cdcl3
160.62
139.03 136.85
83.87
52.10 50.27 44.05 43.35 41.23 31.55 29.47 29.28 25.19 25.01 24.64 22.54 14.09
f1 (ppm)



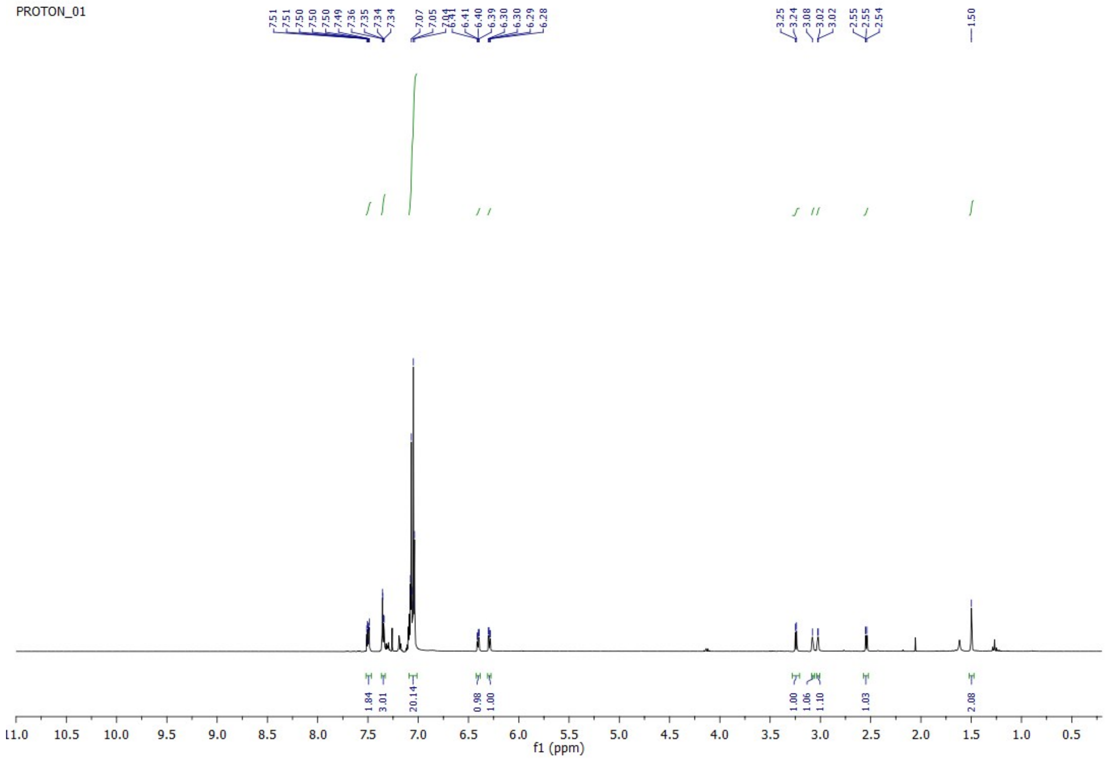
2m

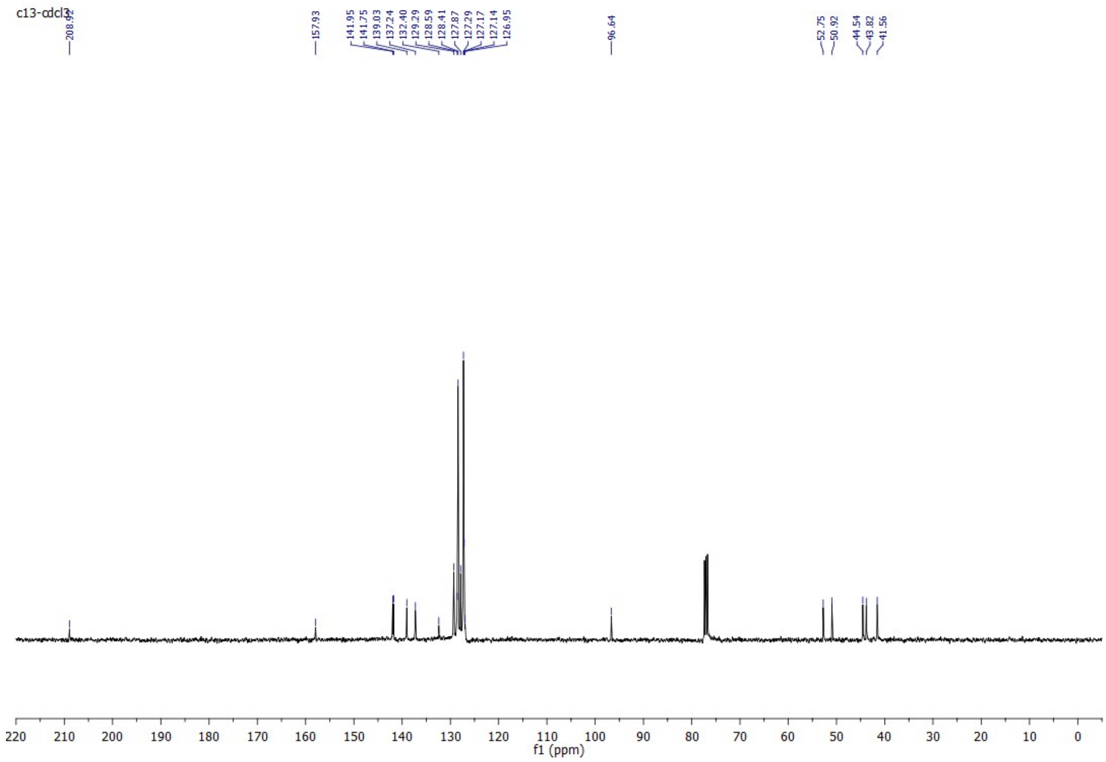


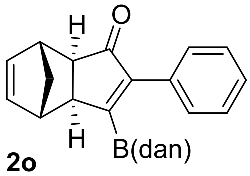



O
H
H
B(bzpin)

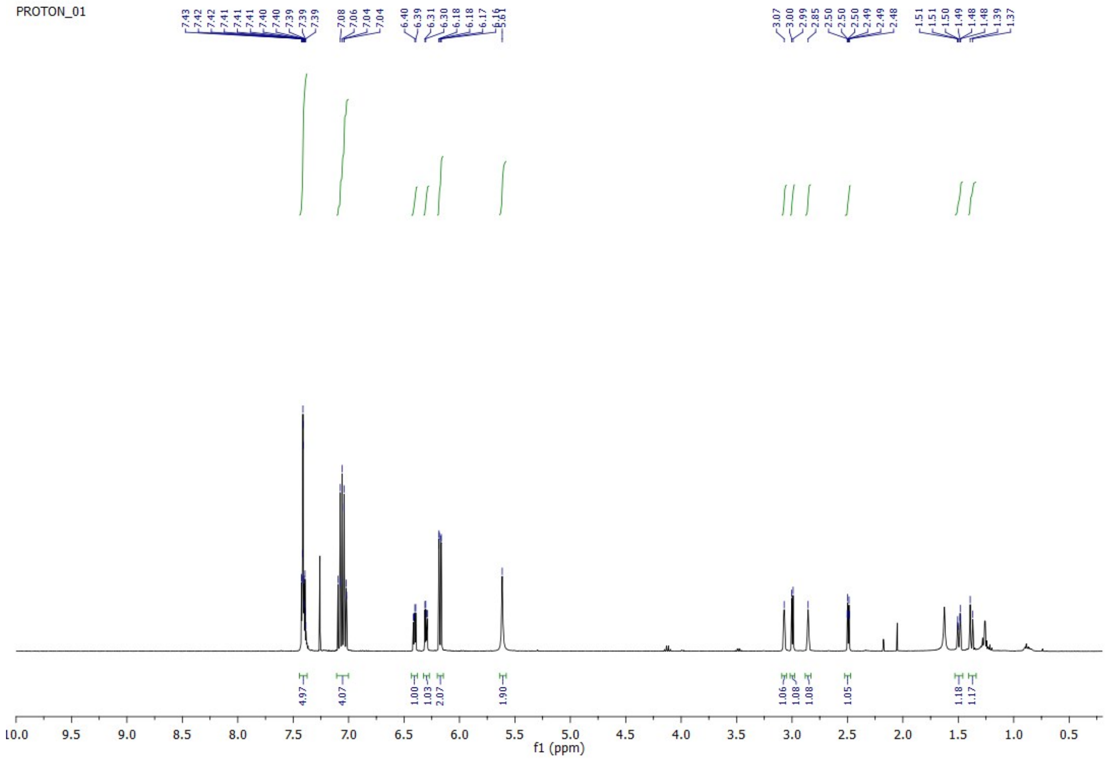
2n

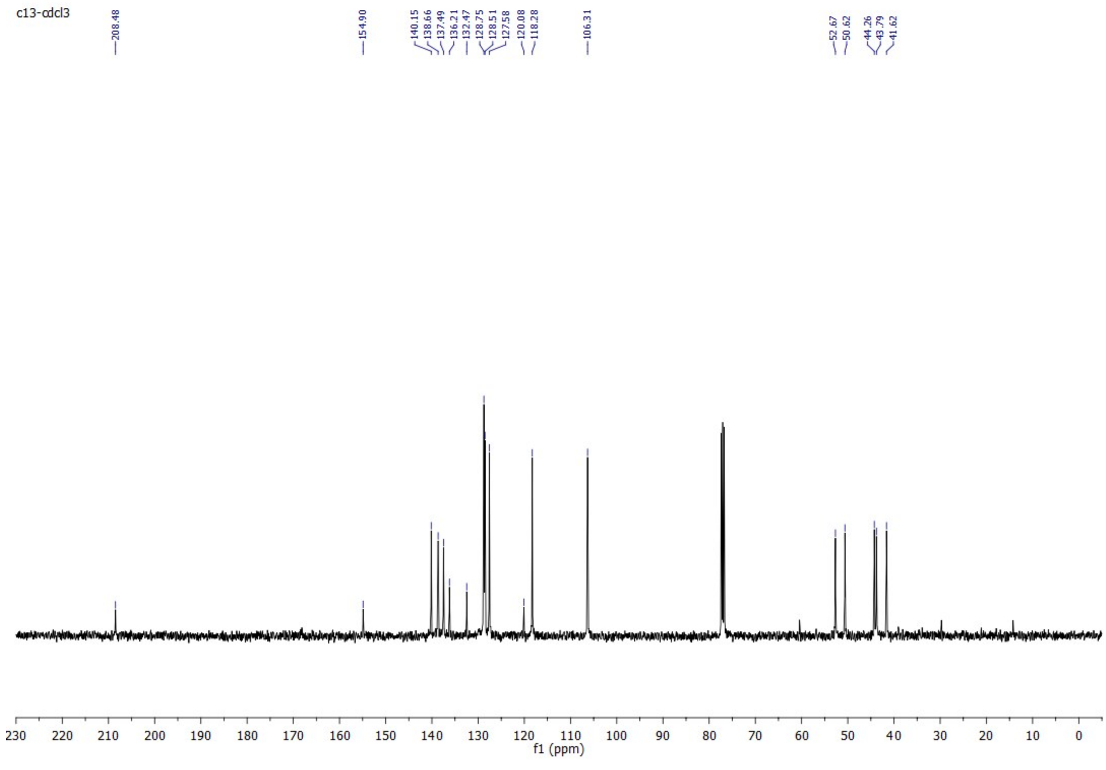

PROTON_01
7.51
7.51
7.50
7.50
7.50
7.49
7.36
7.35
7.34
7.34
7.07
7.05
7.04
6.41
6.41
6.40
6.39
6.30
6.30
6.29
6.28
3.25
3.24
3.08
3.02
3.02
2.55
2.55
2.54
1.50
1.84
3.01
20.14
0.98
1.00
1.00
1.06
1.10
1.03
2.08
f1 (ppm)

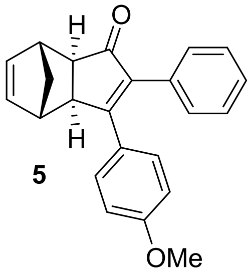

c13-cdcl3
208.92
157.93
141.95
141.75
139.03
137.24
132.40
129.29
128.59
128.41
127.87
127.29
127.17
127.14
126.95
96.64
52.75
50.92
44.54
43.82
41.56
f1 (ppm)



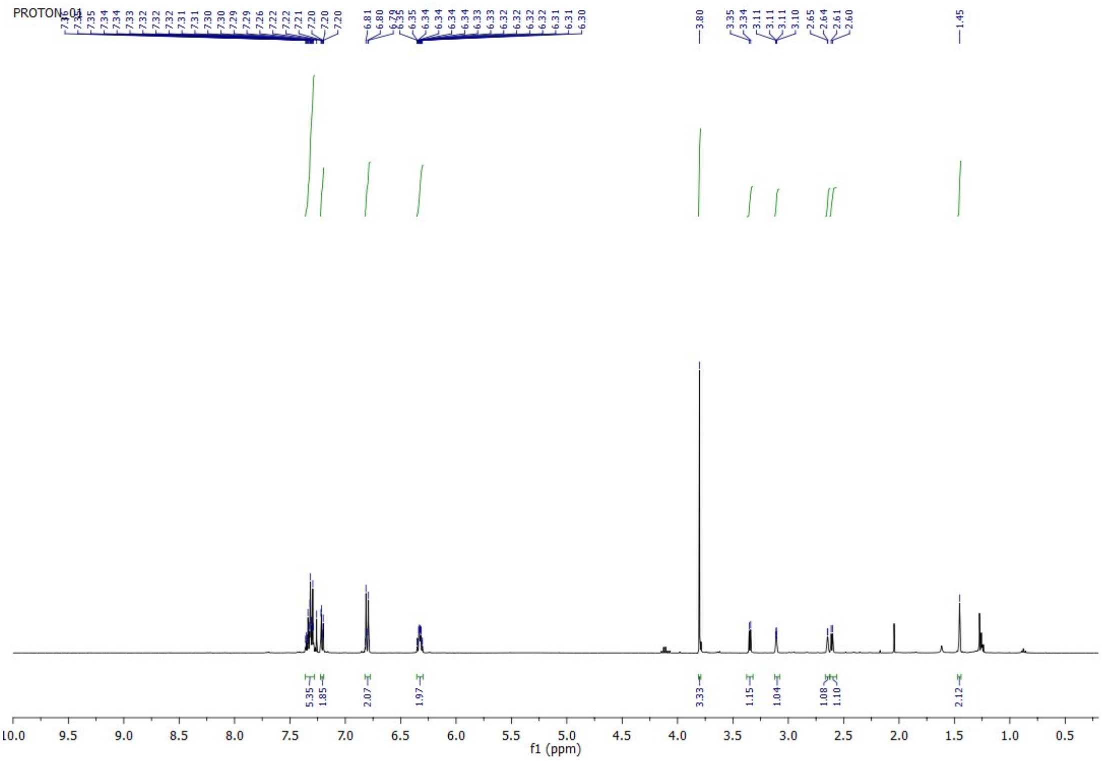
2o

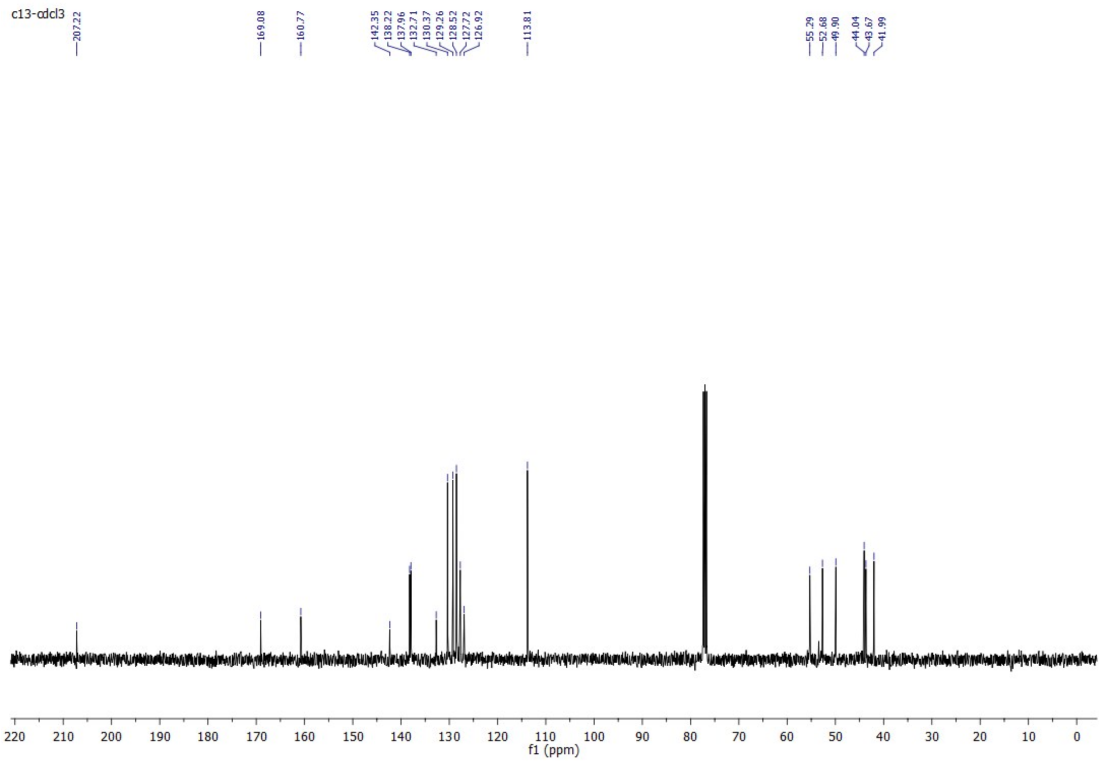


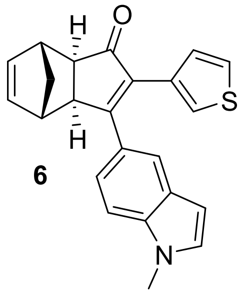




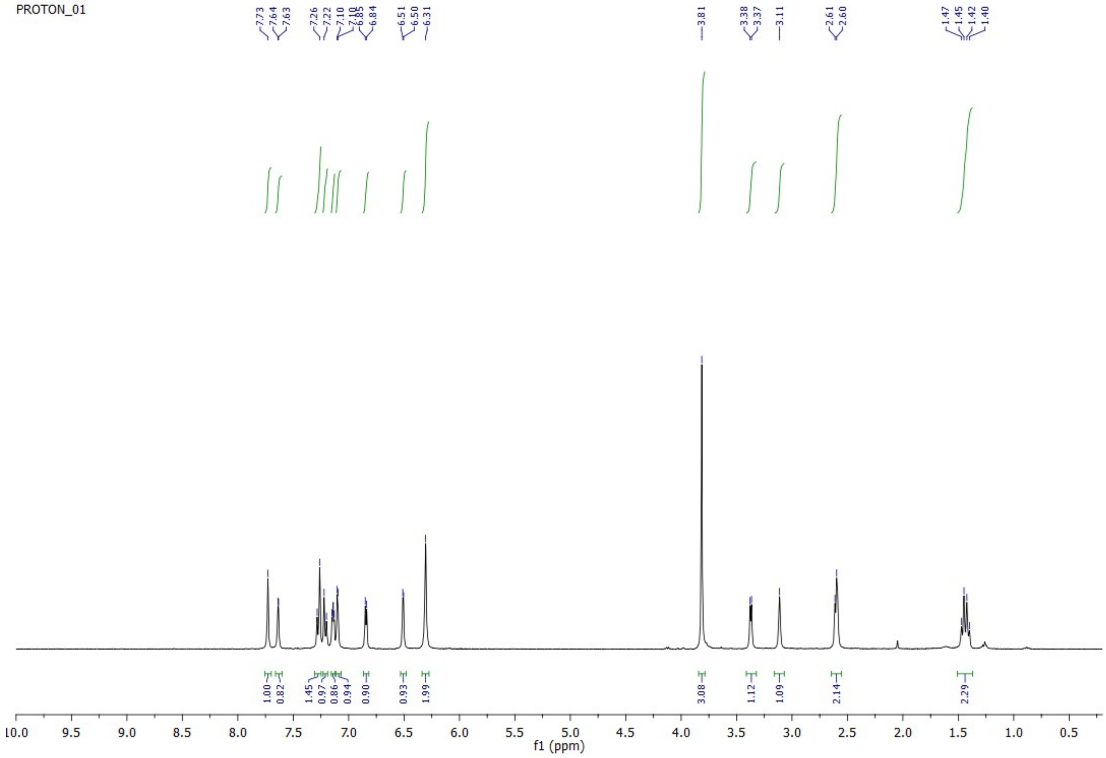
5

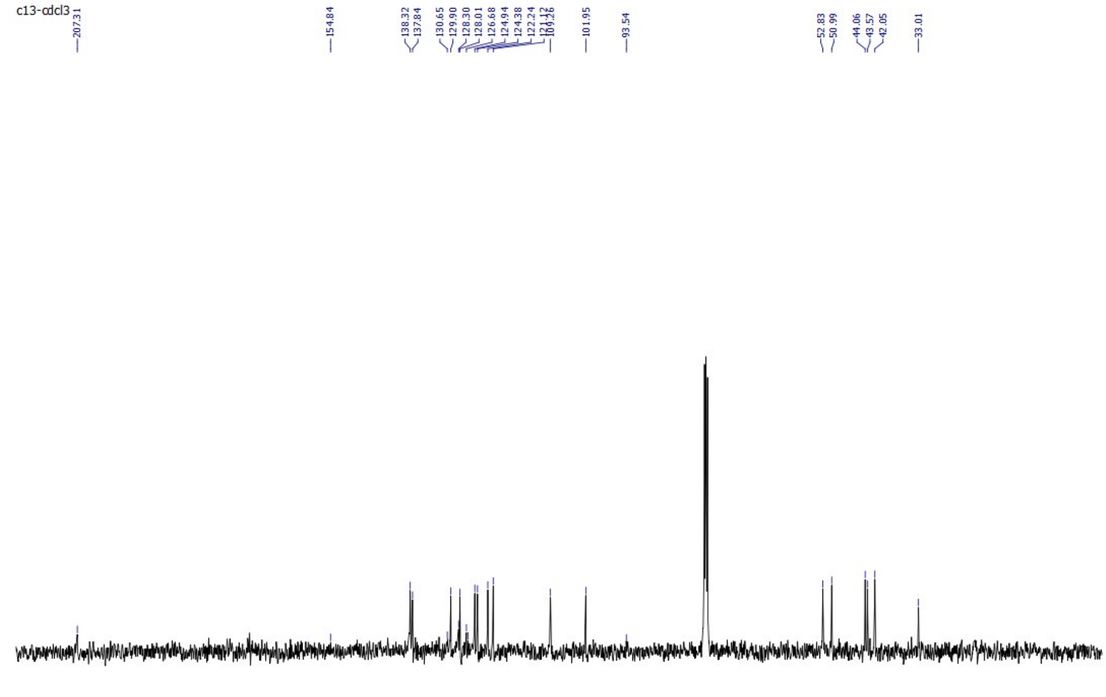


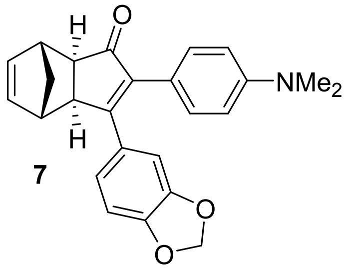




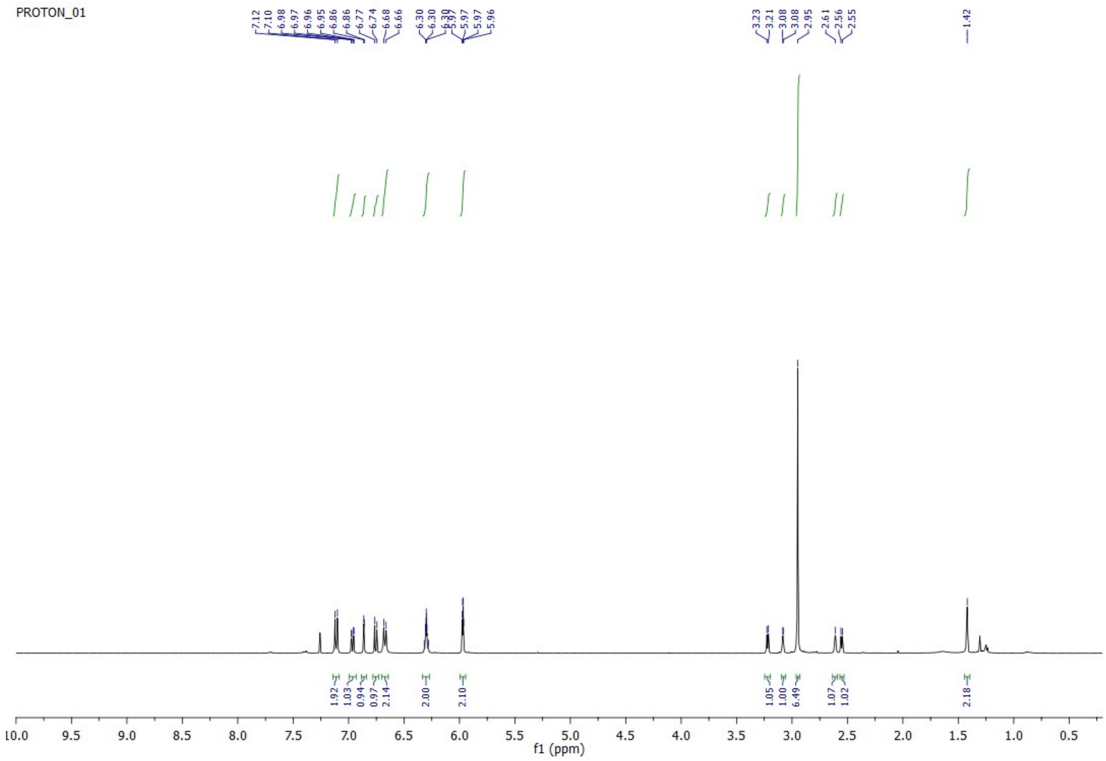
6

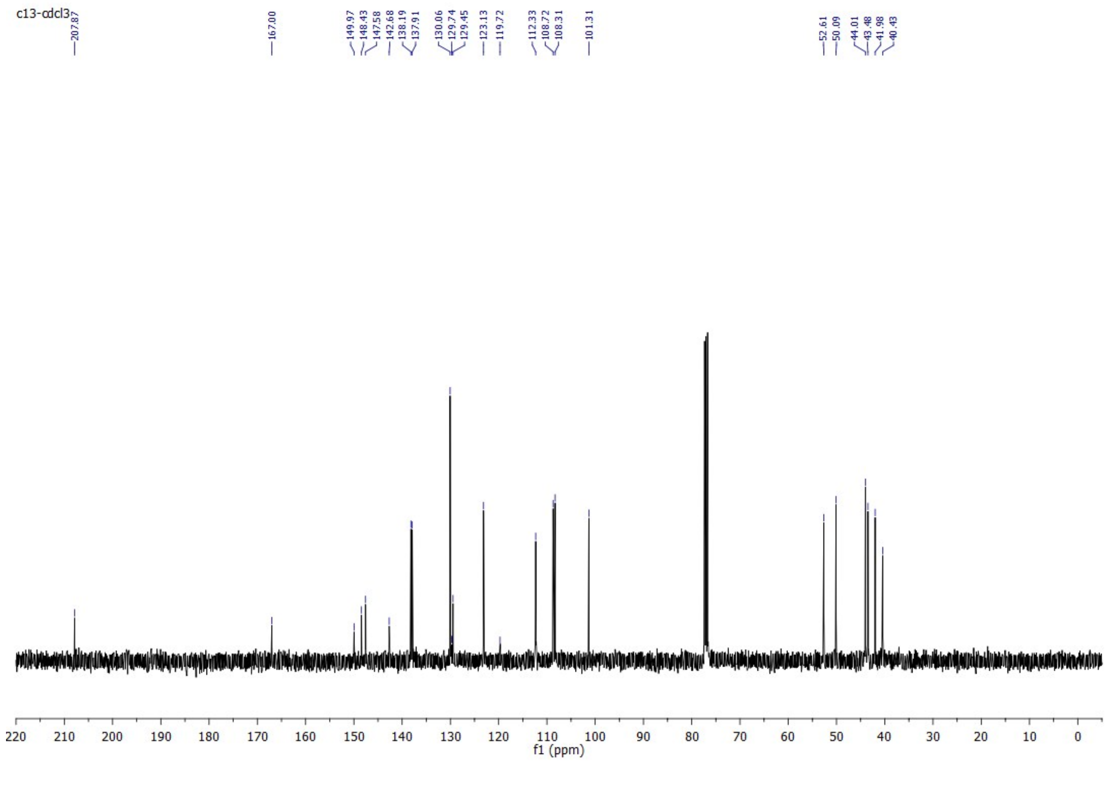

PROTON_01
7.73 7.64 7.63
7.26 7.22 7.10 7.10 6.85 6.84
6.51 6.50 6.31
3.81
3.38 3.37
3.11
2.61 2.60
1.47 1.45 1.42 1.40
1.00 0.82 1.45 0.97 0.86 0.94 0.90 0.93 1.99 3.08 1.12 1.09 2.14 2.29
f1 (ppm)

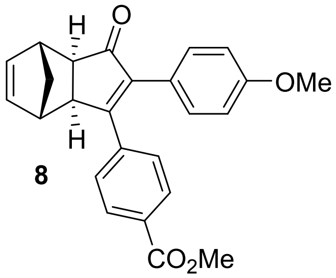

c13-cdcl3
207.31
154.84
138.32 137.84
130.65 129.90 128.30 128.01 126.68 124.94 124.38 122.24 121.12 109.26
101.95
93.54
52.83 50.99
44.06 43.57 42.05
33.01
f1 (ppm)


H
O
NMe2
H
O
O

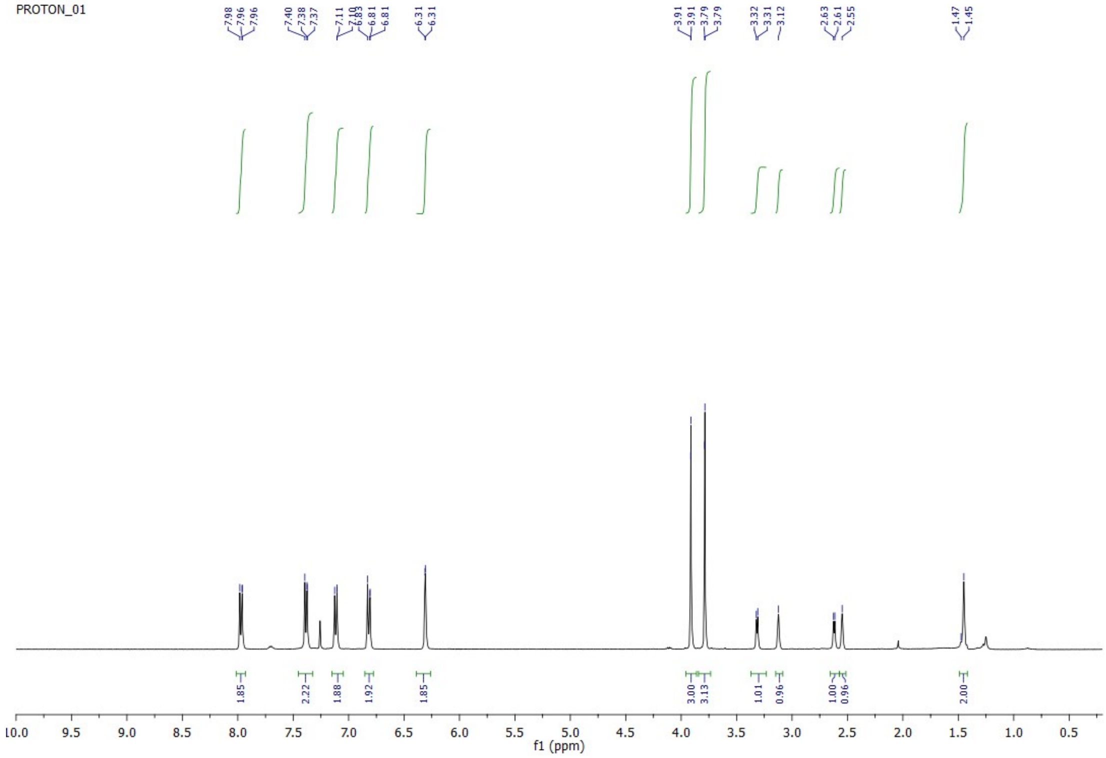
7

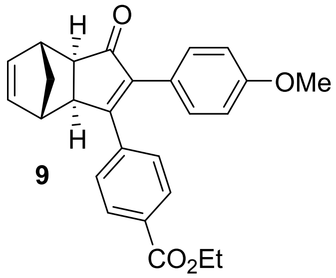

PROTON_01
7.12
7.10
6.98
6.97
6.96
6.95
6.86
6.86
6.77
6.74
6.68
6.66
6.30
6.30
6.30
5.97
5.97
5.97
5.96
3.23
3.21
3.08
3.08
2.95
2.61
2.56
2.55
1.42
1.92
1.03
0.94
0.97
2.14
2.00
2.10
1.05
1.00
6.49
1.07
1.02
2.18
f1 (ppm)

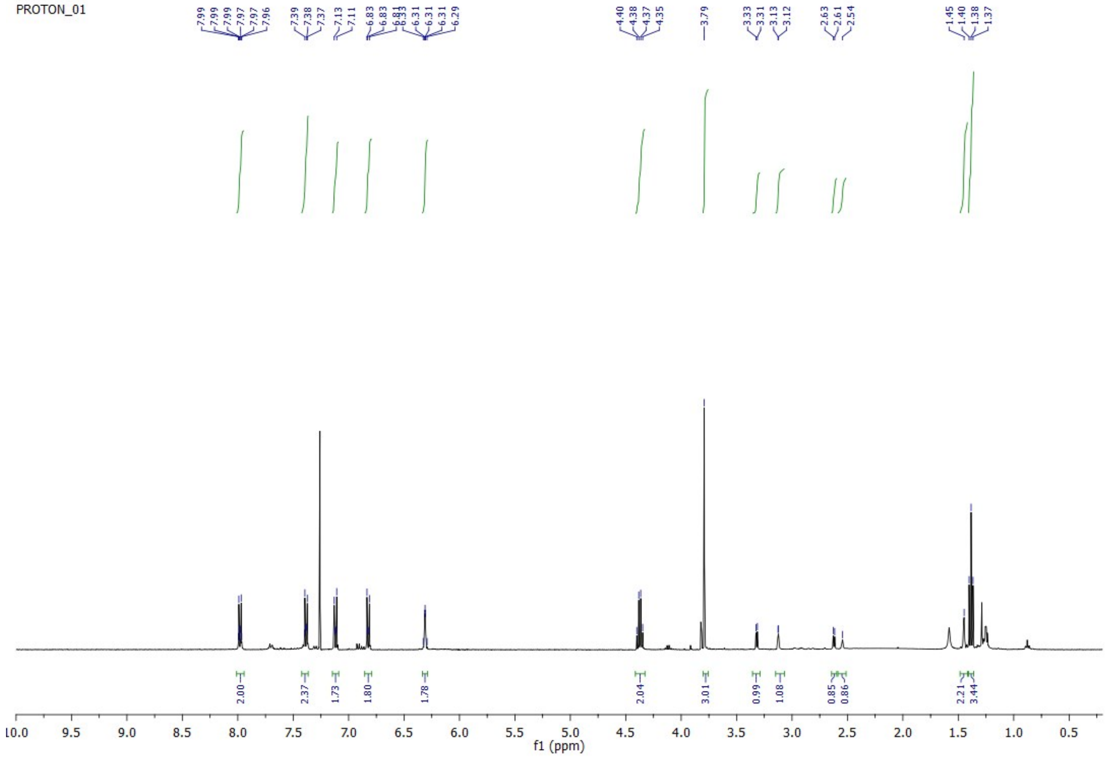

c13-cdcl3
207.87
167.00
149.97
148.43
147.58
142.68
138.19
137.91
130.06
129.74
129.45
123.13
119.72
112.33
108.72
108.31
101.31
52.61
50.09
44.01
43.48
41.98
40.43
f1 (ppm)

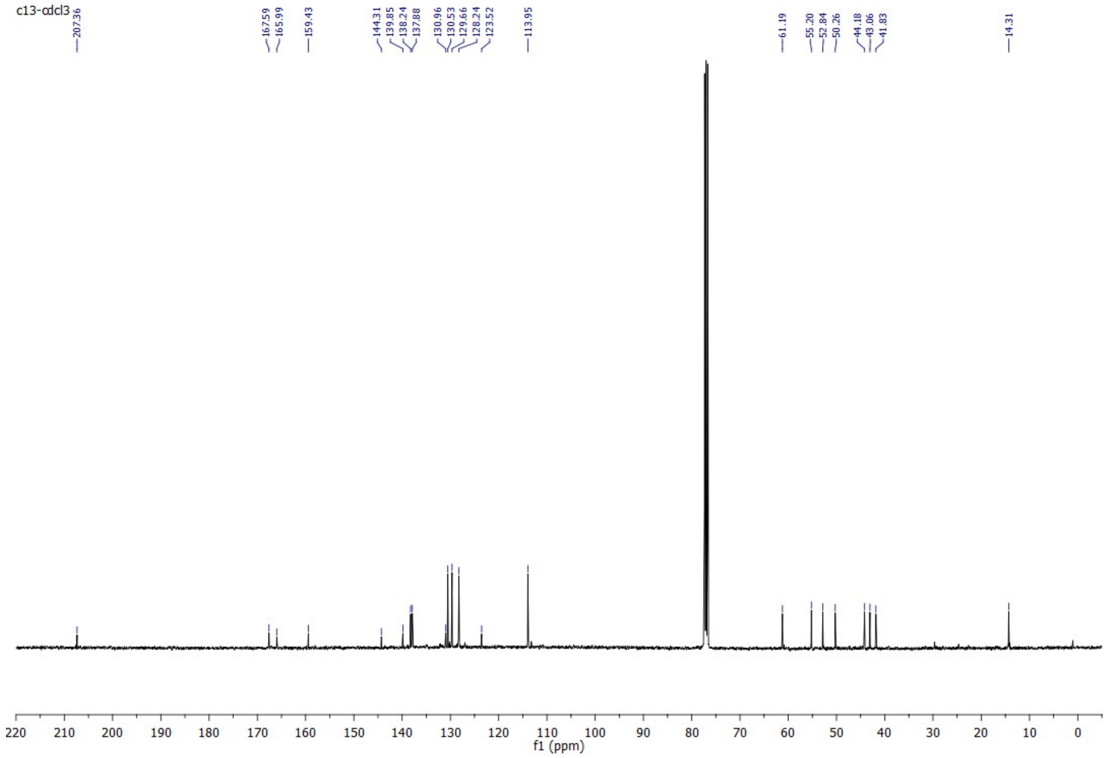


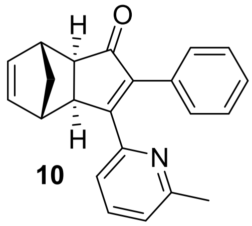
8



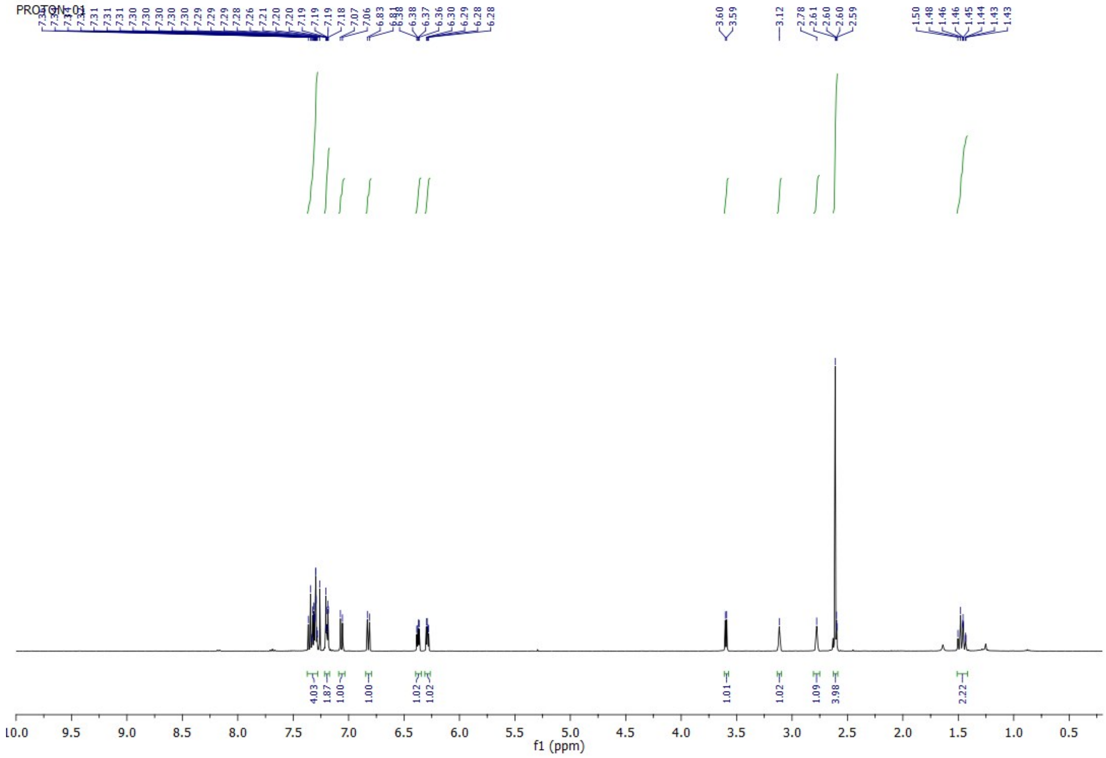

OMe
CO2Et
9

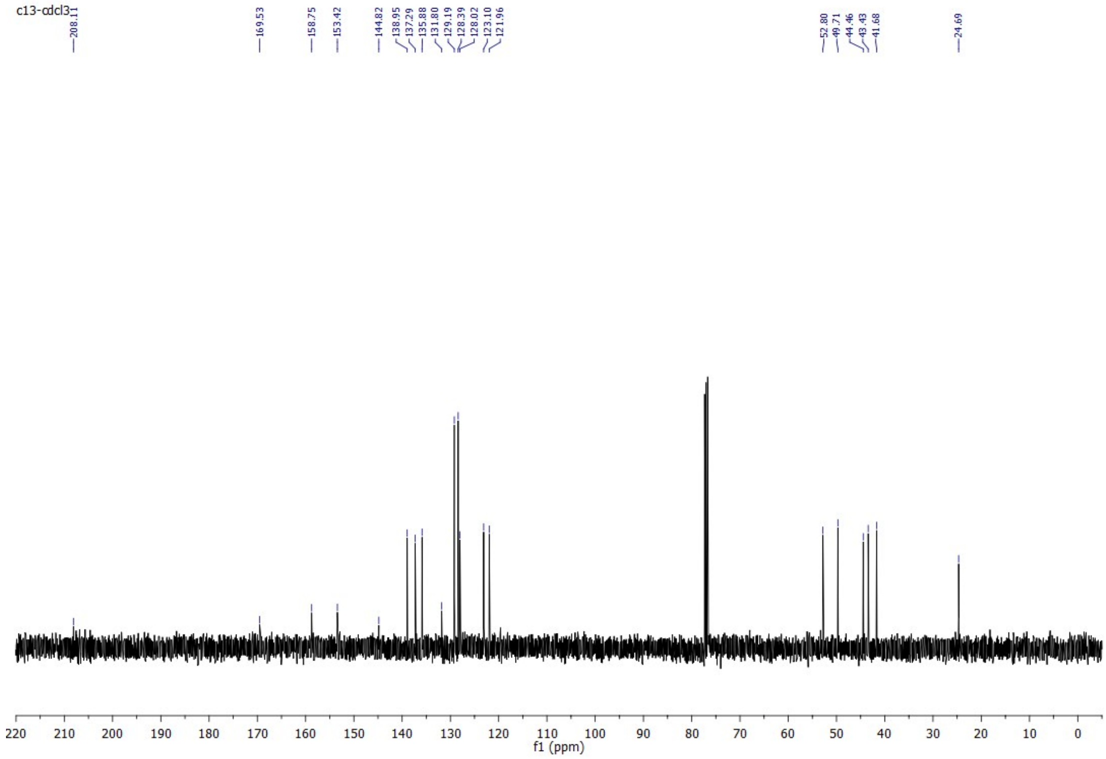

PROTON_01
7.99 7.99 7.99 7.97 7.97 7.96 7.39 7.38 7.37 7.13 7.11 6.83 6.83 6.81 6.33 6.31 6.31 6.31 6.31 6.29
4.40 4.38 4.37 4.35 3.79 3.33 3.31 3.13 3.12 2.63 2.61 2.54 1.45 1.40 1.38 1.37
2.00 2.37 1.73 1.80 1.78 2.04 3.01 0.99 1.08 0.85 0.86 2.21 3.44
f1 (ppm)

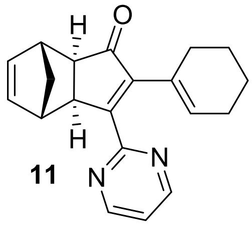

c13-cdcl3
207.36 167.59 165.99 159.43 144.31 139.85 138.24 137.88 130.96 130.53 129.66 128.24 123.52 113.95 61.19 55.20 52.84 50.26 44.18 43.06 41.83 14.31
f1 (ppm)


H
O
H
N

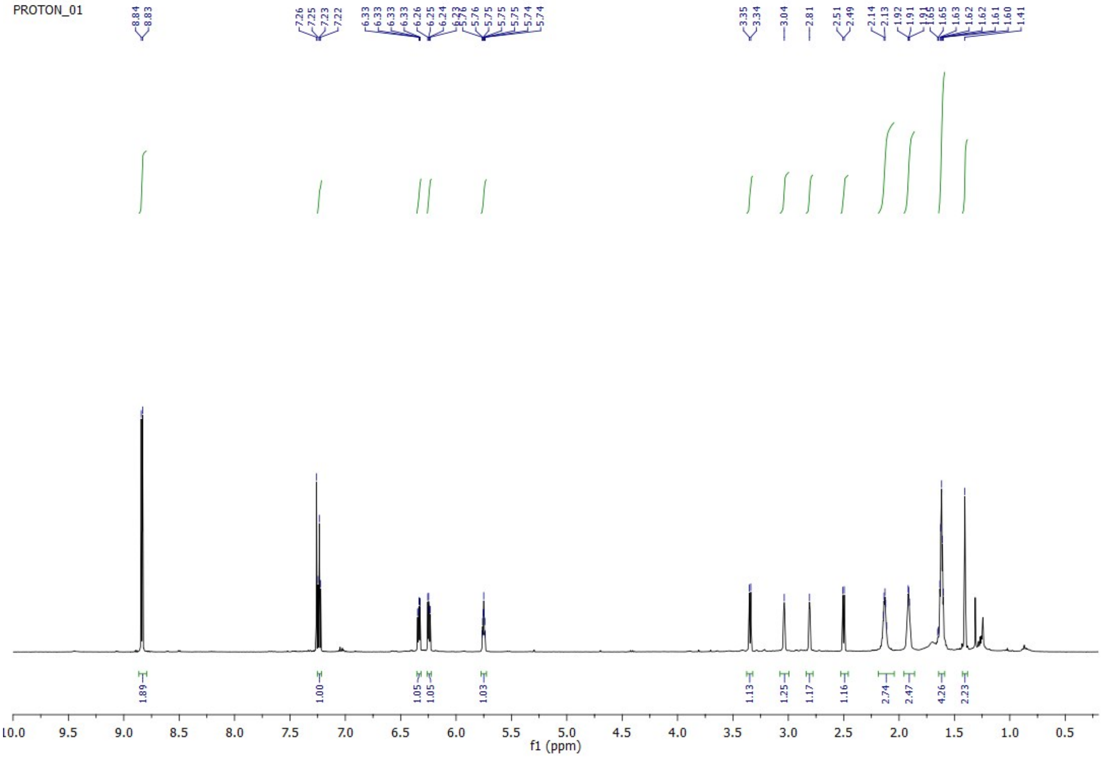
10

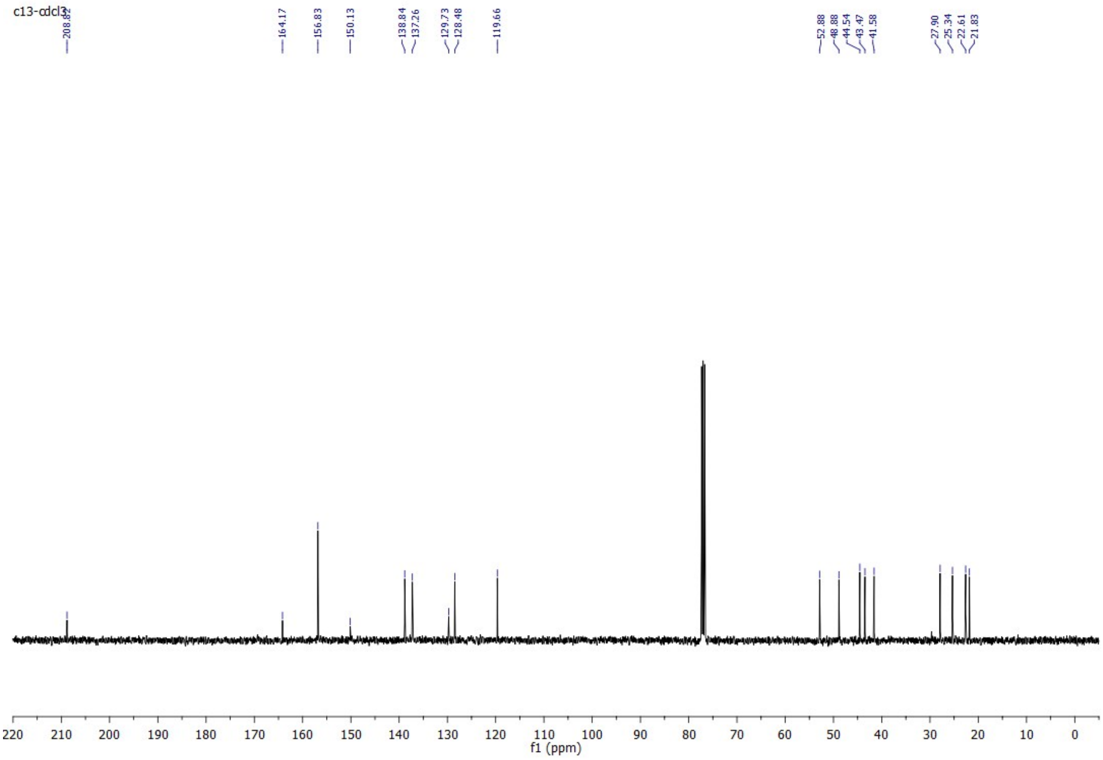

PROTON-01
3.60
3.59
3.12
2.78
2.61
2.60
2.60
2.59
1.50
1.48
1.46
1.46
1.45
1.44
1.43
1.43
4.03
1.87
1.00
1.00
1.02
1.02
1.01
1.02
1.09
3.98
2.22
f1 (ppm)

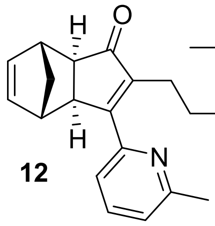

c13-cdcl3
208.11
169.53
158.75
153.42
144.82
138.95
137.29
135.88
131.80
129.19
128.39
128.02
123.10
121.96
52.80
49.71
44.46
43.43
41.68
24.69
f1 (ppm)

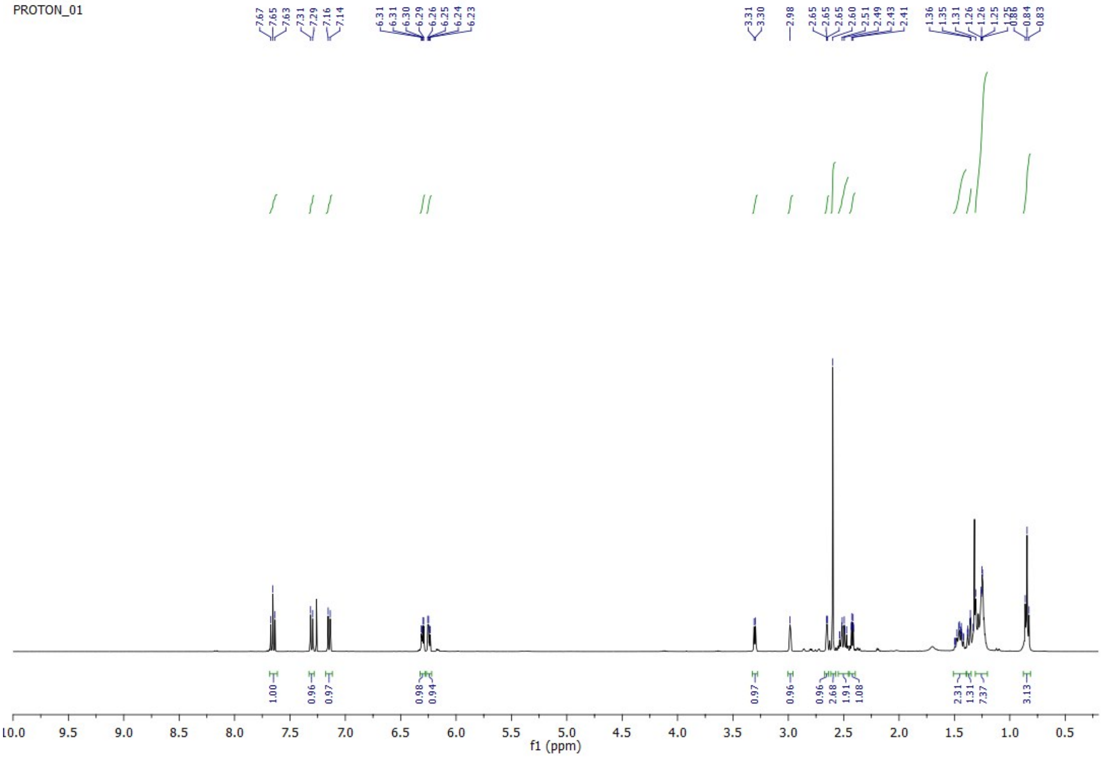


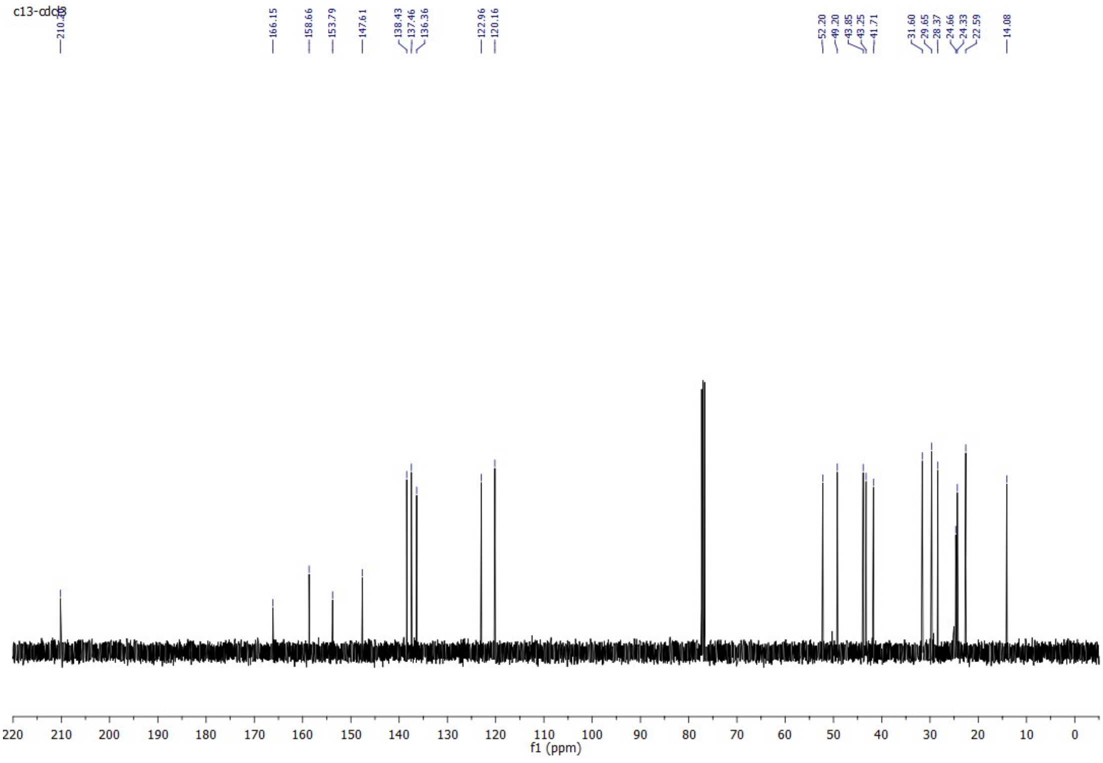
11

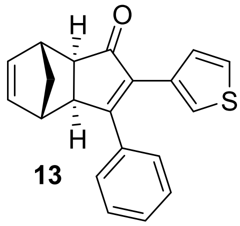

PROTON_01
8.84 8.83
7.26 7.25 7.23 7.22
6.33 6.33 6.33 6.33 6.26 6.25 6.24 6.23
5.76 5.76 5.75 5.75 5.74 5.74
3.35 3.34
3.04
2.81
2.51 2.49
2.14 2.13 1.92 1.91 1.81 1.65 1.65 1.63 1.62 1.62 1.61 1.60 1.41
1.89 1.00 1.05 1.05 1.03 1.13 1.25 1.17 1.16 2.74 2.47 4.26 2.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


c13-cdcl3
208.82
164.17
156.83
150.13
138.84 137.26
129.73 128.48
119.66
52.88 48.88 44.54 43.47 41.58
27.90 25.34 22.61 21.83
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

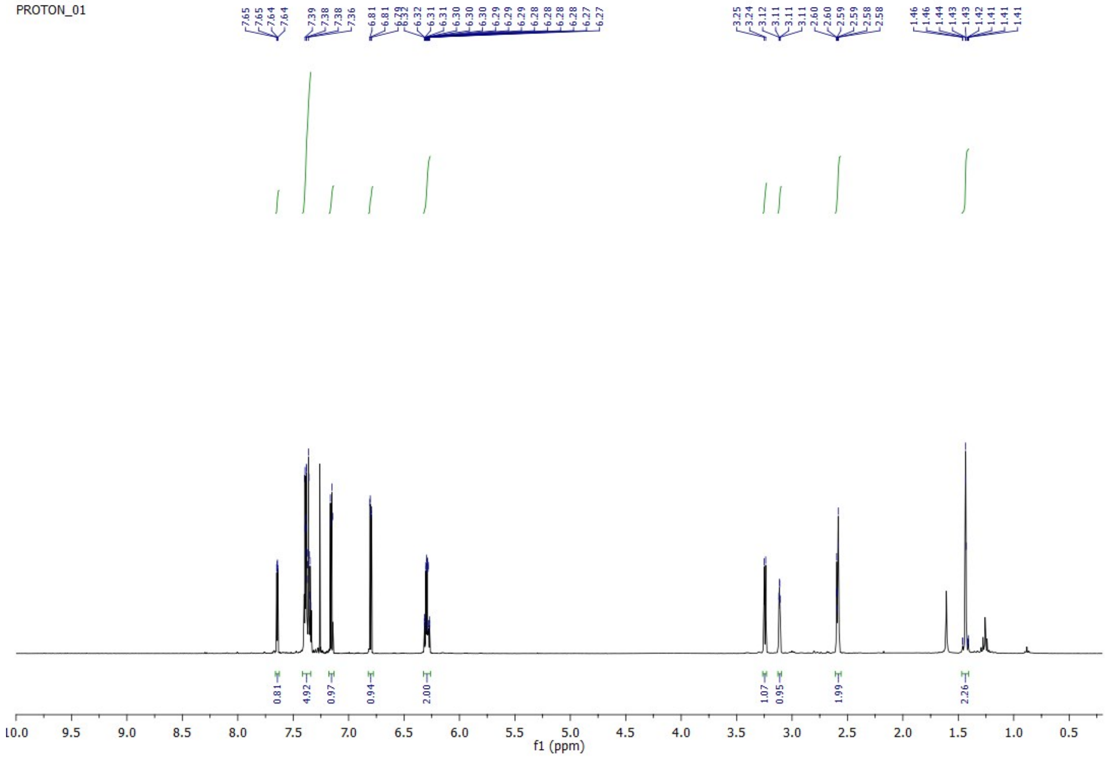

H
O
H
N
12

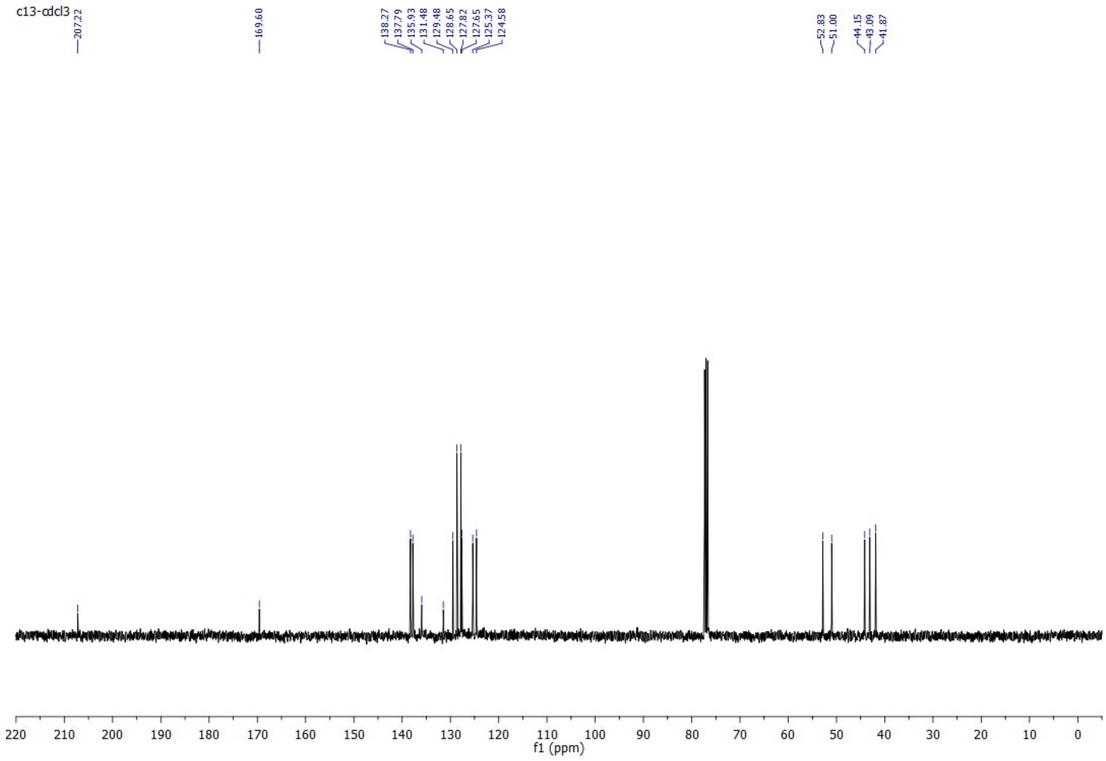

PROTON_01
7.67
7.65
7.63
7.31
7.29
7.16
7.14
6.31
6.31
6.30
6.29
6.26
6.25
6.24
6.23
3.31
3.30
2.98
2.65
2.65
2.65
2.60
2.51
2.49
2.43
2.41
1.36
1.35
1.31
1.26
1.26
1.25
1.25
0.86
0.84
0.83
1.00
0.96
0.97
0.98
0.94
0.97
0.96
0.96
2.68
1.91
1.08
2.31
1.31
7.37
3.13
f1 (ppm)

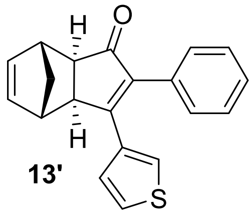

c13-cdcl3
210.30
166.15
158.66
153.79
147.61
138.43
137.46
136.36
122.96
120.16
52.20
49.20
43.85
43.25
41.71
31.60
29.65
28.37
24.66
24.33
22.59
14.08
f1 (ppm)


O
H
H
S

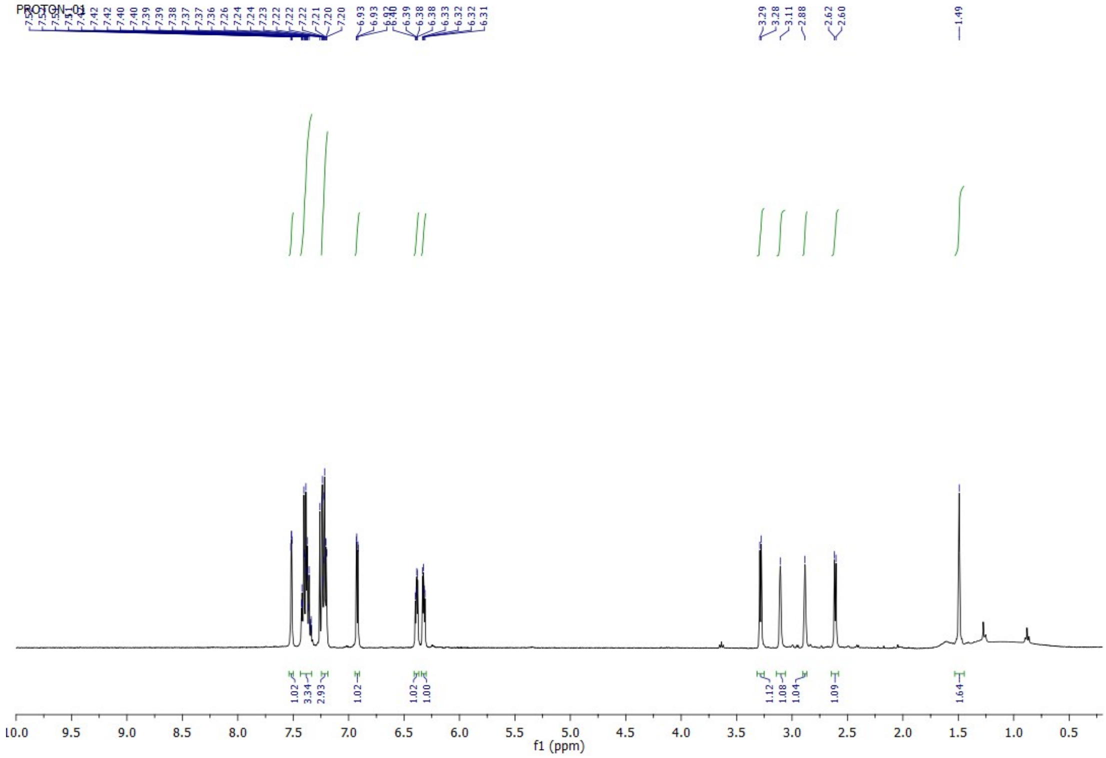
13


PROTON_01
7.65 7.65 7.64 7.64
7.39 7.38 7.38 7.36
6.81 6.81 6.32 6.32 6.32 6.31 6.31 6.30 6.30 6.30 6.29 6.29 6.28 6.28 6.28 6.27 6.27
3.25 3.24 3.12 3.11 3.11 3.11 2.60 2.60 2.59 2.59 2.58 2.58
1.46 1.46 1.44 1.43 1.43 1.42 1.41 1.41 1.41
0.81 4.92 0.97 0.94 2.00 1.07 0.95 1.99 2.26
f1 (ppm)


c13-cdcl3
207.22
169.60
138.27 137.79 135.93 131.48 129.48 128.65 127.82 127.65 125.37 124.58
52.83 51.00 44.15 43.09 41.87
f1 (ppm)


O
H
H
S

13'


PROTON_01
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7.40
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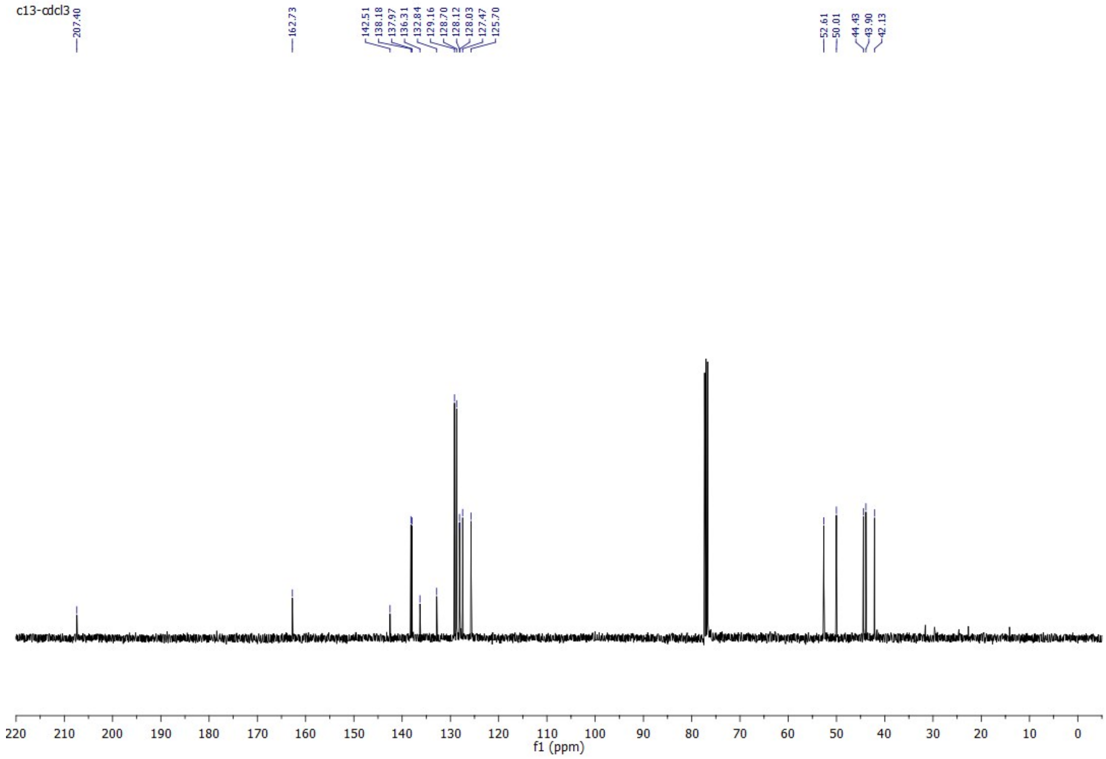
7.38
7.37
7.37
7.36
7.26
7.24
7.24
7.23
7.22
7.22
7.22
7.21
7.20
7.20
6.93
6.93
6.39
6.38
6.38
6.33
6.32
6.32
6.31
3.29
3.28
3.11
2.88
2.62
2.60
1.49
1.02
3.34
2.93
1.02
1.02
1.00
1.12
1.08
1.04
1.09
1.64
f1 (ppm)


c13-cdcl3
207.40
162.73
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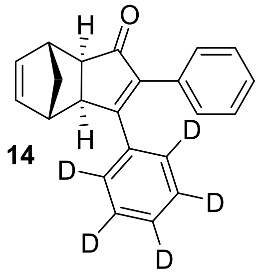
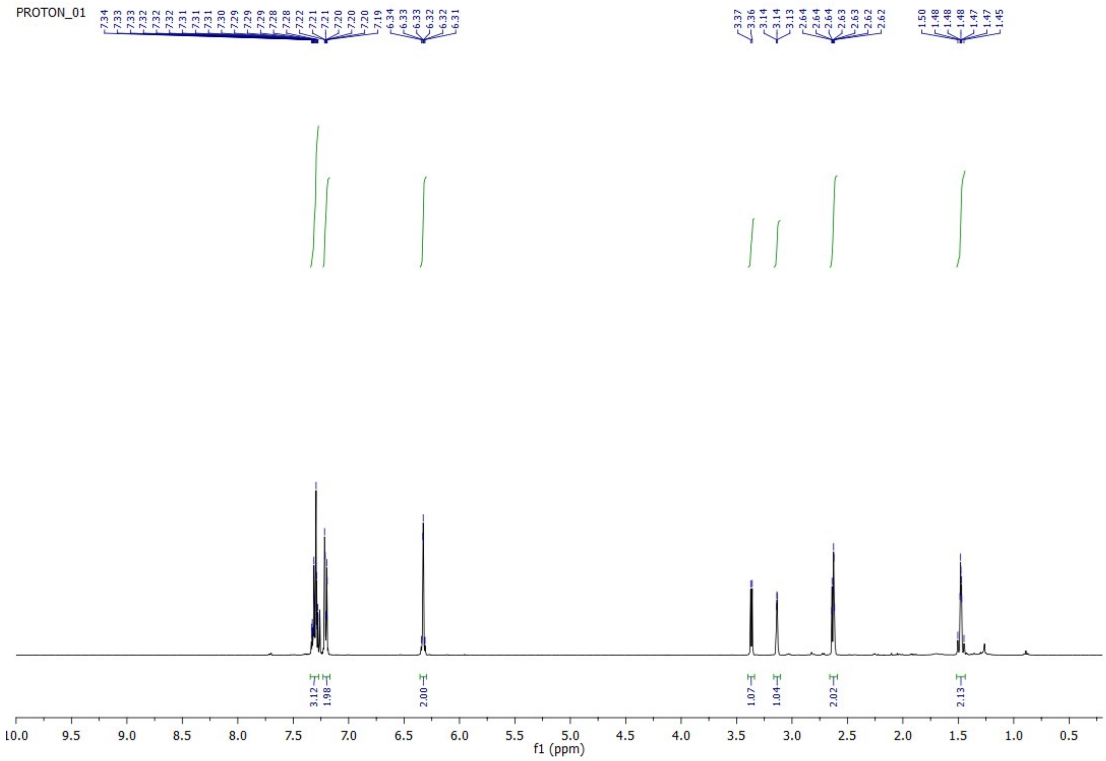
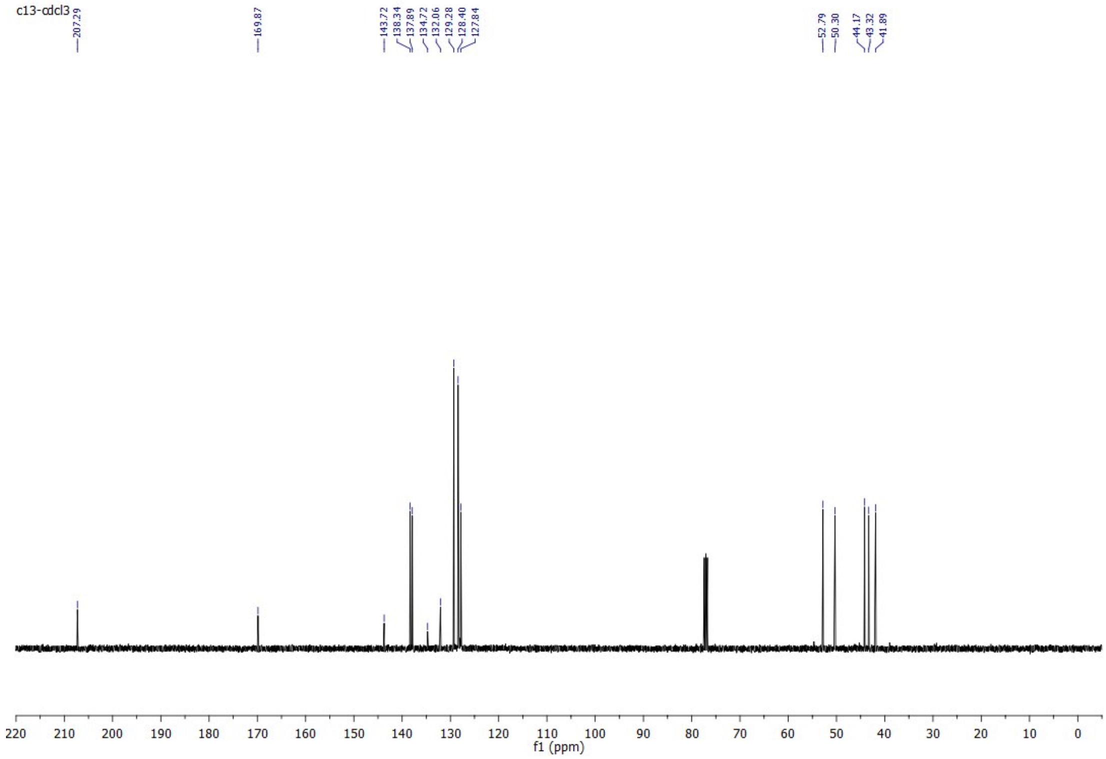
138.18
137.97
136.31
132.84
129.16
128.70
128.12
128.03
127.47
125.70
52.61
50.01
44.43
43.90
42.13
f1 (ppm)



14



PROTON_01
7.34 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.31 7.30 7.29 7.29 7.29 7.28 7.28 7.22 7.21 7.21 7.20 7.20 7.20 7.19 6.34 6.33 6.33 6.32 6.32 6.31
3.37 3.36 3.14 3.14 3.13 2.64 2.64 2.63 2.63 2.63 2.62 2.62 1.50 1.48 1.48 1.48 1.47 1.47 1.45
3.12 1.98 2.00 1.07 1.04 2.02 2.13
f1 (ppm)



c13-cdcl3
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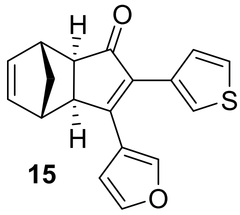
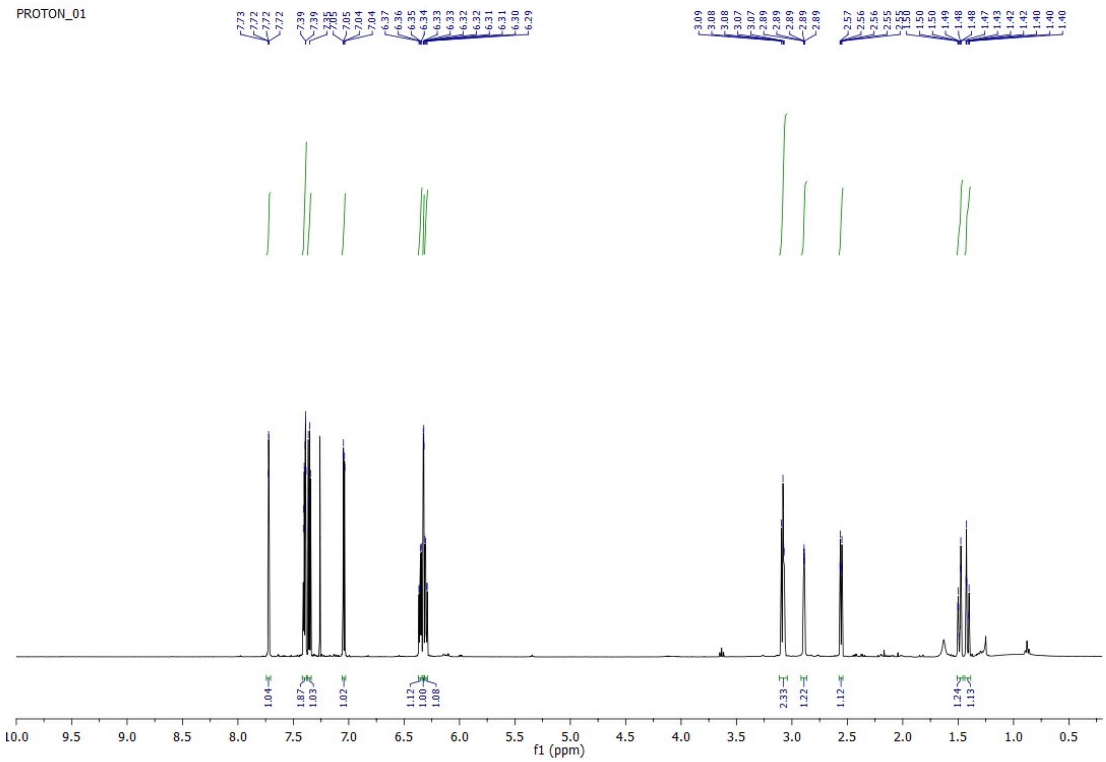
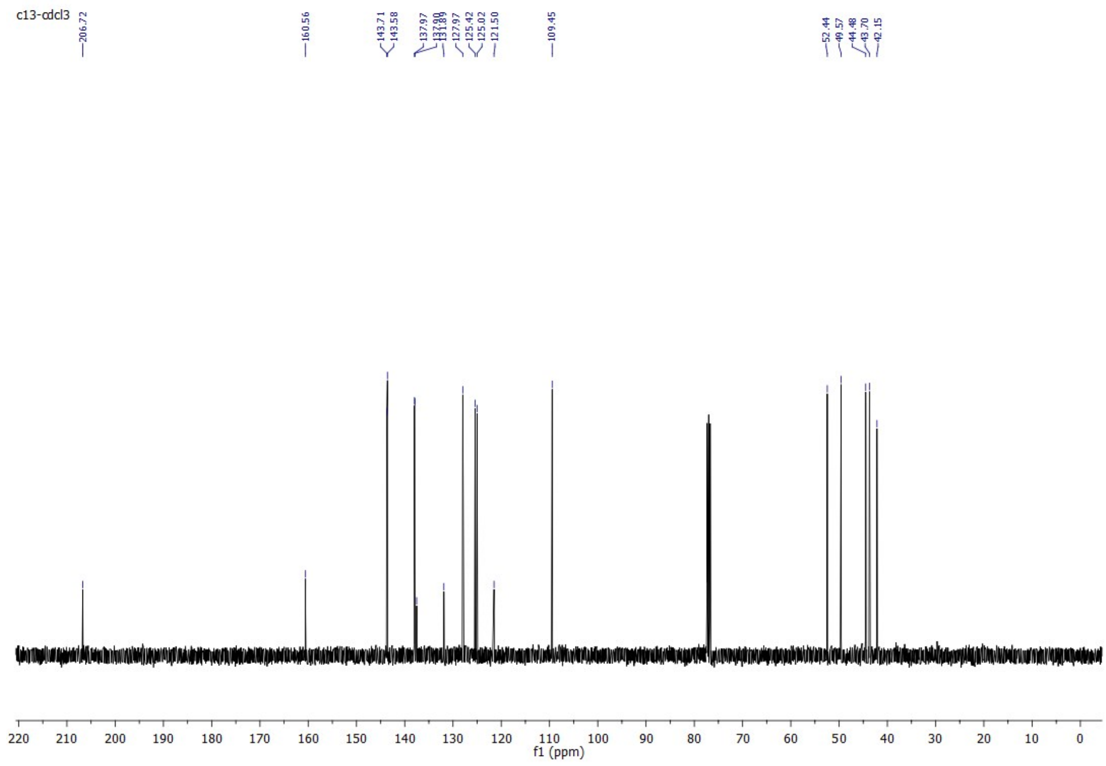
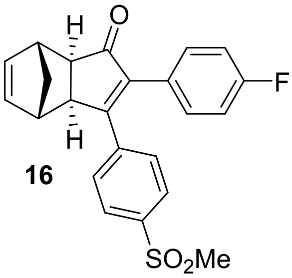
143.72 138.34 137.89 134.72 132.06 129.28 128.40 127.84
52.79 50.30 44.17 43.32 41.89
f1 (ppm)



15

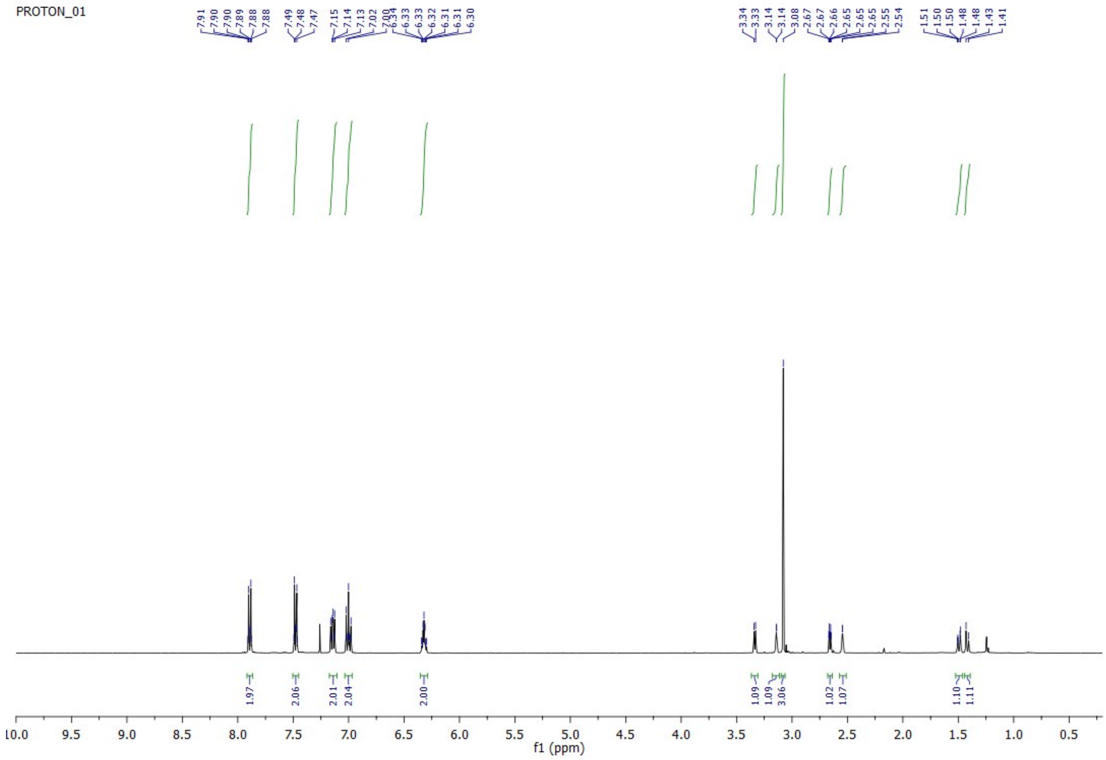




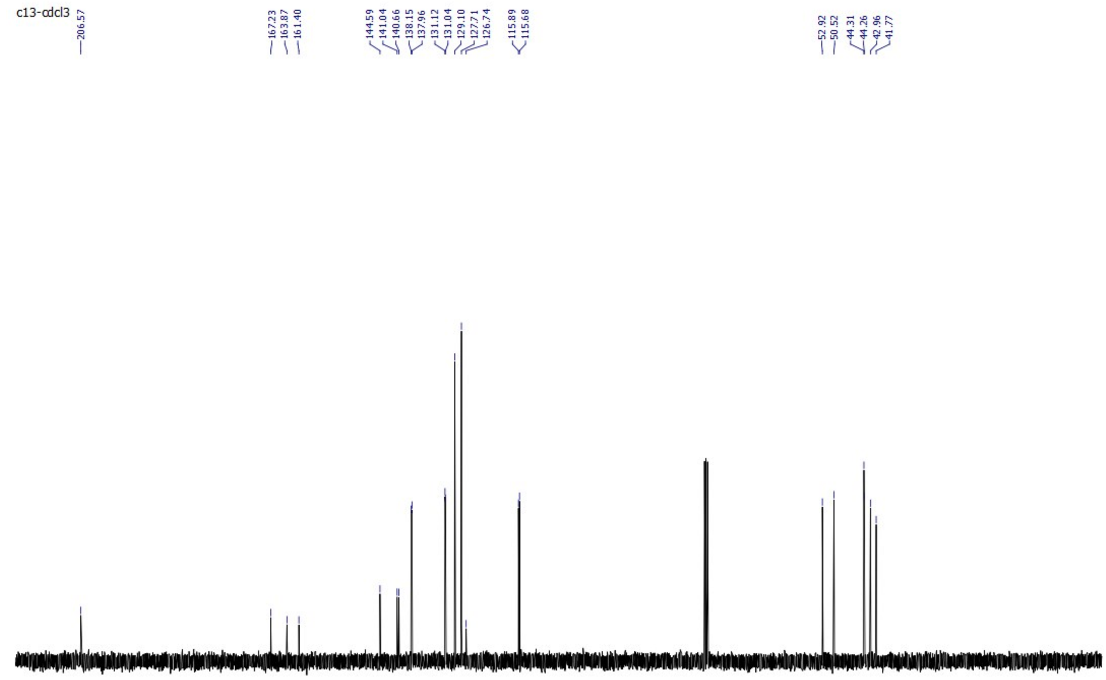


H
O
F
H
SO2Me

16



PROTON_01
7.91 7.90 7.90 7.89 7.88 7.88 7.49 7.48 7.47 7.15 7.14 7.13 7.02 7.00 6.34 6.33 6.33 6.32 6.31 6.31 6.30
3.34 3.33 3.14 3.14 3.08 2.67 2.67 2.66 2.65 2.65 2.55 2.54 1.51 1.50 1.50 1.48 1.48 1.43 1.41
1.97 2.06 2.01 2.04 2.00 1.09 1.09 3.06 1.02 1.07 1.10 1.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



c13-cdcl3
206.57
167.23 163.87 161.40
144.59 141.04 140.66 138.15 137.96 131.12 131.04 129.10 127.71 126.74 115.89 115.68
52.92 50.52 44.31 44.26 42.96 41.77
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)