Supporting Information

Aryne-Mediated Synthesis of Sterically Hindered Arylamines Using TEMPO as the Amine Source

Qiaofeng Liang,† Zhiwen Zhong,† Zhihan Sheng, Bingfeng Sun* and Chenlong Zhu*

School of Pharmaceutical Sciences, Nanjing Tech University, 30 South Puzhu Road, Nanjing, 210000

email: bfsun@njthech.edu.cn and chenlongzhu@njtech.edu.cn

Table of Contents

I. General Experimental Protocols:

Nuclear magnetic resonance (NMR) spectra (^{1}H and ^{13}C) were recorded using a Bruker AX-400 spectrometer. Chemical shifts in ^{1}H NMR spectra recorded in $CDCl_3$ are referenced to $\delta = 7.26$ or (CD_3OD, δ 3.31) (Data are reported according to the following format: chemical shift (ppm) [multiplicity (e.g., s, d, t, q, etc.), coupling constant (s) (in Hz), integral value (to the nearest whole integer), and structural assignment of the proton]. Chemical shifts in ^{13}CNMR spectra are referenced to the carbon atom of $CDCl_3$ (δ 77.16) or (CD_3OD, δ 49.00).

Infrared (IR) spectra were measured on a FT-IR spectrophotometer. The samples were placed on a diamond window as thin films (solids by evaporation from a CH_2Cl_2 solution and liquids by direct deposition) and recorded in the attenuated total reflectance (ATR) mode. The absorption peak maxima are given in cm^{-1}.

High-resolution mass spectrometry (HRMS) measurements were obtained on a Waters Q-TOF Premier Spectrometer (ESI or EI Source).

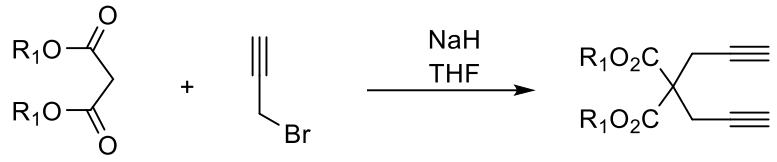
Melting points were obtained on a WRS-1B digital melting-point apparatus.

X-Ray Single Crystal Diffraction Data was recorded on Bruker D8 Quest.

Miscellaneous. Reactions performed above the ambient laboratory temperature were performed in silicone oil baths that had been pre-equilibrated to the temperature of choice before the reaction vessel was immersed. Column chromatography was generally performed on silica gel (300-400 mesh). Reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions and an ethanolic solution of phosphomolybdic acid, and heat as developing agents.

II. Experimental Procedures and Characterization Data for New Compounds

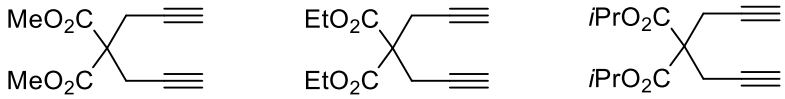
General Procedure A: Synthesis of Diyne S1-S3



S1-S3

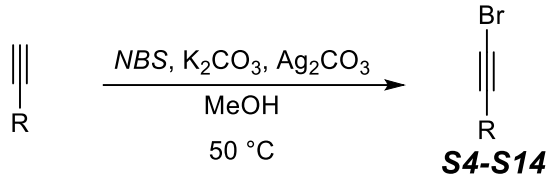
To a stirred solution of sodium hydride (60 % in mineral oil, 2.5 equiv.) in dry THF (e.g., 1 mL on a 1 mmol scale) was added malonate ester (1 eq.) dropwise at 0 °C. The reaction mixture was stirred for 30 minutes while gradually warming to room temperature. It was then cooled back to 0 °C, and propargyl bromide (80% wt in toluene, 2.5 equiv.) was added slowly. The mixture was stirred for 5 hours as it warmed to room temperature. The reaction was quenched with saturated NH_4Cl solution, and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude diyne as a pale yellow solid. Recrystallization from hexanes yielded the white product **S1-S3** in 85%-95% yield.

The proton spectra of **S1**[1], **S2**[2], and **S3**[3] are consistent with previously reported.



S1 ***S2*** ***S3***

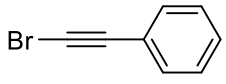
General Procedure B: Synthesis of Bromoacetylene S4-S14



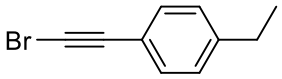
S4-S14

To a stirred solution of alkyne (1.0 equiv.) in MeOH (0.5 M) were added K_2CO_3 (0.5 equiv.), *N*-bromosuccinimide (2.0 equiv.), and Ag_2CO_3 (0.1 equiv.). The reaction mixture was stirred at 50 °C under a nitrogen atmosphere for 2 hours. Upon completion (monitored by TLC), the reaction was cooled to room temperature and quenched with brine. The resulting mixture was extracted with EtOAc. The combined organic layers were washed with water, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using EtOAc/hexanes as the eluent to afford the bromoacetylene products **S4**–**S14** as yellow oils or white solids.

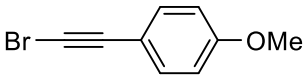
The proton spectra of **S4**[4], **S6**[4], **S7**[5], **S8**[6], **S9**[7], **S10**[8], **S11**[9], **S12**[4], **S13**[10], and **S14**[11] are consistent with previously reported.



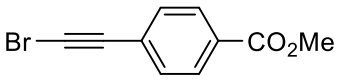
S4



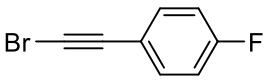
S5



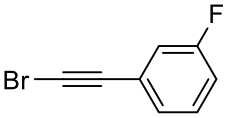
S6



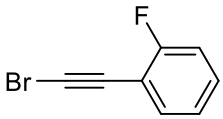
S7



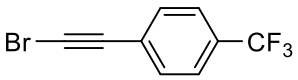
S8



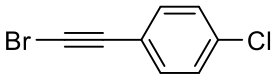
S9



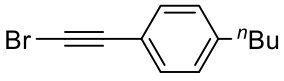
S10



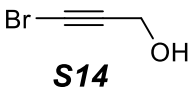
S11



S12

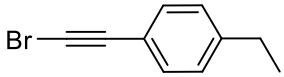


S13



S14

1-(Bromoethynyl)-4-ethylbenzene (S5)



S5

The general reaction procedure B was followed using 1-ethyl-4-ethynylbenzene (1.0 g, 7.7 mmol), K_2CO_3 (534 mg, 3.8 mmol), *N*-bromosuccinimide (2.7 g, 15.4 mmol) and Ag_2CO_3 (211 mg, 0.77 mmol), stirred at 50 °C for 2 h, purification by column chromatography (hexanes 100%) gave the product **S5** (1.5 g, 95%) as a yellow oil.

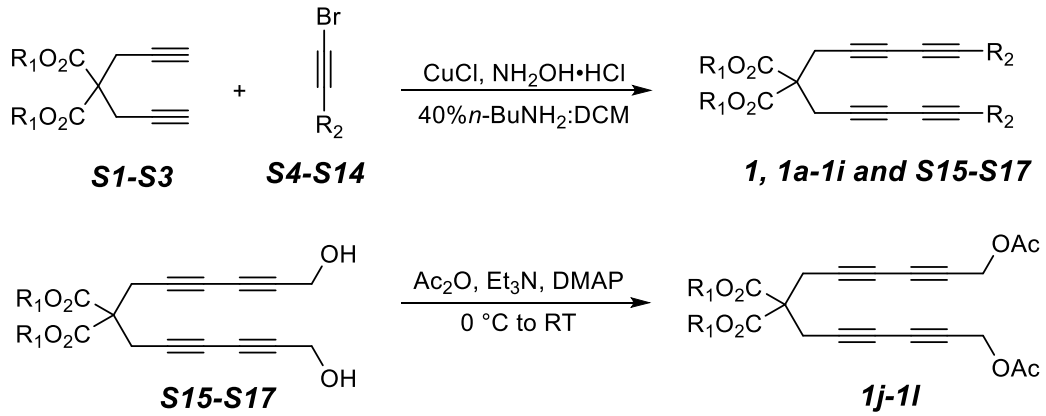
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.35 (m, 2H), 7.19-7.12 (m, 2H), 2.66 (q, *J* = 7.6 Hz, 2H), and 1.24 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 145.3, 132.1 (2C), 128.0 (2C), 120.0, 80.3, 48.9, 29.0, and 15.4.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{10}Br^+$ 208.9960; Found 208.9965.

IR (neat): 3734, 3566, 3028, 2965, 2930, 2198, 1606, 1507, 1454, 1179, and 831 cm^{-1}.

General Procedure C: Synthesis of Tetrayne 1 and 1a-1l

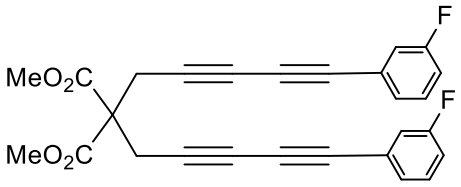


Compounds **1**, **1a-1i** and **S15-S17** were synthesized *via* Cadiot-Chodkiewicz cross-coupling reactions. To a stirred solution of 40% *n*-$BuNH_2$ (3 mL per 1 mmol of substrate) at 0 °C under a nitrogen atmosphere were added CuCl (0.2 equiv), and NH_2OH•HCl (0.6 equiv). A solution of dialkyne (1.0 equiv) in CH_2Cl_2 (1.0 M) was added into the reaction vial, followed by the slow addition of a solution of bromoacetylene (2.5 equiv.) in CH_2Cl_2. The reaction mixture was stirred at 0 °C for an additional 30 minutes. After completion, the reaction mixture was diluted with satd. aq. NH_4Cl and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford **1**, **1a-1i** and **S15-S17** in moderate to good yields.

To a stirred solution of tetraynes **S15-S17** (1 mmol), DMAP (0.2 mmol) and Et_3N (3 mmol) in mixture of THF (e.g., 1 mL on a 1 mmol scale) and CH_2Cl_2 (e.g., 0.5 mL on a 1 mmol scale) at 0 °C was added Ac_2O (3 mmol) dropwise. The resulting mixture was stirred at room temperature for 1 h before it was quenched by the addition of saturated solution of $NaHCO_3$. The layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (hexanes:EtOAc = 10:1) to afford product **1j-1l** (90%, 93%, and 89% respectively) as a yellow oil.

The proton spectra of **1**[12], **1a**[13], **1b**[12], **1c**[14], **1d**[15], **1g**[14], **1h**[16], **1i**[17], **1j**[18] are consistent with those previously reported.

Dimethyl 2,2-bis(5-(3-fluorophenyl)penta-2,4-diyn-1-yl)malonate (1e)



1e

The general reaction procedure C was followed using **S1** (500 mg, 2.1 mmol), **S9** (1.04 g, 5.25 mmol), CuCl (42 mg, 0.42 mmol), $NH_2OH•HCl$ (87 mg, 1.26 mmol), stirred at 0 °C for 30 min, purification by column chromatography (hexanes:EtOAc = 10:1) gave the product **1e** (634 mg, 68%) as a yellow solid.

^{1}H NMR (400 MHz, CD_3OD): δ 7.30-7.23 (m, 4H), 7.14 (ddd, *J* = 8.6, 2.4, 1.2 Hz, 2H), 7.08-7.02 (m, 2H), 3.80 (s, 6H), and 3.20 (s, 4H).

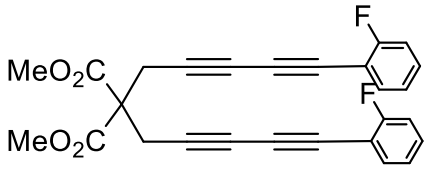
^{13}C NMR (101 MHz, CD_3OD): δ 168.6 (2C), 163.5, 161.1, 130.2, 130.1, 128.6, 128.6, 123.5, 123.4, 119.5, 119.3, 116.9, 116.7, 78.4 (2C), 74.7 (2C), 74.68, 74.67, 68.3 (2C) , 56.6, 53.6 (2C), and 24.3 (2C).

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{19}F_2O_4^+$ 445.1246; Found 445.1239.

IR (neat): 2960, 2555, 1736, 1446, 1300, 1295, 1245, 1024, 900, and 749 cm^{-1}.

m.p.: 116-117 °C.

Dimethyl 2,2-bis(5-(2-fluorophenyl)penta-2,4-diyn-1-yl)malonate (1f)



1f

The general reaction procedure C was followed using **S1** (500 mg, 2.1 mmol), **S10** (1.04 g, 5.25 mmol), CuCl (42 mg, 0.42 mmol), $NH_2OH \cdot HCl$ (87 mg, 1.26 mmol), stirred at 0 °C for 30 min, purification by column chromatography (hexanes:EtOAc = 10:1) gave the product **1f** (569 mg, 61%) as a yellow solid.

^{1}H NMR (400 MHz, CD_3OD): δ 7.47 (td, *J* = 7.3, 1.8 Hz, 2H), 7.39-7.30 (m, 2H), 7.14-7.02 (m, 4H), 3.82 (s, 6H), and 3.23 (s, 4H).

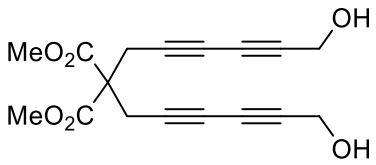
^{13}C NMR (101 MHz, CD_3OD): δ 168.6 (2C), 165.2, 162.7, 134.5, 131.0, 130.9, 124.14, 124.10, 115.8, 115.6, 110.5, 110.3, 78.85, 78.84, 78.55, 78.52, 69.4, 68.34, 68.33, 56.6, 53.6 (2C), and 24.3 (2C).

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{27}H_{19}F_2O_4^+$ 445.1246; Found 445.1241.

IR (neat): 2960, 2550, 1736, 1446, 1300, 1295, 1200, 1024, 900, and 749 cm^{-1}.

m.p.: 115-116.5 °C.

Dimethyl 2,2-bis(6-hydroxyhexa-2,4-diyn-1-yl)malonate (S15)



S15

The general reaction procedure C was followed using **S1** (500 mg, 2.4 mmol), **S14** (1.3 g, 9.6 mmol), CuCl (48 mg, 0.48 mmol), $NH_2OH \cdot HCl$ (100 mg, 1.44 mmol), stirred at 0 °C for 30 min, purification by column chromatography (hexanes:EtOAc = 2:1) gave the product **S15** (418 mg, 55%) as a yellow oil.

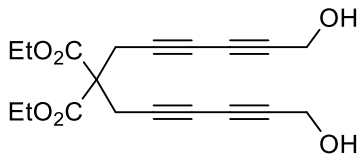
^{1}H NMR (400 MHz, CD_3OD): δ 4.26 (s, 2H), 4.24 (t, *J* = 1.2 Hz, 4H), 3.78 (s, 6H), and 3.06 (t, *J* = 1.1 Hz, 4H).

^{13}C NMR (101 MHz, CD_3OD): δ 169.9 (2C), 78.8 (2C), 77.2 (2C), 74.8 (2C), 69.4, 68.7, 57.7, 53.8 (2C), 50.9 (2C), and 24.6 (2C).

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{17}O_6^+$ 317.1020; Found 317.1024.

IR (neat): 2956, 2539, 1734, 1436, 1326, 1295, 1254, 1214, 1024, 965, and 749cm^{-1}.

Diethyl 2,2-bis(6-hydroxyhexa-2,4-diyn-1-yl)malonate (S16)



S16

The general reaction procedure C was followed using **S2** (500 mg, 2.1 mmol), **S14** (1.1 g, 8.5 mmol), CuCl (42 mg, 0.42 mmol), NH_2OH•HCl (87 mg, 1.3 mmol), stirred at 0 °C for 30 min, purification by column chromatography (hexanes:EtOAc = 2:1) gave the product **S16** (400 mg, 55%) as a yellow oil.

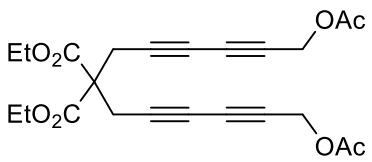
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.25 (t, *J* = 17.4 Hz, 4H), 4.23 (q, *J* = 7.1 Hz, 4H), 3.5 (s, 4H), 2.35 (brs, 2H), and 1.25 (t, *J* = 7.1Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3 (2C), 75.2 (2C), 74.9 (2C), 70.2 (2C), 67.7 (2C), 62.6 (2C), 56.5 (2C), 51.4, 23.9 (2C), 14.1 (2C).

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{21}O_6^+$ 345.1333; Found 345.1337.

IR (neat): 2954, 2541, 1738, 1446, 1331, 1242, 1265, 1234, 1084, 965, 811, 754 and 688 cm^{-1}.

Diethyl 2,2-bis(6-acetoxyhexa-2,4-diyn-1-yl)malonate (1k)



1k

The general reaction procedure C was followed using **S16** (1.1 g, 3.2 mmol), DMAP (40 mg, 0.32 mmol), Et_3N (1.1 mL, 8.0 mmol), Ac_2O (0.76 mL, 8.0 mmol), stirred at 0 °C for 30 min, purification by column chromatography (hexanes:EtOAc = 5:1) gave the product **1k** (1.3 g, 93%) as a yellow oil.

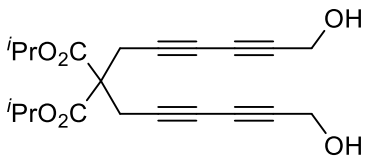
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.68 (d, *J* = 1.3 Hz, 4H), 4.26-4.14 (m, 4H), 3.04 (d, *J* = 2.3 Hz, 4H), 2.12-2.04 (m, 6H), and 1.24 (tt, *J* = 7.1, 1.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.1 (2C), 168.1 (2C), 75.3 (2C), 71.0 (2C), 70.7 (2C), 67.7 (2C), 62.5 (2C), 56.4, 52.4 (2C), 23.8 (2C), 20.7 (2C), and 14.1 (2C).

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{25}O_8^+$ 429.1544; Found 429.1537.

IR (neat): 3467, 2983, 2260, 1737, 1427, 1370, 1221, 1030, 858, and 603 cm^{-1}.

Diisopropyl 2,2-bis(6-hydroxyhexa-2,4-diyn-1-yl)malonate (S17)



S17

The general reaction procedure C was followed using **S3** (685 mg, 2.6 mmol), **S14** (1.4 g, 10.4 mmol), CuCl (52 mg, 0.5 mmol), $NH_2OH•HCl$ (108 mg, 1.56 mmol), stirred at 0 °C for 30 min, purification by column chromatography (hexanes:EtOAc = 2:1) gave the product **S17** (400 mg, 55%) as a yellow oil.

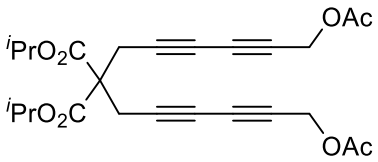
^{1}H NMR (400 MHz, CD_3OD): δ 5.13-5.00 (m, 2H), 4.24 (d, *J* = 1.0 Hz, 4H), 3.01 (d, *J* = 1.2 Hz, 4H), and 1.27 (d, *J* = 6.3 Hz, 12H).

^{13}C NMR (101 MHz, CD_3OD): δ 168.3 (2C), 78.2 (2C), 76.4 (2C), 74.4 (2C), 70.7 (2C), 68.8, 68.8, 68.0, 57.0, 50.3, 50.3, 23.8 (2C), and 21.1 (4C).

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{25}O_6^+$ 373.1646; Found 373.1645.

IR (neat): 2982, 1731, 1212, 1101, 1024, and 749 cm^{-1}.

Diisopropyl 2,2-bis(6-acetoxyhexa-2,4-diyn-1-yl)malonate (1l)



1l

The general reaction procedure C was followed using **S17** (1.2 g, 3.2 mmol), DMAP (40 mg, 0.32 mmol), Et_3N (1.1 mL, 8.0 mmol), Ac_2O (0.76 mL, 8.0 mmol), stirred at 0 °C for 30 min, purification by column chromatography (hexanes:EtOAc = 5:1) gave the product **1l** (1.3 g, 89%) as a yellow oil.

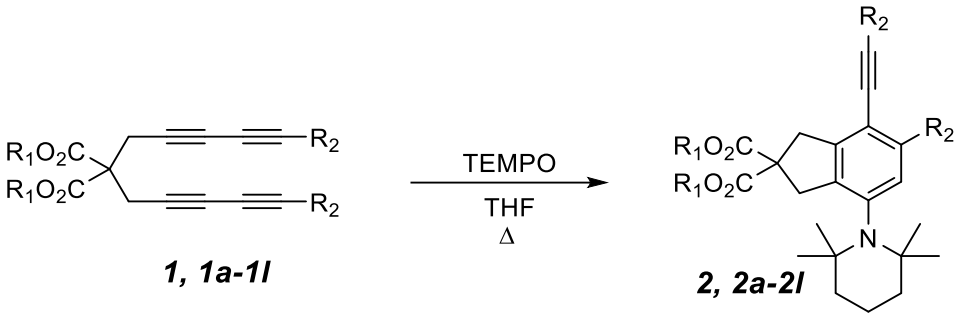
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.07 (m, 2H), 4.70 (s, 4H), 3.03 (s, 4H), 2.09 (s, 6H), and 1.23 (dd, *J* = 6.4, 1.7 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.2 (2C), 167.6 (2C), 75.5 (2C), 71.1 (2C), 70.6 (2C), 70.2 (4C), 67.6 (2C), 56.3, 52.5 (2C), 23.7 (2C), 21.6 (4C), and 20.8 (2C).

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{29}O_8^+$ 457.1857; Found 457.1859.

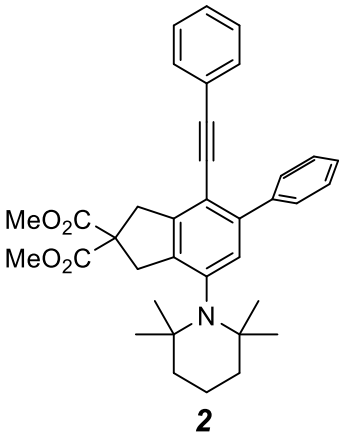
IR (neat): 2983, 1733, 1638, 1424, 1376, 1292, 1216, 1106, 1029, and 602 cm^{-1}.

General Procedure D: Reaction of Tetrayne with TEMPO



Tetraynes **1** and **1a-1l** (1.0 equiv.) and 2,2,6,6-tetramethyl piperdine 1-oxyl (TEMPO) (2.0 equiv.) were dissolved in THF (e.g., 1 mL on a 1 mmol scale) and heated in a screw-capped culture tube in an oil bath under nitrogen atmosphere and at 110 °C for 12 h. Upon completion of the reaction, the mixture was cooled to room temperature, diluted with a saturated aqueous solution of $NaHCO_3$, and extracted with EtOAc. The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford **2** and **2a-2l** in 63–86% yield as white solids or colorless oils.

Dimethyl 5-phenyl-4-(phenylethynyl)-7-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2)



2

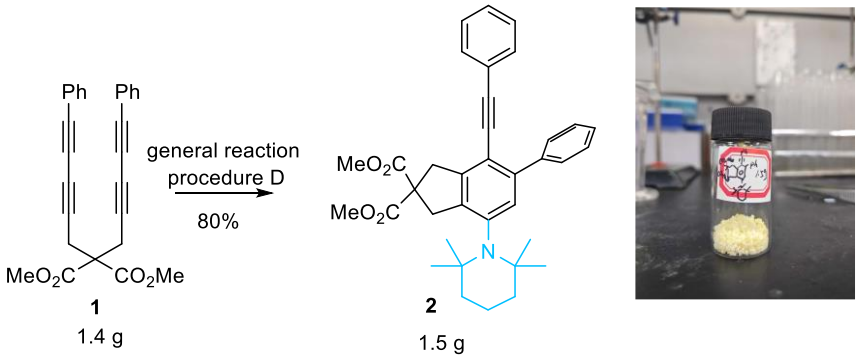
The general reaction procedure D was followed using **1** (168 mg, 0.4 mmol), TEMPO (128 mg, 0.8 mmol), stirred at 110 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 20:1) gave the product **2** (194 mg, 86%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 7.5 Hz, 2H), 7.50-7.42 (m, 2H), 7.40-7.34 (m, 3H), 7.33-7.23 (m, 4H), 3.95-3.65 (m, 10H), and 1.95-0.66 (m, 8H).

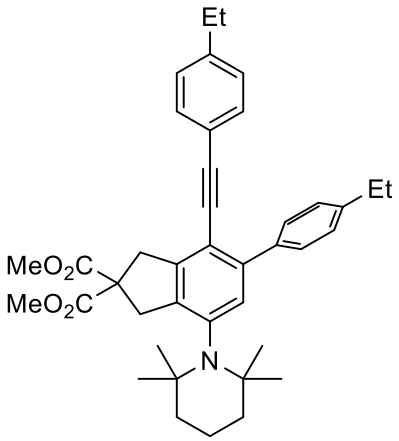
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.2, 144.1, 143.9, 142.7, 142.6, 140.7, 132.3, 131.4, 129.5, 128.3, 128.1, 127.94, 127.86, 127.3, 123.7, 115.2, 95.6, 87.4, 59.7, 55.5, 53.0, 42.2, 41.54, 41.46, 32.4, 25.6, and 18.5.
HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{40}NO_4^+$ 550.2952; Found 550.2949.

IR (neat): 3568, 3292, 2969, 2928, 1754, 1648, 1491, 1377, 1275, 1198, 1065, 912, and 754 cm^{-1}.
m.p.: 172-173.5 °C.

Gram-scale results are shown below:



Dimethyl 5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-7-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2a)



2a

The general reaction procedure D was followed using **1a** (156 mg, 0.3mmol), TEMPO (93 mg, 0.6 mmol), stirred at 110 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 30:1) gave the product **2a** (141 mg, 78%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.60 (m, 2H), 7.31 (m, 5H), 7.16 (m, 2H), 3.85 (s, 2H), 3.79 (s, 6H), 3.74 (s, 2H), 2.81-2.70 (m, 2H), 2.71-2.63 (m, 2H), 1.73-1.54 (m, 6H), 1.39-1.21 (m, 12H), 1.16-1.03 (m, 1H), and 0.90-0.83 (m, 5H).

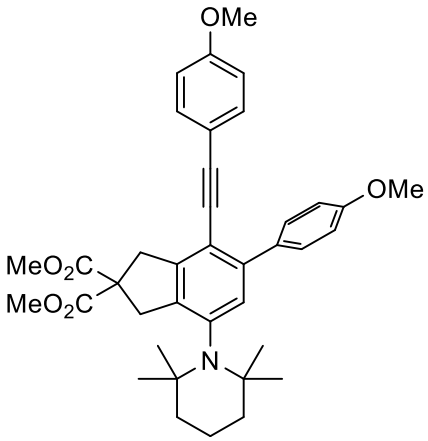
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.2, 144.5, 143.8, 143.7, 143.5, 143.2, 142.4, 142.3, 138.1, 132.2, 131.4, 129.3, 127.8, 127.4, 120.9, 115.3, 59.6, 55.4, 52.9, 42.2, 41.5, 41.46, 32.4, 28.9 28.7, 25.5, 18.4, 15.6, and 15.5.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{40}H_{48}NO_4^+$ 606.3578; Found 606.3583.

IR (neat): 3350, 2089, 1737, 1639, 1489, 1455, 1237, 832, and 644 cm^{-1}.

m.p.: 169-170 °C.

Dimethyl 5-(4-methoxyphenyl)-4-((4-methoxyphenyl)ethynyl)-7-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2b)



2b

The general reaction procedure D was followed using **1b** (134 mg, 0.28 mmol), TEMPO (89 mg, 0.57 mmol), stirred at 110 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 20:1) gave the product **2b** (94 mg, 74%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.7 Hz, 2H), 7.39-7.32 (m, 2H), 7.27 (d, *J* = 13.1 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.90-6.82 (m, 2H), 3.90 (s, 3H), 3.86-3.77 (m, 11H), 3.71 (s, 2H), and 1.09 (m, 18H).

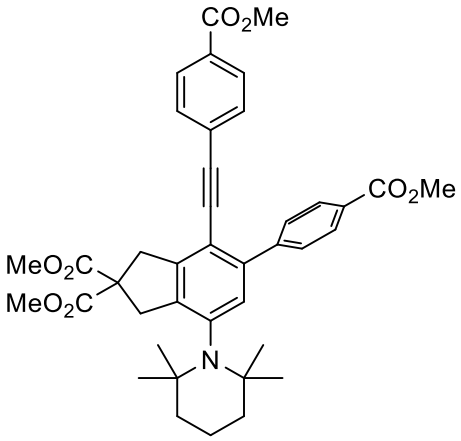
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.3, 159.6, 159.0, 143.8, 143.6, 142.2, 141.9, 133.5, 132.9, 132.2, 130.6, 116.0, 115.4, 114.0, 113.4, 95.6, 86.3, 59.7, 55.5, 55.4, 53.0, 42.3, 41.6, 32.5, 25.6, and 18.5.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{38}H_{44}NO_6^+$ 610.3163; Found 610.3167.

IR (neat): 2932, 1731, 1510, 1338, 1247, 1031, 873, and 750 cm^{-1}.

m.p.: 170-171.2 ºC.

Dimethyl 5-(4-(methoxycarbonyl)phenyl)-4-((4-(methoxycarbonyl)phenyl)ethynyl)-7-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylat (2c)



2c

The general reaction procedure D was followed using **1c** (100 mg, 0.21 mmol), TEMPO (66 mg, 0.4 mmol), stirred at 110 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 50:1) gave the product **2c** (96 mg, 75%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16-8.09 (m, 2H), 8.01-7.93 (m, 2H), 7.76-7.68 (m, 2H), 7.43-7.35 (m, 2H), 7.28 (s, 1H), 3.95 (s, 3H), 3.91 (s, 3H), 3.82 (s, 2H), 3.76 (s, 6H), 3.71 (s, 2H), and 1.73-0.75 (m, 18H).

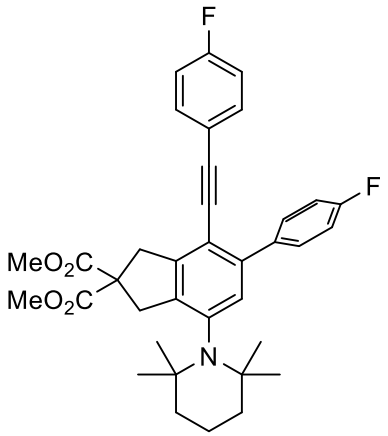
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.0, 167.1, 166.6, 145.2, 144.9, 144.5, 143.8, 141.7, 132.4, 131.3, 129.6, 129.5, 129.44, 129.37, 129.1, 128.0, 95.2, 90.0, 59.7, 55.6, 53.1, 52.33, 52.27, 42.2, 41.5, 41.4, 32.4, 25.6, and 18.4.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{40}H_{44}NO_8^+$ 666.3061; Found 666.3057.

IR (neat): 2500, 2068, 1742, 1738, 1639, 1492, 1240, 1200, 1093, 825, and 620 cm^{-1}.

m.p.: 170-171.5 ºC.

Dimethyl 5-(4-fluorophenyl)-4-((4-fluorophenyl)ethynyl)-7-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2d)



2d

The general reaction procedure D was followed using **1d** (102 mg, 0.23 mmol), TEMPO (72 mg, 0.45 mmol), stirred at 110 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 50:1) gave the product **2d** (100 mg, 75%) as a white solid.

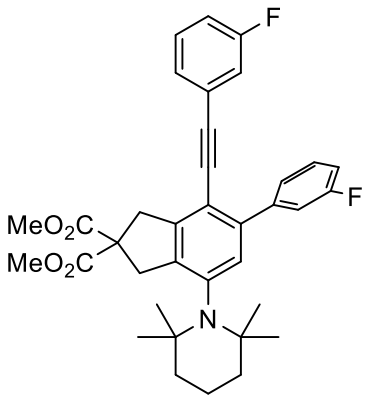
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.56 (m, 2H), 7.33 (tt, J = 5.3, 2.3 Hz, 2H), 7.22 (s, 1H), 7.18-7.08 (m, 2H), 7.04-6.94 (m, 2H), 3.92-3.62 (m, 10H), and 1.68-0.78 (m, 18H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.2, 163.8, 163.6, 161.3, 161.2, 144.3, 143.9, 143.0, 141.5, 136.8, 133.33, 133.25, 132.3, 131.1, 131.0, 119.6, 115.9, 115.6, 115.1, 115.0, 114.8 , 94.7, 86.9, 59.7, 55.5, 53.1, 42.2, 41.53, 41.45, 32.5, 25.6, and 18.5.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{38}F_2NO_4^+$ 586.2763; Found 586.2763.

IR (neat): 2950, 2500, 2038, 1738, 1680, 1547, 1499, 1221, 1198, 1088, and 749 cm^{-1}.

m.p.: 185.6-186.8 ºC.

Dimethyl 5-(3-fluorophenyl)-4-((3-fluorophenyl)ethynyl)-7-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2e)



2e

The general reaction procedure D was followed using **1e** (160 mg, 0.36 mmol), TEMPO (113 mg, 0.72 mmol), stirred at 110 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 50:1) gave the product **2e** (166 mg, 79%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.36 (m, 3H), 7.30-7.24 (m, 2H), 7.17-6.96 (m, 4H), 3.81 (s, 2H), 3.76 (s, 6H), 3.71 (s, 2H), 1.69-1.53 (m, 6H), 1.30 (s, 6H), and 0.83 (s, 6H).

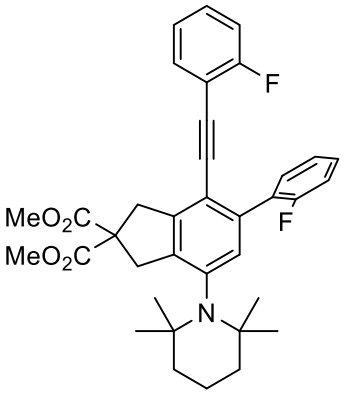
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.1, 163.8, 163.7, 161.3, 161.2, 144.7, 144.3, 143.5, 142.8, 142.7, 141.4, 132.3, 130.1, 130.0, 129.5, 129.4, 127.4, 127.3, 125.4, 125.3, 125.2, 125.1, 118.3, 118.0, 116.5, 116.3, 115.8, 115.6, 114.8, 114.4, 114.2, 94.8, 94.7, 87.9, 59.7, 55.6, 53.1, 42.2, 41.6, 41.4, 32.4, 25.6, and 18.5.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{38}F_2NO_4^+$ 586.2763; Found 586.2766.

IR (neat): 3100, 2850, 2200, 1740, 1725, 1647, 1600, 1465, 1370, 1201, 878, and 685 cm^{-1}.

m.p.: 186.1-187.6 °C.

Dimethyl 5-(2-fluorophenyl)-4-((2-fluorophenyl)ethynyl)-7-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2f)



2f

The general reaction procedure D was followed using **1f** (116 mg, 0.26 mmol), TEMPO (82 mg, 0.52 mmol), stirred at 110 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 50:1) gave the product **2f** (130 mg, 85%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (td, *J* = 7.6, 1.8 Hz, 1H), 7.38 (tdd, *J* = 7.3, 5.0, 1.8 Hz, 1H), 7.31 (q, *J* = 2.8 Hz, 2H), 7.28-7.16 (m, 3H), 7.06 (q, *J* = 8.2 Hz, 2H), 3.86 (s, 2H), 3.78 (s, 6H), 3.74 (s, 2H), 1.62 (q, *J* = 3.6 Hz, 6H), 1.30 (s, 6H), and 0.86 (s, 6H).

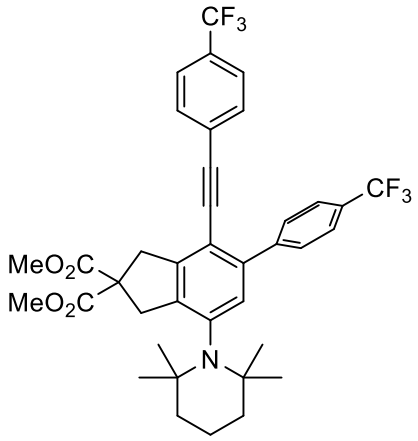
^{13}C NMR (101 MHz, $CDCl_3$): δ 163.8, 161.3, 161.1, 158.6, 144.2, 143.9, 143.4, 136.5, 133.3, 133.2, 132.4, 132.3, 129.9, 129.8, 129.4, 129.3, 128.3, 128.1, 124.0 123.9, 123.64, 123.61, 116.2, 115.9, 115.7, 115.6, 115.4, 112.3, 112.2, 59.7, 55.6, 53.1, 42.3, 41.7, 41.4, 32.5, 25.3, and 18.5.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{38}F_2NO_4^+$ 586.2763; Found 586.2767.

IR (neat): 2980, 2530, 2029, 1740, 1725, 1680, 1547, 1460, 1077, and 736 cm^{-1}.

m.p.: 183-183.5 °C.

Dimethyl 7-(2,2,6,6-tetramethylpiperidin-1-yl)-5-(4-(trifluoromethyl)phenyl)-4-((4-(trifluoromethyl)phenyl)ethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2g)



2g

The general reaction procedure D was followed using **1g** (150 mg, 0.27 mmol), TEMPO (84 mg, 0.54 mmol), stirred at 110 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 50:1) gave the product **2g** (148 mg, 80%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (q, *J* = 8.3 Hz, 4H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.27 (s, 1H), 3.86-3.70 (m, 10H), 1.61 (t, *J* = 7.5 Hz, 5H), 1.30 (s, 6H), and 0.84 (s, 6H).

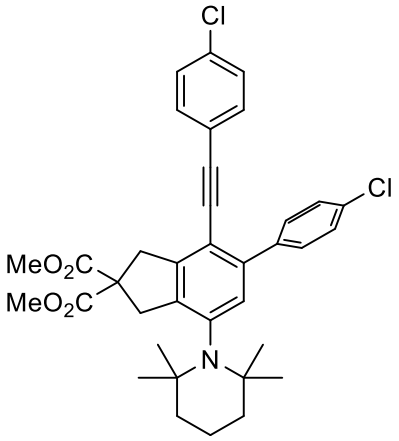
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.0, 145.0, 144.6, 144.3, 144.0, 141.5, 132.5, 131.6, 129.8, 125.5, 125.4, 125.1, 125.0, 114.7, 94.6, 89.2, 59.7, 55.6, 53.1, 42.2, 41.6, 41.5, 32.5, 25.6, and 18.4.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{38}H_{38}F_6NO_4^+$ 686.2700; Found 686.2695.

IR (neat):3100, 2850, 2500, 2200, 1738, 1720, 1588, 1275, 1220, 1155, 1088, 824, and 750 cm^{-1}.

m.p.: 168-169 °C.

Dimethyl 5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-7-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2h)



2h

The general reaction procedure D was followed using **1h** (100 mg, 0.21 mmol), TEMPO (66 mg, 0.4 mmol), stirred at 110 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 50:1) gave the product **2h** (96 mg, 75%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.27 (s, 4H), 7.20 (s, 1H), 3.78-3.73 (m, 10H), 3.68 (s, 2H), and 1.74-0.48 (m, 16H).

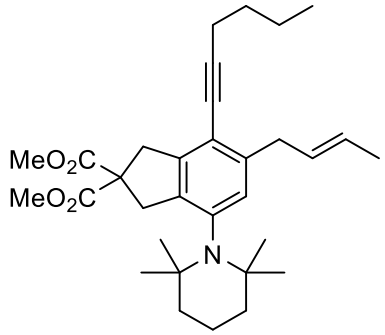
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.9, 144.4, 144.0, 143.1, 141.2, 139.0, 134.2, 133.3, 132.5, 132.1, 130.6, 128.6, 128.0, 127.97, 121.8, 114.7, 94.6, 87.9, 71.8, 59.5, 55.4, 55.2, 53.1, 52.9, 42.1, 41.4, 41.3, 32.3, 25.5, 22.6, and 18.3.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{38}Cl_2NO_4^+$ 618.2172; Found 618.2167.

IR (neat): 2500, 2068, 1639, 1490, 1238, 1198, 1089, 824, and 671 cm^{-1}.

m.p.: 171-172 °C.

Dimethyl (*E*)-5-(but-2-en-1-yl)-4-(hex-1-yn-1-yl)-7-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2i)



2i

The general reaction procedure D was followed using **1i** (120 mg, 0.3 mmol), TEMPO (93 mg, 0.6 mmol), stirred at 110 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 20:1) to afford compound **2m** (11 mg, 5%) as a colorless oil and followed by the slower eluting **2i** (104 mg, 63%) as a colorless oil.

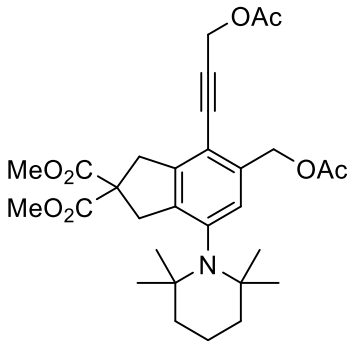
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.48 (s, 1H), 4.72-4.61 (m, 2H), 3.75 (s, 6H), 3.65 (s, 2H), 3.32 (s, 2H), 2.70-2.61 (m, 2H), 2.44 (t, *J* = 6.9 Hz, 2H), 1.98 (t, *J* = 7.3 Hz, 2H), 1.68-1.28 (m, 20H), and 0.94 (td, *J* = 7.3, 3.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.4, 145.8, 145.1, 143.0, 142.0, 122.5, 112.1, 110.2, 107.8, 94.6, 77.7, 59.2, 53.8, 53., 41.4, 40.7, 38.2, 38.1, 34.8, 33.2, 31.4, 28.6, 22.7, 22.4, 22.1, 21.8, 19.5, 14.2, and 13.8.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{32}H_{46}NO_4^+$ 508.3421; Found 508.3425.

IR (neat): 3450, 2954, 2931, 2858, 1647, 1605, 1505, 1433, 1362, 1248, 1197, 1070, 885, and 778 cm^{-1}.

Dimethyl 5-(acetoxymethyl)-4-(3-acetoxyprop-1-yn-1-yl)-7-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2j)



2j

The general reaction procedure D was followed using **1j** (100 mg, 0.25 mmol), TEMPO (78 mg, 0.5 mmol), stirred at 120 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 10:1) gave the product **2j** (100 mg, 74%) as a colorless oil.

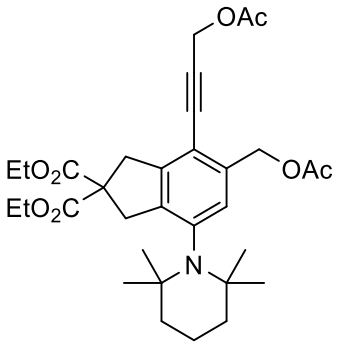
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 2.7 Hz, 1H), 5.19 (t, *J* = 2.3 Hz, 2H), 4.93 (t, *J* = 2.4 Hz, 2H), 3.76-3.49 (m, 10H), 2.12 (dt, *J* = 7.8, 2.2 Hz, 6H), and 1.70-0.66 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.0, 171.0, 170.4, 144.6, 144.2, 144.0, 136.6, 131.5, 115.3, 90.9, 82.0, 64.9, 59.7, 55.5, 53.0, 52.96, 42.2, 41.4, 41.0 32.3, 25.3, 21.1, 20.9, and 18.4.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{40}NO_8^+$ 542.2748; Found 542.2744.

IR (neat): 3380, 1737, 1638, 1434, 1377, 1362, 1236, 1174, 1129, 1027, and 605 cm^{-1}.

Diethyl 5-(acetoxymethyl)-4-(3-acetoxyprop-1-yn-1-yl)-7-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2k)



2k

The general reaction procedure D was followed using **1k** (107 mg, 0.25 mmol), TEMPO (78 mg, 0.5 mmol), stirred at 120 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 20:1) gave the product **2k** (106 mg, 75%) as a colorless oil.

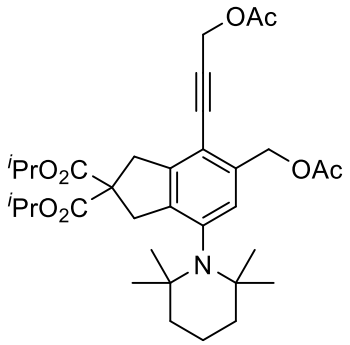
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (s, 1H), 5.19 (s, 2H), 4.93 (s, 2H), 4.18 (q, *J* = 7.0 Hz, 4H), 3.63 (d, *J* = 13.3 Hz, 4H), 2.12 (dd, *J* = 7.2, 1.5 Hz, 6H), and 1.69-0.58 (m, 24H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.6, 171.0, 170.4, 144.6, 144.3, 144.1, 136.4, 131.5, 115.3, 90.8, 82.0, 64.9, 61.9, 59.7, 55.4, 53.0, 42.2, 41.23, 40.8, 32.4, 25.3, 21.1, 20.9, 18.4, and 14.2.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{32}H_{44}NO_8^+$ 570.3061; Found 570.3068.

IR (neat): 3420, 2974, 1639, 1377, 1363, 1235, 1183, 1129, 1066, 1027, and 605 cm^{-1}.

Diisopropyl 5-(acetoxymethyl)-4-(3-acetoxyprop-1-yn-1-yl)-7-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2l)



2l

The general reaction procedure D was followed using **1l** (98 mg, 0.2 mmol), TEMPO (67 mg, 0.4 mmol), stirred at 120 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 30:1) gave the product **2l** (81 mg, 72%) as a colorless oil.

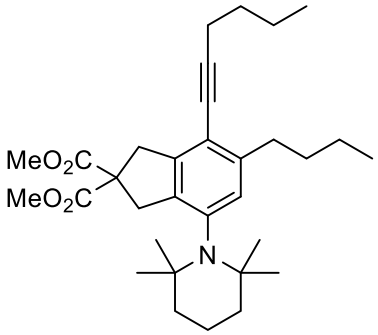
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (s, 1H), 5.18 (s, 2H), 5.08-4.96 (m, 2H), 4.93 (s, 2H), 3.60 (s, 4H), 2.11 (d, *J* = 5.9 Hz, 6H), and 1.71-0.67 (m, 30H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.2, 171.0, 170.4, 144.6, 144.5, 144.2, 136.5, 131.4, 115.3, 90.8, 82.1, 69.3, 65.0, 59.7, 55.4, 53.6, 53.0, 42.2, 41.2, 40.9, 32.5, 25.3, 21.7, 21.66, 21.1, 20.9, and 18.5.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{34}H_{48}NO_8^+$ 598.3374; Found 598.3371.

IR (neat): 3458, 2978, 2933, 1645, 1455, 1376, 1237, 1188, 1105, 1027, 910, and 825 cm^{-1}.

Dimethyl 5-butyl-4-(hex-1-yn-1-yl)-7-(2,2,6,6-tetramethylpiperidin-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (2m)



2m

Tetrayne **1i** (120 mg, 0.3 mmol) and 2,2,6,6-Tetramethylpiperidine (TMP) (100 µL, 0.6 mmol), THF (2 mL) were heated in a screw-capped culture tube in an oil bath and stirred at 110 °C for 12 h. After the completion of reaction, the mixture was cooled to room temperature, and diluted with saturated solution of NH_4Cl (5 mL), extracted with CH_2Cl_2 (3x10 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (hexanes:EtOAc = 20:1) to afford **2m** (82.5 mg, 50%) as a colorless oil and followed by the slower eluting **2i** (20.5 mg, 10%) as a colorless oil.

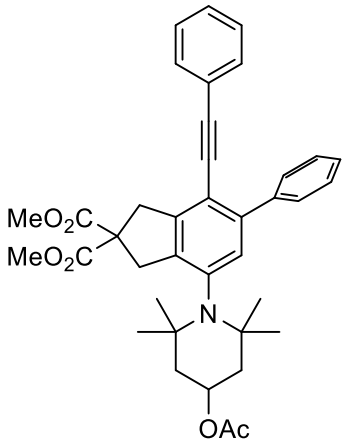
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (s, 1H), 3.71 (s, 6H), 3.63 (s, 2H), 3.57 (s, 2H), 2.73-2.67 (m, 2H), 2.47 (t, *J* = 6.9 Hz, 2H), 1.63-1.47 (m, 10H), 1.40-1.30 (m, 2H), 1.25 (s, 7H), 0.94 (dt, *J* = 8.6, 7.3 Hz, 7H), and 0.73 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.4, 143.2, 142.9, 142.8, 140.5, 131.4, 117.0, 97.1, 59.7, 55.3, 52.9, 42.3, 41.5, 41.3, 34.3, 33.1, 32.4, 31.2, 25.4, 22.6, 22.1, 19.5, 18.6, 14.2, and 13.8.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{32}H_{48}NO_4^+$ 510.3578; Found 510.3576.

IR (neat): 3450, 2954, 2931, 2858, 1737, 1505, 1433, 1362, 1248, 1197, 1070, 875, and 764 cm^{-1}.

Dimethyl 7-(4-acetoxy-2,2,6,6-tetramethylpiperidin-1-yl)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (5)



5

The general reaction procedure D was followed using **1** (110 mg, 0.26 mmol), 4-*acetyl*-TEMPO (107 mg, 0.5 mmol), stirred at 110 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 20:1) gave the product **5** (112 mg, 71%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.68 (m, 2H), 7.57-7.26 (m, 9H), 5.35 (s, 1H), 3.94-3.66 (m, 10H), 2.19-2.02 (m, 6H), and 1.81-0.89 (m, 13H).

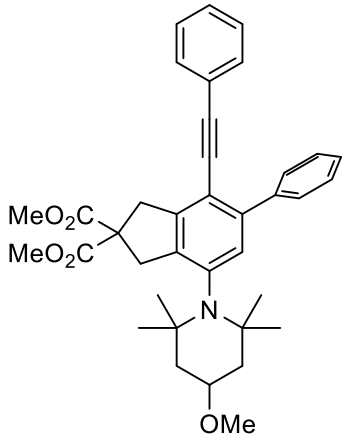
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.2, 170.0, 143.2, 142.1, 142.0, 141.6, 139.6, 131.2, 130.6, 128.6, 127.5, 127.4, 127.2, 126.6, 122.7, 114.9, 95.0, 86.3, 67.2, 58.8, 55.8, 52.3, 46.2, 40.6, 31.6, 25.6, and 20.8.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{38}H_{42}NO_6^+$ 608.3007; Found 608.3005.

IR (neat): 2972, 1735, 1491, 1464, 1435, 1379, 1365, 1244, 1178, 1030, 953, and 776 cm^{-1}.

m.p.: 176-176.9 °C.

Dimethyl 7-(4-methoxy-2,2,6,6-tetramethylpiperidin-1-yl)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (6)



6

The general reaction procedure D was followed using **1** (140 mg, 0.3 mmol), 4-*methoxy*-TEMPO (112 mg, 0.6 mmol), stirred at 110 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 30:1) gave the product **6** (118 mg, 68%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.62 (m, 2H), 7.50-7.43 (m, 2H), 7.41-7.33 (m, 3H), 7.32-7.25 (m, 3H), 7.23 (s, 1H), 3.82 (s, 2H), 3.80 (s, 1H), 3.76 (s, 6H), 3.67 (s, 2H), 3.41 (s, 3H), 2.03 (dd, *J* = 12.0, 4.0 Hz, 2H), and 1.68-0.86 (m, 14H).

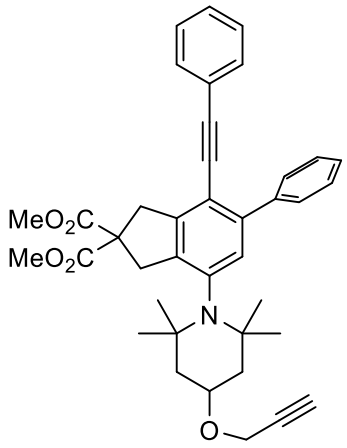
^{13}C NMR (101 MHz, $CDCl_3$): δ 171.9, 143.8, 143.1, 142.5, 142.4, 140.4, 132.0, 131.2, 130.3, 129.2, 128.7, 128.1, 128.0, 127.7, 127.1, 123.4, 115.4, 95.6, 87.0, 72.8, 59.4, 56.4, 55.3, 53.2, 52.8, 47.3, 41.2, 32.3, and 26.4.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{37}H_{42}NO_5^+$ 580.3057; Found 580.3063.

IR (neat): 3442, 2971, 2093, 1736, 1640, 1492, 1378, 1364, 1201, 1032, 911, and 776, 526 cm^{-1}.

m.p.: 181-1812 °C.

Dimethyl 5-phenyl-4-(phenylethynyl)-7-(2,2,6,6-tetramethyl-4-(prop-2-yn-1-yloxy)piperidin-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (7)



7

The general reaction procedure D was followed using **1** (110 mg, 0.26 mmol), 4-*propargyloxy*-TEMPO (105 mg, 0.5 mmol), stirred at 110 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 20:1) gave the product **7** (101 mg, 65%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.62 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.41-7.20 (m, 7H), 4.25 (d, *J* = 2.4 Hz, 2H), 4.05 (s, 1H), 3.93-3.63 (m, 10H), 2.61-2.31 (m, 1H), 2.08-2.00 (m, 2H), and 1.74-0.85 (m, 14H).

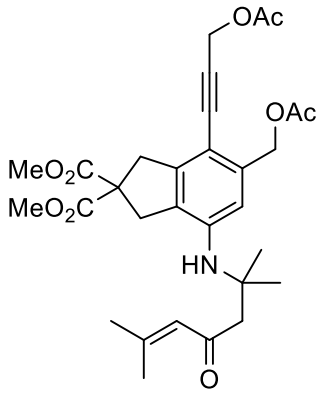
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.2, 144.2, 143.2, 142.8, 142.7, 140.6, 132.2, 131.5, 129.5, 128.4, 128.3, 128.0, 127.5, 123.6, 115.8, 95.9, 87.3, 80.5, 74.1, 71.1, 59.7, 56.8, 55.1, 53.1, 47.6, 41.5, 32.6, and 26.7.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{39}H_{42}NO_5^+$ 604.3057; Found 604.3052.

IR (neat): 3588, 3568, 3288, 2970, 1731, 1597, 1491, 1465, 1434, 1634, 1336, 1237, 1190, 1175, 1082, 1032, 910, 756, 701, and 691 cm^{-1}.

m.p.: 182-182.8 ºC.

Dimethyl 5-(acetoxymethyl)-4-(3-acetoxyprop-1-yn-1-yl)-7-((2,6-dimethyl-4-oxohept-5-en-2-yl)amino)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (8)



8

The general reaction procedure D was followed using **1j** (162 mg, 0.4 mmol), 4-*oxo*-TEMPO (125 mg, 0.8 mmol), stirred at 110 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 10:1) gave the product **8** (96 mg, 43%) as a yellow oil.

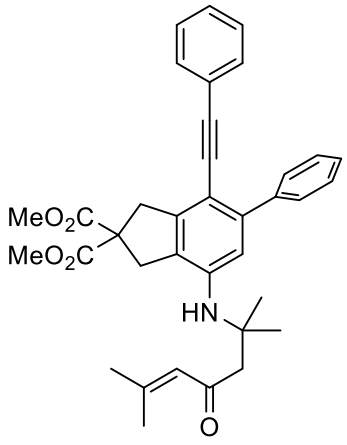
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71 (s, 1H), 5.98 (m, 1H), 5.16 (s, 2H), 4.91 (s, 2H), 3.76 (s, 6H), 3.65 (s, 2H), 3.40 (s, 2H), 2.71 (s, 2H), 2.11 (s, 6H), 2.10 (s, 3H), 1.83 (d, *J* = 1.3 Hz, 3H), and 1.25 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.0, 172.1, 171.0, 170.5, 156.8, 144.2, 143.3, 138.3, 126.0, 125.2, 112.3, 106.0, 88.6, 82.8, 65.3, 59.1, 56.5, 55.7, 54.1, 53.9, 53.7, 53.3, 53.2, 41.2, 38.2, 32.0, 28.4, 27.9, 21.1, and 21.0.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{30}H_{38}NO_9^+$ 556.2541; Found 556.2536.

IR (neat): 3364, 2936, 2190, 1736, 1685, 1598, 1581, 1509, 1430, 1365, 1249, 1198, 958, 833, and 758 cm^{-1}.

Dimethyl 7-((2,6-dimethyl-4-oxohept-5-en-2-yl)amino)-5-phenyl-4-(phenylethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (9)



9

The general reaction procedure D was followed using **1** (160 mg, 0.39 mmol), 4-*oxo*-TEMPO (120 mg, 0.78 mmol), stirred at 110 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 20:1) gave the product **9** (109 mg, 50%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.63 (m, 2H), 7.50-7.35 (m, 3H), 7.35-7.24 (m, 6H), 6.79 (s, 1H), 6.04 (d, *J* = 2.2 Hz, 1H), 3.93-3.46 (m, 10H), 2.79 (s, 2H), 2.16 (s, 3H), 1.87 (s, 3H), and 1.52 (s, 6H).

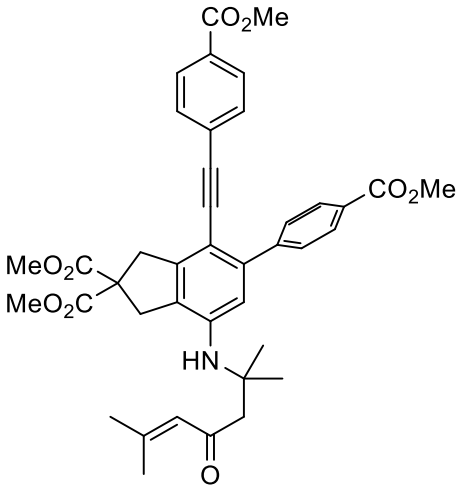
^{13}C NMR (101 MHz, $CDCl_3$): δ 200.0, 172.3, 156.6, 144.4, 144.0, 142.9, 141.5, 131.1, 129.5, 128.3, 127.9, 127.5, 127.3, 125.3, 125.3, 124.4, 113.2, 106.5, 93.7, 88.4, 59.2, 54.0, 53.8, 53.2, 41.7, 38.5, 28.6, 27.9, and 21.0.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{38}NO_5^+$ 564.2744; Found 564.2748.

IR (neat): 3381, 3021, 2189, 1735, 1696, 1605, 1562, 1511, 1434, 1368, 1163, 1074, 963, and 758 cm^{-1}.

m.p.: 141-142 °C.

Dimethyl 7-((2,6-dimethyl-4-oxohept-5-en-2-yl)amino)-5-(4-(methoxycarbonyl)phenyl)-4-((4-(methoxycarbonyl)phenyl)ethynyl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (10)



10

The general reaction procedure D was followed using **1c** (120 mg, 0.23 mmol), 4-*oxo*-TEMPO (72 mg, 0.46 mmol), stirred at 110 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 10:1) gave the product **10** (80 mg, 52%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16-8.07 (m, 2H), 7.94-7.90 (m, 2H), 7.73-7.65 (m, 2H), 7.38-7.26 (m, 2H), 6.73 (s, 1H), 6.03 (q, *J* = 1.3 Hz, 1H), 3.93 (d, *J* = 21.8 Hz, 3H), 3.82-3.78 (m, 3H), 3.52 (s, 8H), 2.75 (s, 2H), 2.13 (d, *J* = 1.2 Hz, 1H), 1.86 (d, *J* = 1.3 Hz, 3H), 1.49 (m, 10H).

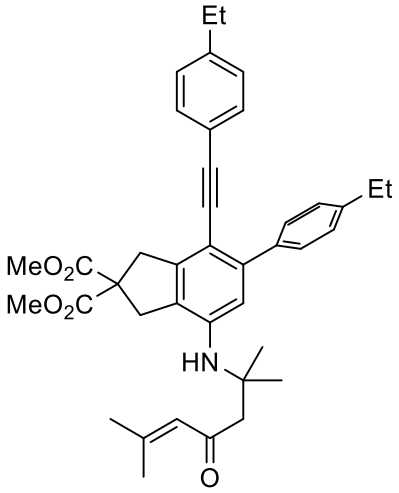
^{13}C NMR (101 MHz, $CDCl_3$): δ 200.0, 172.2, 167.2, 166.8, 157.0, 146.1, 144.5, 143.7, 143.5, 130.9, 129.6, 129.7, 129.3, 129.1, 128.9, 128.8, 125.9, 125.2, 112.7, 105.5, 93.5, 91.4, 59.2, 54.0, 53.9, 53.3, 52.3, 41.7, 38.4, 28.4, 27.9, and 21.0.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{40}H_{42}NO_9^+$ 680.2754; Found 680.2752.

IR (neat): 3359, 3007, 2185, 1726, 1694, 1610, 1585, 1564, 1514, 1437, 1368, 1256, 1194, 967, and 757 cm^{-1}.

m.p.: 146.3-147 °C.

Dimethyl 5-(4-ethylphenyl)-4-((4-ethylphenyl)ethynyl)-7-(2,2,6,6-tetramethyl-4-oxopiperidin-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (11)



11

The general reaction procedure D was followed using **1a** (100 mg, 0.2 mmol), 4-*oxo*-TEMPO (67 mg, 0.4 mmol), stirred at 120 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 20:1) gave the product **11** (53 mg, 45%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 4H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.79 (s, 1H), 6.03 (s, 1H), 3.88-3.49 (m, 10H), 2.91-2.60 (m, 6H), 2.15 (s, 3H), and 1.97-1.17 (m, 16H).

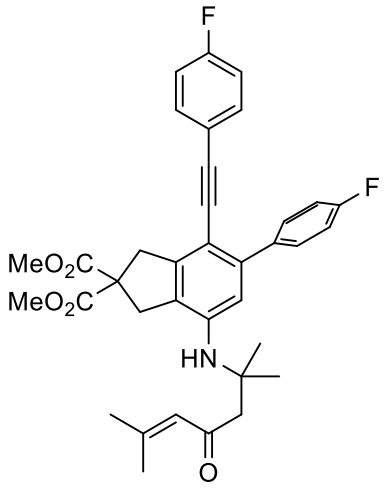
^{13}C NMR (101 MHz, $CDCl_3$): δ 200.1, 172.3, 156.5, 144.1, 143.8, 143.77, 143.2, 142.5, 138.7, 131.0, 129.3, 127.8, 127.3, 125.2, 125.0 121.5, 113.0, 106.5, 93.7, 87.7, 86.4, 72.3, 67.3, 59.04, 53.9, 53.7, 53.6, 53.2, 41.7, 38.3, 33.1, 28.9, 28.7, 28.5, 27.9, 22.4, 20.9, 15.7, and 15.6.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{40}H_{46}NO_5^+$ 620.3371; Found 620.3371.

IR (neat): 3359, 3004, 2215, 1736, 1710, 1654, 1562, 1515, 1441, 1367, 1253, 1166, 1078, 965 and 756 cm^{-1}.

m.p.: 144-145 °C.

Dimethyl 5-(4-fluorophenyl)-4-((4-fluorophenyl)ethynyl)-7-(2,2,6,6-tetramethyl-4-oxopiperidin-1-yl)-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (12)



12

The general reaction procedure D was followed using **1d** (102 mg, 0.2 mmol), 4-*oxo*-TEMPO (71 mg, 0.4 mmol), stirred at 120 °C for 12 h, purification by column chromatography (hexanes:EtOAc = 20:1) gave the product **7** (66 mg, 55%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.33-7.22 (m, 3H), 7.12 (t, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.70 (s, 1H), 6.02 (s, 1H), 3.80 (s, 8H), 3.51 (s, 2H), 2.75 (s, 1H), 2.13 (d, *J* = 1.2 Hz, 3H), 1.86 (d, *J* = 1.3 Hz, 3H), and 1.48 (s, 8H).

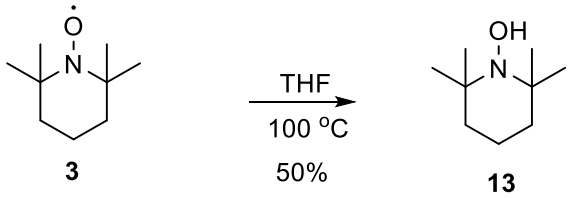
^{13}C NMR (101 MHz, $CDCl_3$): δ 200.1, 172.2, 163.6, 163.3, 161.1, 156.9, 143.9, 143.3, 142.9, 137.4, 132.9, 132.8, 131.0, 130.95, 125.3, 125.2, 120.2, 115.7, 115.5, 114.9, 114.7, 112.9, 106.1, 92.6, 87.7, 59.1, 54.0, 53.8, 53.3, 41.6, 38.4, 28.4, 28.0, and 21.0.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{36}F_2NO_5^+$ 600.2556; Found 600.2556.

IR (neat): 3365, 2953, 2203, 1735, 1676, 1603, 1577, 1507, 1435, 1367, 1285, 1248, 1221, 1093, 911, and 730cm^{-1}.

m.p.: 151-151.9 ºC.

2,2,6,6-Tetramethylpiperidin-1-ol (13)



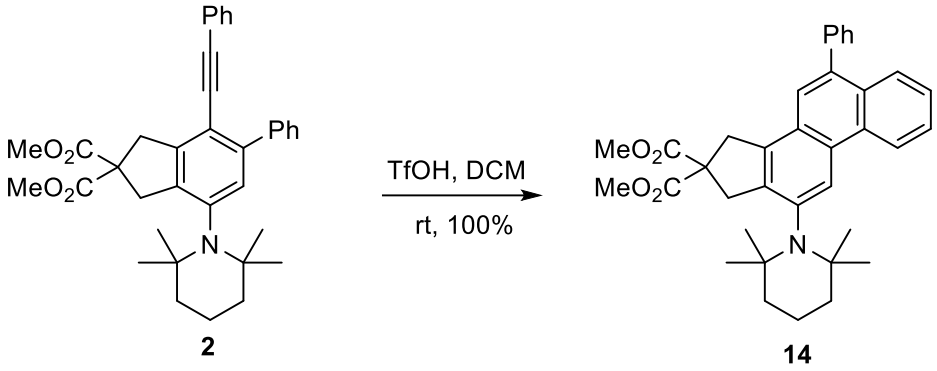
3 **13**

A solution of the TEMPO **3** (100 mg, 0.37 mmol) in THF (5 mL) was heated in a screw-capped culture tube in an oil bath held at 110 °C. After 4 h the solution was allowed to cool to room temperature and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 4:1) afforded the **13** (50 mg, 50%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.52 (s, 6H), and 1.17 (s, 12H).

The proton spectrum of **13** is consistent with the previously reported.[19]

Dimethyl 7-iodo-6-phenyl-12-(2,2,6,6-tetramethylpiperidin-1-yl)-15,17-dihydro-16*H*-cyclopenta[*a*]phenanthrene-16,16-dicarboxylate (14)



2 **14**

To a stirred solution of **2** (95 mg, 0.17 mmol) in CH_2Cl_2, was added TfOH (70 µL, 0.86 mmol) dropwise at room temperature. The resulting mixture was stirred at room temperature for 2 h. The solution was then quenched with satd. aq. $NaHCO_3$, extracted with CH_2Cl_2 (3 × 10 mL), and washed with brine (10 mL). The combined organic layer was dried and concentrated. The residue was purified by flash chromatography (silica gel, hexanes:EtOAc = 10:1). afforded product **14** (95 mg, 100%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70-8.63 (m, 1H), 8.57 (s, 1H), 7.91 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.70-7.61 (m, 2H), 7.59-7.41 (m, 6H), 4.00 (s, 2H), 3.87 (s, 2H), 3.74 (s, 6H), 1.74-1.59 (m, 6H), 1.48 (s, 6H), and 0.82 (s, 6H).

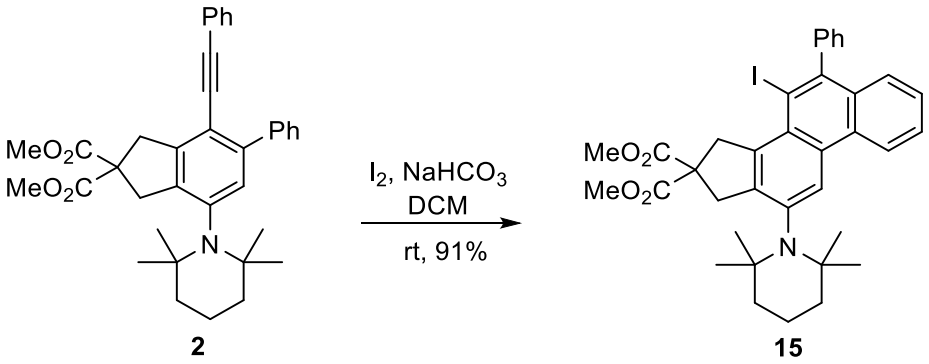
^{13}C NMR (101 MHz, $CDCl_3$): δ 172.4, 143.3, 142.8, 141.1, 138.7, 137.2, 131.0, 130.8, 130.2, 129.5, 128.4, 127.5, 127.2, 126.7, 126.2, 126.0, 125.0, 123.7, 122.9, 60.2, 55.6, 53.0, 42.4, 42.0, 40.0, 32.4, 25.6, and 18.6.

HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{40}NO_4^+$ 550.2952; Found 550.2950.

IR (neat): 2900, 1738, 1646, 1430, 1380, 1264, 1220, 1174, 1111, 1035, 950, 825, and 738 cm^{-1}.

m.p.: 238-239.2 °C.

Dimethyl 7-iodo-6-phenyl-12-(2,2,6,6-tetramethylpiperidin-1-yl)-15,17-dihydro-16*H*-cyclopenta[*a*]phenanthrene-16,16-dicarboxylate (15)



2 **15**

To a stirred solution of **2** (90 mg, 0.16 mmol) in CH_2Cl_2 (1.5 mL) were added I_2 (63 mg, 0.48 mmol) and $NaHCO_3$ (42 mg, 0.48 mmol) at room temperature in the dark under N_2 atmosphere. The resulting mixture was stirred for 10 hours before quenched by satd. aq. Na_2SO_3 solution, extracted with CH_2Cl_2 (3 × 10 mL), and washed with brine (10 mL). The combined organic layer was dried and concentrated. The residue was purified by flash chromatography (silica gel, hexanes:EtOAc = 10:1) to give product **15** (101 mg, 91%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.60 (m, 2H), 7.49-7.41 (m, 3H), 7.35-7.28 (m, 3H), 7.12-7.09 (m, 2H), 3.77 (s, 3H), 3,75 (s， 3H), 3.73-3.55 (m, 4H), 1.61 (m, 6H), 1.32 (s, 3H), 1.30 (s, 3H), 0.88 (s, 3H), and 0.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 172.1, 172.0, 147.0, 144.4, 143.9, 140.8, 138.8, 138.3, 138.2, 133.3, 131.4, 129.8, 128.5, 128.2, 127,4, 127.3, 100.4, 97.8, 60.4, 55.5, 53.0, 42.2, 41.2, 40.4, 32.6, 25.6, and 18.5.

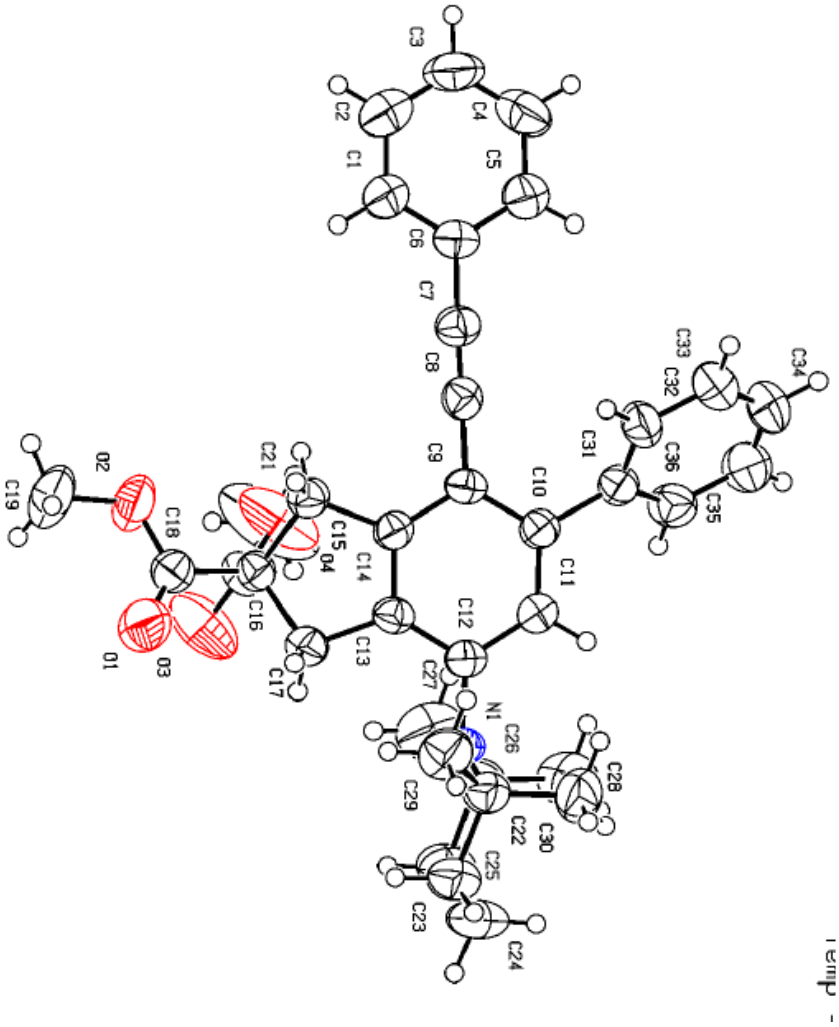
HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{36}H_{39}INO_4^+$ 676.1918; Found 676.1917.

IR (neat): 2900, 2930, 1738, 1646, 1430, 1380, 1264, 1220, 1174, 1111, 1035, 998, 950, 912, 825, 738, and 556 cm^{-1}.

m.p.: 243.4-244°C.

III. Crystal Data and Structure Refinement for Compound 2

Crystal preparation: Compound **2** (15 mg) were dissolved in hexane/CH_2Cl_2 = 2:1 (3 mL) in 10 mL round bottom flask and the resultant solution were allowed to slowly evaporate at room temperature to get pure crystals suitable for X-ray diffraction analysis.



X-ray crystal structure of **2** with thermal ellipsoids drawn at the 35% probability level [CCDC: 2430137]

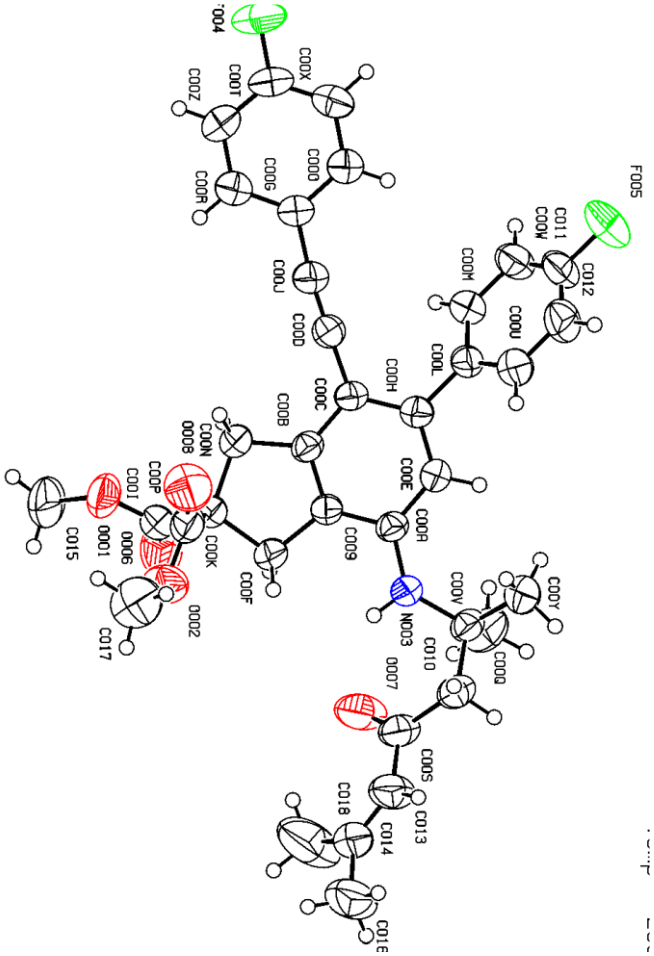
Table 1. Crystal data and structure refinement for **2**

Identification code	**2**
Empirical formula	$C_{36}H_{39}NO_4$
Formula weight	549.68
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	15.532(7)
b/Å	11.970(5)
c/Å	17.168(6)
α/°	90
β/°	104.089(9)
γ/°	90
Volume/Å^3	3096(2)
Z	4
ρ_{calc}g/cm^3	1.179
μ/mm^{-1}	0.076
F(000)	1176.0
Crystal size/mm^3	0.22 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.654 to 50.158

Index ranges	$-16 \leq h \leq 18$, $-14 \leq k \leq 14$, $-20 \leq l \leq 17$
Reflections collected	33160
Independent reflections	5428 [R_{int} = 0.1139, R_{sigma} = 0.1151]
Data/restraints/parameters	5428/0/376
Goodness-of-fit on F^2	0.982
Final R indexes [I>=2σ (I)]	R_1 = 0.0779, wR_2 = 0.1473
Final R indexes [all data]	R_1 = 0.2001, wR_2 = 0.2060
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.19

IV. Crystal Data and Structure Refinement for Compound 12

Crystal preparation: Compound **12** (20 mg) were dissolved in hexane/CH_2Cl_2 = 2:1 (4 mL) in 20 mL round bottom flask and the resultant solution were allowed to slowly evaporate at room temperature to get pure crystals suitable for X-ray diffraction analysis.



X-ray crystal structure of **12** with thermal ellipsoids drawn at the 35% probability level [CCDC: 2470156]

Table 2. Crystal data and structure refinement for **12**

Identification code	**12**
Empirical formula	$C_{36}H_{35}F_2NO_5$
Formula weight	599.65
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	10.7387(5)
b/Å	11.1188(6)
c/Å	14.8160(7)
α /°	77.588(2)
β /°	72.7770(10)
γ /°	69.889(2)
Volume/Å^3	1574.03(14)
Z	2
ρ_{calc}g/cm^3	1.265
μ /mm^{-1}	0.092
F(000)	632.0
Crystal size/mm^3	0.22 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.584 to 50.134
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17

Reflections collected	21143
Independent reflections	5494 [R_{int} = 0.0408, R_{sigma} = 0.0459]
Data/restraints/parameters	5494/0/402
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2 σ (I)]	R_1 = 0.0554, wR_2 = 0.1279
Final R indexes [all data]	R_1 = 0.1048, wR_2 = 0.1523
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.21

V. References for the Supporting Information

[1] L. Severa, J. Vávra, A. Kohoutová, M. Čížková, T. Šálová, J. Hývl, D. Šaman, R. Pohl, L. Adriaenssens, and F. Teplý, Air-tolerant C–C bond formation *via* organometallic ruthenium catalysis: Diverse catalytic pathways involving (C_5Me_5) Ru or (C_5H_5) Ru are robust to molecular oxygen, *Tetrahedron Lett.*, 2009, **50**, 4526–4528.

[2] R. K. Singh, A convenient synthesis of diethyl dialkyl-and dibenzylmalonates *via* extractive alkylation. *Synthesis*, 1985, **1985** , 54–55.

[3] Gao, X.; Li, W.; Chen, Y.; Wu, R.; Zhu, S. Dirhodium-catalyzed [2+2+2] cycloaddition of 1, 6-diynes and alkynes. *J. Org. Chem.* **2024**, *89*, 17248–17259.

[4] A. Leyva-Pérez, P. Rubio-Marqués, S. S. Al-Deyab, S. I. Al-Resayes, and A. Corma, Cationic gold catalyzes ω-bromination of terminal alkynes and subsequent hydroaddition reactions, *ACS Catal.*, 2011, **1**, 601–606.

[5] S. Desrat, C. Remeur, C. Geny, G. Riviere, C. Colas, V. Dumontet, N. Birlirakis, B. Iorga, and F. Roussi, From meiogynin a to the synthesis of dual inhibitors of Bcl-xL and Mcl-1 anti-apoptotic proteins, *Chem. Comm.*, 2014, **50**, 8593–8596.

[6] Y. S. Feng, Z. Q. Xu, L. Mao, F. F. Zhang, and H. J. Xu, Copper catalyzed decarboxylative alkynylation of quaternary α-cyano acetate salts, *Org. Lett.*, 2013, **15**, 1472–1475.

[7] S. Krishna Moodapelly, G. V. Sharma, and V. Ramana Doddi, Controlled reactivity of 1, 8-diazabicyclo [5.4. 0] undec-7-ene (DBU) in the selective synthesis of 1-(bromoethynyl) arenes, *Adv. Syn. Catal.*, 2017, **359**, 1535–1540.

[8] Z. Chen, H. Jiang, Y. Li, and C. Qi, Highly efficient two-step synthesis of (Z)-2-halo-1-iodoalkenes from terminal alkynes, *Chem. Comm.*, 2010, **46**, 8049–8051.

[9] K. Watanabe, T. Mino, E. Ishikawa, M. Okano, T. Ikematsu, Y. Yoshida, M. Sakamoto, K. Sato, and K. Yoshida, Synthesis of *o*-allyloxy (ethynyl) benzene derivatives by Cu-catalyzed Suzuki–Miyaura-type reaction and their transformations into heterocyclic compounds, *Eur. J. Org. Chem.*, 2017, **2017**, 2359–2368.

[10] W. Shi, Z. Guan, P. Cai, and H. Chen, Highly efficient and recyclable catalyst for the direct chlorination, bromination and iodination of terminal alkynes, *J. Catal.*, 2017, **353**, 199–204.

[11] X. Ouyang, F. W. Fowler, and J. W. Lauher, Single-crystal-to-single-crystal topochemical polymerizations of a terminal diacetylene: Two remarkable transformations give the same conjugated polymer, *J. Am. Chem. Soc.*, 2003, **125**, 12400–12401.

[12] M. X. Zhang, W. Shan, Z. Chen, J. Yin, G. A. Yu, and S. H. Liu, Diels–Alder reactions of arynes in situ generated from DA reaction between bis-1, 3-diynes and alkynes, *Tetrahedron Lett.*, 2015, **56**, 6833–6838.

[13] W. Xu, X. Li, L. Zou, X. Li, Z. Zhang, S. Ali, Z. Wang, P. Li, and H. Zheng, Access to fully substituted dihydroindazoles *via* hexadehydro-Diels–Alder/[3+ 2] cycloaddition, *J. Org. Chem.*, 2023, **88**, 14736 –14747.

[14] F. Xu, X. Xiao, and T. R. Hoye, Photochemical hexadehydro-Diels–Alder reaction, *J. Am. Chem. Soc.*, 2017, **139**, 8400–8403.

[15] L. Yao, Q. Hu, Y. Lei, L. Bao, and Y. Hu, C-O/C-S difunctionalized benzene derivativesvia multicomponent coupling of tetraynes, *Org. Chem. Front.*, 2020, **7**, 3633–3637.

[16] W. Xu, P. Li, Y. Li, Z. Kou, K. Li, H. Li, S. Ali, J. Pan, Z. Wang, and H. Zheng, Iodonium (III) ylide: An iodoalkylation reagent with aryne, *J. Org. Chem.*, 2025, **90**, 2372–2385.

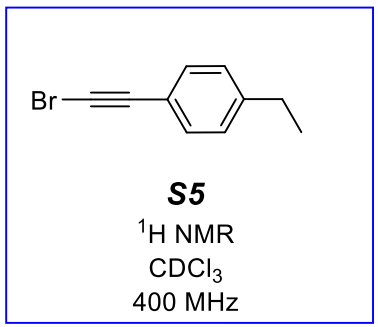
[17] S. Ghorai, and D. Lee, Synthesis of imides, imidates, amidines, and amides by intercepting the aryne–isocyanide adduct with weak nucleophiles, *Org. Lett.*, 2019, **21**, 7390–7393.

[18] B. S. Chinta, S. Arora, and T. R. Hoye,Trapping reactions of benzynes initiated by intramolecular nucleophilic addition of a carbonyl oxygen to the electrophilic zryne, *Org. Lett.*, 2021, **24**, 425–429.

[19] F. G. Bordwell, and W.-Z. Liu, Solvent effects on homolytic bond dissociation energies of hydroxylic acids, *J. Am. Chem. Soc.*, 1996, **118**, 10819–10823.

V. Copies of ^{1}H, ^{13}C Spectra

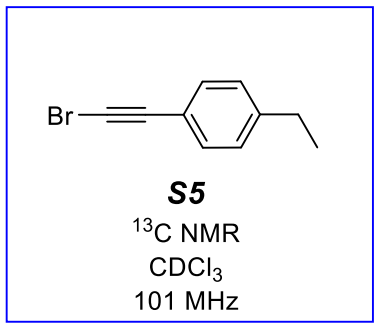
S5/H

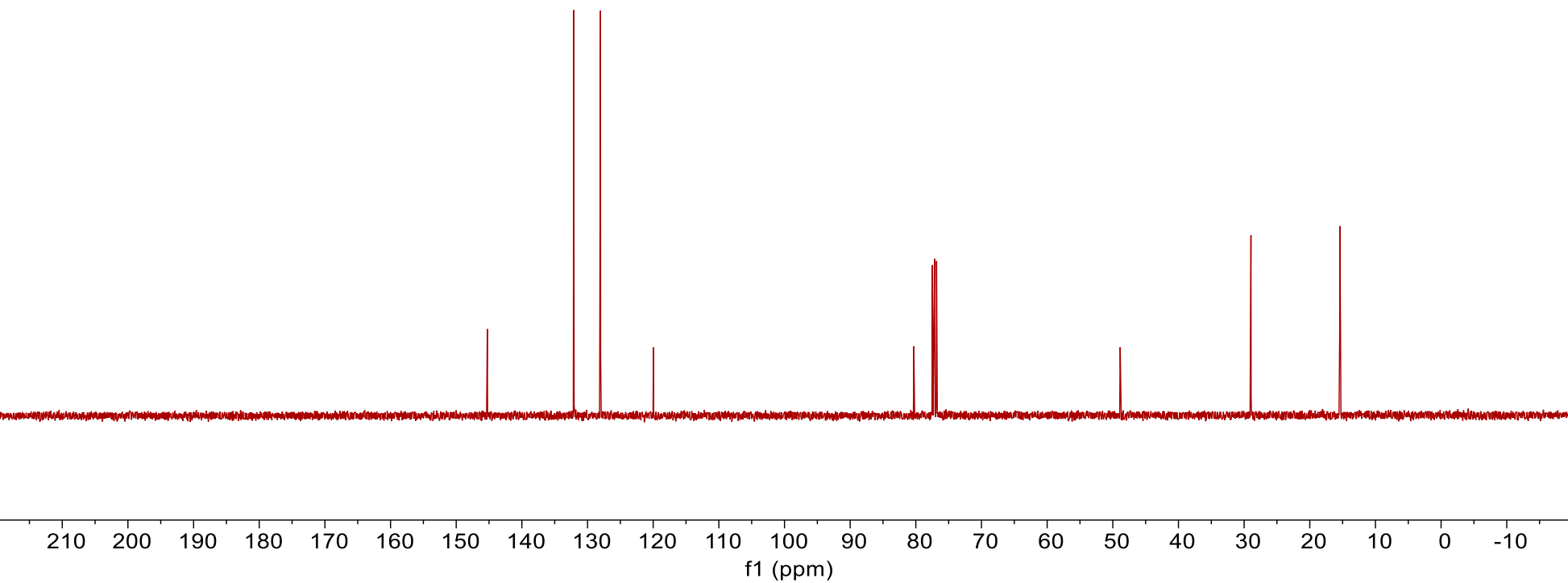

Br
S5
1H NMR
CDCl3
400 MHz

7.40
7.40
7.39
7.38
7.37
7.17
7.16
7.15
7.15
2.69
2.67
2.65
2.63
1.26
1.24
1.22
1.93
1.96
2.00
3.02
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
0.0
f1 (ppm)

S5/C

145.26
132.09
128.02
119.98
80.31
48.88
28.96
15.40

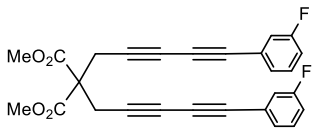




7.29 7.27 7.26 7.25 7.25 7.24 7.24 7.24 7.23 7.23 7.16 7.16 7.15 7.15 7.14 7.13 7.13 7.13 7.12 7.07 7.07 7.06 7.06 7.05 7.05 7.05 7.05 7.04 7.04 7.03 7.03 7.02 — 3.80 — 3.20

LQF, ZZW, SZH, SBF & ZCL SI

1e/H

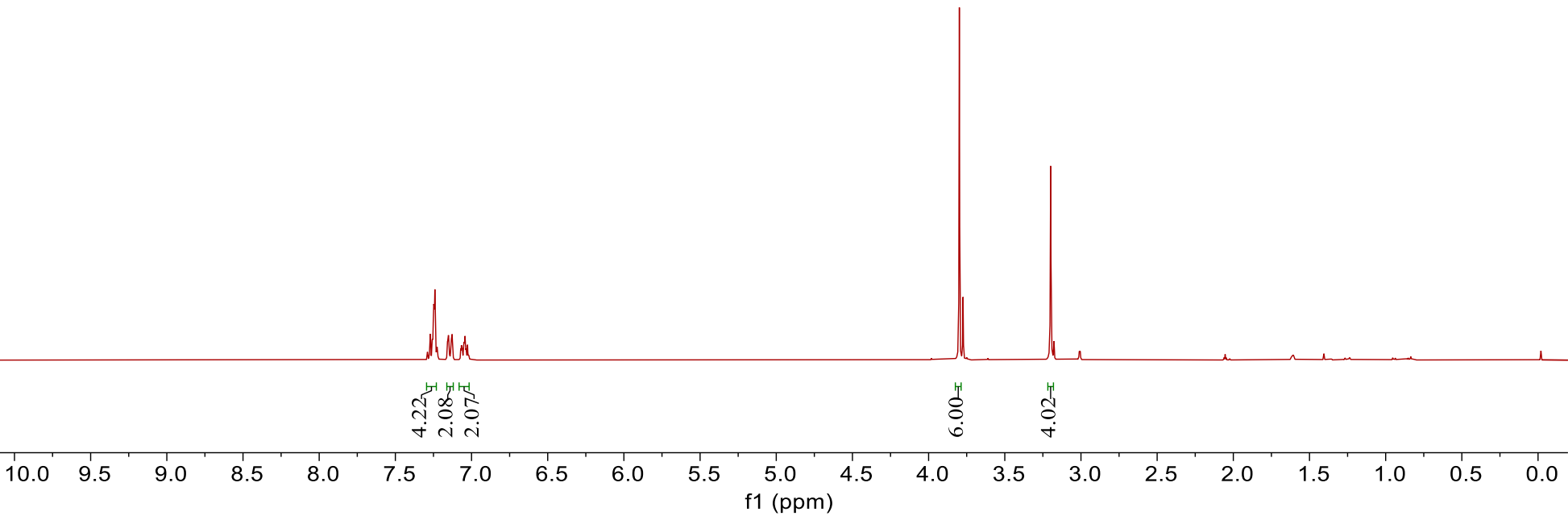


1e

^{1}H NMR

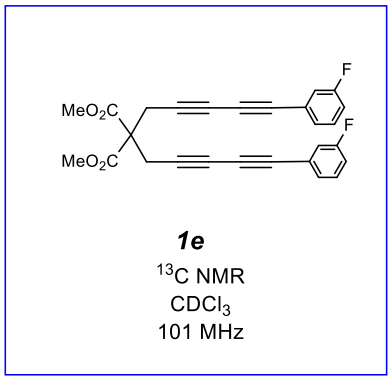
$CDCl_3$

400 MHz

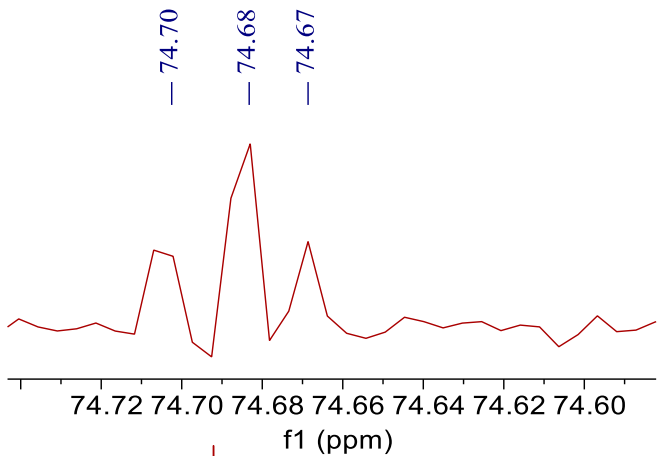


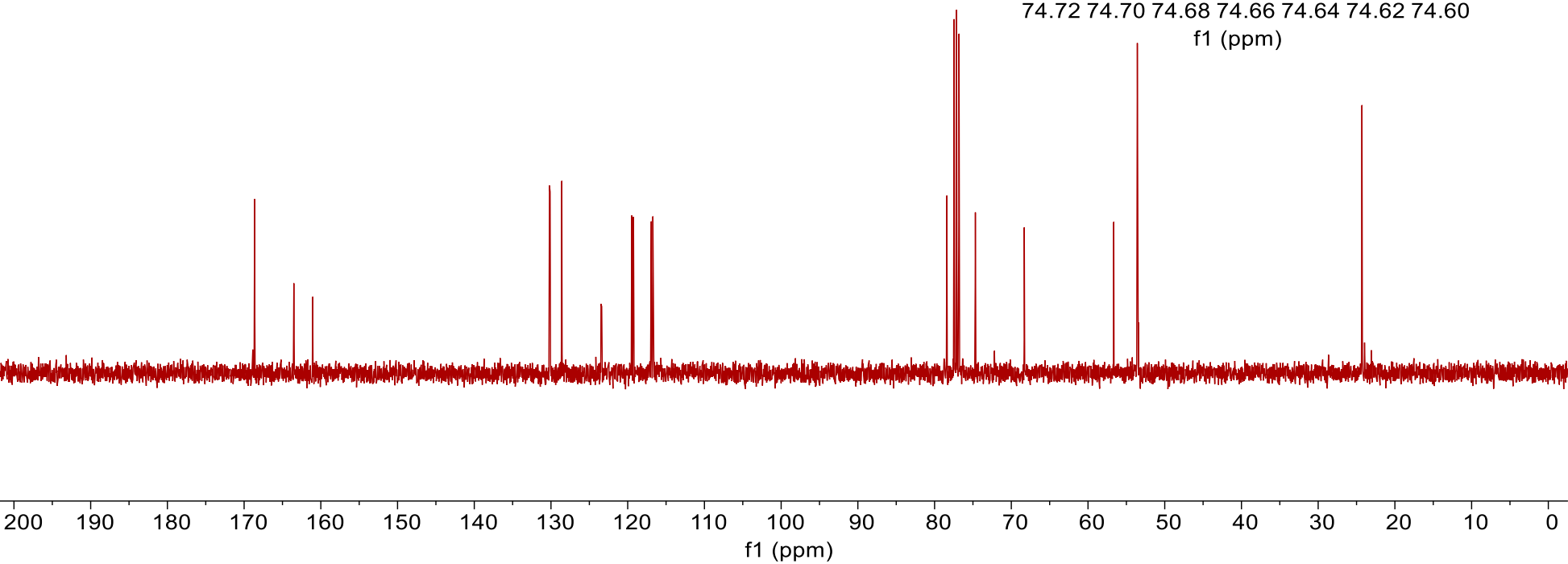
1e/C

168.63
163.52
161.06
130.20
130.11
128.62
128.59
123.48
123.39
119.47
119.25
116.93
116.72
78.40
74.70
74.68
74.67
68.31
56.64
53.57
24.29

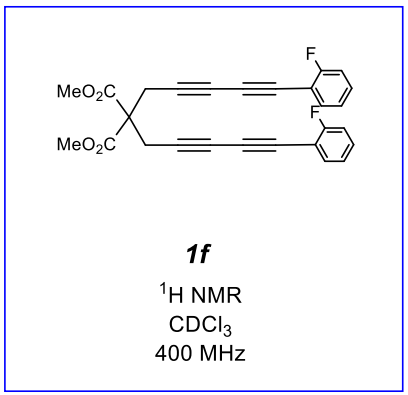


1e
^{13}C NMR
$CDCl_3$
101 MHz





1f/H

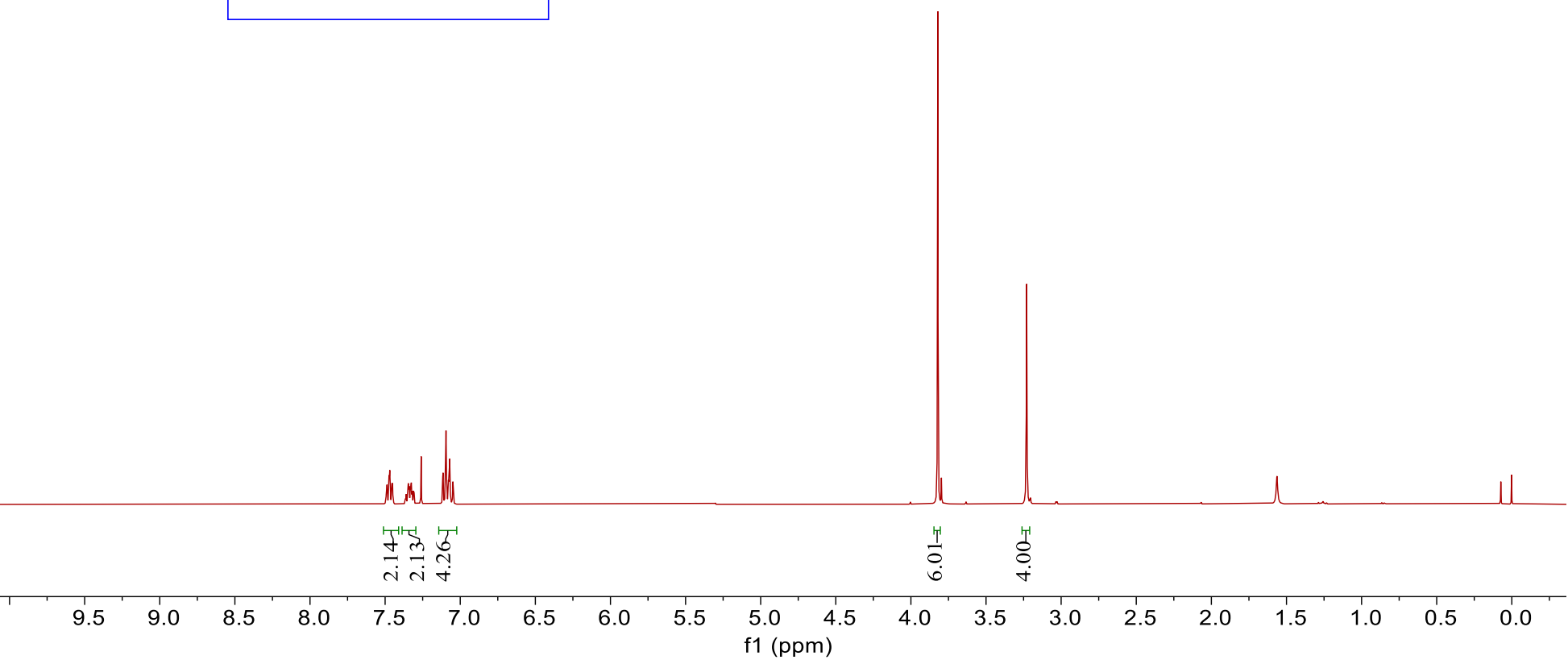


1f

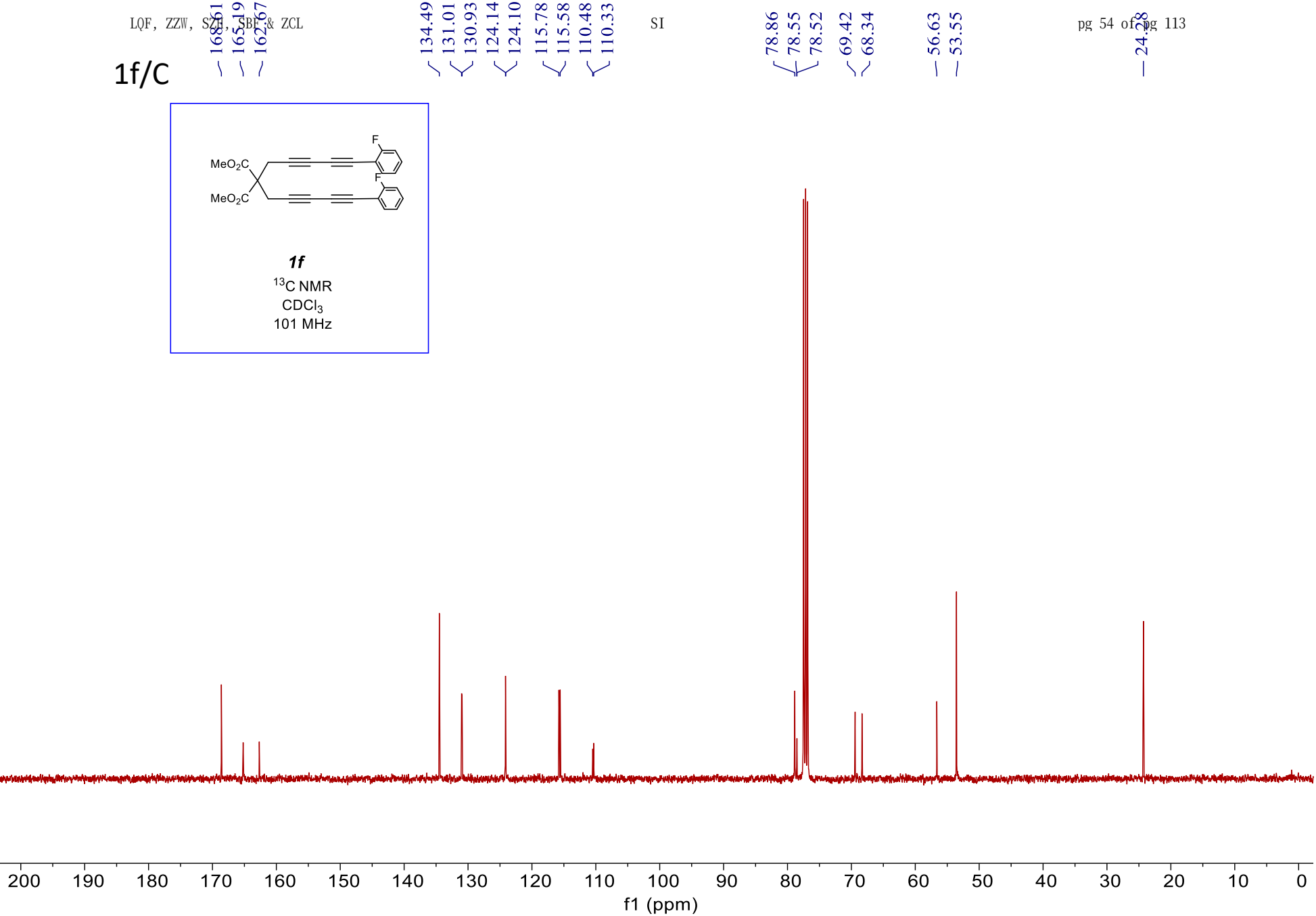
^{1}H NMR

$CDCl_3$

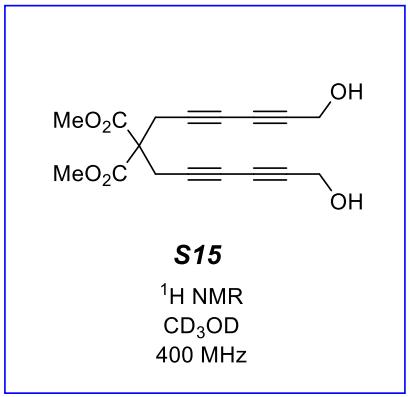
400 MHz

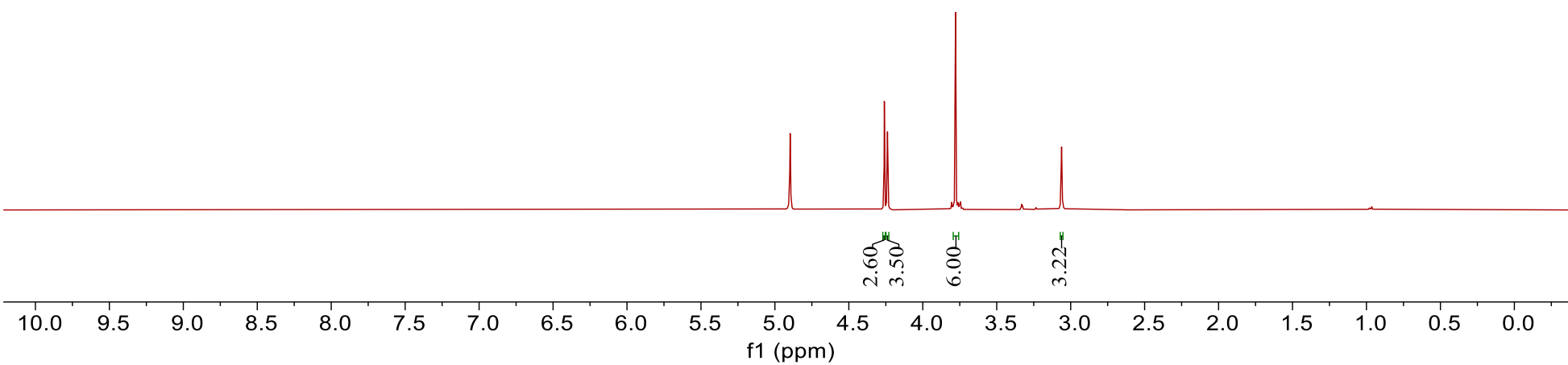


1f/C

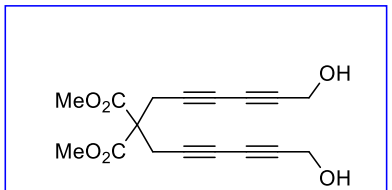

168.61
165.19
162.67
134.49
131.01
130.93
124.14
124.10
115.78
115.58
110.48
110.33
78.86
78.55
78.52
69.42
68.34
56.63
53.55
24.28
MeO2C
MeO2C
F
F
1f
13C NMR
CDCl3
101 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S15/H


MeO2C
MeO2C
OH
OH
S15
1H NMR
CD3OD
400 MHz


4.26
4.24
4.24
4.24
3.78
3.06
3.06
3.06
2.60
3.50
6.00
3.22
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
0.0
f1 (ppm)

S15/C



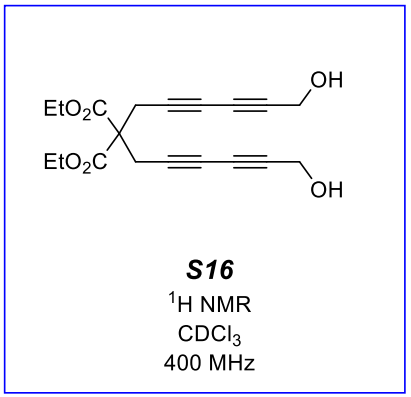
S15

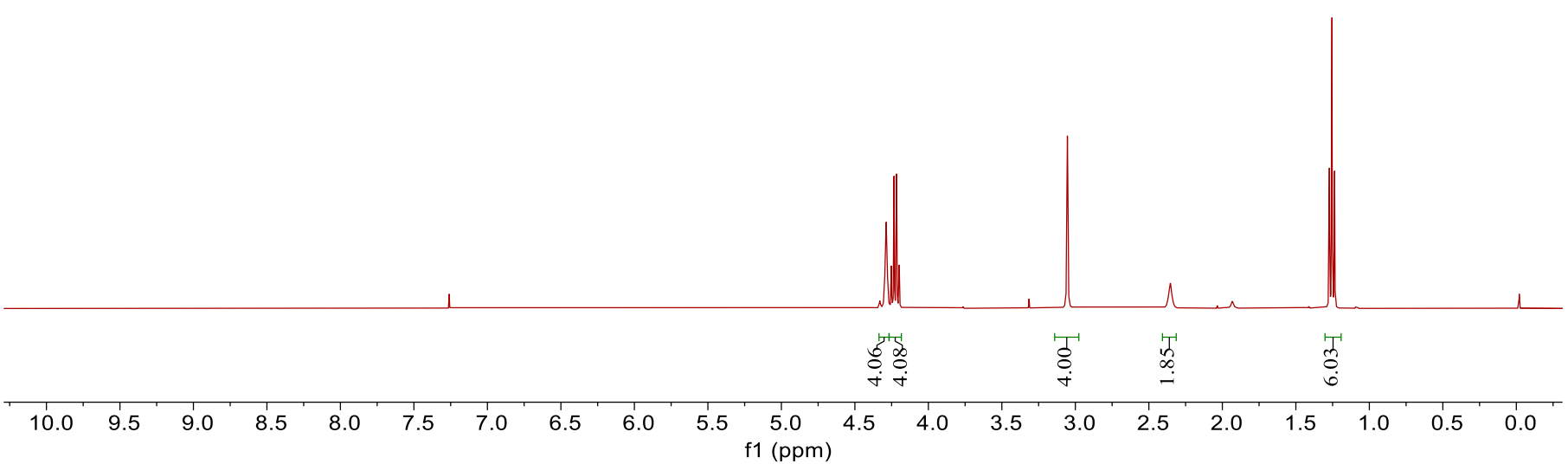
^{13}C NMR

CD_3OD

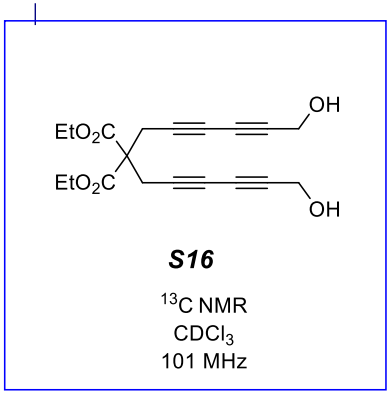
101 MHz

S16/H


OH
EtO2C
EtO2C
OH
S16
1H NMR
CDCl3
400 MHz


4.29
4.25
4.23
4.22
4.20
3.05
2.35
1.27
1.25
1.24
4.06
4.08
4.00
1.85
6.03
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 0.0
f1 (ppm)

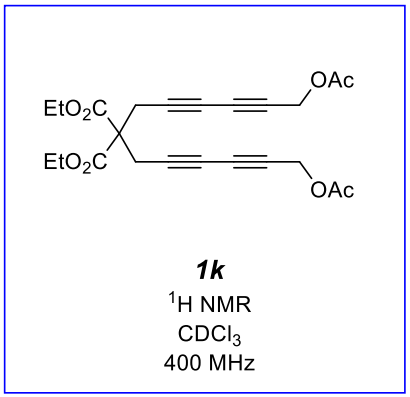
S16/C

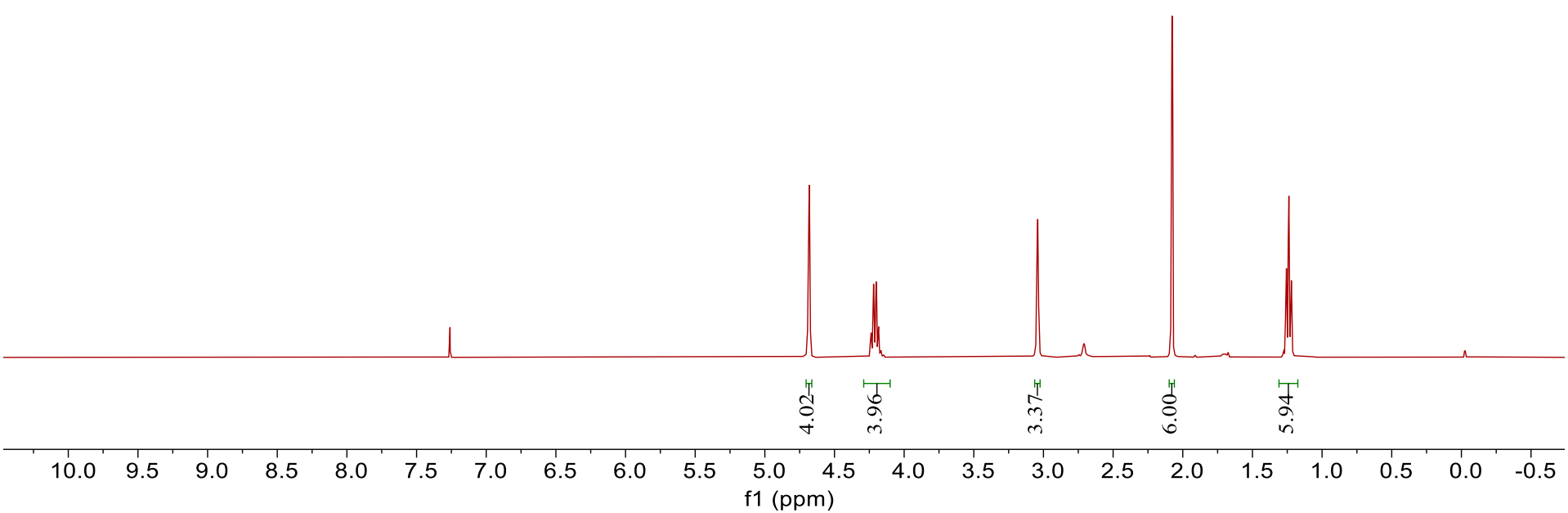


S16

^{13}C NMR
$CDCl_3$
101 MHz

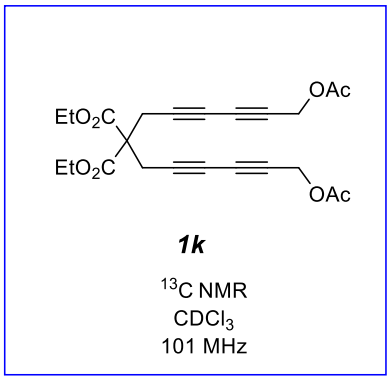
1k/H

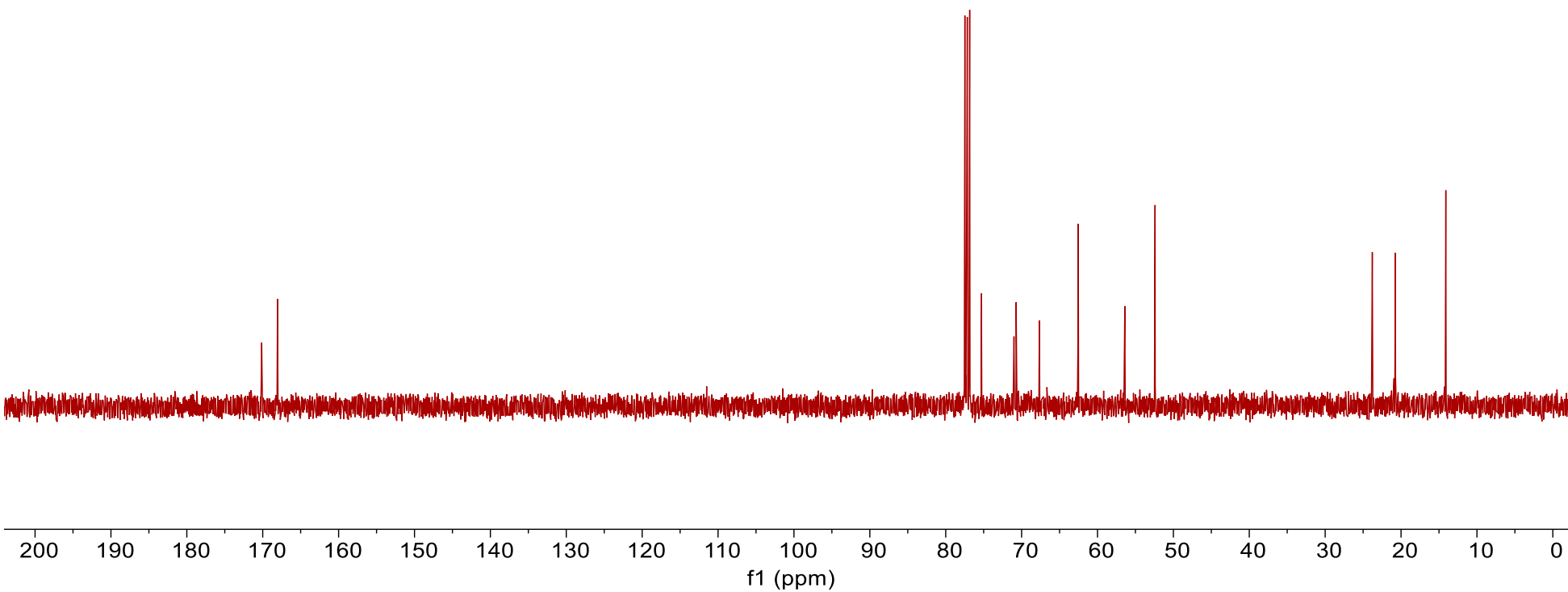

OAc
EtO2C
EtO2C
OAc
1k
1H NMR
CDCl3
400 MHz


4.68
4.68
4.24
4.24
4.23
4.22
4.22
4.22
4.21
4.20
4.20
4.19
4.18
4.18
4.17
4.17
4.16
3.05
3.04
2.10
2.08
2.08
2.07
2.05
1.26
1.26
1.25
1.24
1.24
1.23
1.23
1.22
1.22
4.02
3.96
3.37
6.00
5.94
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
0.0
-0.5
f1 (ppm)

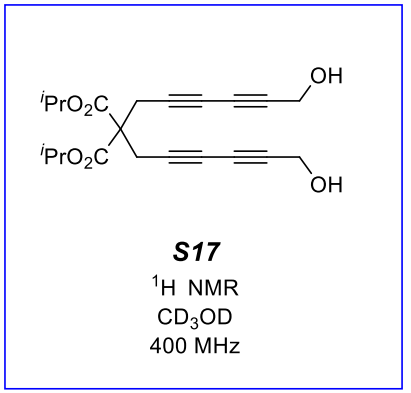
170.14
168.05
75.28
71.00
70.72
67.66
62.54
56.40
52.41
23.79
20.74
14.10

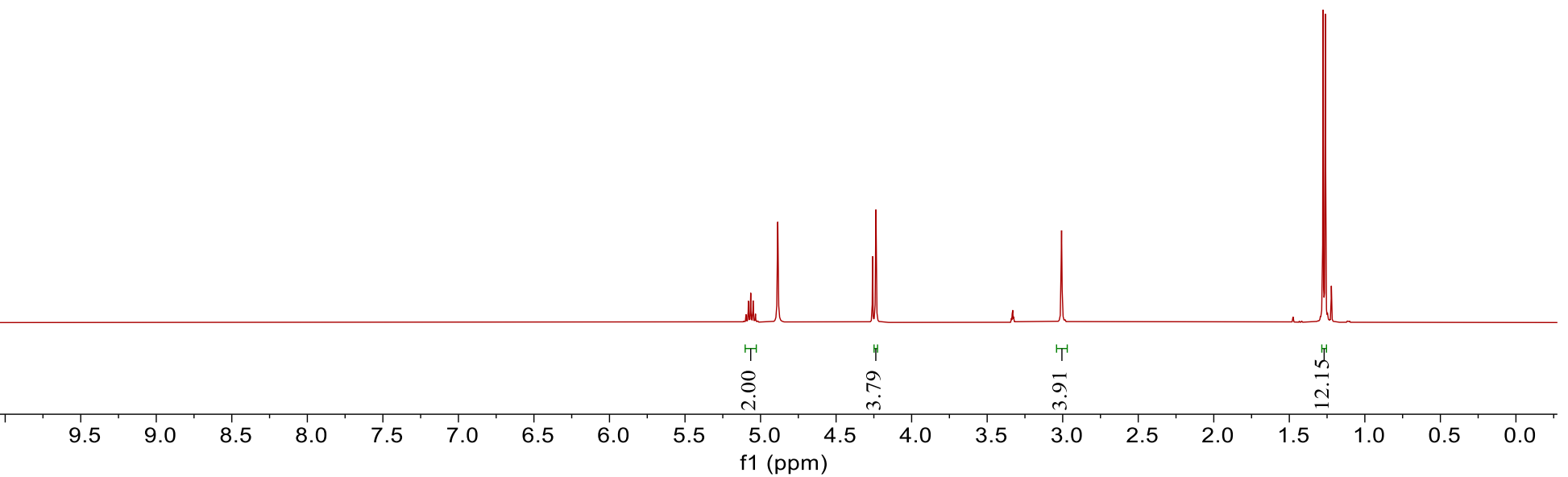
1k/C



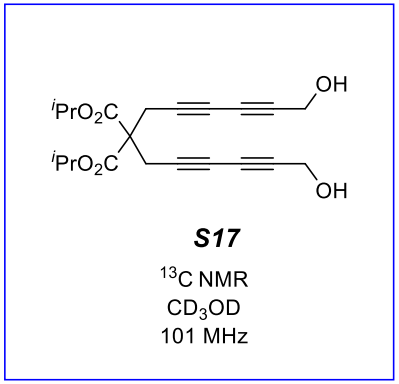


S17/H


OH
$^{i}PrO_2C$
$^{i}PrO_2C$
OH
S17
^{1}H NMR
CD_3OD
400 MHz

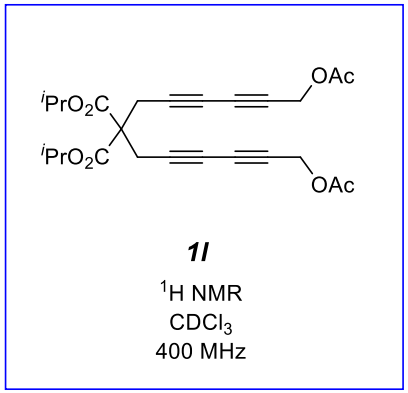

5.08
5.06
5.05
4.24
4.24
4.23
3.01
3.01
2.98
1.29
1.28
1.28
1.26
1.25
2.00
3.79
3.91
12.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

S17/C


OH
$^{i}PrO_2C$
$^{i}PrO_2C$
OH
S17
^{13}C NMR
CD_3OD
101 MHz

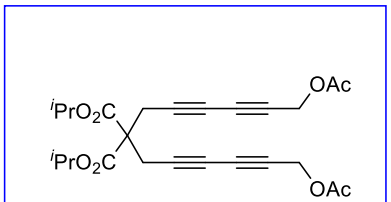
168.30
78.17
76.44
74.42
70.71
68.84
68.79
68.01
56.95
50.31
50.28
23.77
21.10
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

1l/H


OAc
$^{i}PrO_2C$
$^{i}PrO_2C$
OAc
1l
^{1}H NMR
$CDCl_3$
400 MHz

5.12
5.10
5.09
5.09
5.07
5.06
5.04
5.03
4.70
3.03
2.09
1.24
1.24
1.23
1.22
2.09
4.02
4.03
6.00
12.19
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
0.0
f1 (ppm)

1l/C



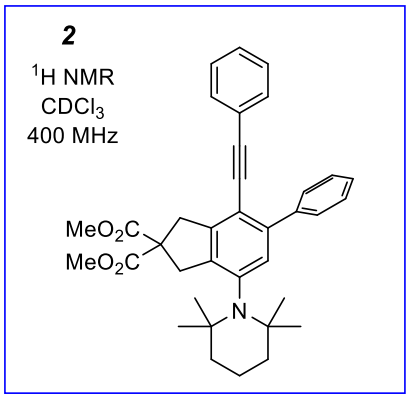
1l

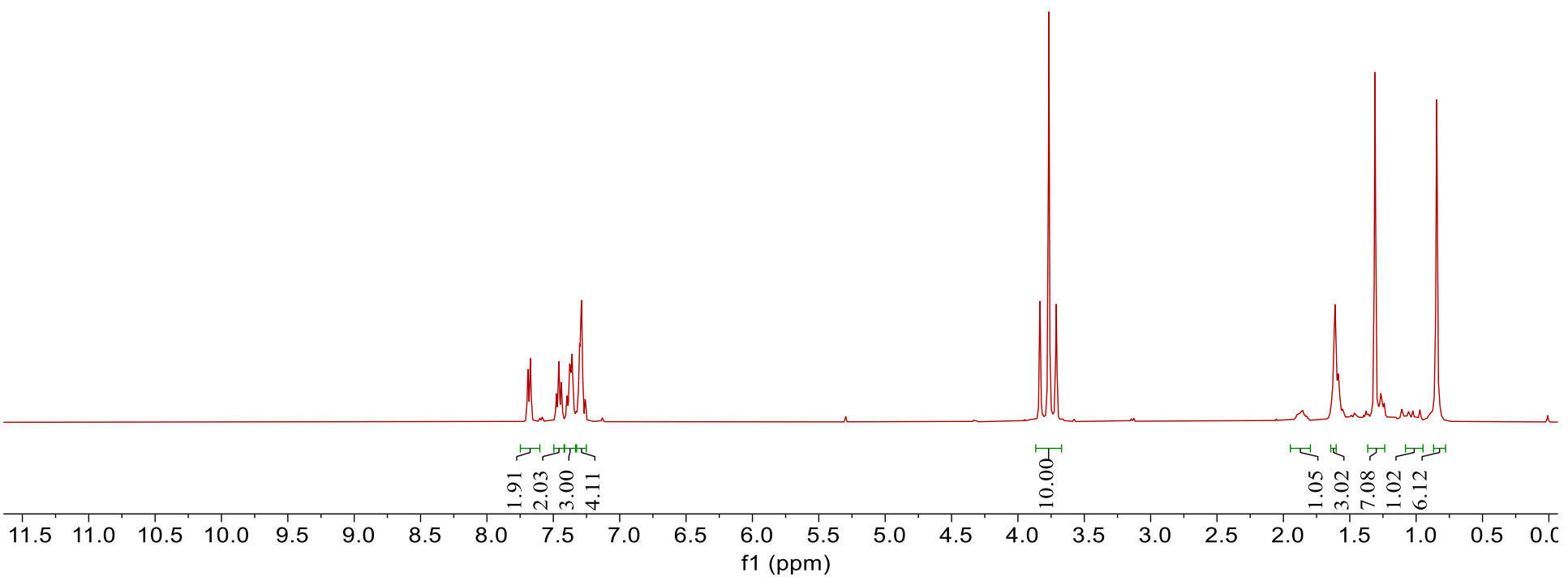
^{13}C NMR

$CDCl_3$

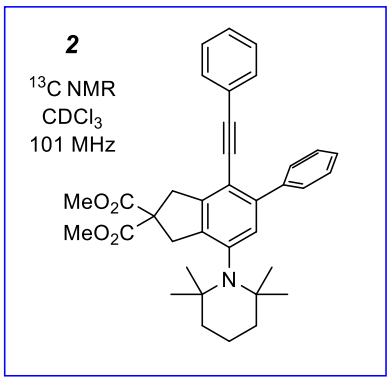
101 MHz

2/H


2
^{1}H NMR
$CDCl_3$
400 MHz
MeO_2C
MeO_2C
N


7.69
7.67
7.48
7.46
7.46
7.44
7.38
7.38
7.37
7.36
7.36
7.30
7.29
7.29
7.28
3.83
3.78
3.77
3.76
3.71
1.61
1.59
1.31
0.85
1.91
2.03
3.00
4.11
10.00
1.05
3.02
7.08
1.02
6.12
11.5 11.0 10.5 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 0.0
f1 (ppm)

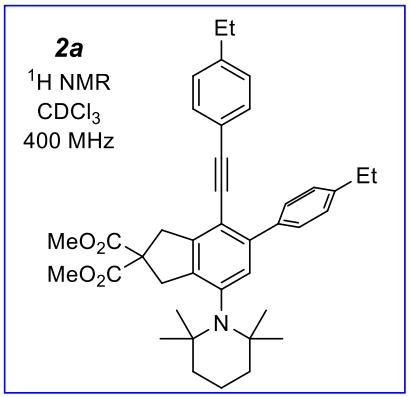
2/C

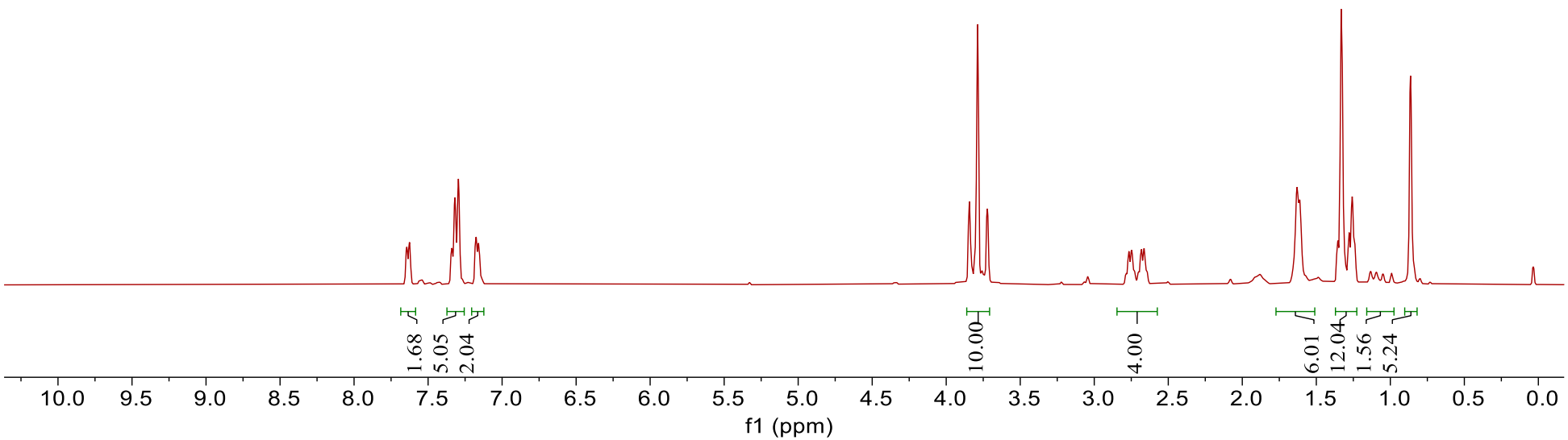

2
^{13}C NMR
$CDCl_3$
101 MHz
MeO_2C
MeO_2C
N

152.20
144.12
143.86
142.72
142.59
140.74
132.31
131.42
129.47
128.32
128.12
127.94
127.86
127.30
123.68
115.22
95.59
87.41
59.67
55.45
53.00
42.22
41.54
41.46
32.43
25.56
19.45
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

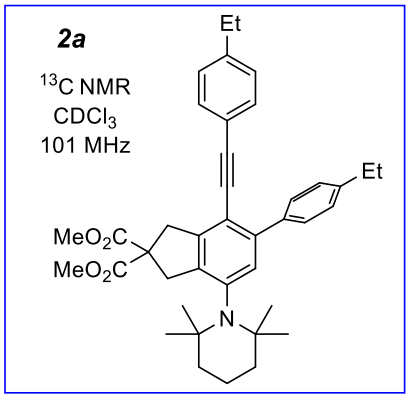
7.35 7.34 7.33 7.32 7.30 7.29 7.16 7.15 3.85 3.84 3.83 3.81 3.79 3.79 3.78 3.76 3.75 3.73 3.72 3.72 2.79 2.78 2.77 2.76 2.75 2.75 2.73 2.71 2.70 2.69 2.68 2.67 2.66 2.64 1.63 1.61 1.36 1.35 1.34 1.33 1.33 1.28 1.28 1.26 1.26 1.24 0.87 0.86

2a/H



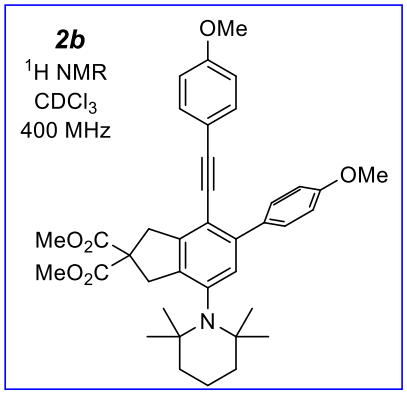


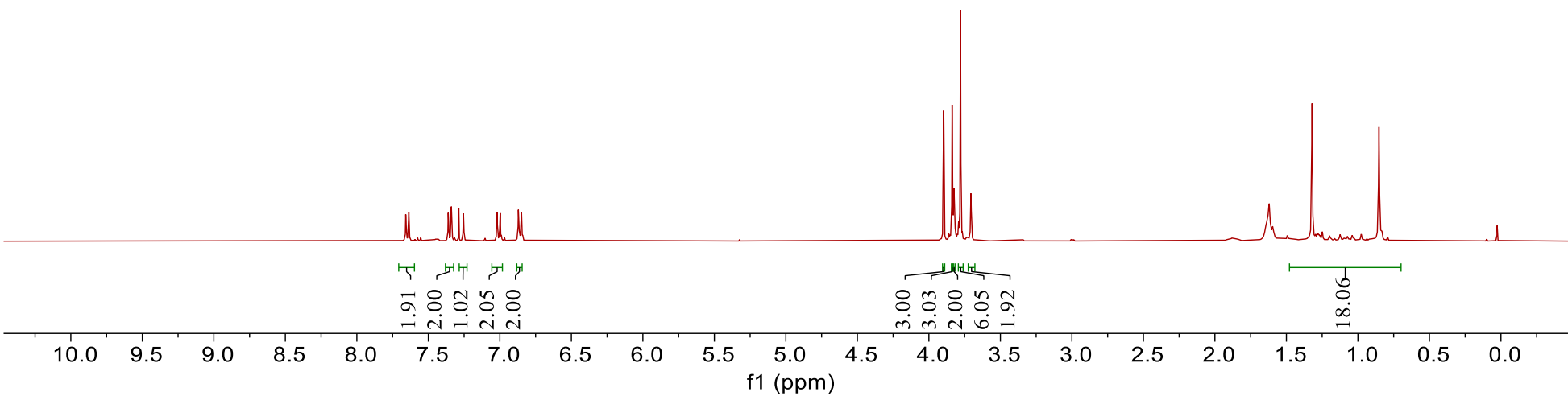
2a/C


2a
^{13}C NMR
$CDCl_3$
101 MHz
Et
Et
MeO_2C
MeO_2C
N

172.21
144.47
143.84
143.68
143.19
142.38
142.34
138.09
132.18
131.37
129.32
127.84
127.37
120.94
115.32
59.61
55.38
52.92
42.20
41.51
41.46
32.39
28.87
28.66
25.53
18.43
15.62
15.46
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

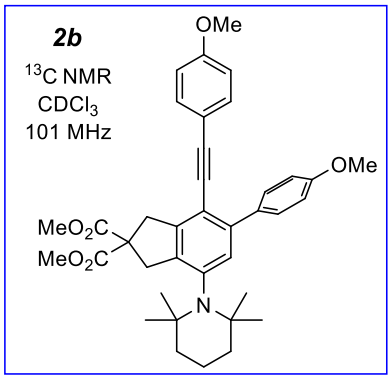
2b/H


2b
1H NMR
CDCl3
400 MHz
OMe
OMe
MeO2C
MeO2C
N


7.66
7.64
7.36
7.36
7.34
7.34
7.33
7.29
7.25
7.02
7.00
6.87
6.87
6.85
3.90
3.84
3.83
3.83
3.82
3.78
3.71
1.32
0.85
1.91
2.00
1.02
2.05
2.00
3.00
3.03
2.00
6.05
1.92
18.06
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
0.0
f1 (ppm)

SI

2b/C



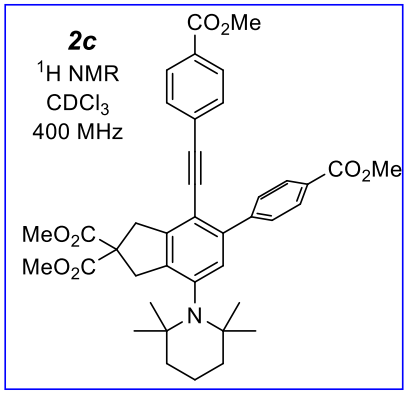
172.32
159.57
158.98
143.77
143.61
142.23
141.90
133.45
132.92
132.18
130.60
115.99
115.42
114.03
113.37
95.62
86.33
59.73
55.46
55.44
53.02
42.30
41.55
32.49
25.62
18.52

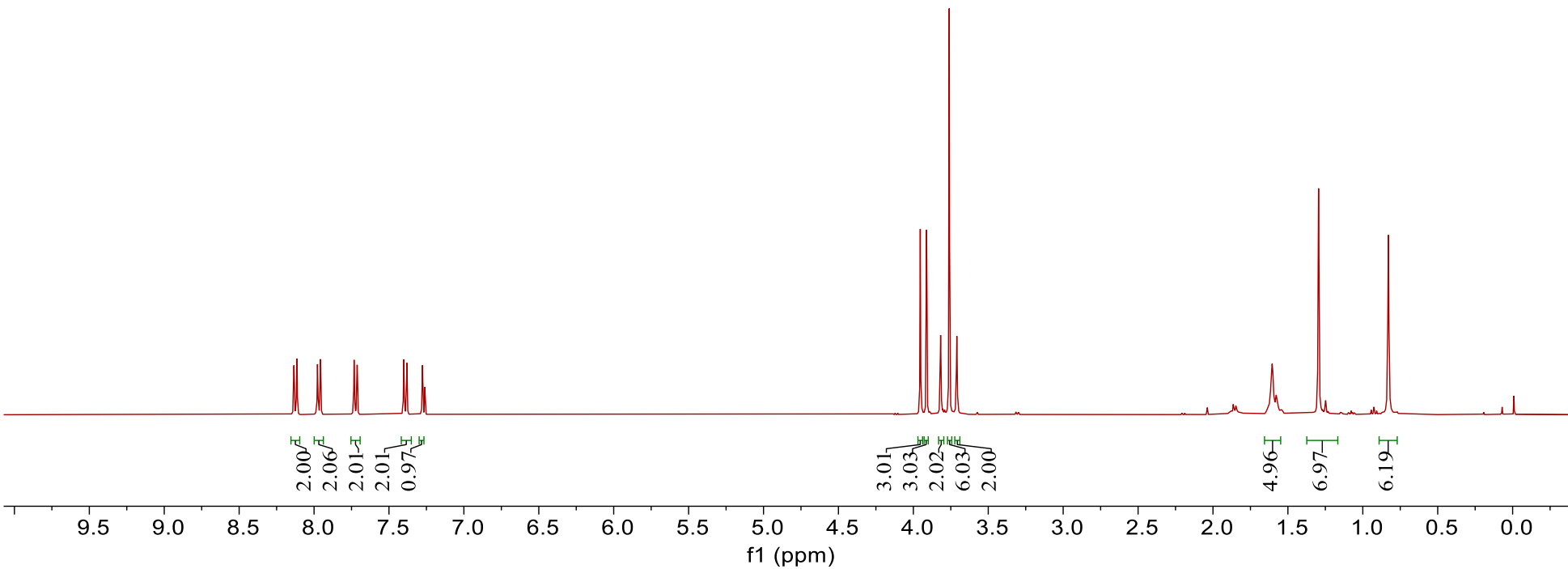
8.13 8.13 8.12 8.11 7.98 7.97 7.96 7.96 7.73 7.73 7.72 7.71 7.40 7.40 7.38 7.38 7.28

3.95 3.91 3.82 3.76 3.71

1.62 1.60 1.58 1.30 0.83

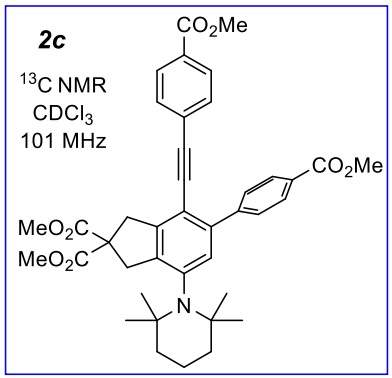
2c/H

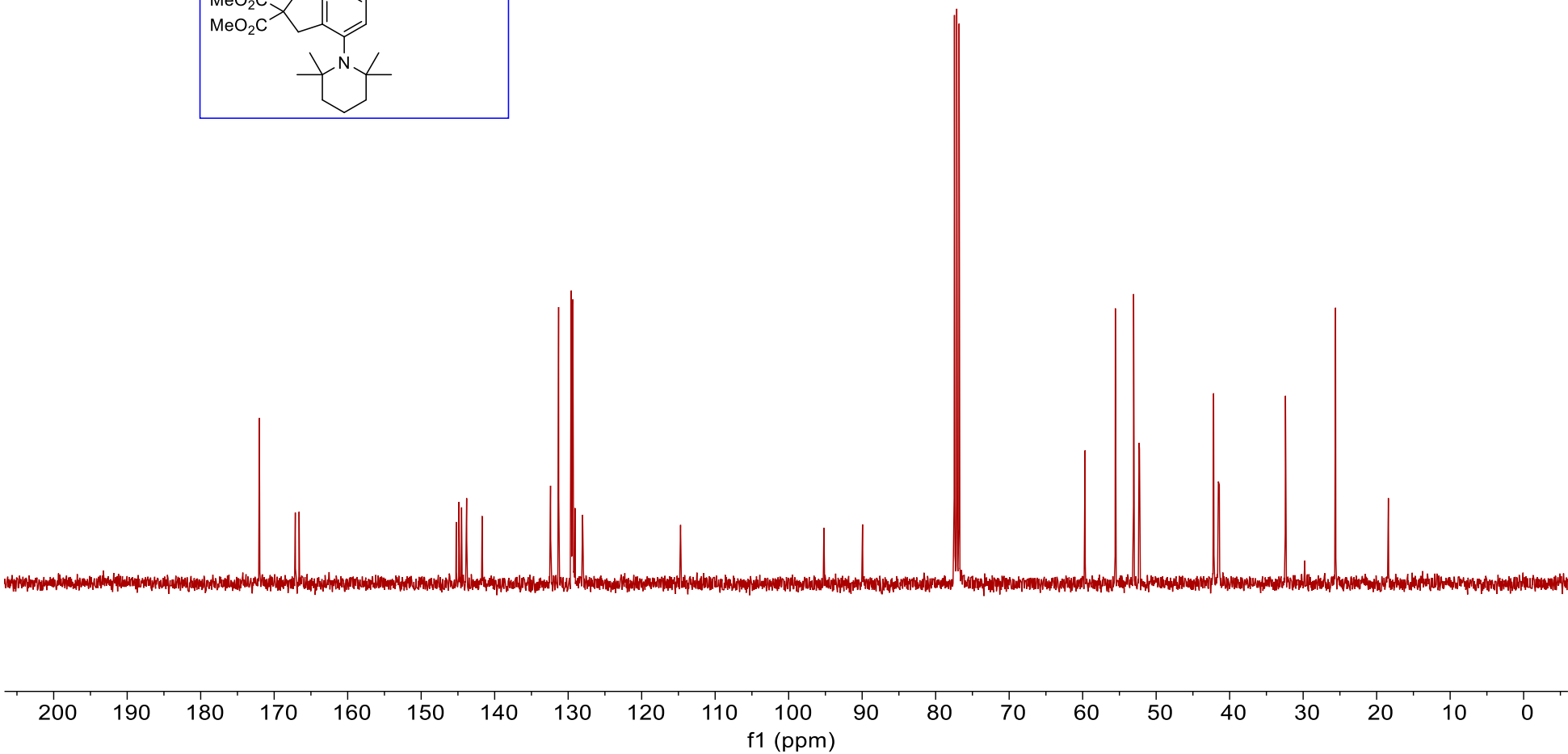


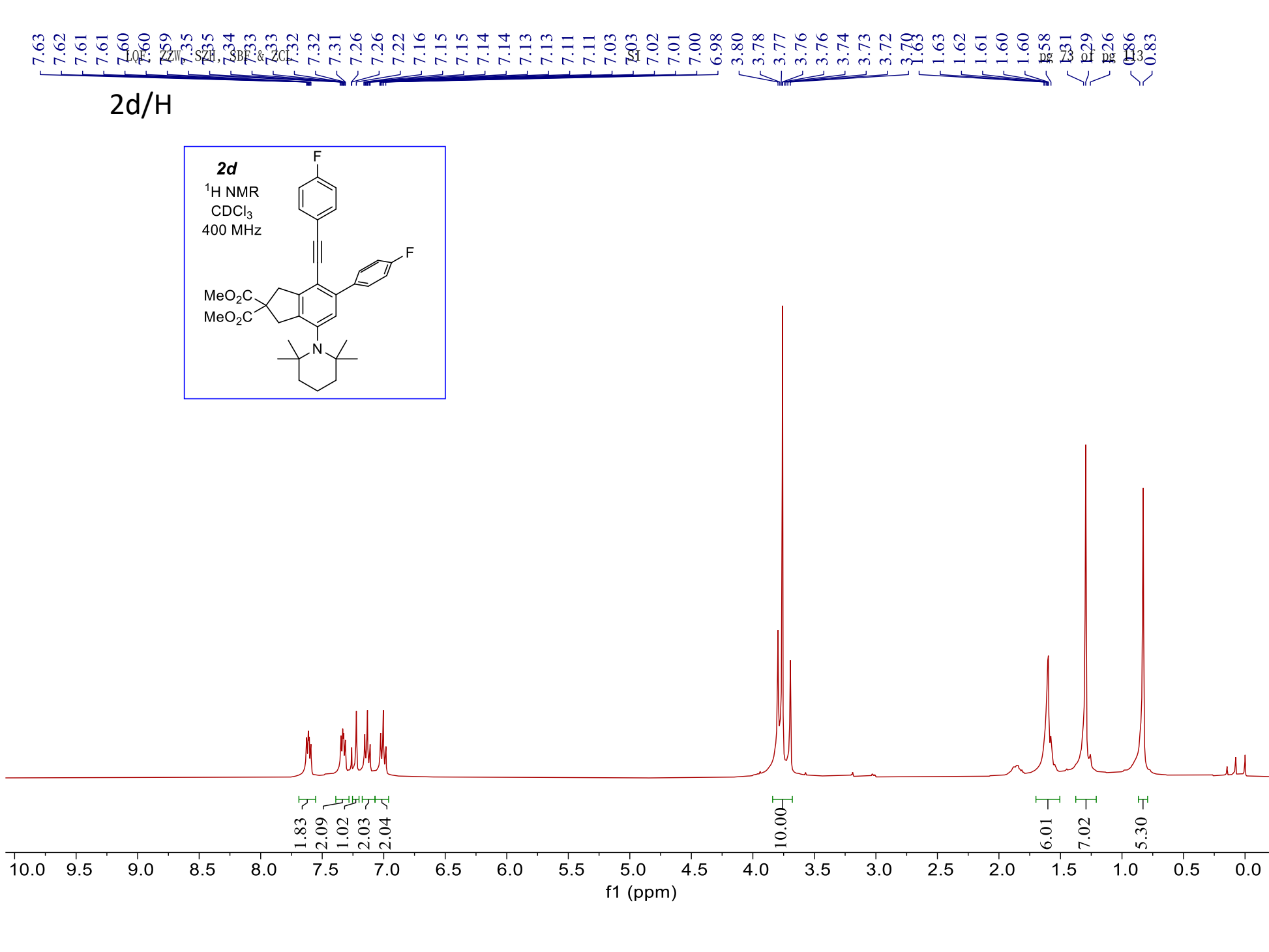


172.01
167.12
166.61
145.23
144.87
144.51
143.81
141.71
132.40
131.30
129.58
129.48
129.44
129.37
129.07
128.04
95.21
89.95
59.67
55.55
53.06
52.33
52.27
42.18
41.54
41.41
32.40
25.59
18.41

2c/C

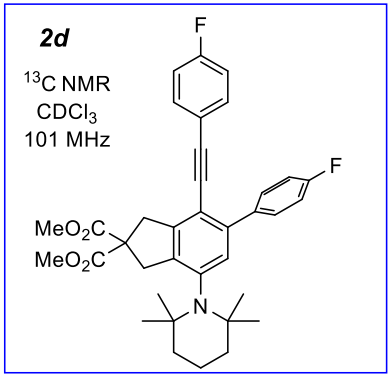


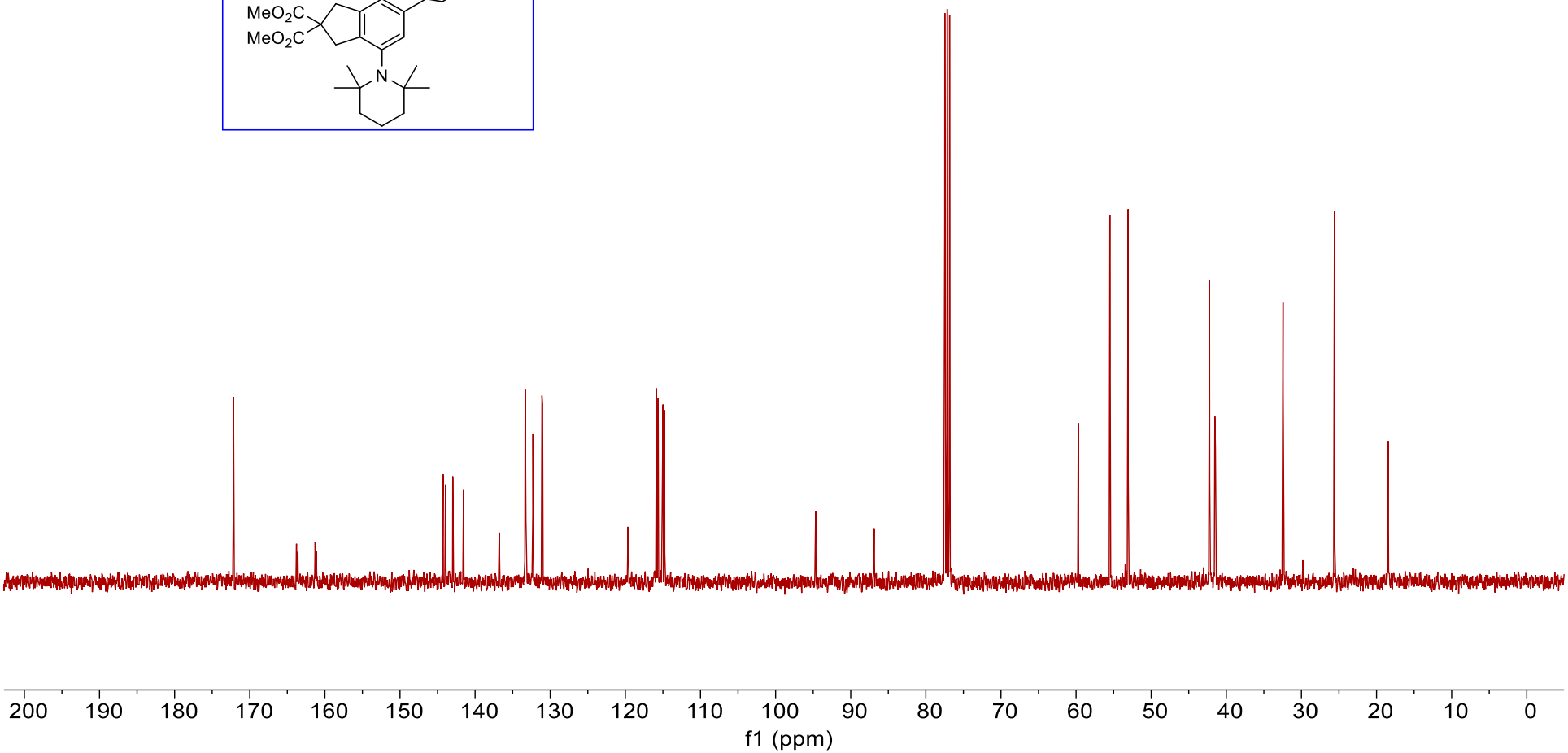



7.63
7.62
7.61
7.61
7.60
7.60
7.59
7.35
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.26
7.26
7.22
7.16
7.15
7.15
7.14
7.14
7.13
7.13
7.11
7.11
7.03
7.03
7.02
7.01
7.00
6.98
3.80
3.78
3.77
3.76
3.76
3.74
3.73
3.72
3.70
1.63
1.63
1.62
1.61
1.60
1.60
1.58
1.31
1.29
1.26
0.86
0.83
LQF-ZZW-SZH, SBF-&-ZC
2d/H
2d
1H NMR
CDCl3
400 MHz
F
F
MeO2C
MeO2C
N
1.83
2.09
1.02
2.03
2.04
10.00
6.01
7.02
5.30
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
0.0
f1 (ppm)

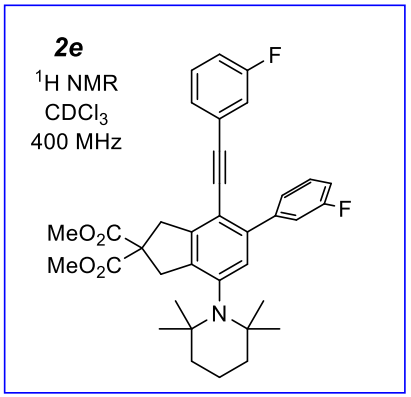
172.16 163.78 163.59 161.30 161.15 144.26 143.94 142.97 141.54 136.79 133.33 133.25 132.30 131.10 131.02 119.64 115.85 115.63 115.10 114.99 114.78 SI 94.67 86.89 59.71 55.50 53.07 42.23 41.53 41.45 32.45 25.60 18.46

2d/C



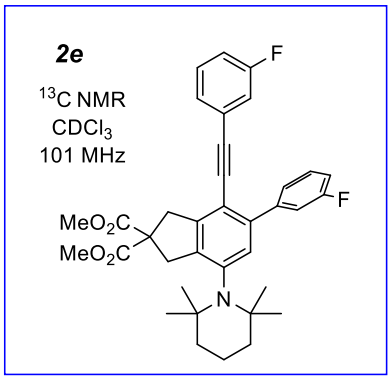


2e/H


2e
1H NMR
CDCl3
400 MHz
F
F
MeO2C
MeO2C
N

3.06
2.35
4.11
2.07
6.08
2.00
5.83
6.68
6.17
f1 (ppm)

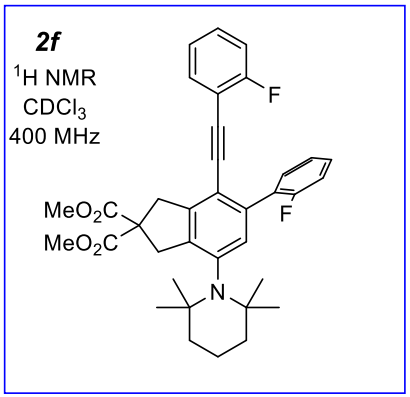
2e/C

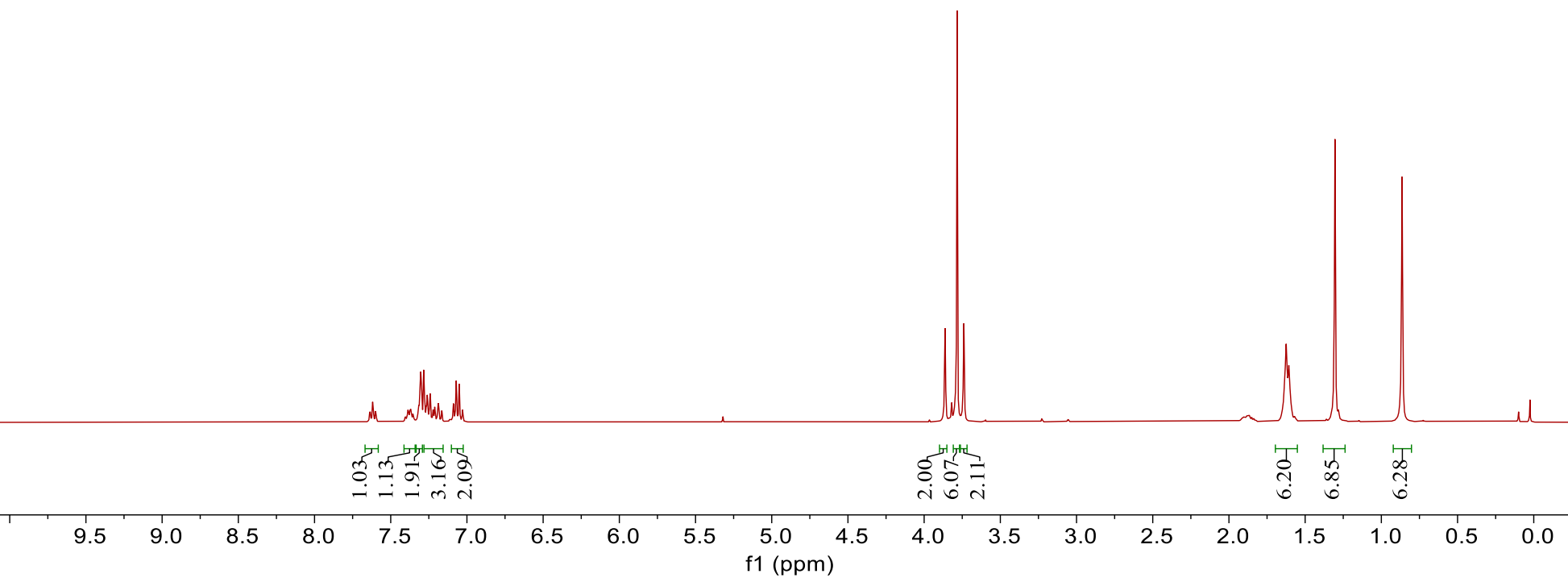

2e
13C NMR
CDCl3
101 MHz
F
F
MeO2C
MeO2C
N

172.09
163.77
163.69
161.33
161.24
144.65
144.29
143.52
142.84
142.76
141.43
132.28
130.05
129.97
129.54
129.46
127.36
127.33
125.35
125.25
125.18
118.25
118.03
116.51
116.29
115.76
115.55
114.81
114.39
114.18
94.77
94.73
87.91
59.70
55.55
53.08
42.23
41.56
41.43
32.44
25.62
18.45
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

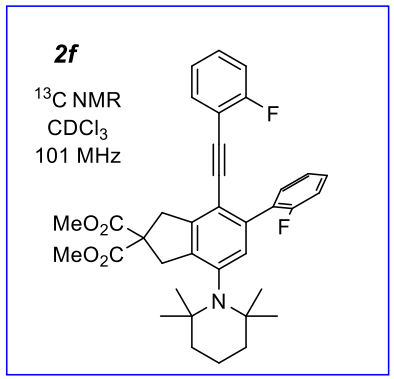

7.64
7.63
7.62
7.61
7.60
7.60
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.35
7.35
7.32
7.32
7.31
7.30
7.30
7.28
7.28
7.27
7.26
7.26
7.25
7.24
7.24
7.22
7.22
7.21
7.21
7.19
7.19
7.18
7.17
7.16
7.09
7.09
7.07
7.05
7.03
3.86
3.79
3.78
3.74
1.65
1.64
1.63
1.62
1.61
1.60
1.59
1.57
1.33
1.30
1.28
0.86

2f/H


2f
1H NMR
CDCl3
400 MHz
F
MeO2C
MeO2C
F
N

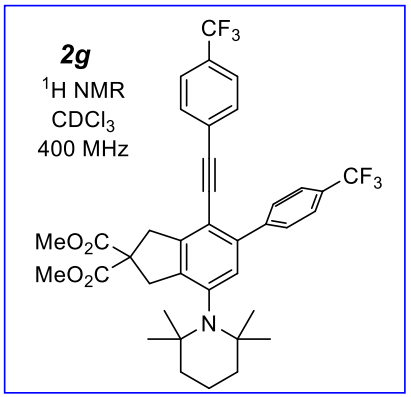

1.03
1.13
1.91
3.16
2.09
2.00
6.07
2.11
6.20
6.85
6.28
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

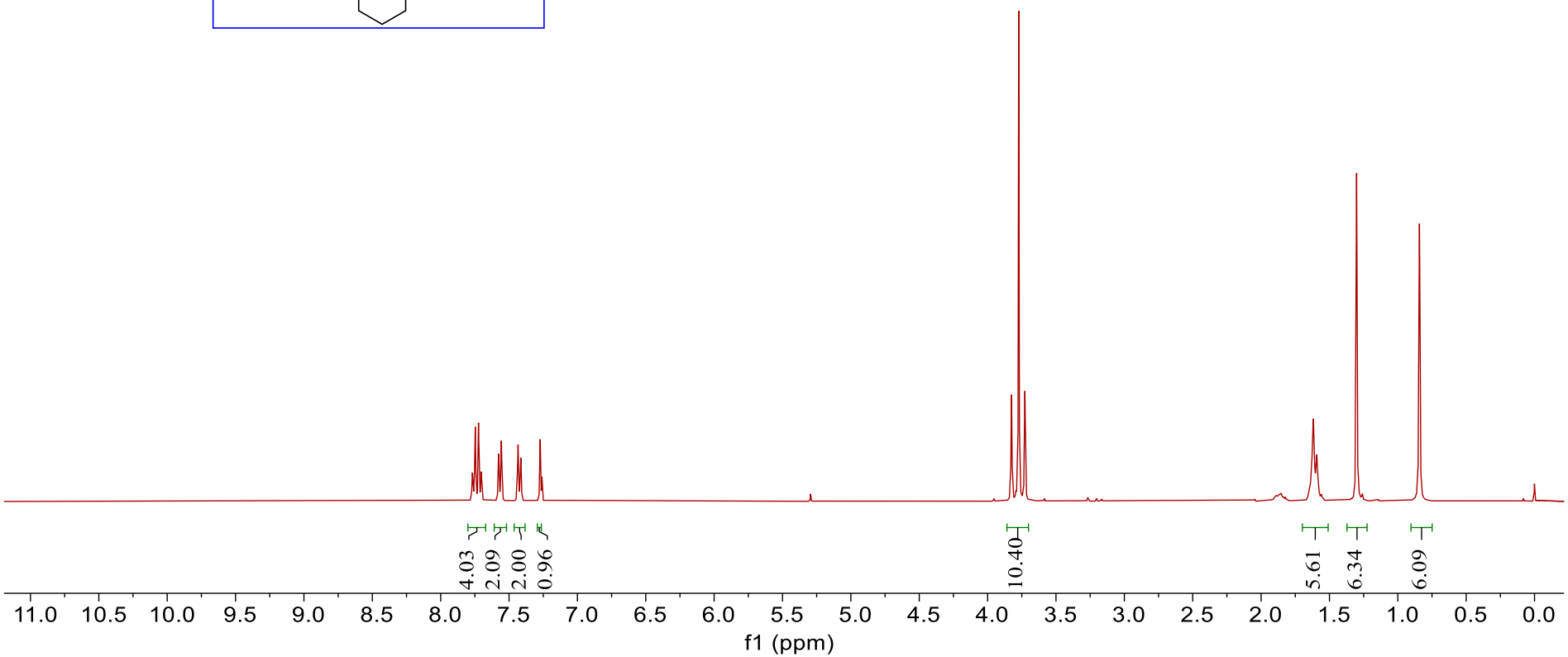
2f/C


2f
13C NMR
CDCl3
101 MHz
MeO2C
MeO2C
F
F
N

163.83
161.92
161.10
158.64
144.15
143.87
143.44
136.53
133.34
133.20
132.37
132.34
129.92
129.84
129.37
129.28
128.25
128.11
123.93
123.90
123.64
123.61
116.15
115.92
115.70
115.64
115.43
112.31
112.15
59.70
55.58
53.06
42.29
41.71
41.41
32.46
25.24
18.50
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

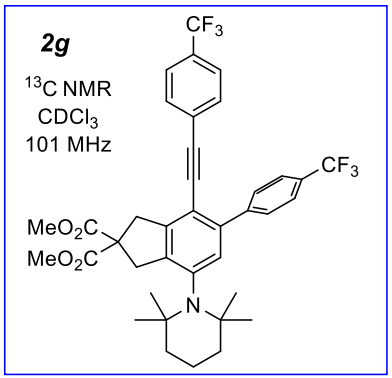
2g/H

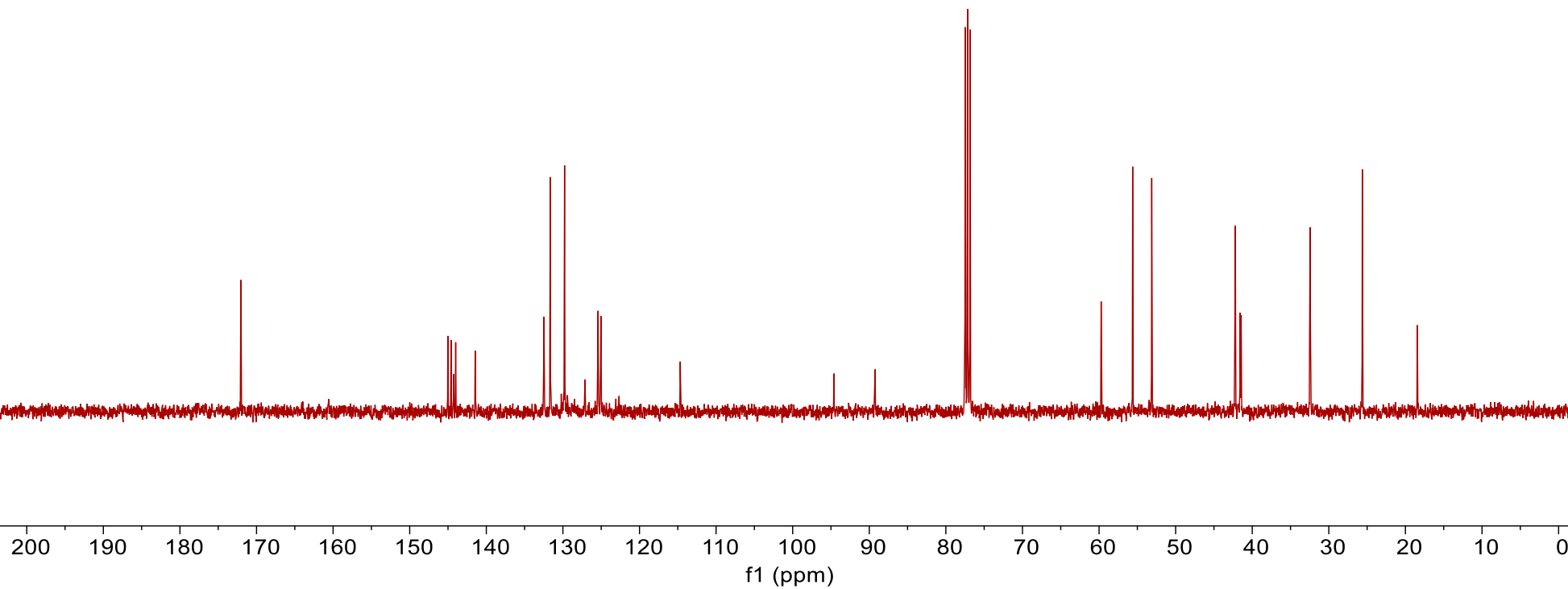

2g
1H NMR
CDCl3
400 MHz
CF3
CF3
MeO2C
MeO2C
N


7.77
7.75
7.72
7.70
7.58
7.56
7.43
7.41
7.27
3.83
3.77
3.76
3.73
1.65
1.64
1.63
1.62
1.59
1.30
0.84
4.03
2.09
2.00
0.96
10.40
5.61
6.34
6.09
11.0 10.5 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 0.0
f1 (ppm)

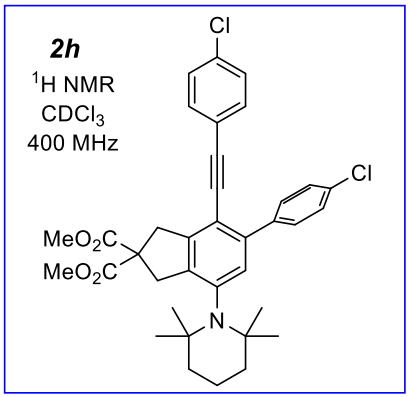
2g/C

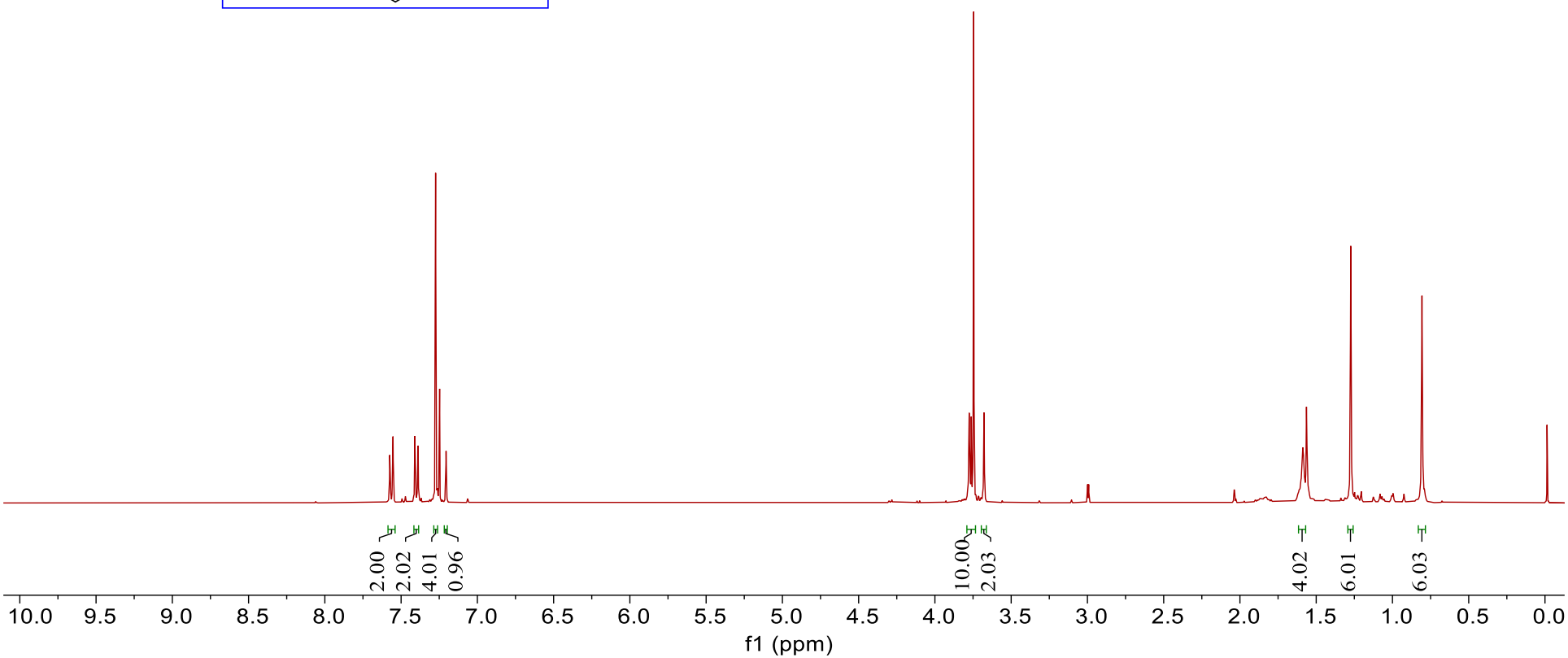
172.04
145.02
144.59
144.26
144.00
141.45
132.48
131.64
129.78
125.45
125.41
125.06
125.03
114.67
94.61
89.23
59.72
55.61
53.12
42.22
41.58
41.45
32.45
25.63
18.44



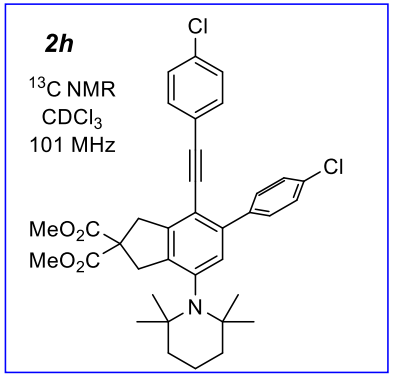


2h/H


2h
1H NMR
CDCl3
400 MHz
Cl
Cl
MeO2C
MeO2C
N

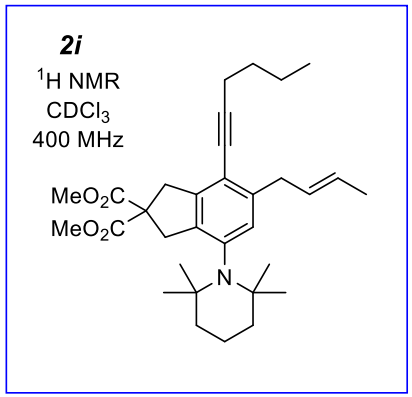

7.55
7.41
7.39
7.27
7.25
7.20
3.78
3.76
3.75
3.68
1.61
1.60
1.59
1.27
1.25
1.20
0.81
2.00
2.02
4.01
0.96
10.00
2.03
4.02
6.01
6.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2h/C



171.93
144.35
144.01
143.14
141.19
138.99
134.17
133.26
132.48
132.12
130.58
128.64
128.04
127.97
121.78
114.72
94.61
87.88
71.77
59.53
55.36
55.16
53.14
52.91
42.06
41.37
41.28
32.27
25.45
22.61
18.28

2i/H


2i
1H NMR
CDCl3
400 MHz
MeO2C
MeO2C
N

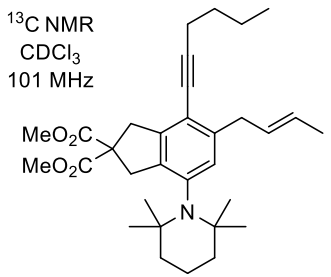
6.48
4.69
4.69
4.65
4.65
4.64
3.75
3.74
3.65
3.32
2.67
2.65
2.65
2.45
2.44
2.42
2.00
1.98
1.96
1.65
1.65
1.64
1.58
1.56
1.56
1.32
1.32
0.96
0.95
0.94
0.93
0.92
0.91
1.00
2.00
6.00
2.02
1.98
2.00
2.00
2.00
20.11
6.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

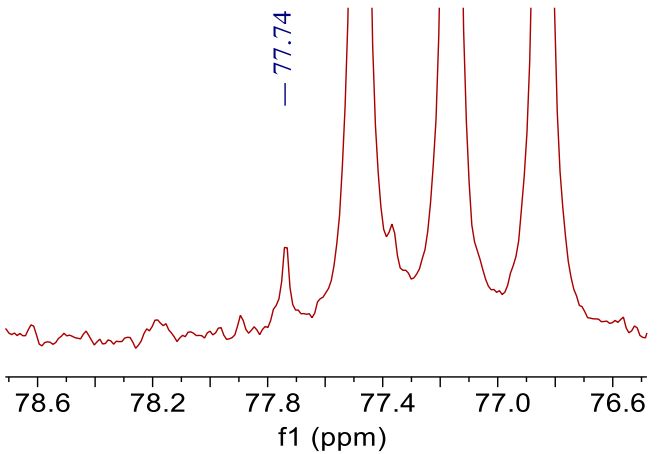
172.39
145.78
145.10
143.00
142.00
122.48
112.11
110.24
107.83
94.62
77.74
59.22
53.76
53.20
41.43
40.74
38.05
34.75
33.24
31.37
28.56
22.73
22.36
22.09
21.76
19.53
14.19
13.81

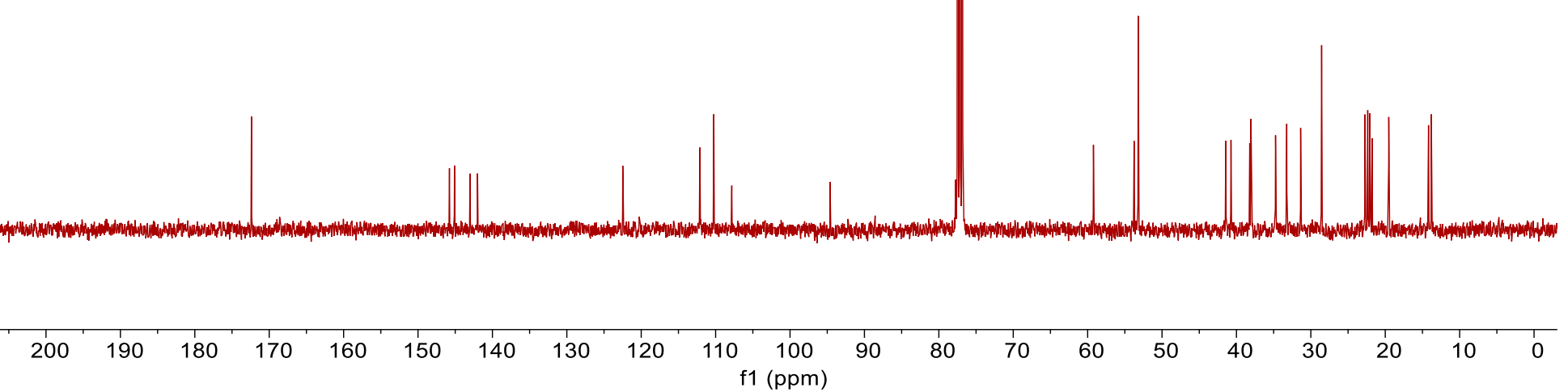
2i/C

2i

^{13}C NMR
$CDCl_3$
101 MHz

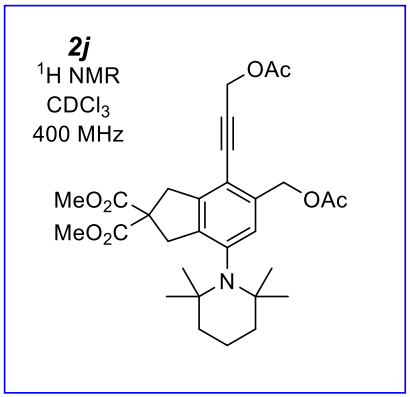


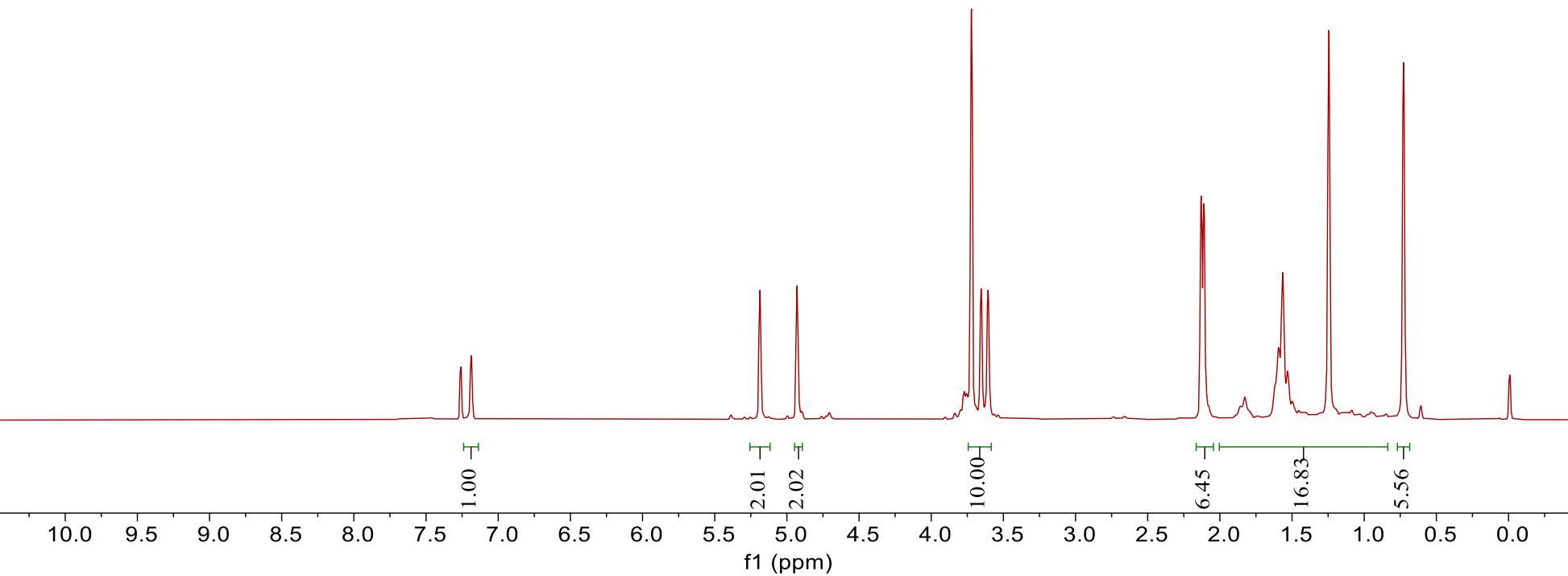




LQF, ZZW, SZH, SBF & ZCL

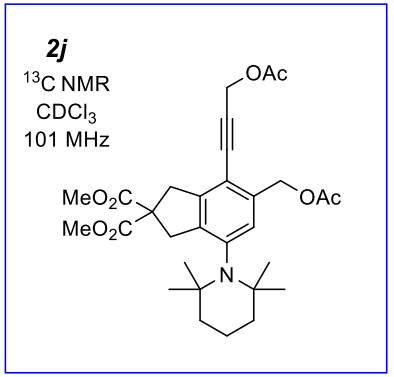
2j/H



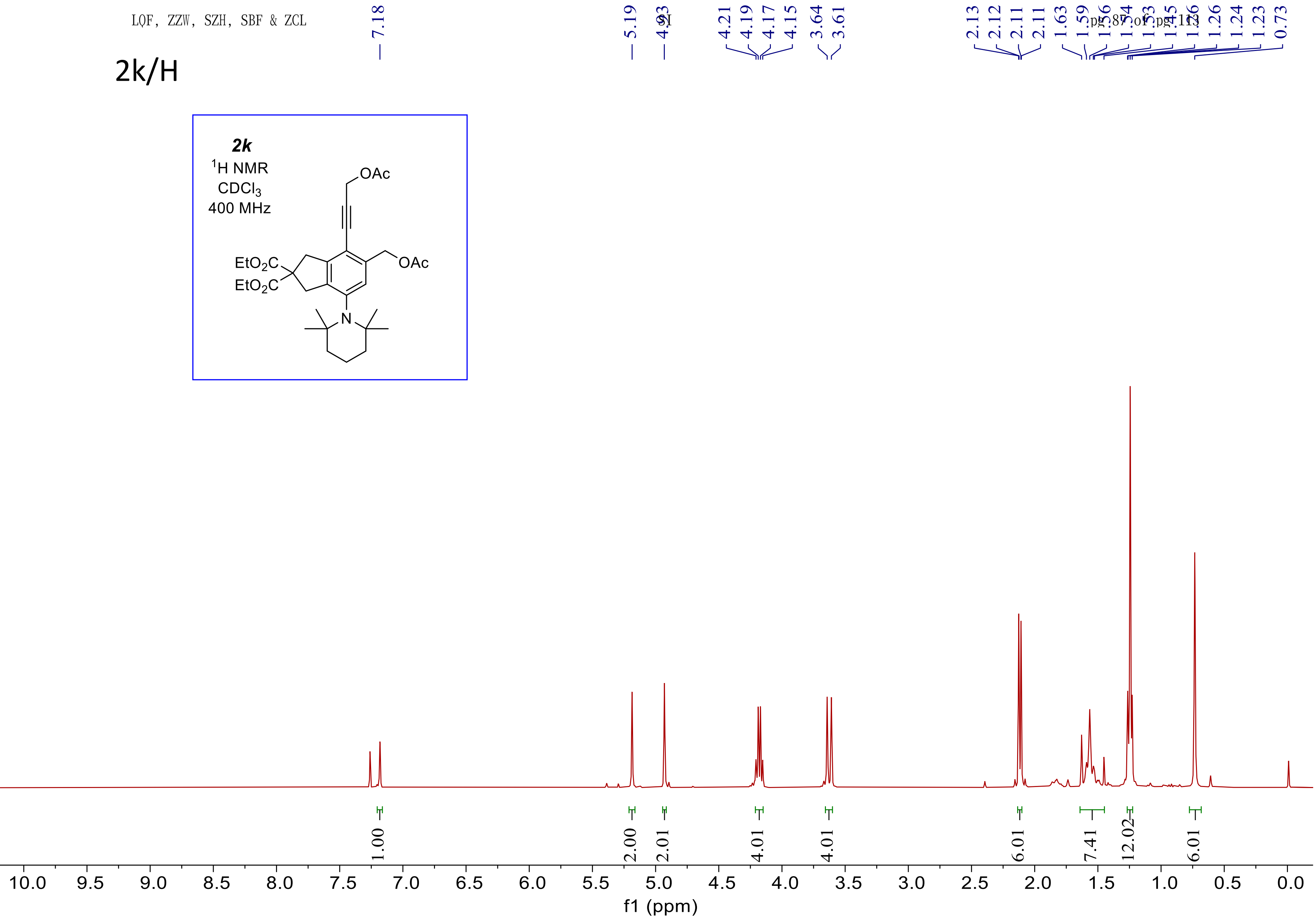


171.98
170.99
170.42
144.64
144.19
144.02
136.56
131.52
115.32
90.90
81.99
64.92
59.69
55.49
53.04
52.96
42.23
41.42
40.96
32.33
25.33
21.08
20.94
18.44

2j/C

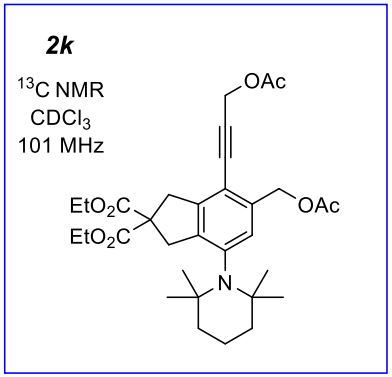


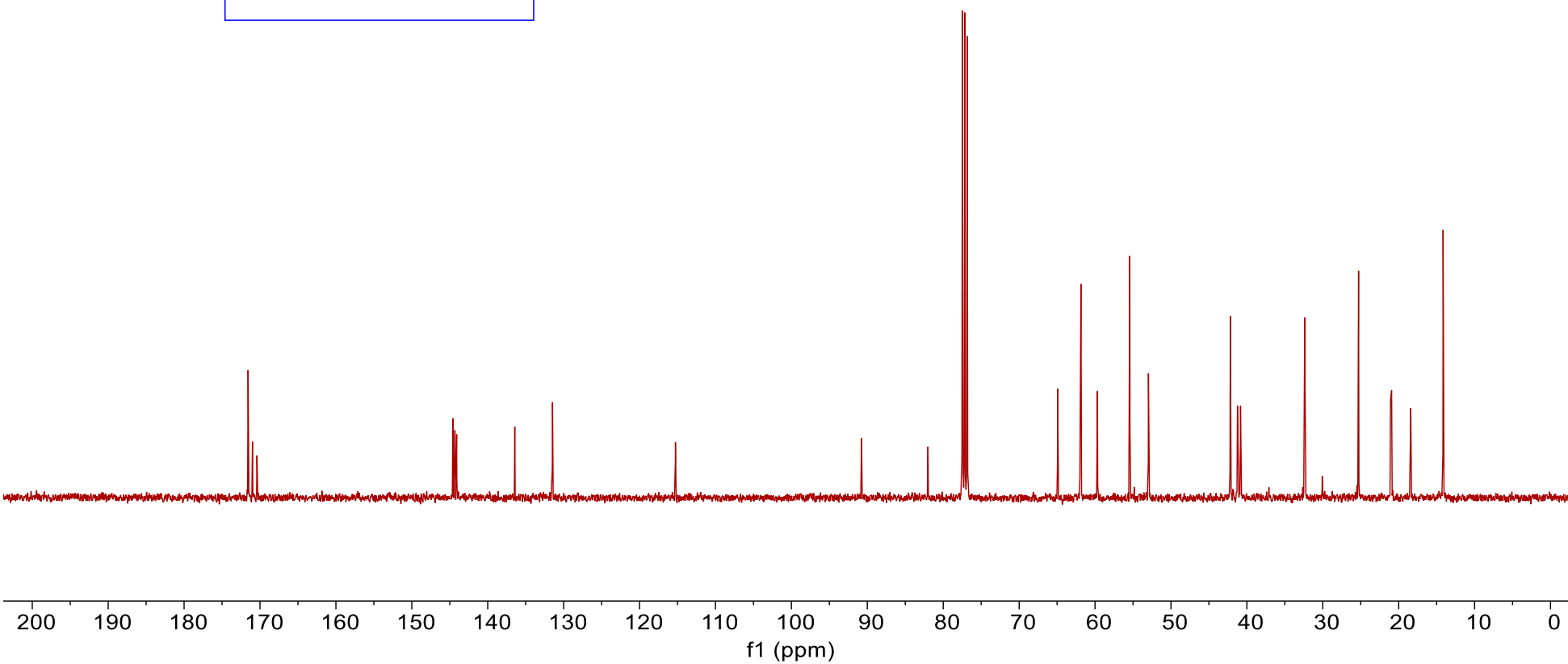
2k/H


2k
^{1}H NMR
$CDCl_3$
400 MHz
OAc
OAc
EtO_2C
EtO_2C
N
7.18
5.19
4.93
4.21
4.19
4.17
4.15
3.64
3.61
2.13
2.12
2.11
2.11
1.63
1.59
1.56
1.54
1.53
1.45
1.26
1.26
1.24
1.23
0.73
1.00
2.00
2.01
4.01
4.01
6.01
7.41
12.02
6.01
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 0.0
f1 (ppm)

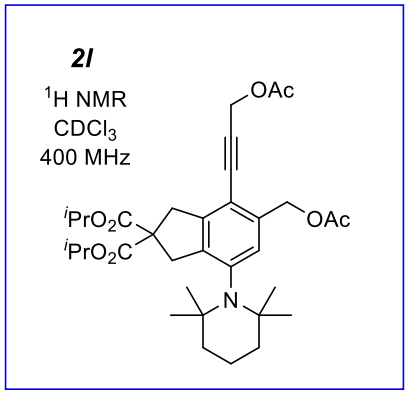
171.57
170.99
170.41
144.58
144.33
144.09
136.44
131.47
115.27
90.76
82.01
64.93
61.86
59.68
55.42
52.97
42.18
41.23
40.84
32.37
25.29
21.08
20.93
18.41
14.15

2k/C



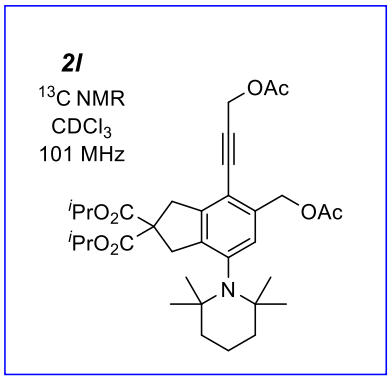


2l/H


2l
1H NMR
CDCl3
400 MHz
OAc
OAc
iPrO2C
iPrO2C
N

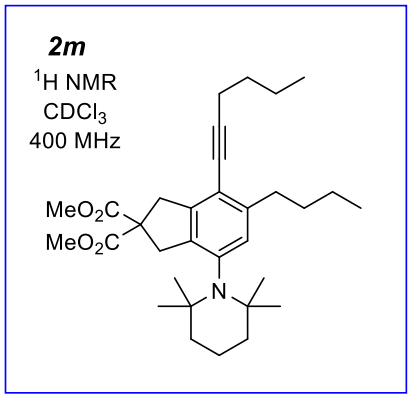
7.17
5.18
5.04
5.03
5.01
5.00
4.93
3.60
2.12
2.10
1.56
1.25
1.24
1.24
1.23
1.21
0.73
1.00
2.02
2.04
2.03
4.01
6.04
7.46
20.07
6.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

2l/C


2l
^{13}C NMR
$CDCl_3$
101 MHz
OAc
OAc
$^{i}PrO_2C$
$^{i}PrO_2C$
N

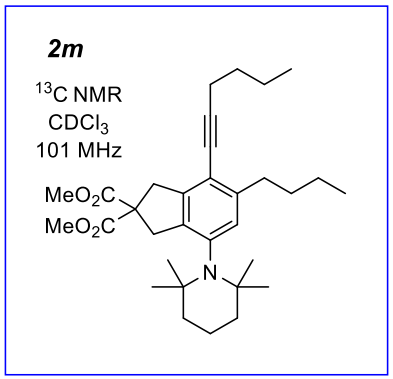
173.16
170.98
170.38
144.60
144.48
144.17
136.45
131.43
115.29
90.77
82.11
69.34
64.96
59.67
55.44
53.55
53.00
42.23
41.20
40.85
32.49
25.33
21.68
21.66
21.06
20.91
18.45
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2m/H


2m
1H NMR
CDCl3
400 MHz
MeO2C
MeO2C
N

1.00
6.19
2.01
2.01
2.19
2.21
6.40
4.38
2.16
6.90
7.28
6.04
f1 (ppm)

2m/C



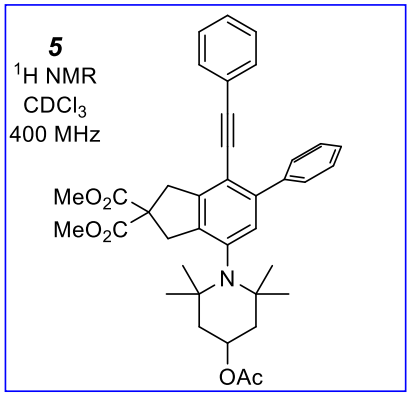
172.43 143.20 142.91 142.84 140.54 131.35 116.95 97.12 59.73 55.26 52.91 42.32 41.46 41.34 34.34 33.11 32.42 31.20 25.44 22.63 22.12 19.50 18.57 14.16 13.78

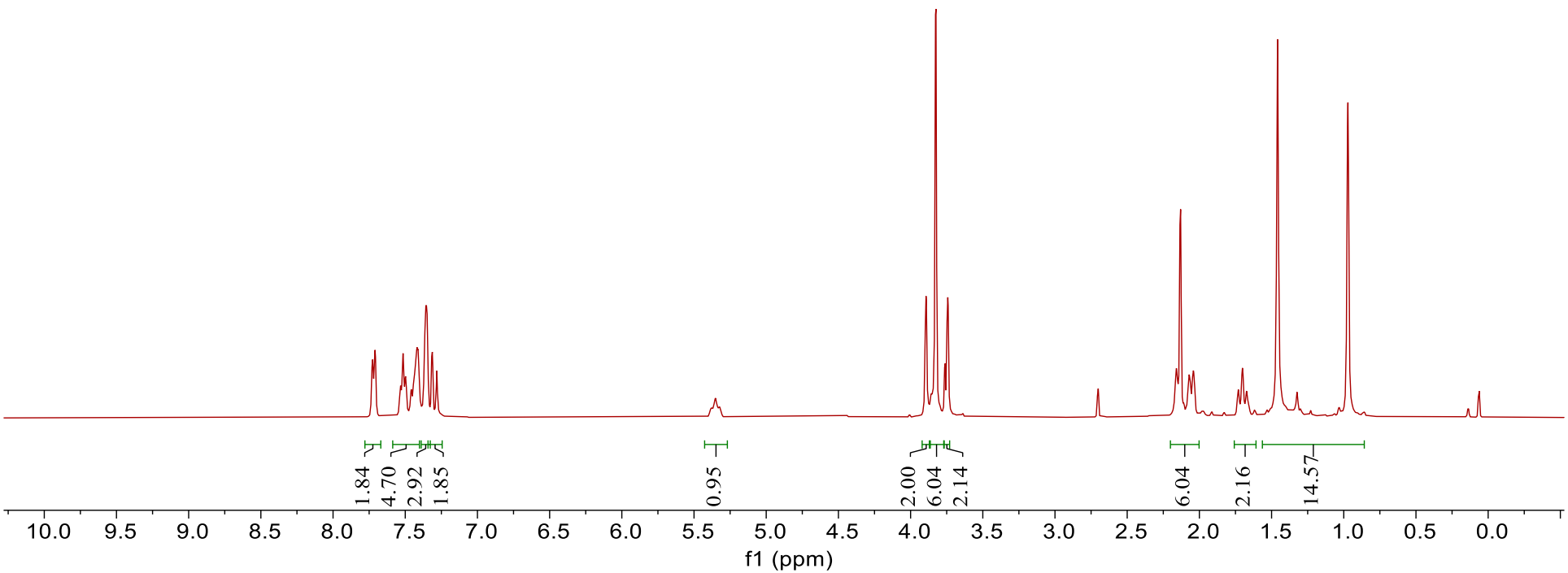
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

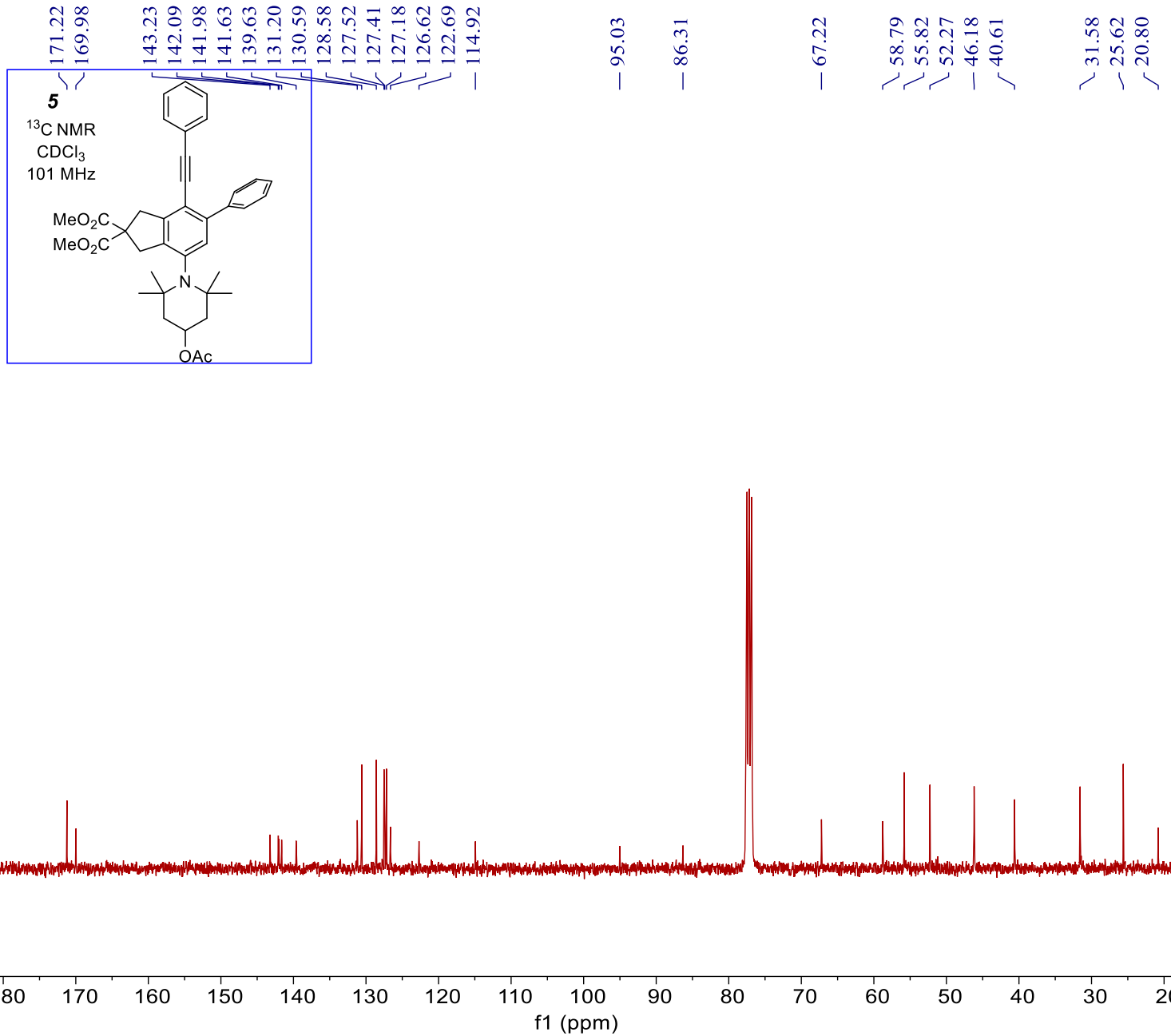
7.73 7.71 7.70 7.53 7.52 7.50 7.49 7.46 7.44 7.44 7.43 7.42 7.41 7.40 7.37 7.36 7.35 7.34 7.32 7.31 7.28 — 5.35 — 3.90 3.89 3.89 3.85 3.83 3.82 3.76 3.76 3.75 3.74 3.74 2.16 2.13 2.13 2.11 2.10 2.07 2.04 2.03 1.73 1.70 1.67 1.46 1.45 1.32 0.97 0.97

5/H



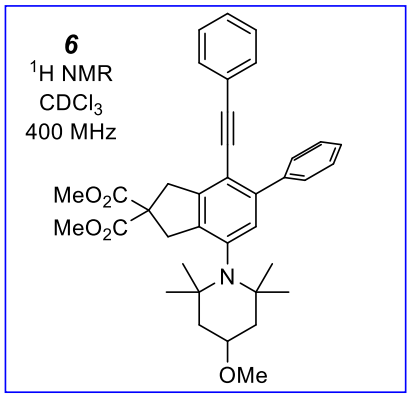


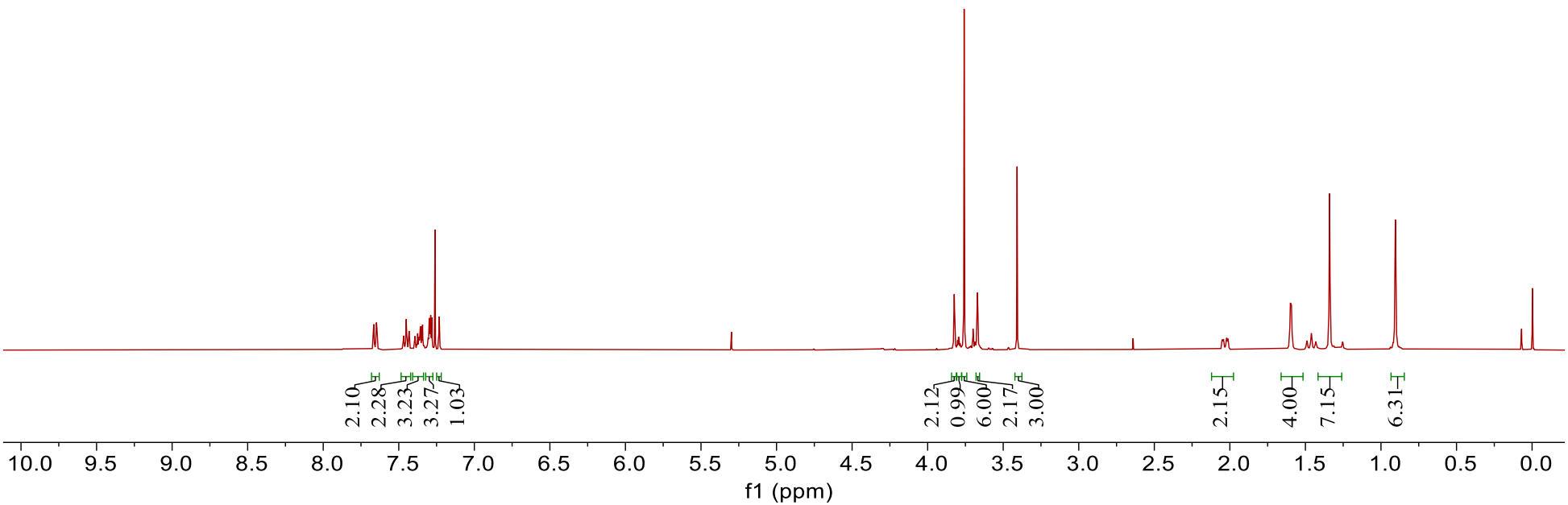
5/C


171.22
169.98
143.23
142.09
141.98
141.63
139.63
131.20
130.59
128.58
127.52
127.41
127.18
126.62
122.69
114.92
95.03
86.31
67.22
58.79
55.82
52.27
46.18
40.61
31.58
25.62
20.80
5
13C NMR
CDCl3
101 MHz
MeO2C
MeO2C
N
OAc
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

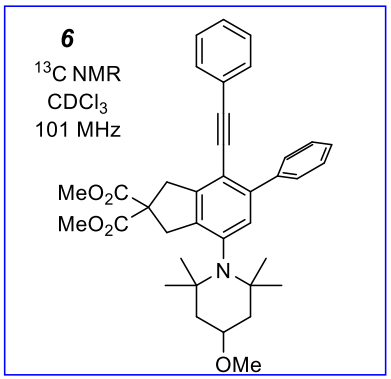
7.67 7.67 7.65 7.65 7.64 7.47 7.47 7.45 7.45 7.44 7.43 7.43 7.39 7.39 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.31 7.30 7.30 7.30 7.29 7.29 7.29 7.29 7.28 7.23 3.82 3.81 3.80 3.80 3.79 3.76 3.70 3.69 3.67 3.41 2.05 2.05 2.04 2.02 2.01 1.60 1.59 1.49 1.46 1.43 1.34 1.25 0.92 0.90

6/H





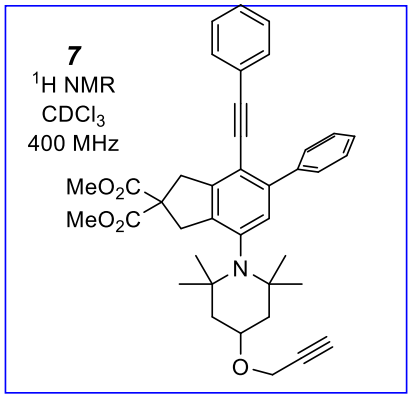
6/C

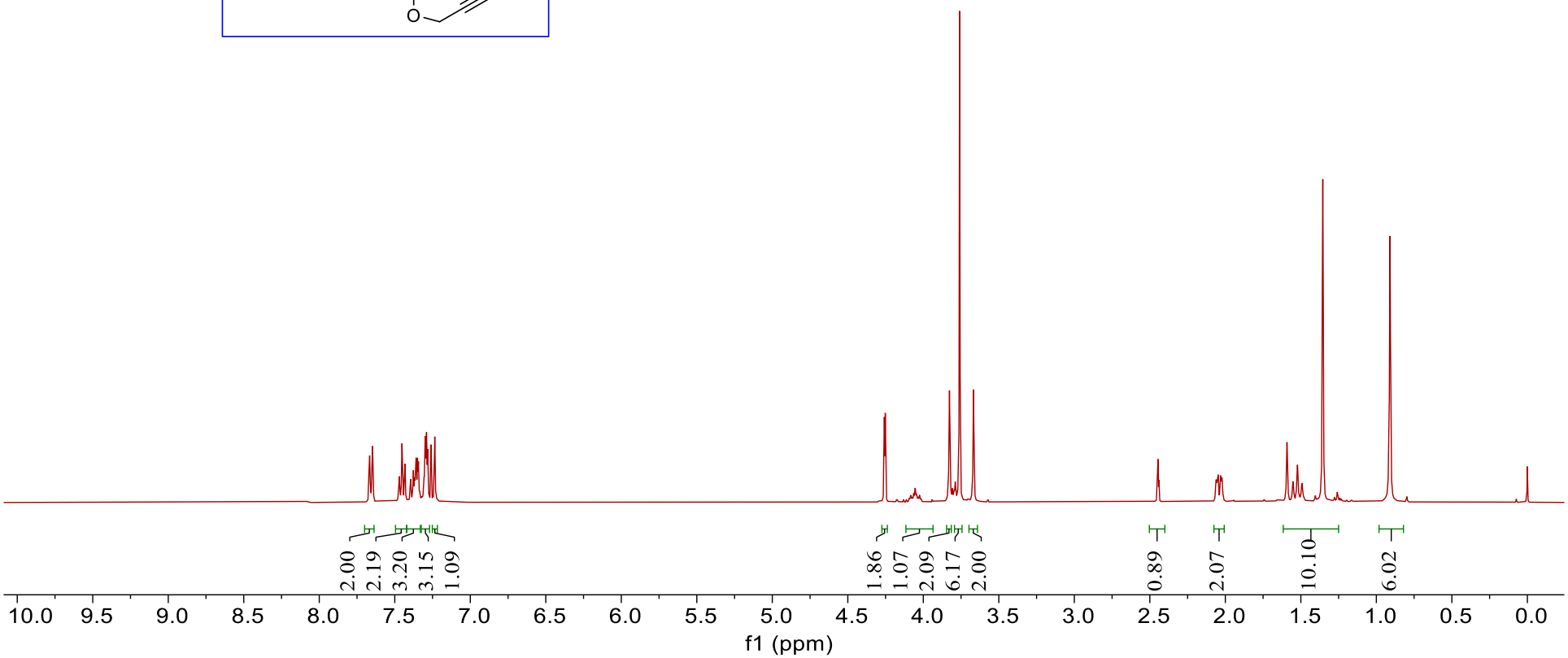


171.85
143.84
133.05
132.46
132.43
140.38
131.96
131.19
130.27
129.19
128.65
128.08
127.95
127.73
127.14
123.36
115.42
95.58
87.00
72.77
59.41
56.38
55.26
53.18
52.76
47.28
41.24
32.34
26.39

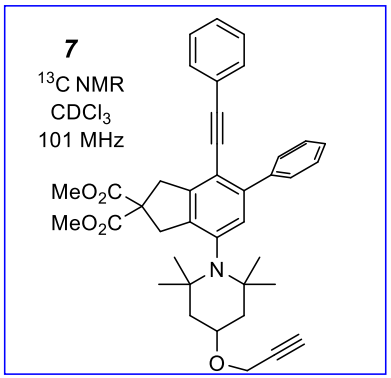
7.67 7.67 7.66 7.65 7.65 7.65 7.47 7.45 7.45 7.44 7.43 7.40 7.38 7.37 7.36 7.36 7.36 7.35 7.35 7.34 7.31 7.30 7.30 7.29 7.28 7.26 7.24 7.23 SI 4.29 4.26 4.25 4.22 4.05 3.83 3.79 3.76 3.67 2.45 2.45 2.44 2.44 2.06 2.05 2.05 2.03 2.02 1.59 1.55 1.52 1.49 1.35 0.91

7/H



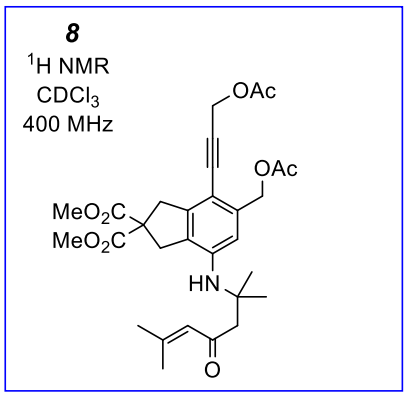


7/C


7
^{13}C NMR
$CDCl_3$
101 MHz
MeO_2C
MeO_2C
N
O

172.15
144.16
143.23
142.78
142.70
140.64
132.21
131.49
129.49
128.39
128.26
128.03
127.45
123.63
115.76
95.90
87.27
80.48
74.09
71.08
59.69
56.77
55.11
53.08
47.60
41.53
32.61
26.68
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

8/H


8
1H NMR
CDCl3
400 MHz
OAc
OAc
MeO2C
MeO2C
HN
O

6.71
5.99
5.99
5.99
5.98
5.98
5.16
4.91
3.76
3.65
3.40
2.71
2.11
2.11
2.10
1.84
1.84
1.25
1.06
1.00
2.00
1.95
6.08
2.05
2.01
1.91
9.17
3.00
6.49
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)

8/H

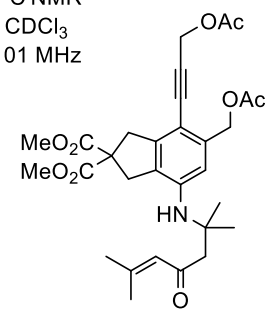
199.97 172.05 171.03 170.48 156.76 144.20 143.26 138.29 125.98 125.15 112.26 106.04 88.62 82.82 65.25 59.11 56.46 55.68 54.11 53.91 53.67 53.28 53.19 53.15 41.19 38.21 31.95 28.37 27.86 21.09 20.95

8

^{13}C NMR

$CDCl_3$

101 MHz



7.69 7.69 7.67 7.66 7.64 7.54 7.52 7.51 7.49 7.47 7.45 7.43 7.41 7.40 7.40 7.39 7.38 7.36 7.34 7.34 7.33 7.32 7.32 7.31 7.30 7.29 7.27 7.27 7.26 7.25 7.24 7.23 7.14 7.12 6.88 6.79 6.78 6.77 6.61 6.04 6.04 5.97 3.90 3.86 3.82 3.81 3.79 3.79 3.78 3.76 3.54 2.79 2.16 2.07 1.87 1.84 1.67 1.52 1.40 1.33

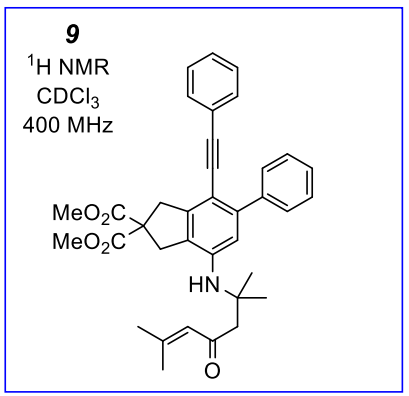
9/H

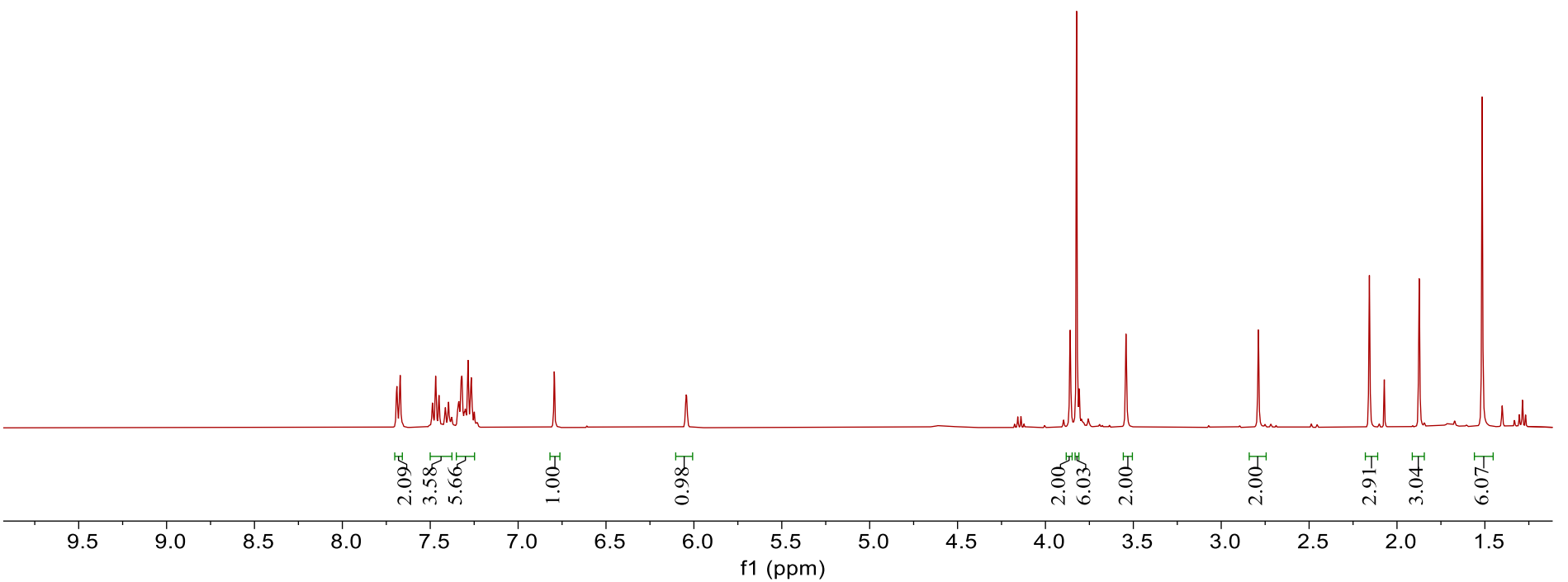
9

^{1}H NMR

$CDCl_3$

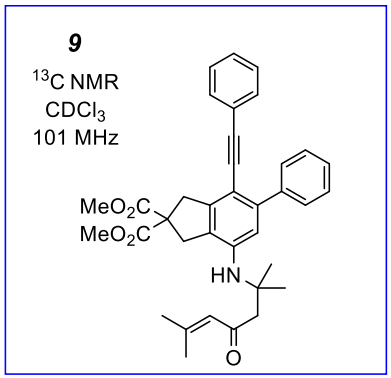
400 MHz





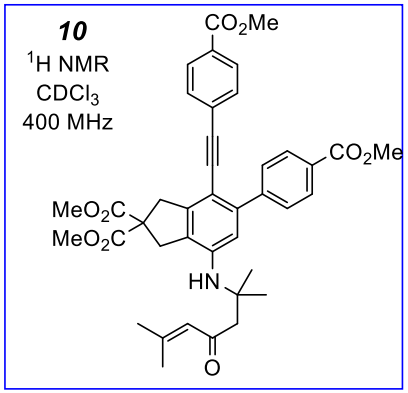
200.04
172.30
156.56
144.43
143.99
142.85
141.50
131.09
129.48
128.26
127.92
127.48
127.31
125.30
125.26
124.38
119.18
106.46
93.66
88.39
59.20
53.99
53.80
53.21
41.74
38.45
26.55
27.88
20.95

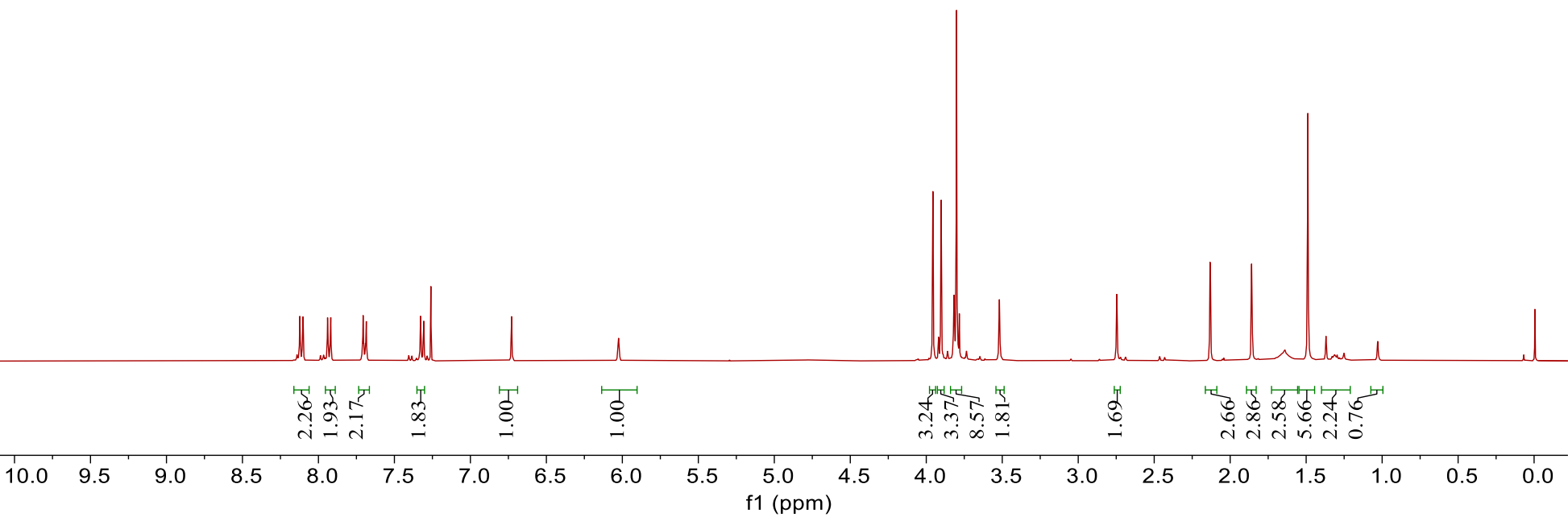
9/C



8.12 8.12 8.11 8.10 7.94 7.94 7.92 7.92 7.71 7.71 7.70 7.69 7.69 7.68 7.33 7.33 7.32 7.31 7.31 6.73 6.03 6.03 6.02 6.02 3.96 3.92 3.91 3.90 3.86 3.82 3.80 3.79 3.78 3.74 3.52 2.75 2.13 2.13 1.86 1.86 1.64 1.49 1.37 1.03

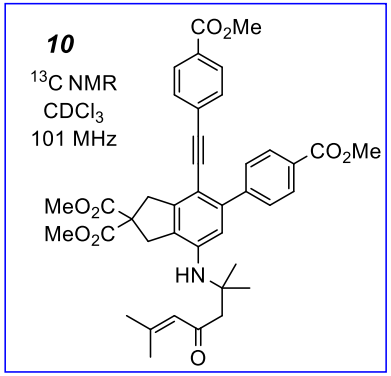
10/H



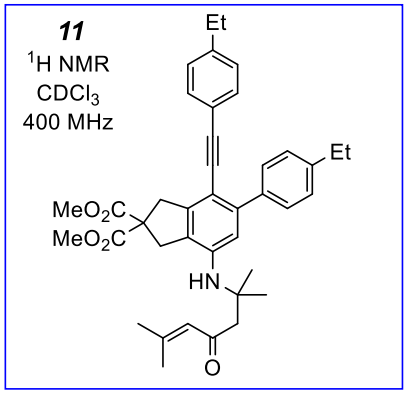


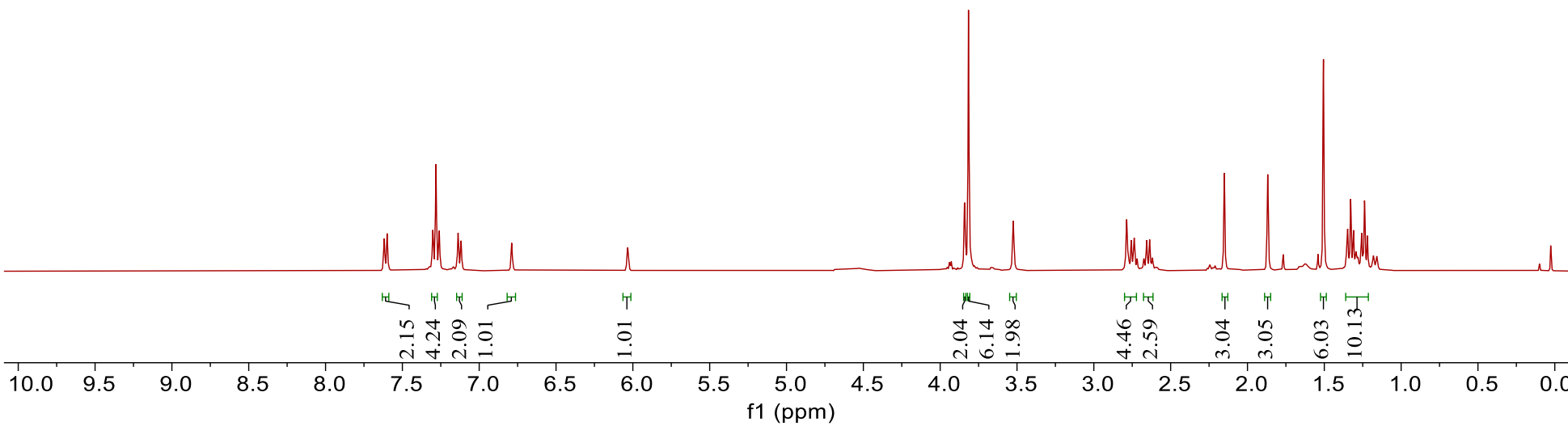
199.97
172.18
166.23
166.80
157.01
146.09
144.48
143.68
143.45
130.89
129.56
129.47
129.34
129.09
128.90
128.75
125.93
125.21
112.72
105.53
93.49
91.39
59.18
54.05
53.90
53.29
52.30
41.69
38.43
28.40
27.94
21.02

10/C

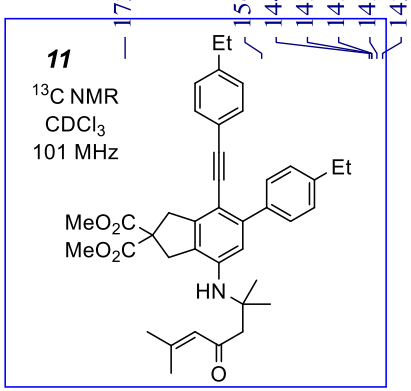


11/H

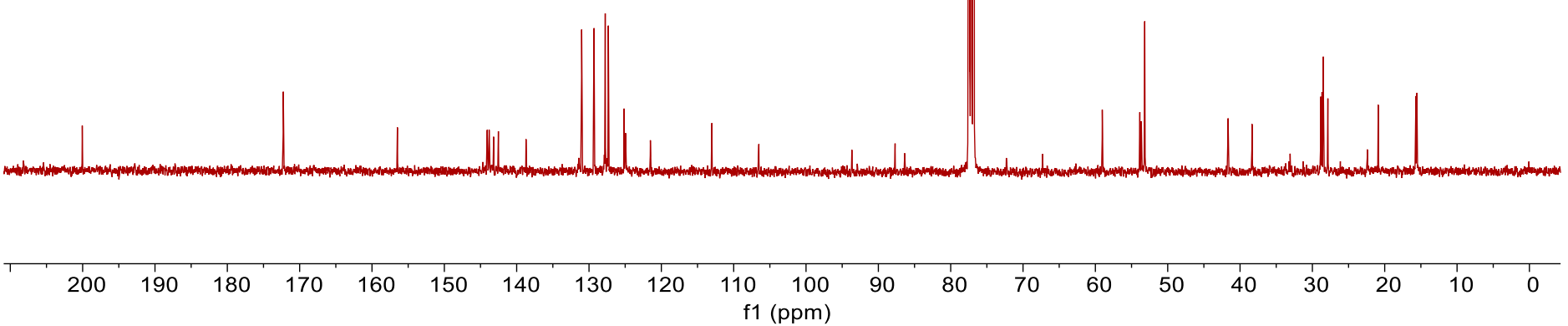

11
^{1}H NMR
$CDCl_3$
400 MHz
Et
Et
MeO_2C
MeO_2C
HN
O


7.62
7.60
7.30
7.28
7.14
7.12
6.79
6.03
3.84
3.82
3.52
2.79
2.78
2.76
2.74
2.66
2.64
2.15
1.87
1.51
1.35
1.33
1.31
1.24
2.15
4.24
2.09
1.01
1.01
2.04
6.14
1.98
4.46
2.59
3.04
3.05
6.03
10.13
f1 (ppm)

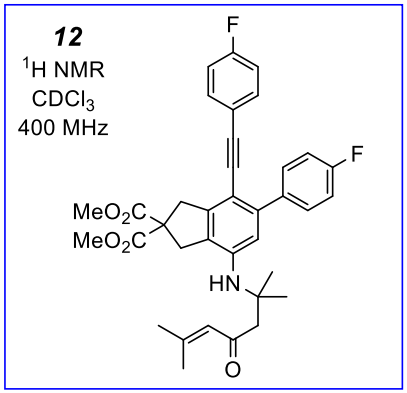
11/C

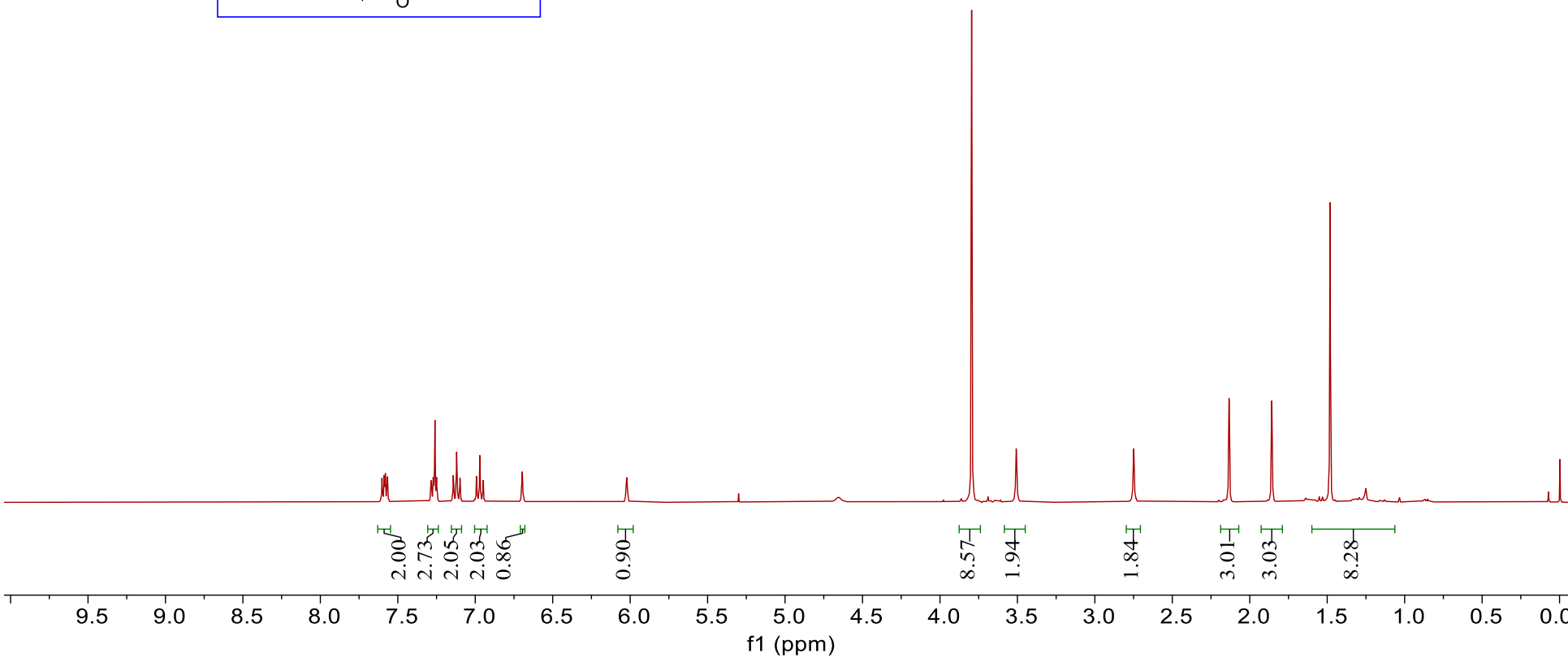


200.05 172.26 156.49 144.07 143.81 143.77 143.19 142.53 138.71 131.01 129.31 127.76 127.33 125.15 124.95 121.51 113.02 106.52 93.66 87.69 86.36 72.31 67.29 59.04 53.86 53.65 53.61 53.17 41.65 38.34 33.08 28.85 28.67 28.49 27.86 22.41 20.90 15.69 15.55



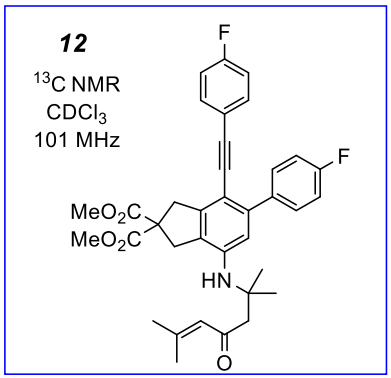
12/H


12
1H NMR
CDCl3
400 MHz
F
F
MeO2C
MeO2C
HN
O

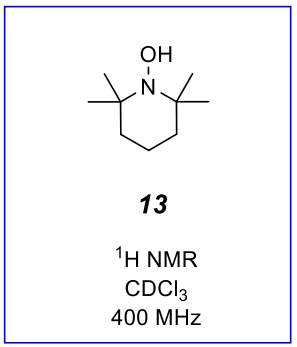

7.80
7.79
7.78
7.77
7.27
7.26
7.26
7.25
7.14
7.12
7.10
6.99
6.97
6.70
6.02
3.80
3.78
3.51
2.75
2.20
2.17
2.17
2.14
2.13
1.88
1.86
1.86
1.84
1.60
1.55
1.55
1.53
1.48
1.45
2.00
2.73
2.05
2.03
0.86
0.90
8.57
1.94
1.84
3.01
3.03
8.28
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

200.06 172.23 163.55 163.33 161.10 156.88 143.93 143.28 142.86 137.42 132.86 132.77 131.02 130.95 125.31 125.17 120.24 115.69 115.47 114.88 114.67 112.86 106.05 92.57 87.73 59.10 53.96 53.81 53.28 41.64 38.35 28.40 27.96 20.99

12/C



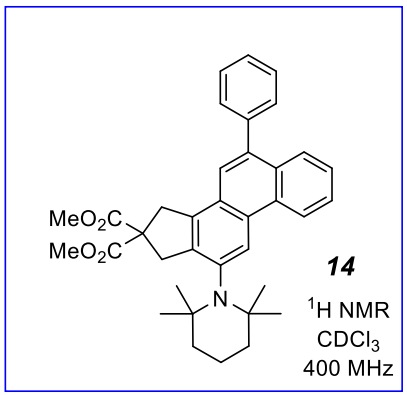
13/H


OH
N
13
^{1}H NMR
$CDCl_3$
400 MHz

1.56
1.21
6.02
12.00
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 0.0 -0.5
f1 (ppm)

8.68 8.66 8.65 8.57 7.93 7.92 7.90 7.90 7.68 7.68 7.66 7.66 7.65 7.65 7.64 7.64 7.57 7.56 7.56 7.56 7.55 7.55 7.54 7.54 7.54 7.53 7.53 7.52 7.52 7.52 7.51 7.51 7.51 7.50 7.50 7.50 7.49 7.49 7.48 7.48 7.47 7.47 7.46 7.46 4.00 3.87 3.74 1.70 1.69 1.68 1.67 1.66 1.65 1.64 1.63 1.59 1.48 0.82

14/H



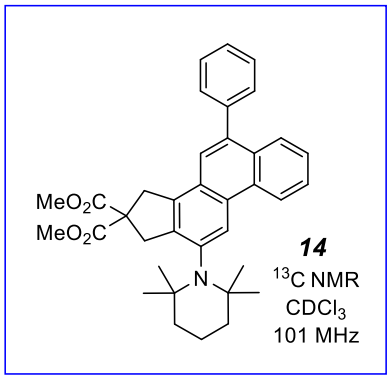
0.95 0.96 0.95 1.99 6.14 1.96 1.98 6.00 5.65 6.33 6.07

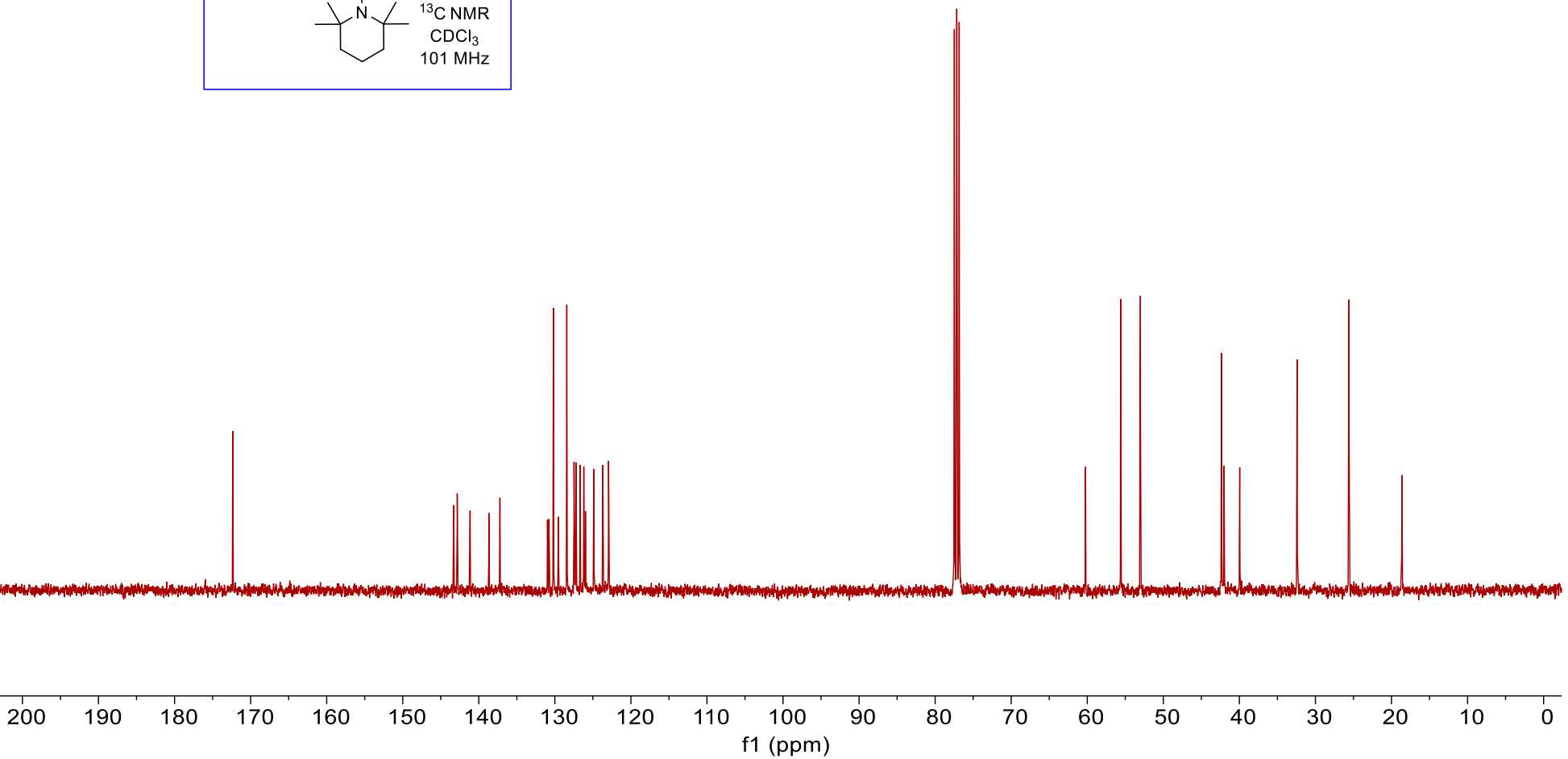
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

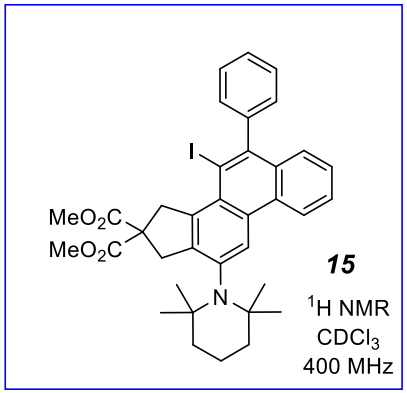
14/C

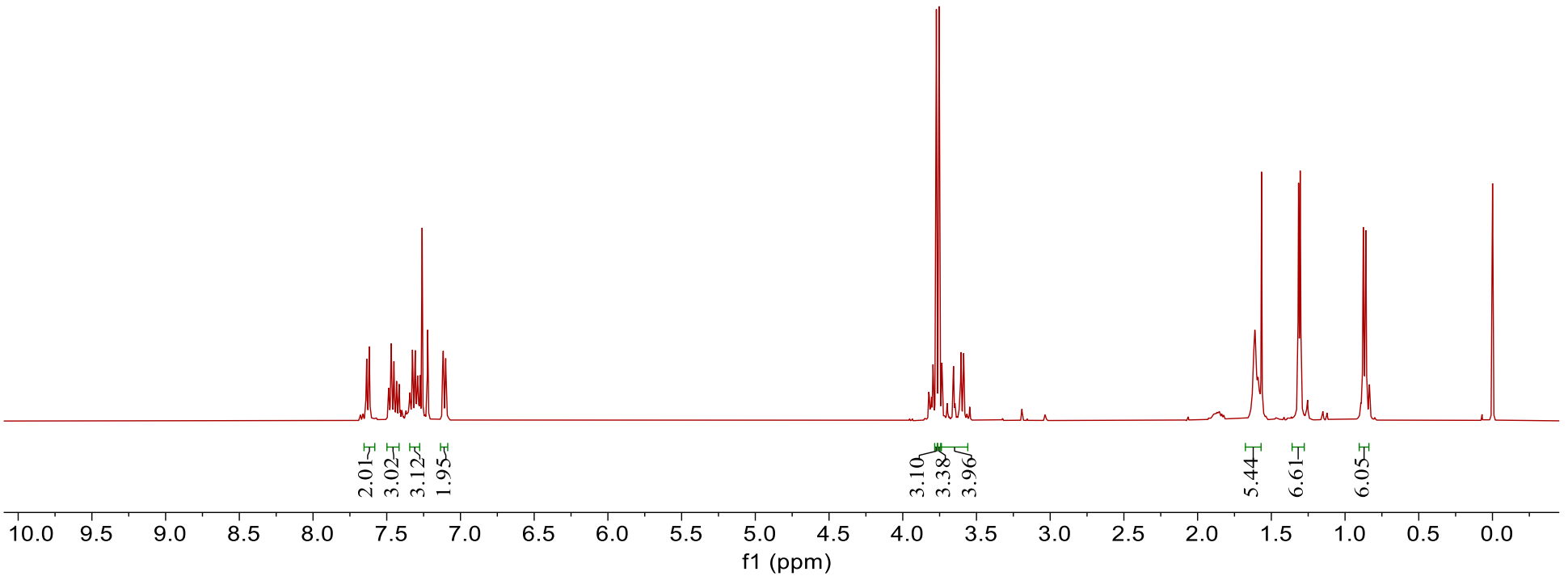
172.35
143.31
142.83
141.14
138.67
137.22
130.97
130.77
130.19
129.51
128.43
127.48
127.23
126.68
126.19
125.97
124.88
123.71
122.94
60.23
55.61
53.01
42.35
42.02
39.96
32.41
25.89
18.63



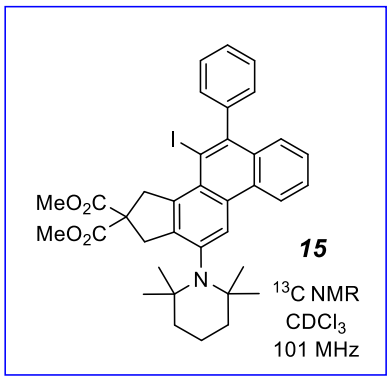


15/H


I
MeO2C
MeO2C
N
15
1H NMR
CDCl3
400 MHz


2.01
3.02
3.12
1.95
3.10
3.38
3.96
5.44
6.61
6.05
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 0.0
f1 (ppm)

15/C


I
MeO2C
MeO2C
N
15
13C NMR
CDCl3
101 MHz

172.09
144.96
144.36
143.87
140.75
138.77
138.33
138.18
133.27
129.76
128.49
128.18
127.85
127.37
100.33
97.75
60.40
55.36
53.02
42.22
41.23
40.44
32.59
32.52
25.58
25.52
18.48
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)