Electronic Supplementary Information

Access toward Fluorenone Derivatives through Solvent-Free Ruthenium Trichloride Mediated [2 + 2 + 2] Cycloadditions

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Contents

I. General informations 2

II. Synthesis of starting materials 3

III. Ru-catalyzed [2+2+2] cycloaddition reactions 18

IV. Valorization of [2+2+2] cycloadducts 28

V. ORTEP diagram for the structure of compound 3h 32

VI. NMR spectra for new compounds 33

I. General informations

All manipulations were carried out under an argon atmosphere. ^{1}H NMR and ^{13}C NMR were recorded on Bruker AV300 or AV400 instruments. ^{19}F NMR was recorded using a Bruker AV 300 (282 MHz). All signals are expressed as ppm (δ) and are referenced to the non-deuterated solvent peak $CHCl_3$ (7.26 ppm for ^{1}H and 77.16 for ^{13}C of $CDCl_3$). Coupling constants (J) are gave in Hz and refer to apparent peak multiplicities. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Melting point were determined in a Kofler Heizbank 7841 equipment and are uncorrected.

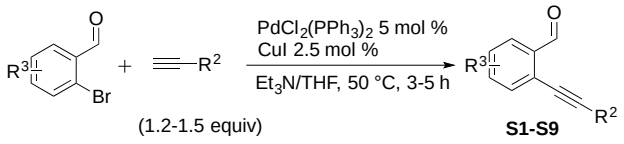
Mass spectrometry analyses (direct introduction by chemical ionization with ammoniac or electrospray) were performed at the Ecole Nationale Supérieure de Chimie de Paris (ENSCP). High resolution mass spectra were performed at the University Pierre and Marie Curie (Paris) or at the Faculty of Pharmacy.

Sigma-Aldrich Silica gel (high-purity grade, pore size 60 Å, 230-400 mesh particle size, 40-63 µm particle size) was employed for flash column chromatography. Analytical thin layer chromatography (TLC) was carried out using commercial silica-gel plates (Merck 60 F254), spots were detected with UV light (254 nm) and revealed with a $KMnO_4$ or *para*-anisaldehyde stain solution.

All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

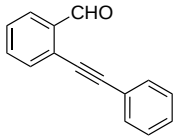
II. Synthesis of starting materials

General procedure for Sonogashira coupling reaction for the synthesis of substrates S1-S9:



$PdCl_2(PPh_3)_2$ (5 mol %) and CuI (2.5 mol %) were added to a NEt_3/THF (1:1, 5.0 M) solution containing aryl halide (1.0 equiv), alkyne (1.2-1.5 equiv). The mixture was stirred at 50 °C for 3-5 h. When the reaction was complete (TLC monitoring), the mixture was cooled to room temperature. A saturated aqueous solution of ammonium chloride was added and the mixture was stirred for 5 minutes. The organic layer was extracted with ethyl acetate (×3), washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to afford compounds **S1-S9**.

2-(phenylethynyl)benzaldehyde (S1).

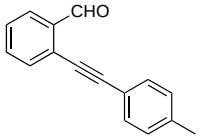


Chemical Formula: $C_{15}H_{10}O$
Exact Mass: 206.0732

Starting from 2-bromobenzaldehyde (1.0 g, 5.4 mmol) and phenylacetylene (0.71 mL, 6.5 mmol, 1.2 equiv). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 100/0 to 98/2) afforded **S1** (0.85 g, 76%) as an orange oil.

Spectral data obtained were in agreement with data reported in the literature.[1]

2-(*p*-tolylethynyl)benzaldehyde (S2).



Chemical Formula: $C_{16}H_{12}O$
Exact Mass: 220.0888

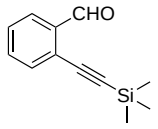
Starting from 2-bromobenzaldehyde (2.5 g, 13.5 mmol) and 4-ethynyltoluene (1.88 mL, 16.2 mmol, 1.2 equiv). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 99/1 to 98/2) afforded

[1] Sakamoto, T.; Kondo, Y.; Miura, N.; Hayashi, K.; Yamanaka, H. *Heterocycles* **1986**, *24*, 2311.

S2 (2.3 g, 80%) as a white solid. m.p. 32 –34 °C.

Spectral data obtained were in agreement with data reported in the literature.[2]

2-((trimethylsilyl)ethynyl)benzaldehyde (S3).

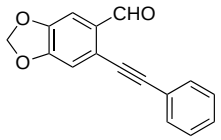


Chemical Formula: $C_{12}H_{14}OSi$
Exact Mass: 202.0814

Starting from 2-bromobenzaldehyde (3.68 g, 20.0 mmol) and trimethysilylacetylene (3.3 mL, 24.0 mmol, 1.2 equiv). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 98/2 to 90/10) afforded **S3** (3.5 g, 87%) as a white solid. m.p. 56 – 58 °C.

Spectral data obtained were in agreement with data reported in the literature.[1]

6-(phenylethynyl)benzo[*d*][1,3]dioxole-5-carbaldehyde (S4).

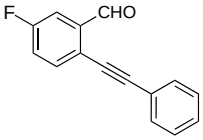


Chemical Formula: $C_{16}H_{10}O_3$
Exact Mass: 250.0630

Starting from 2-bromo-4,5-methylenedioxybenzaldehyde (2.3 g, 10.0 mmol) and phenylacetylene (1.2 mL, 11.2 mmol, 1.1 equiv). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 99/1 to 98/2) afforded **S4** (1.8 g, 72%) as a white solid. m.p. 118 – 120 °C.

Spectral data obtained were in agreement with data reported in the literature.[3]

5-fluoro-2-(phenylethynyl)benzaldehyde (S5).



Chemical Formula: $C_{15}H_9FO$
Exact Mass: 224.0637

Starting from 2-bromo-5-fluorobenzaldehyde (2.0 g, 10.0 mmol) and phenylacetylene (1.23 g, 12.0 mmol, 1.2 equiv). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 98/2 to 95/5) afforded **S5** (1.55 g, 70%) as a pale yellow solid. m.p. 54 – 56 °C.

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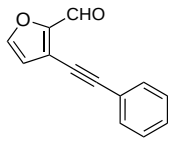
[2] Alfonsi, M.; Dell'Acqua, M.; Facoetti, D.; Arcadi, A.; Abbiati G.; Rossi, E. *Eur. J. Org. Chem.* **2009**, 2852.
[3] Huang, Q.-H.; Hunter, J. A.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 3437.

Spectral data obtained were in agreement with data reported in the literature.[4]

3-(phenylethynyl)furan-2-carbaldehyde (S6).

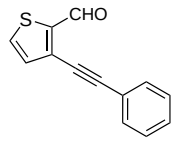


Chemical Formula: $C_{13}H_8O_2$
Exact Mass: 196.0524

Starting from 3-bromofuran-2-carbaldehyde (0.59 g, 3.4 mmol) and phenylacetylene (0.41 g, 4 mmol, 1.2 equiv). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 98/2 to 95/5) afforded **S6** (0.4 g, 50%) as an orange oil.

Spectral data obtained were in agreement with data reported in the literature.[5]

3-(phenylethynyl)thiophene-2-carbaldehyde (S7).

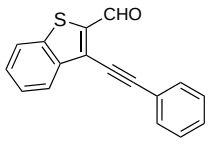


Chemical Formula: $C_{13}H_8OS$
Exact Mass: 212.0296

Starting from 3-bromothiophene-2-carbaldehyde (1.0 g, 5.23 mmol) and phenylacetylene (0.64 g, 6.28 mmol, 1.2 equiv). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 98/2 to 95/5) afforded **S7** (0.92 g, 83%) as a brown oil.

Spectral data obtained were in agreement with data reported in the literature.[6]

3-(phenylethynyl)benzo[*b*]-thiophene-2-carbaldehyde (S8).



Chemical Formula: $C_{17}H_{10}OS$
Exact Mass: 262.0452

Starting from 3-bromobenzo[*b*]thiophene-2-carbaldehyde (0.72 g, 3.0 mmol) and phenylacetylene (0.37 g, 3.6 mmol, 1.2 equiv). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 99/1 to 98/2) afforded **S8** (0.4 g, 50%) as a yellow solid. m.p. 114 – 116 °C.

Spectral data obtained were in agreement with data reported in the literature.[7]

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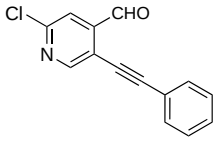
[4] Obika,S.; Kono, H.; Yasui, Y.; Yanada, R.; Takemoto, Y. *J. Org. Chem.* **2007**, *72*, 4462.
[5] Sagar, P.; Fröhlich, R.; Würthwein, E.-U. *Angew. Chem. Int. Ed.* **2004**, *43*, 5694.
[6] Okamoto, N.; Sakurai, K.; Ishikura, M.; Takeda, K.; Yanada, R. *Tetrahedron Lett.* **2009**, *50*, 4167.

2-chloro-5-(phenylethynyl)isonicotinaldehyde (S9).



Chemical Formula: $C_{14}H_8ClNO$
Exact Mass: 241.0294

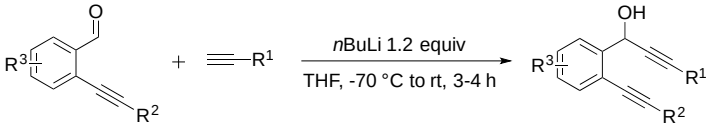
Starting from 5-bromo-2-chloroisonicotinaldehyde (0.44 g, 2.0 mmol) and phenylacetylene (0.21 g, 2.1 mmol, 1.05 equiv). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 98/2 to 95/5) afforded **S9** (0.26 g, 54%) as a yellow solid. m.p. 69 – 71 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.55 (s, 1H), 8.74 (s, 1H), 7.75 (s, 1H), 7.63 – 7.52 (m, 2H), 7.47 – 7.36 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.4, 154.6, 151.6, 142.8, 132.0, 130.0, 128.8, 121.5, 120.8, 120.4, 100.1, 81.1.

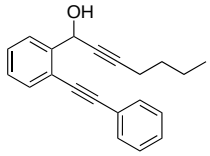
MS (CI, NH_3): m/z = 242 $[M + H]^+$.

General procedure for the synthesis of substrates M1-M10:



To a THF solution of alkynes (1.2 equiv, 5.0 M) was added *n*BuLi (1.3 equiv, 2.2 M in THF) at -70 °C. The mixture was warmed to 0 °C and stirred for 1 h. The resulting solution was cooled to -70 °C again and a solution of compound **S1-S9** (1.0 equiv) in THF was added over 10 min. Then the mixture was warmed to room temperature and stirred for 2-3 h before addition of a saturated aqueous ammonium chloride solution. The organic layer was extracted with ethyl acetate (×3), washed with water and brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to afford compounds **M1-M10**.

1-(2-(phenylethynyl)phenyl)hept-2-yn-1-ol (M1).



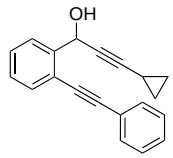
Chemical Formula: $C_{21}H_{20}O$
Exact Mass: 288.1514

[7] Lyaskovskyy, V.; Fröhlich R.; Würthwein, E.-U. *Synthesis* **2007**, *14*, 2135.

Starting from 2-(phenylethynyl)benzaldehyde **S1** (2.6 g, 12.6 mmol) and 1-hexyne (2.16 mL, 18.0 mmol, 1.5 equiv). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 95/5 to 90/10) afforded **M1** (3.3 g, 92%) as a pale orange oil.

Spectral data obtained were in agreement with data reported in the literature.[8]

3-cyclopropyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-ol (M2).

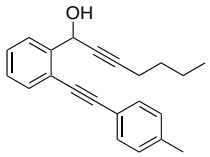


Chemical Formula: $C_{20}H_{16}O$
Exact Mass: 272.1201

Starting from 2-(phenylethynyl)benzaldehyde **S1** (1.1 g, 5.3 mmol) and cyclopropylacetylene (0.58 mL, 7.0 mmol, 1.3 equiv). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 95/5 to 90/10) afforded **M2** (1.2 g, 92%) as a pale yellow oil.

Spectral data obtained were in agreement with data reported in the literature.[8]

1-(2-(*p*-tolylethynyl)phenyl)hept-2-yn-1-ol (M3).

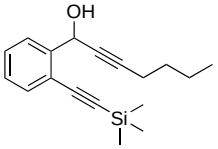


Chemical Formula: $C_{22}H_{22}O$
Exact Mass: 302.1671

Starting from 2-(*p*-tolylethynyl)benzaldehyde **S2** (1.0 g, 4.6 mmol) and 1-hexyne (0.68 mL, 5.9 mmol, 1.3 equiv). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 95/5 to 90/10) afforded **M3** (1.19 g, 87%) as a pale oil.

Spectral data obtained were in agreement with data reported in the literature.[9]

1-(2-((trimethylsilyl)ethynyl)phenyl)hept-2-yn-1-ol (M4).



Chemical Formula: $C_{18}H_{24}OSi$
Exact Mass: 284.1596

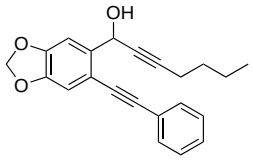
Starting from 2-((trimethylsilyl)ethynyl)benzaldehyde **S3** (1.5 g, 7.4 mmol) and 1-hexyne (1.1 mL, 9.6

[8] Chen, Y.-F.; Chen, M.; Liu, Y.-H. *Angew. Chem. Int. Ed.* **2012**, *51*, 6181.
[9] Schmittel, M.; Keller, M.; Kiau, S.; Strittmatter, M. *Chem. Eur. J.* **1997**, *3*, 807.

mmol, 1.3 equiv). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 95/5 to 90/10) afforded **M4** (1.7 g, 80%) as a colorless oil.

Spectral data obtained were in agreement with data reported in the literature.[10]

1-(6-(phenylethynyl)benzo[*d*][1,3]dioxol-5-yl)hept-2-yn-1-ol (M5).



Chemical Formula: $C_{22}H_{20}O_3$
Exact Mass: 332.1412

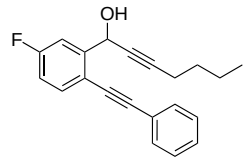
Starting from 6-(phenylethynyl)benzo[*d*][1,3]dioxole-5-carbaldehyde **S4** (1.0 g, 4.0 mmol) and 1-hexyne (0.6 mL, 5.2 mmol, 1.3 equiv). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 95/5 to 90/10) afforded **M5** (1.27 g, 96%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.47 (m, 2H), 7.40 – 7.29 (m, 3H), 7.24 (s, 1H), 6.96 (s, 1H), 6.01 (s, 2H), 5.92 (d, *J* = 2.0 Hz, 1H), 2.46 (d, *J* = 4.6 Hz, 1H), 2.27 (td, *J* = 7.0, 2.0 Hz, 2H), 1.55 – 1.33 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.5, 147.4, 138.6, 131.6, 128.5, 123.2, 114.9, 111.7, 107.6, 101.8, 93.4, 87.7, 86.8, 79.5, 63.2, 30.8, 22.1, 18.7, 13.7.

MS (CI, NH_3): m/z = 315 $[M + H - H_2O]^+$.

1-(5-fluoro-2-(phenylethynyl)phenyl)hept-2-yn-1-ol (M6).



Chemical Formula: $C_{21}H_{19}FO$
Exact Mass: 306.1420

Starting from 5-fluoro-2-(phenylethynyl)benzaldehyde **S5** (0.9 g, 4.1 mmol) and 1-hexyne (0.6 mL, 5.2 mmol, 1.3 equiv). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 95/5 to 90/10) afforded **M6** (1.16 g, 92%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 3H), 7.46 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.01 (td, *J* = 8.3, 2.7 Hz, 1H), 5.91 (s, 1H), 2.56 (d, *J* = 4.9 Hz, 1H), 2.27 (td, *J* = 7.0, 1.9 Hz, 2H), 1.54 – 1.34 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8 (d, *J* = 247.5 Hz), 145.8 (d, *J* = 7.1 Hz), 134.4 (d, *J* = 8.2 Hz), 131.7,

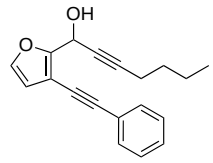
[10] Schmittel, M.; Strittmatter, M.; Mahajan, A. A.; Vavilala, C.; Cinar, M. E.; Maywald, M. *Arkivoc* **2007**, 66.

128.8, 128.6, 123.0, 117.5 (d, *J* = 3.3 Hz), 115.4 (d, *J* = 22.0 Hz), 114.2 (d, *J* = 23.6 Hz), 94.6, 88.2, 85.9, 79.0, 63.1, 30.7, 22.1, 18.7, 13.7.

^{19}F NMR (282 MHz, ($CDCl_3$) *δ* -110.5 (dd, *J* = 14.1, 8.5 Hz).

MS (CI, NH_3): m/z = 289 $[M + H - H_2O]^+$.

1-(3-(phenylethynyl)furan-2-yl)hept-2-yn-1-ol (M7).



Chemical Formula: $C_{19}H_{18}O_2$
Exact Mass: 278.1307

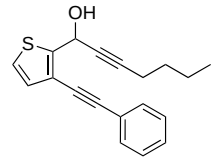
Starting from 3-(phenylethynyl)furan-2-carbaldehyde **S6** (0.43 g, 2.2 mmol) and 1-hexyne (0.37 mL, 3.3 mmol, 1.5 equiv). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 95/5 to 90/10) afforded **M7** (0.45 g, 74%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.50 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.37 (d, *J* = 1.8 Hz, 1H), 7.37 – 7.29 (m, 3H), 6.48 (d, *J* = 1.8 Hz, 1H), 5.72 – 5.65 (m, 1H), 2.38 (d, *J* = 6.9 Hz, 1H), 2.25 (td, *J* = 7.0, 2.0 Hz, 2H), 1.56 – 1.44 (m, 2H), 1.44 – 1.32 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) *δ* 155.3, 142.3, 131.6, 128.5, 123.2, 113.4, 105.0, 93.6, 87.9, 79.9, 57.2, 30.6, 22.1, 18.7, 13.7.

MS (ESI, NH_3): m/z = 261 $[M + H - H_2O]^+$.

1-(3-(phenylethynyl)thiophen-2-yl)hept-2-yn-1-ol (M8).



Chemical Formula: $C_{19}H_{18}OS$
Exact Mass: 294.1078

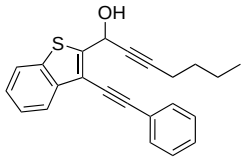
Starting from 3-(phenylethynyl)thiophene-2-carbaldehyde **S7** (0.92 g, 4.33 mmol) and 1-Hexyne (0.65 mL, 5.6 mmol, 1.3 equiv). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 95/5 to 90/10) afforded **M8** (1.13 g, 89%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.46 (m, 2H), 7.35 (dd, *J* = 6.5, 2.7 Hz, 3H), 7.23 (d, *J* = 5.2 Hz, 1H), 7.08 (d, *J* = 5.2 Hz, 1H), 6.05 – 5.88 (m, 1H), 2.48 (d, *J* = 5.1 Hz, 1H), 2.28 (td, *J* = 6.9, 2.0 Hz, 2H), 1.47 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4, 131.7, 130.1, 128.6, 128.5, 124.7, 123.1, 120.2, 93.5, 87.6, 82.8, 79.2, 59.4, 30.6, 22.1, 18.6, 13.7.

MS (CI, NH_3): m/z = 277 $[M + H - H_2O]^+$.

1-(3-(phenylethynyl)benzo[*b*]thiophen-2-yl)hept-2-yn-1-ol (M9).



Chemical Formula: $C_{23}H_{20}OS$
Exact Mass: 344.1235

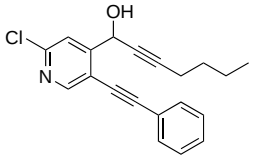
Starting from 3-(phenylethynyl)benzo[*b*]thiophene-2-carbaldehyde **S8** (0.4 g, 1.5 mmol) and 1-hexyne (0.26 mL, 2.25 mmol, 1.5 equiv). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 95/5 to 90/10) afforded **M9** (0.46 g, 89%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 8.02 – 7.91 (m, 1H), 7.87 – 7.79 (m, 1H), 7.65 – 7.55 (m, 2H), 7.49 – 7.33 (m, 5H), 6.25 – 6.14 (m, 1H), 2.54 (d, *J* = 5.1 Hz, 1H), 2.29 (td, *J* = 7.0, 2.0 Hz, 2H), 1.52 – 1.36 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 149.3, 139.6, 138.1, 131.8, 128.8, 128.6, 125.6, 125.0, 123.4, 123.0, 122.8, 115.9, 96.4, 88.3, 81.4, 78.8, 60.1, 30.6, 22.1, 18.7, 13.7.

MS (ESI, NH_3): m/z = 327 $[M + H - H_2O]^+$.

1-(2-chloro-5-(phenylethynyl)pyridin-4-yl)hept-2-yn-1-ol (M10).



Chemical Formula: $C_{20}H_{18}ClNO$
Exact Mass: 323.1077

Starting from 2-chloro-5-(phenylethynyl)isonicotinaldehyde **S9** (0.25 g, 1.04 mmol) and 1-hexyne (0.15 mL, 1.3 mmol, 1.3 equiv). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 95/5 to 90/10) afforded **M10** (0.24 g, 71%) as a yellow oil.

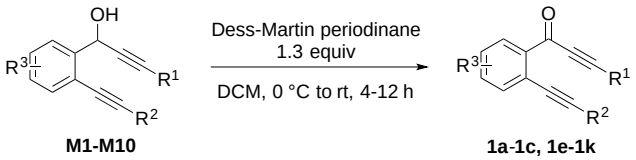
^{1}H NMR (300 MHz, $CDCl_3$) *δ* 8.51 (s, 1H), 7.67 (s, 1H), 7.59 – 7.49 (m, 2H), 7.44 – 7.33 (m, 3H), 5.82 – 5.75 (m, 1H), 2.66 (d, *J* = 5.1 Hz, 1H), 2.36 – 2.18 (m, 2H), 1.53 – 1.32 (m, 4H), 0.85 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) *δ* 153.8, 152.5, 151.3, 131.8, 129.4, 128.7, 122.3, 121.3, 117.4, 98.9, 89.0, 82.7, 62.2, 30.5, 22.1, 18.6, 13.6.

MS (CI, NH_3): m/z = 324 $[M + H]^+$.

General procedure for the synthesis of diynes (1a-1k):

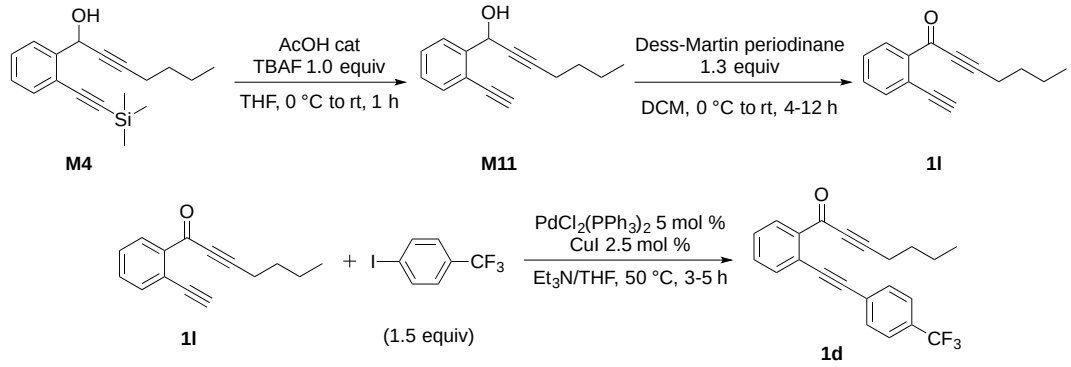
Procedure A:



M1-M10 **1a-1c, 1e-1k**

Dess-Martin periodinane (1.3 equiv) was added to a solution of **M1**-**M10** (1 equiv) in anhydrous CH_2Cl_2 (5 M) at 0 °C and the resulting mixture was stirred at room temperature for 4-12 h. When the reaction was complete (TLC monitoring), the reaction mixture was filtered through a pad of celite. A saturated aqueous solution of $NaHCO_3$ was added to the organic layer and the resulting mixture was stirred for 20 minutes, washed with water and brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to afford compounds **1a**-**1c** and **1e**-**1k**.

Procedure B:



M4 **M11** **1l**

1l (1.5 equiv) **1d**

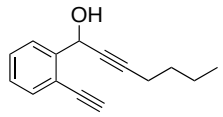
a) To a solution of **M4** (1.7 g, 6 mmol) in THF (20 mL) was added acetic acid (a few drops as catalyst) and TBAF (6 mL, 1.0 M in THF) at 0 °C under stirring and the mixture was allowed to stir at room temperature for 1 h. The resulting mixture was quenched with water, the organic layer washed with saturated aqueous solution of $NaHCO_3$, water and brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography to afford the corresponding product **M11** (1.13 g, 89%).

b) Dess-Martin periodinane (1.3 equiv, 6.1 mmol) was added to a solution of **M11** (1 equiv, 4.7 mmol) in anhydrous CH_2Cl_2 (30 mL) at 0 °C and the resulting mixture was stirred at room temperature for 12 h. When the reaction was complete (TLC monitoring), the reaction mixture was filtered through a pad of celite. A saturated aqueous solution of $NaHCO_3$ was added to the organic layer and the resulting mixture was stirred for 20 minutes, washed with water and brine, dried over $MgSO_4$, filtered and

concentrated under reduced pressure. The residue was purified by column chromatography to afford compound **1l** (0.82 g, 83%).

c) $PdCl_2(PPh_3)_2$ (5 mol %) and CuI (2.5 mol %) were added to a NEt_3/THF (1:1, 5 mL) solution containing aryl halide (1.2 equiv) and the above terminal alkyne **1l** (1.0 equiv). The mixture was stirred at 50 °C for 3-5 h under argon. When the reaction was complete (TLC monitoring), a saturated aqueous solution of ammonium chloride was added and the mixture was stirred for 5 minutes. The organic layer was extracted with ethyl acetate (×3), washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to afford compounds **1d**.

1-(2-ethynylphenyl)hept-2-yn-1-ol (M11).

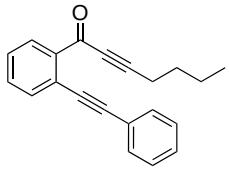


Chemical Formula: $C_{15}H_{16}O$
Exact Mass: 212.1201

Starting from 1-(2-((trimethylsilyl)ethynyl)phenyl)-hept-2-yn-1-ol **M4** (1.7 g, 6 mmol) and TBAF (6 mL, 1.0 M in THF). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 95/5 to 90/10) afforded **M11** (1.13 g, 89%) as a pale oil.

Spectral data obtained were in agreement with data reported in the literature.[9]

1-(2-(phenylethynyl)phenyl)hept-2-yn-1-one (1a).



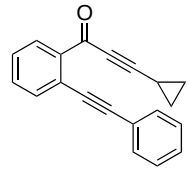
Chemical Formula: $C_{21}H_{18}O$
Exact Mass: 286.1358

Starting from 1-(2-(phenylethynyl)phenyl)hept-2-yn-1-ol **M1** (1.7 g, 5.9 mmol) and Dess-Martin periodinane (3.25 g, 7.6 mmol, 1.3 equiv). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 100/0 to 98/2) afforded **1a** (1.6 g, 94%) as a pale yellow oil.

Spectral data obtained were in agreement with data reported in the literature.[11]

3-cyclopropyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-one (1b).

[11] Tang, J.-M.; Liu, T.-A.; Liu, R.-S. *J. Org. Chem.* **2008**, *73*, 8479.



Chemical Formula: $C_{20}H_{14}O$
Exact Mass: 270.1045

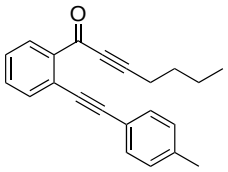
Starting from 3-cyclopropyl-1-(2-(phenylethynyl)phenyl)prop-2-yn-1-ol **M2** (1.1 g, 4.0 mmol) and Dess-Martin periodinane (2.2 g, 5.2 mmol, 1.3 equiv). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 99/1 to 98/2) afforded **1b** (0.82 g, 75%) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$), δ 8.07 – 8.02 (m, 1H), 7.66 – 7.58 (m, 3H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.38 – 7.33 (m, 3H), 1.49 – 1.41 (m, 1H), 0.99 – 0.93 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$), δ 177.6, 138.8, 134.3, 132.2, 132.0, 131.5, 128.7, 128.4, 128.0, 123.5, 122.9, 101.6, 95.3, 88.4, 10.0, 0.3.

MS (ESI, NH_3): m/z = 271 $[M + H]^+$.

1-(2-(*p*-tolylethynyl)phenyl)hept-2-yn-1-one (1c).



Chemical Formula: $C_{22}H_{20}O$
Exact Mass: 300.1514

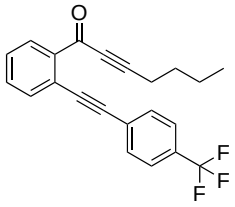
Starting from 1-(2-(*p*-tolylethynyl)phenyl)hept-2-yn-1-ol **M3** (1.1 g, 3.64 mmol) and Dess-Martin periodinane (2.0 g, 4.73 mmol, 1.3 equiv). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) afforded **1c** (1.0 g, 91%) as a pale yellow solid. m.p. 35 – 37 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 1H), 7.68 – 7.58 (m, 1H), 7.56 – 7.46 (m, 3H), 7.45 – 7.37 (m, 1H), 7.20 – 7.13 (m, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.62 – 1.52 (m, 2H), 1.50 – 1.38 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 138.9, 138.5, 134.3, 132.3, 132.0, 131.8, 129.2, 127.8, 123.3, 120.4, 97.2, 95.6, 87.9, 81.0, 29.9, 22.2, 21.7, 19.2, 13.6.

MS (ESI, NH_3): m/z = 301 $[M + H]^+$.

1-(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)hept-2-yn-1-one (1d).



Chemical Formula: $C_{22}H_{17}F_3O$
Exact Mass: 354.1231

Starting from 1-(2-ethynylphenyl)hept-2-yn-1-one **1l** (0.5 g, 2.38 mmol) and 4-iodobenzotrifluoride (0.71 g, 2.62 mmol, 1.1 equiv). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 99/1 to 98/2) afforded **1d** (0.55 g, 65%) as a brown solid. m.p. 35 – 37 °C.

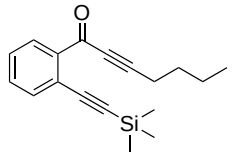
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 – 8.11 (m, 1H), 7.75 – 7.68 (m, 2H), 7.68 – 7.58 (m, 3H), 7.58 – 7.52 (m, 1H), 7.51 – 7.44 (m, 1H), 2.46 (t, *J* = 7.1 Hz, 2H), 1.67 – 1.55 (m, 2H), 1.52 – 1.38 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 138.7, 134.5, 132.5, 132.2, 132.2, 150.33 (d, J_{C-F} = 32.3 Hz), 128.6, 127.3, 125.9, 125.4, 125.4, 122.3, 122.2, 97.3, 93.3, 90.8, 80.7, 29.9, 22.2, 19.1, 13.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ -63.8 (s).

MS (ESI, NH_3): m/z = 355 $[M + H]^+$.

1-(2-((trimethylsilyl)ethynyl)phenyl)hept-2-yn-1-one (1e).



Chemical Formula: $C_{18}H_{22}OSi$
Exact Mass: 282.1440

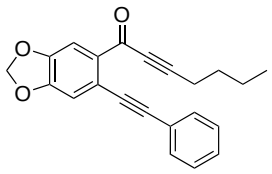
Starting from 1-(2-((trimethylsilyl)ethynyl)phenyl)hept-2-yn-1-ol **M4** (2.06 g, 10.0 mmol) and Dess-Martin periodinane (5.1 g, 12.0 mmol, 1.2 equiv). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) afforded **1e** (2.06 g, 74%) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 – 7.96 (m, 1H), 7.61 – 7.51 (m, 1H), 7.48 – 7.41 (m, 1H), 7.41 – 7.35 (m, 1H), 2.45 (t, *J* = 7.1 Hz, 2H), 1.68 – 1.54 (m, 2H), 1.38 – 1.52 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.27 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 139.0, 135.1, 132.1, 131.7, 128.2, 122.6, 103.3, 100.9, 96.8, 80.7, 29.9, 22.2, 19.1, 13.6, -0.1.

MS (ESI, NH_3): m/z = 283 $[M + H]^+$.

1-(6-(phenylethynyl)benzo[*d*][1,3]dioxol-5-yl)hept-2-yn-1-one (1f).



Chemical Formula: $C_{22}H_{18}O_3$
Exact Mass: 330.1256

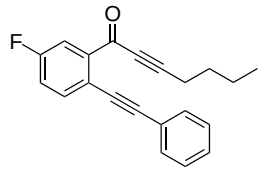
Starting from 1-(6-(phenylethynyl)benzo[*d*][1,3]dioxol-5-yl)hept-2-yn-1-ol **M5** (1.25 g, 3.8 mmol) and Dess-Martin periodinane (2.07 g, 4.9 mmol, 1.3 equiv). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 95/5 to 90/10) afforded **1f** (0.9 g, 77%) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 3H), 7.36 – 7.31 (m, 3H), 7.05 (s, 1H), 6.09 (s, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 1.63 – 1.53 (m, 2H), 1.46 – 1.37 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 176.0, 151.1, 147.8, 133.9, 132.0, 128.6, 128.4, 123.6, 119.0, 113.6, 111.4, 102.5, 96.8, 94.3, 88.6, 80.8, 30.0, 22.2, 19.2, 13.6.

MS (ESI, NH_3): m/z = 331 $[M + H]^+$.

1-(5-fluoro-2-(phenylethynyl)phenyl)hept-2-yn-1-one (1g).



Chemical Formula: $C_{21}H_{17}FO$
Exact Mass: 304.1263

Starting from 1-(5-fluoro-2-(phenylethynyl)phenyl)hept-2-yn-1-ol **M6** (1.1 g, 3.6 mmol) and Dess-Martin periodinane (1.98 g, 4.7 mmol, 1.3 equiv). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) afforded **1g** (0.95 g, 87%) as an orange oil.

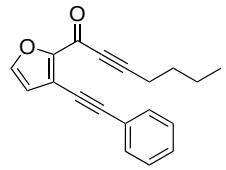
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 9.1, 2.7 Hz, 1H), 7.66 – 7.54 (m, 3H), 7.39 – 7.32 (m, 3*H*), 7.27 – 7.19 (m, 1H), 2.44 (t, *J* = 7.1 Hz, 2H), 1.66 – 1.51 (m, 2H), 1.50 – 1.36 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4, 161.8 (d, *J* = 249.8 Hz), 140.4 (d, *J* = 6.8 Hz), 136.2 (d, *J* = 7.5 Hz), 132.0, 128.8, 128.5, 123.3, 119.8 (d, *J* = 21.8 Hz), 119.1, 118.4 (d, *J* = 23.3 Hz),, 98.2, 95.0, 87.4, 80.6, 29.9, 22.2, 19.2, 13.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ -111.4 (dd, *J* = 14.1, 8.5 Hz).

MS (ESI, NH_3): m/z = 305 $[M + H]^+$.

1-(3-(phenylethynyl)furan-2-yl)hept-2-yn-1-one (1h).



Chemical Formula: $C_{19}H_{16}O_2$
Exact Mass: 276.1150

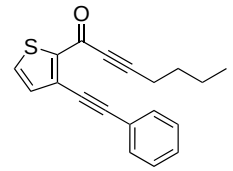
Starting from 1-(3-(phenylethynyl)furan-2-yl)hept-2-yn-1-ol **M7** (0.45 g, 1.6 mmol) and Dess-Martin periodinane (0.89 g, 2.1 mmol, 1.3 equiv). Purification on silica gel (Petroleum ether/Ethyl acetate gradient 98/2 to 95/5) afforded **1h** (0.18 g, 40%) as an orange oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.50 (m, 3H), 7.41 – 7.31 (m, 3H), 6.67 (d, J = 1.6 Hz, 1H), 2.37 (t, J = 7.2 Hz, 2H), 1.59 – 1.42 (m, 2H), 1.40 – 1.26 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 152.7, 146.4, 131.9, 129.2, 128.6, 122.7, 116.4, 116.3, 98.0, 97.8, 80.8, 79.7, 29.8, 22.2, 19.2, 13.6.

MS (ESI, NH_3): m/z = 277 $[M + H]^+$.

1-(3-(phenylethynyl)thiophen-2-yl)hept-2-yn-1-one (1i).



Chemical Formula: $C_{19}H_{16}OS$
Exact Mass: 292.0922

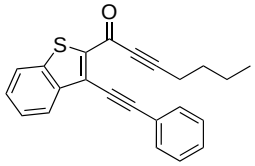
Starting from 1-(3-(phenylethynyl)thiophen-2-yl)hept-2-yn-1-ol **M8** (1.12 g, 3.8 mmol) and Dess-Martin periodinane (2.1 g, 4.9 mmol, 1.3 equiv). Purification on silica gel (Petroleum ether/Ethyl acetate gradient 99/1 to 98/2) afforded **1i** (0.6 g, 55%) as a yellow solid. m.p. 33 – 35 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 – 7.52 (m, 3H), 7.42 – 7.31 (m, 3H), 7.28 – 7.19 (m, 1H), 2.36 (t, J = 7.1 Hz, 2H), 1.52 – 1.45 (m, 2H), 1.41 – 1.28 (m, 2H), 0.85 (t, J = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 144.3, 133.3, 132.5, 131.9, 129.1, 128.6, 126.9, 123.0, 97.5, 96.3, 84.4, 80.3, 29.9, 22.2, 19.2, 13.6.

MS (CI, NH_3): m/z = 293 $[M + H]^+$.

1-(3-(phenylethynyl)benzo[*b*]thiophen-2-yl)hept-2-yn-1-one (1j).



Chemical Formula: $C_{23}H_{18}OS$
Exact Mass: 342.1078

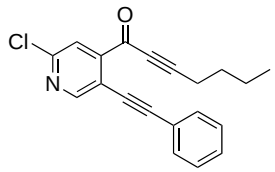
Starting from 1-(3-(phenylethynyl)benzo[*b*]thiophen-2-yl)hept-2-yn-1-ol **M9** (0.46 g, 1.34 mmol) and Dess-Martin periodinane (0.74 g, 1.7 mmol, 1.3 equiv). Purification on silica gel (Petroleum ether/Ethyl acetate gradient 98/2 to 95/5) afforded **1j** (0.34 g, 74%) as a yellow solid. m.p. 90 – 92 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 – 8.09 (m, 1H), 7.88 – 7.62 (m, 1H), 7.72 – 7.62 (m, 2H), 7.58 – 7.45 (m, 2H), 7.45 – 7.34 (m, 3H), 2.41 (t, *J* = 7.2 Hz, 2H), 1.62 – 1.48 (m, 2H), 1.45 – 1.29 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 144.3, 140.7, 140.5, 132.0, 129.3, 128.7, 128.6, 125.6, 123.3, 122.9, 99.7, 98.8, 83.1, 80.6, 77.5, 77.2, 76.8, 29.9, 22.2, 19.4, 13.6.

MS (ESI, NH_3): m/z = 343 $[M + H]^+$.

1-(2-chloro-5-(phenylethynyl)pyridin-4-yl)hept-2-yn-1-one (1k).



Chemical Formula: $C_{20}H_{16}ClNO$
Exact Mass: 321.0920

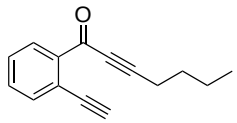
Starting from 1-(2-chloro-5-(phenylethynyl)pyridin-4-yl)hept-2-yn-1-ol **M10** (0.23 g, 0.71 mmol) and Dess-Martin periodinane (0.39 g, 0.92 mmol, 1.3 equiv). Purification on silica gel (Petroleum ether/Ethyl acetate gradient 98/2) afforded **1k** (0.16 g, 70%) as a yellow solid. m.p. 34 – 36 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (d, *J* = 0.6 Hz, 1H), 7.85 (d, *J* = 0.6 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.42 – 7.33 (m, 3H), 2.46 (t, *J* = 7.1 Hz, 2H), 1.63 – 1.54 (m, 2H), 1.50 – 1.35 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 175.2, 154.7, 150.8, 146.4, 132.1, 129.5, 128.6, 124.3, 122.5, 117.2, 100.5, 98.9, 84.1, 80.2, 29.7, 22.2, 19.3, 13.6.

MS (CI, NH_3): m/z = 322 $[M + H]^+$.

1-(2-ethynylphenyl)hept-2-yn-1-one (1l)



Chemical Formula: $C_{15}H_{14}O$
Exact Mass: 210.1045

Starting from 1-(2-ethynylphenyl)hept-2-yn-1-ol **M11** (1.0 g, 4.7 mmol) and Dess-Martin periodinane (2.59 g, 6.1 mmol, 1.3 equiv). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 95/5 to 90/10) afforded **1l** (0.82 g, 83%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 – 8.06 (m, 1H), 7.66 – 7.56 (m, 1H), 7.54 – 7.41 (m, 2H), 3.39 (s, 1H), 2.47 (t, J = 7.0 Hz, 2H), 1.68 – 1.58 (m, 2H), 1.48 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 139.2, 135.5, 132.3, 131.8, 128.6, 121.7, 97.4, 82.9, 82.1, 80.8, 29.9, 22.2, 19.1, 13.6.

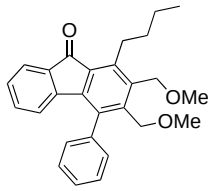
MS (CI, NH_3): m/z = 211 $[M + H]^+$.

III. Ru-catalyzed [2+2+2] cycloaddition reactions.

General procedure for the synthesis of fluorenone and heterofluorenone derivatives 3a-3q.

A sealed tube was equipped with $RuCl_3 \cdot nH_2O$ (5 mol%) and diyne **1** (1 equiv), followed by the addition of alkyne **2** (2 equiv) under argon atmosphere. The tube was sealed and the reaction mixture was stirred for the required time at 50-80 °C. When the reaction was complete (TLC monitoring), the crude reaction mixture was directly purified by flash chromatography over silica gel to afforded cycloadducts **3**.

1-butyl-2,3-bis(methoxymethyl)-4-phenyl-9*H*-fluoren-9-one (3a).



Chemical Formula: $C_{27}H_{28}O_3$
Exact Mass: 400.2038

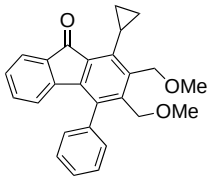
Starting from diyne **1a** (100 mg, 0.35 mmol), 1,4-dimethoxy-2-butyne **2a** (80 mg, 0.7 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (3.6 mg, 0.0175 mmol). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 98/2 to 95/5) afforded **3a** (101 mg, 72%) as a yellow solid. m.p. 88 – 90 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 1H), 7.54 – 7.46 (m, 3H), 7.36 – 7.28 (m, 2H), 7.13 (td, *J* = 7.5, 0.9 Hz, 1H), 7.04 (td, *J* = 7.5, 1.2 Hz, 1H), 5.94 (d, *J* = 7.5 Hz, 1H), 4.57 (s, 2H), 4.19 (s, 2H), 3.51 (s, 3H), 3.29 – 3.20 (m, 2H), 3.18 (s, 3H), 1.67 – 1.49 (m, 4H), 1.02 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.6, 144.8, 143.6, 142.9, 142.4, 138.3, 137.6, 137.0, 135.2, 134.1, 130.8, 129.6, 128.9, 128.5, 128.1, 123.6, 123.2, 68.5, 67.4, 58.9, 58.6, 33.6, 27.3, 23.5, 14.1.

HRMS (ESI^+): calcd. for $C_{27}H_{28}O_3Na$ $[M+Na]^+$: 423.1931, found 423.1928.

1-cyclopropyl-2,3-bis(methoxymethyl)-4-phenyl-9*H*-fluoren-9-one (3b).



Chemical Formula: $C_{26}H_{24}O_3$
Exact Mass: 384.1725

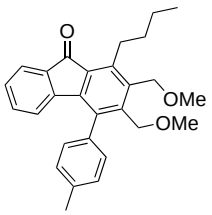
Starting from diyne **1b** (100 mg, 0.37 mmol), 1,4-dimethoxy-2-butyne **2a** (85 mg, 0.74 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (3.8 mg, 0.0185 mmol). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) afforded **3b** (90 mg, 63%) as a yellow solid. m.p. 166 – 168 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 1H), 7.53 – 7.46 (m, 3H), 7.35 – 7.29 (m, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.04 (td, *J* = 7.5, 1.2 Hz, 1H), 5.92 (d, *J* = 7.5 Hz, 1H), 4.81 (s, 2H), 4.20 (s, 2H, *CH*), 3.51 (s, 3H), 3.17 (s, 3H), 2.11 – 1.99 (m, 1H), 1.26 – 1.17 (m, 2H), 0.71 – 0.68 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.4, 143.8, 143.4, 142.9, 142.6, 139.5, 138.1, 137.8, 135.1, 134.0, 133.2, 129.5, 128.8, 128.5, 128.1, 123.6, 123.1, 68.4, 68.2, 59.0, 58.7, 10.9, 8.4.

HRMS (ESI^+): calcd. for $C_{26}H_{24}O_3Na$ $[M+Na]^+$: 407.1618, found 407.1623.

1-butyl-2,3-bis(methoxymethyl)-4-(*p*-tolyl)-9*H*-fluoren-9-one (3c).



Chemical Formula: $C_{28}H_{30}O_3$
Exact Mass: 414.2195

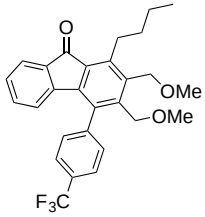
Starting from diyne **1c** (102 mg, 0.35 mmol), 1,4-dimethoxy-2-butyne **2a** (80 mg, 0.7 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (3.6 mg, 0.0175 mmol). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) afforded **3c** (101 mg, 71%) as a yellow solid. m.p. 86 – 88 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.24 – 7.17 (m, 2H), 7.17 – 7.02 (m, 2H), 6.02 (d, *J* = 7.5 Hz, 1H), 4.57 (s, 2H), 4.19 (s, 2H), 3.51 (s, 3H), 3.28 – 3.18 (m, 2H), 3.20 (s, 3H), 2.49 (s, 3H), 1.66 – 1.51 (m, 4H), 1.02 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.7,144.6,143.8,143.0, 142.6, 137.8, 137.6, 137.1, 135.1, 134.1, 130.7, 129.6, 129.4, 128.4, 123.6, 123.3, 68.5, 67.4, 58.9, 58.5, 33.6, 27.3, 23.5, 21.5, 14.1.

HRMS (ESI^+): calcd. for $C_{28}H_{30}O_3Na$ $[M+Na]^+$: 437.2087, found 437.2087.

1-butyl-2,3-bis(methoxymethyl)-4-(4-(trifluoromethyl)-phenyl)-9*H*-fluoren-9-one (3d).



Chemical Formula: $C_{28}H_{27}F_3O_3$
Exact Mass: 468.1912

Starting from diyne **1d** (100.0 mg, 0.28 mmol), 1,4-dimethoxy-2-butyne **2a** (80 mg, 0.56 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (2.9 mg, 0.014 mmol). Purification on silica gel (Cyclohexane/Ethyl acetate gradient from 98/2 to 95/5) afforded **3d** (85 mg, 65%) as a brown solid. m.p. 113 – 115 °C.

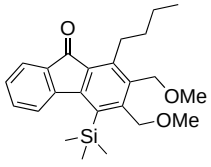
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.59 (dd, *J* = 7.3, 0.6 Hz, 1H), 7.49 (d, *J* = 7.9 Hz, 2H), 7.17 (td, *J* = 7.5, 1.0 Hz, 1H), 7.08 (td, *J* = 7.6, 1.3 Hz, 1H), 5.91 (d, *J* = 7.5 Hz, 1H), 4.55 (s, 2H), 4.11 (s, 2H), 3.51 (s, 3H), 3.30 – 3.20 (m, 2H), 3.17 (s, 3H), 1.64 – 1.50 (m, 4H), 1.02 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.3, 145.4, 143.2, 142.7, 142.3, 142.1, 137.9, 135.5, 135.2, 134.3, 130.9, 130.3, 128.9, 125.8, 125.8, 124.0, 122.9, 68.4, 67.3, 59.0, 58.7, 33.7, 27.4, 23.5, 14.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -63.4 (s).

HRMS (ESI^+): calcd. for $C_{28}H_{27}F_3O_3Na$ $[M+Na]^+$: 491.1805, found 491.1803.

1-butyl-2,3-bis(methoxymethyl)-4-(trimethylsilyl)-9*H*-fluoren-9-one (3e).



Chemical Formula: $C_{24}H_{32}O_3Si$
Exact Mass: 396.2121

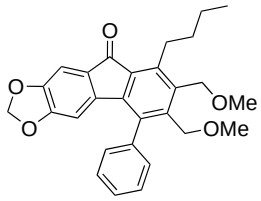
Starting from diyne **1e** (99.0 mg, 0.35 mmol), 1,4-dimethoxy-2-butyne **2a** (80 mg, 0.7 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (3.6 mg, 0.0175 mmol). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) afforded **3e** (81 mg, 58%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (t, J = 7.5 Hz, 2H), 7.42 (td, J = 7.5, 1.2 Hz, 1H), 7.30 – 7.20 (m, 1H), 4.59 (s, 2H), 4.47 (s, 2H), 3.44 (s, 3H), 3.34 (s, 3H), 3.26 – 3.15 (m, 2H), 1.58 – 1.44 (m, 4H), 0.98 (t, J = 6.6 Hz, 3H), 0.46 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 152.9, 151.9, 145.5, 144.6, 135.4, 135.3, 133.2, 130.7, 128.5, 125.9, 123.5, 71.9, 67.3, 58.5, 57.7, 33.5, 27.0, 23.4, 14.1, 2.8.

HRMS (ESI^+): calcd. for $C_{24}H_{32}O_3SiNa$ $[M+Na]^+$: 419.2013, found 419.2008.

8-butyl-6,7-bis(methoxymethyl)-5-phenyl-9*H*-fluoreno[2,3-d][1,3]dioxol-9-one (3f).



Chemical Formula: $C_{28}H_{28}O_5$
Exact Mass: 444.1937

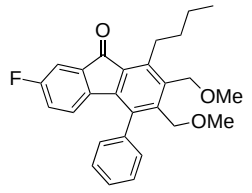
Starting from diyne **1f** (115.5 mg, 0.35 mmol), 1,4-dimethoxy-2-butyne **2a** (80 mg, 0.7 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (3.6 mg, 0.0175 mmol). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) afforded **3f** (105 mg, 68%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 3H), 7.33 – 7.27 (m, 2H), 6.99 (s, 1H), 5.88 (s, 2H), 5.32 (s, 1H), 4.53 (s, 2H), 4.14 (s, 2H), 3.49 (s, 3H), 3.22 – 3.15 (m, 2H), 3.16 (s, 3H), 1.61 – 1.49 (m, 4H), 1.00 (t, J = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.0, 152.4, 147.9, 144.2, 142.0, 140.6, 138.0, 137.0, 136.0, 131.2, 130.1, 129.6, 128.9, 128.2, 104.6, 104.5, 101.9, 68.5, 67.4, 58.9, 58.6, 33.7, 27.2, 23.5, 14.1.

HRMS (ESI^+): calcd. for $C_{28}H_{28}O_5Na$ $[M+Na]^+$: 467.1829, found 467.1830.

1-butyl-7-fluoro-2,3-bis(methoxymethyl)-4-phenyl-9*H*-fluoren-9-one (3g).



Chemical Formula: $C_{27}H_{27}FO_3$
Exact Mass: 418.1944

Starting from diyne **1g** (106 mg, 0.35 mmol), 1,4-dimethoxy-2-butyne **2a** (80 mg, 0.7 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (3.6 mg, 0.0175 mmol). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) afforded **3g** (98 mg, 65%) as a yellow oil.

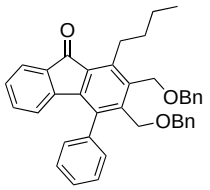
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 3H), 7.35 – 7.27 (m, 2H), 7.22 (dd, *J* = 7.2, 2.4 Hz, 1H), 6.72 (td, *J* = 8.7, 2.4 Hz, 1H), 5.86 (dd, *J* = 8.1, 4.5 Hz, 1H), 4.56 (s, 2H), 4.17 (s, 2H), 3.50 (s, 3H), 3.26 – 3.18 (m, 2H), 3.18 (s, 3H), 1.66 – 1.51 (m, 4H), 1.01 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 163.2 (d, *J* = 247.5 Hz), 145.2, 142.8, 142.4, 139.4 (d, *J* = 2.8 Hz), 138.1, 137.5, 137.4, 136.7, 131.0 (d, *J* = 1.6 Hz), 129.5, 129.0, 128.3, 124.6 (d, *J* = 7.7 Hz), 120.2 (d, *J* = 22.5 Hz), 111.1 (d, *J* = 23.6 Hz), 68.5, 67.4, 59.0, 58.6, 33.6, 27.4, 23.5, 14.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -113.6 (dd, *J* = 11.3, 8.5 Hz).

HRMS (ESI^+): calcd. for $C_{27}H_{27}FO_3Na$ $[M+Na]^+$: 441.1836, found 441.1837.

2,3-bis((benzyloxy)-methyl)-1-butyl-4-phenyl-9*H*-fluoren-9-one (3h).



Chemical Formula: $C_{39}H_{36}O_3$
Exact Mass: 552.2664

Starting from diyne **1a** (100 mg, 0.35 mmol) and 1,4-bis(benzyloxy)but-2-yne[12] **2b** (186 mg, 0.7 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (3.6 mg, 0.0175 mmol). The excess of alkyne was removed by bulb to bulb distillation (condition: 3.0×10^{-3} mbar, 175℃ for 20 minutes). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) afforded **3h** (156 mg, 81%) as a yellow solid. m.p. 145 – 147 °C.

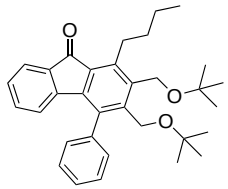
^{1}H NMR (300 MHz, $CDCl_3$), δ 7.58 – 7.53 (m, 1H), 7.53 – 7.46 (m, 3H), 7.40 – 7.27 (m, 10H), 7.22 – 7.17 (m, 2H), 7.13 (td, *J* = 7.5, 0.9 Hz, 1H), 7.04 (td, *J* = 7.5, 1.2 Hz, 1H), 5.93 (d, *J* = 7.5 Hz, 1H), 4.53 (s, 2H), 4.50 (s, 2H), 4.16 (s, 2H), 4.15 (s, 2H), 3.23 – 3.12 (m, 2H), 1.57 – 1.41 (m, 4H), 0.97 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ 194.7, 144.9, 143.7, 143.0, 142.6, 138.2, 138.0, 137.7, 137.1, 135.2, 134.1, 130.8, 129.7, 128.9, 128.7, 128.6, 128.5, 128.3, 128.1, 127.9, 123.7, 123.2, 73.6, 73.3, 66.2, 64.7, 33.7, 27.4, 23.5, 14.1

HRMS (ESI^+): calculated for $C_{33}H_{40}O_3Na^+$ $[M+Na^+]$: 507.2870, found 507.2867.

2,3-bis(*tert*-butoxymethyl)-1-butyl-4-phenyl-9*H*-fluoren-9-one (3i).

[12] Arai, A.; Ichikizaki, I. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1571.



Chemical Formula: $C_{33}H_{40}O_3$
Exact Mass: 484.2977

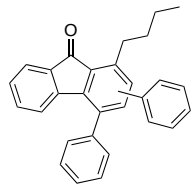
Starting from diyne **1a** (100 mg, 0.35 mmol) and 1,4-di-*tert*-butoxybut-2-yne[13] **2c** (139 mg, 0.7 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (3.6 mg, 0.0175 mmol). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 99/1 to 98/2) afforded **3i** (140 mg, 83%) as a yellow solid. m.p. 158 – 160 °C.

^{1}H NMR (300 MHz, $CDCl_3$), *δ* 7.58 – 7.52 (m, 1H), 7.56 – 7.44 (m, 3H), 7.39 – 7.29 (m, 2H), 7.11 (td, *J* = 7.5, 0.9 Hz, 1H), 7.02 (td, *J* = 7.5, 1.2 Hz, 1H), 5.89 (d, *J* = 7.5 Hz, 1H), 4.55 (s, 2H), 4.19 (s, 2H), 3.28 – 3.15 (m, 2H), 1.72 – 1.51 (m, 4H), 1.36 (s, 9H), 1.03 (t, *J* = 6.9 Hz, 3H), 1.01 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$), *δ* 194.8, 145.1, 143.9, 143.3, 142.8, 138.4, 138.3, 137.3, 135.2, 134.0, 130.7, 129.9, 128.7, 128.3, 128.0, 123.5, 123.1, 73.7, 73.6, 57.9, 56.8, 33.7, 27.9, 27.6, 27.5, 23.7, 14.1.

HRMS (ESI^+): calculated for $C_{39}H_{36}O_3Na^+$ [M+Na^+]: 575.2557, found 575.2551.

1-butyl-3,4-diphenyl-9*H*-fluoren-9-one and 1-butyl-2,4-diphenyl-9*H*-fluoren-9- one (3j)



Chemical Formula: $C_{29}H_{24}O$
Exact Mass: 388.1827

Starting from diyne **1a** (200 mg, 0.7 mmol), phenyl acetylene **2d** (93 mg, 1.4 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (7.2 mg, 0.035 mmol). Purification on silica gel (Petroleum ether/Ethyl acetate 99/1) afforded the title regioisomer compounds **3j** (191 mg, 70%) in the ratio of 73/27 as a orange solid.

Major product: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.66-7.58 (m, 1H), 7.34-7.30 (m, 3H), 7.20-7.05 (m, 10H), 6.22 – 6.13 (m, 1H), 3.15 (t, *J* = 7.8 Hz, 2H), 1.75-1.65 (m, 2H), 1.55-1.46 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.7, 148.0, 144.1, 143.8, 143.1, 140.4, 138.3, 135.3, 134.6, 134.1, 132.8, 130.4, 130.0, 129.6, 128.6, 128.5, 127.8, 127.7, 127.1, 123.6, 123.3, 33.1, 31.2, 23.0, 14.1.

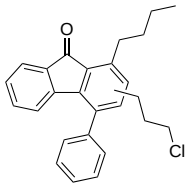
[13] Mallesha, N.; Rao, S. P.; Suhas, R.; Gowda, D. C, *Tetrahedron Lett*. **2012**, *53*, 641.

Minor product: **^{1}H NMR** (300 MHz, $CDCl_3$), δ 7.66-7.58 (m, 1H), 7.50-7.33 (m, 10H), 7.22-7.05 (m, 3H), 6.77-6.72 (m, 1H), 3.08-3.03 (m, 1H), 1.55-1.46 (m, 2H), 1.37-1.30 (m, 2H), 0.82 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ 194.9, 144.2, 143.7, 142.2, 141.2, 140.4, 139.7, 137.9, 135.7, 135.1, 134.1, 131.4, 129.4, 129.1, 129.0 128.8, 128.3, 128.1, 127.4, 123.8, 123.0, 33.3, 27.7, 23.1,13.8.

HRMS (ESI^+): calculated for $C_{29}H_{24}ONa^+$ [M+Na^+]: 411.1719, found 411.1722.

1-butyl-3-(3-chloropropyl)-4-phenyl-9*H*-fluoren-9-one and 1-butyl-2-(3-chloropropyl)-4-phenyl-9*H*-fluoren-9-one (3k)



Chemical Formula: $C_{26}H_{25}ClO$
Exact Mass: 388.1594

Starting from diyne **1a** (200 mg, 0.7 mmol), 5-chloro-1-pentyne **2e** (143 mg, 1.4 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (7.2 mg, 0.035 mmol). Purification on silica gel (Petroleum ether/Ethyl acetate 99/1) afforded the title regioisomer compounds **3k** (165 mg, 61%) in the ratio of 55/45 as a orange oil.

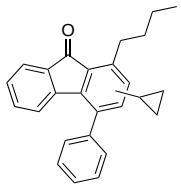
Major product: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57-7.50 (m, 4H), 7.30-7.27 (m, 2H), 7.19 -7.11 (m, 1H), 7.05 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.01 (s, 1H), 5.95-5.92 (m, 1H), 3.40 (t, *J* = 6.6 Hz, 2H), 3.08 (t, *J* = 7.7 Hz, 2H), 2.57-2.52 (m, 2H), 1.91-1.86 (m, 2H), 1.68-1.64 (m, 2H), 1.52-1.46 (m, 2H), 0.99 (t, *J* = 7.7 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 194.7, 146.3, 144.1, 144.0, 143.1, 138.2, 135.4, 135.2, 134.0, 131.6, 129.4, 129.3, 129.0, 128.4, 128.2, 123.6, 123.0, 44.4, 33.6, 33.1, 31.2, 30.6, 22.9, 14.1.

Minor product **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.59-7.57 (m, 1H), 7.49-7.49 (m, 2H), 7.45-7.40 (m, 3H), 7.16 -7.11 (m, 3H), 6.67-6.63 (m, 1H), 3.62 (t, *J* = 6.3 Hz, 2H), 3.20-3.12 (m, , 2H), 2.88-2.78 (m, 2H), 2.12-2.04 (m, 2H), 1.59-1.53 (m, 4H), 1.09 (t, *J* = 7.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 143.8, 142.6, 140.9, 140.3, 139.9, 137.2, 136.0, 135.0, 134.7, 134.1, 131.5, 129.1, 128.8, 128.1, 123.8, 122.8, 44.6, 34.0, 33.3, 29.1, 26.9, 23.5, 14.1.

HRMS (ESI^+): calculated for $C_{26}H_{25}ClONa^+$ [M+Na^+]: 411.1486, found 411.1490.

1-butyl-3-cyclopropyl-4-phenyl-9*H*-fluoren-9-one and 1-butyl-3-cyclopropyl-4-phenyl -9*H*-fluoren-9-one (3l)



Chemical Formula: $C_{26}H_{24}O$
Exact Mass: 352.1827

Starting from diyne **1a** (200 mg, 0.7 mmol), cyclopropyl acetylene **2f** (93 mg, 1.4 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (7.2 mg, 0.035 mmol). Purification on silica gel (Petroleum ether/Ethyl acetate 99/1) afforded the title regioisomer compounds **3l** (208 mg, 84%) in the ratio of 67/33 as a orange oil.

Major product: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.60 – 7.45 (m, 4H), 7.39 – 7.33 (m, 2H), 7.15 – 7.08 (m, 2H), 6.56 (s, 1H), 6.04 – 5.98 (m, 1H), 3.05 (t, *J* = 7.8 Hz, 2H), 1.68 – 1.55 (m, 3H), 1.51 – 1.40 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H), 0.86 – 0.74 (m, 2H), 0.75 – 0.64 (m, 2H).

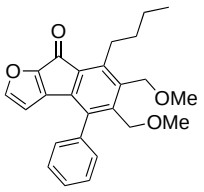
^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5, 149.6, 144.2, 144.1, 142.6, 138.9, 136.0, 133.8, 129.7, 129.1, 128.3, 127.9, 125.3, 123.5, 123.1, 33.1, 31.5, 22.9, 14.1, 12.5, 10.2.

Minor product: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.60 – 7.45 (m, 4H), 7.43 – 7.39 (m, 2H), 7.04 (td, *J* = 7.5, 1.4 Hz, 2H), 6.88 (s, 1H), 6.64 – 6.60 (m, 1H), 3.35 (t, *J* = 7.8 Hz, 2H), 2.05 – 1.97 (m, 1H), 1.68 – 1.50 (m, 4H), 1.02 (t, *J* = 7.8 Hz, 3H), 0.86 – 0.74 (m, 2H), 0.75 – 0.64 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 195.2, 143.9, 143.4, 140.2, 139.4, 135.8, 135.2, 134.0, 133.3, 131.1, 129.1 128.8, 128.6, 128.2, 128.0, 123.7, 122.7, 32.6, 27.0, 23.5, 14.0, 12.5, 7.8.

HRMS (ESI^+): calculated for $C_{26}H_{24}OH^+$ [$M+H^+$]: 353.1900, found 353.1900.

7-butyl-5,6-bis(methoxymethyl)-4-phenyl-8*H*-indeno[2,1-*b*]furan-8-one (3m).



Chemical Formula: $C_{25}H_{26}O_4$
Exact Mass: 390.1831

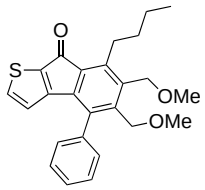
Starting from diyne **1h** (97 mg, 0.35 mmol) and 1,4-dimethoxy-2-butyne **2a** (80 mg, 0.7 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (3.6 mg, 0.0175 mmol). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) afforded **3m** (75 mg, 55 %) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.38 (m, 3H), 7.35 – 7.27 (m, 3H), 5.40 (d, *J* = 1.7 Hz, 1H), 4.49 (s, 2H), 4.16 (s, 2H), 3.48 (s, 3H), 3.23 (s, 3H), 3.13 – 3.02 (m, 2H), 1.60 – 1.46 (m, 4H), 0.99 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 179.6, 154.6, 151.3, 145.0, 144.6, 140.9, 138.2, 137.7, 135.1, 134.8, 131.6, 129.7, 128.4, 128.0, 108.0, 68.8, 67.4, 58.9, 58.5, 33.7, 26.7, 23.4, 14.1.

HRMS (ESI^+): calculated for $C_{25}H_{26}O_4Na^+$ [M+Na^+]: 413.1723, found 413.1723.

7-butyl-5,6-bis(methoxymethyl)-4-phenyl-8*H*-indeno[2,1-*b*]thiophen-8-one (3n).



Chemical Formula: $C_{25}H_{26}O_3S$
Exact Mass: 406.1603

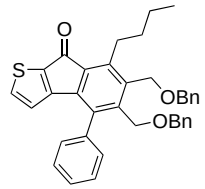
Starting from diyne **1i** (102 mg, 0.35 mmol) and 1,4-dimethoxy-2-butyne **2a** (80 mg, 0.7 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (3.6 mg, 0.0175 mmol). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) afforded **3n** (101 mg, 71%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$), δ 7.49 – 7.43 (m, 3H), 7.34 (d, *J* = 4.5 Hz, 1H), 7.33 – 7.27 (m, 2H), 5.62 (d, *J* = 4.8 Hz, 1H), 4.51 (s, 2H), 4.16 (s, 2H), 3.49 (s, 3H), 3.19 (s, 3H), 3.17 – 3.07 (m, 2H), 1.62 – 1.47 (m, 4H), 1.00 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ 186.6, 157.2, 144.6, 141.2, 139.3, 138.5, 138.1, 137.3, 134.8, 133.7, 129.8, 128.5, 128.0, 122.3, 68.8, 67.4, 58.9, 58.5, 33.7, 26.9, 23.5, 14.1.

HRMS (ESI^+): calcd. for $C_{25}H_{26}O_3SNa$ [M+Na]$^+$: 429.1495, found 429.1494.

5,6-bis((benzyloxy)-methyl)-7-butyl-4-phenyl-8*H*-indeno[2,1-*b*]thiophen-8-one (3o).



Chemical Formula: $C_{37}H_{34}O_3S$
Exact Mass: 558.2229

Starting from diyne **1i** (102 mg, 0.35 mmol) and 1,4-bis(benzyloxy)-but-2-yne[13] **2b** (186 mg, 0.7 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (3.6 mg, 0.0175 mmol). The excess of alkyne was removed by bulb to bulb distillation (condition: $3.0x10^{-3}$ mbar, 175℃ for 20 minutes). Purification on silica gel (Petroleum

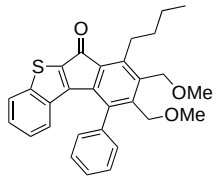
ether/Ethyl acetate gradient from 98/2 to 95/5) afforded **3o** (121 mg, 62%) as a yellow solid. m.p. 124 – 126 °C.

^{1}H NMR (300 MHz, $CDCl_3$), δ 7.48 – 7.42 (m, 3H), 7.38 – 7.27 (m, 11H), 7.22 – 7.17 (m, 2H), 5.62 (d, J = 4.8 Hz, 1H), 4.49 (s, 2H), 4.48 (s, 2H), 4.17 (s, 2H), 4.15 (s, 2H), 3.13 – 3.03 (m, 2H), 1.52 – 1.38 (m, 4H), 0.95 (t, J = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ 186.6, 157.2, 144.6, 141.5, 139.3, 138.5, 138.0, 137.4, 137.3, 134.9, 133.7, 129.8, 128.6, 128.6, 128.5, 128.3, 128.1, 128.0, 127.9, 122.3, 73.5, 73.2, 66.4, 64.7, 33.7, 26.9, 23.4, 14.0.

HRMS (ESI^+): calculated for $C_{37}H_{34}O_3SNa^+$ [M+Na^+]: 581.2121, found 581.2115.

7-butyl-8,9-bis(methoxymethyl)-10-phenyl-6*H*-benzo[b]indeno[1,2-*d*]thiophen-6-one (3p).



Chemical Formula: $C_{29}H_{28}O_3S$
Exact Mass: 456.1759

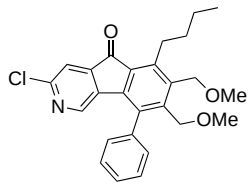
Starting from diyne **1j** (120 mg, 0.35 mmol) and 1,4-dimethoxy-2-butyne **2a** (80 mg, 0.7 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (3.6 mg, 0.0175 mmol). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) afforded **3p** (124 mg, 78 %) as a red solid. m.p. 135 – 137 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 1H), 7.51 – 7.40 (m, 5H), 7.20 – 7.10 (m, 1H), 6.83 – 6.72 (m, 1H), 5.19 (d, J = 8.6 Hz, 1H), 4.52 (s, 2H), 4.10 (s, 2H), 3.51 (s, 3H), 3.24 – 3.11 (m, 2H), 3.19 (s, 3H), 1.69 – 1.52 (m, 4H), 1.03 (t, J = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.4, 151.6, 147.4, 144.6, 142.1, 141.3, 140.2, 139.9, 137.4, 135.0, 133.2, 132.6, 131.2, 128.7, 128.4, 126.6, 126.3, 125.1, 124.0, 68.9, 67.4, 59.0, 58.6, 33.6, 27.0, 23.5, 14.0.

HRMS (ESI^+): calcd. for $C_{29}H_{28}O_3SNa$ [M+Na]$^+$: 479.1651, found 479.1650.

6-butyl-3-chloro-7,8-bis(methoxymethyl)-9-phenyl-5*H*-indeno[1,2-*c*]pyridin-5-one (3q).



Chemical Formula: $C_{26}H_{26}ClNO_3$
Exact Mass: 435.1601

Starting from diyne **1k** (112 mg, 0.35 mmol), 1,4-dimethoxy-2-butyne **2a** (80 mg, 0.7 mmol, 2.0 equiv) and $RuCl_3 \cdot nH_2O$ (3.6 mg, 0.0175 mmol). Purification on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) afforded **3q** (91 mg, 60%) as a yellow solid. m.p. 94 – 96 °C.

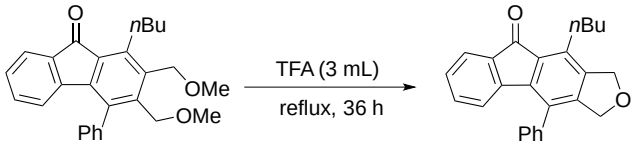
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 3H), 7.40 (d, J = 0.9 Hz, 1H), 7.32 – 7.27 (m, 2H), 6.90 (d, J = 1.2 Hz, 1H), 4.57 (s, 2H), 4.22 (s, 2H), 3.51 (s, 3H), 3.24 – 3.15 (m, 2H), 3.20 (s, 3H), 1.60 – 1.52 (m, 4H), 1.01 (t, J = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.9, 151.7, 146.4, 144.2, 143.7, 141.5, 138.8, 137.8, 137.6, 136.0, 130.3, 129.4, 129.1, 128.9, 128.8, 118.1, 67.3, 59.1, 58.7, 33.5, 27.6, 23.5, 14.0.

HRMS (ESI^+): calcd. for $C_{26}H_{26}ClNO_3Na$ $[M+Na]^+$: 458.1493, found 458.1494.

IV. Valorization of [2+2+2] cycloadducts

Synthesis of 10-butyl-4-phenyl-1*H*-fluoreno[2,3-*c*]furan-9(3H)-one (4).



3a **4**

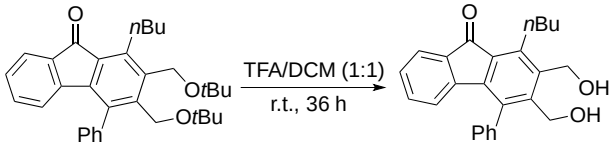
A solution of **3a** (400 mg, 1.0 mmol) in trifluoroacetic acid (3 mL) was refluxed for 36 h. Evaporation of the excess of trifluoroacetic acid under reduced pressure gave a residue which was purified by column chromatography on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) to afforded compound **4** (300 mg, 85%) as a yellow solid. m.p. 109 – 111 °C.

^{1}H NMR (300 MHz, $CDCl_3$), δ 7.60 – 7.55 (m, 1H), 7.53 – 7.47 (m, 3H), 7.37 – 7.32 (m, 2H), 7.18 – 7.05 (m, 2H), 6.38 (d, J = 7.2 Hz, 1H), 5.17 (s, 1H), 4.86 (s, 1H), 2.97 (t, J = 7.5 Hz, 2H), 1.68 – 1.54 (m, 2H), 1.52 – 1.40 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ 194.3, 145.4, 143.6, 142.7, 139.9, 137.8, 137.5, 135.4, 134.1, 131.2, 129.8, 129.3, 128.5, 123.8, 122.8, 73.9, 73.3, 32.2, 29.0, 23.2, 14.1.

HRMS (ESI^+): calculated for $C_{25}H_{22}O_2Na^+$ $[M+Na^+]$: 377.1512, found 377.1515.

Synthesis of 1-butyl-2,3-bis(hydroxymethyl)-4-phenyl-9*H*-fluoren-9-one (5).



3i **5**

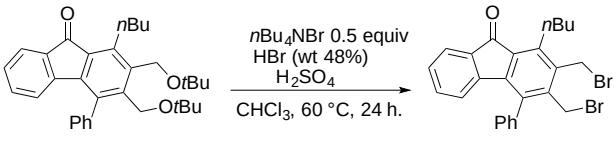
To a solution of **3i** (100 mg, 0.21 mmol) in CH_2Cl_2 (1 mL) was added trifluoroacetic acid (1 mL, large excess amount). The reacton mixture was stirred at room temperature for 36 h. When the reaction was complete (TLC monitoring), CH_2Cl_2 and the excess of trifluoroacetic acid were evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) to afforded compound **5** (60 mg, 75%) as a yellow solid. m.p. 166 – 168 °C.

^{1}H NMR (300 MHz, $CDCl_3$), δ 7.66 – 7.60 (m, 1H), 7.58 – 7.51 (m, 3H), 7.34 – 7.27 (m, 2H), 7.22 (td, J = 7.5, 0.9 Hz, 1H), 7.11 (td, J = 7.5, 1.2 Hz, 1H), 5.96 (d, J = 7.5 Hz, 1H), 5.57 (s, 2H), 5.22 (s, 2H), 3.33 – 3.22 (m, 2H), 1.63 – 1.52 (m, 4H), 1.01 (t, J = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ 193.7, 145.4, 144.9, 142.7, 138.2, 138.0, 136.5, 134.9, 134.7, 133.1, 132.1, 129.6, 129.6, 129.2, 124.2, 123.6, 63.7, 62.7, 33.8, 27.4, 23.4, 13.9.

HRMS (ESI^+): calculated for $C_{25}H_{24}O_3Na^+$ [M+Na^+]: 395.1618, found 395.1619.

Synthesis of 2,3-bis(bromomethyl)-1-butyl-4-phenyl-9*H*-fluoren-9-one (6).



3i **6**

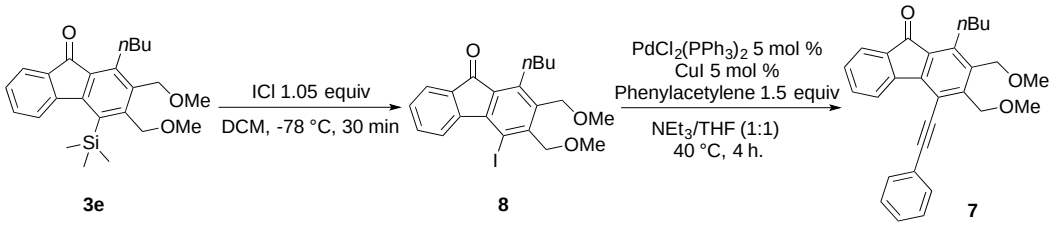
To a solution of **3i** (480 mg, 1.0 mmol) in $CHCl_3$ (10 mL) were added nBu$_4$NBr (0.16 g, 0.5 mmol), aq. HBr (48% in water, 3 mL) and conc. H_2SO_4 (0.3 mL). The resulting mixture was heated at 60 °C for 24 h. At the end of the reaction (TLC monitoring), the reaction mixture was poured into water (50 mL). The product was extracted with CH_2Cl_2 (3×30 mL) and the combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (Petroleum ether/Dichloromethane = 2/1) to afford compound **6** (444 mg, 90%) as a yellow solid. m.p. 132 – 133 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 7.50 (m, 4H), 7.48 – 7.35 (m, 2H), 7.17 (td, *J* = 7.5, 0.9 Hz, 1H), 7.07 (td, *J* = 7.6, 1.3 Hz, 1H), 5.88 (d, *J* = 7.5 Hz, 1H), 4.79 (s, 2H), 4.42 (s, 2H), 3.37 – 3.13 (m, 2H), 1.75 – 1.50 (m, 4H), 1.04 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 194.0, 144.5, 143.8, 143.1, 142.1, 137.0, 136.9, 136.8, 135.0, 134.4, 131.2, 129.4, 129.3, 129.1, 128.9, 123.9, 123.4, 33.3, 27.5, 27.3, 26.3, 23.5, 14.0.

HRMS (ESI^+): calcd. for $C_{25}H_{22}Br_2OH$ $[M+H]^+$: 497.0110, found 497.0109.

Synthesis of 1-butyl-2,3-bis(methoxymethyl)-4-(phenylethynyl)-9*H*- fluoren-9-one (7).



3e **8** **7**

a) To a solution of **3e** (0.56 g, 1.41 mmol) in CH_2Cl_2 (10 mL) was added a solution of iodine monochloride (240 mg, 1.5 mmol) in DCM (2 mL) at -78 °C and the mixture was allowed to warm to room temperature and stirred for additional 30 minutes. The reaction was quenched with aqueous saturated $Na_2S_2O_3$ and extracted with CH_2Cl_2 (3×30 mL). The organic layer was washed with brine and dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) to afford compound **8** (0.53 g, 84%) as a yellow solid. m.p. 93 – 95 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.98 – 8.87 (m, 1H), 7.67 (dd, *J* = 7.3, 0.6 Hz, 1H), 7.56 (td, *J* = 7.7, 1.3 Hz, 1H), 7.35 (td, *J* = 7.4, 0.8 Hz, 1H), 4.74 (s, 2H), 4.55 (s, 2H), 3.54 (s, 3H), 3.48 (s, 3H), 3.18 (t, *J* = 7.5 Hz, 2H), 1.55 – 1.44 (m, 4H), 0.98 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 147.8, 146.5, 145.3, 144.2, 138.9, 135.1, 133.8, 133.1, 129.6, 124.1, 122.9, 95.8, 75.2, 67.8, 59.0, 58.9, 33.5, 27.0, 23.4, 14.0.

HRMS (ESI^+): calcd. for $C_{21}H_{23}IO_3Na$ $[M+Na]^+$: 473.0584, found 473.0580.

b) $PdCl_2(PPh_3)_2$ (5 mol%, 19.6 mg) and CuI (5 mol%, 2.7 mg) were added to a NEt_3/THF (1:1, 2 mL) solution containing iodo-substituted fluorenone **8** (0.56 mmol, 250 mg), phenylacetylene (1.5 equiv, 86 mg). The mixture was stirred at 40 °C for 4 h under argon. When the reaction was complete (TLC monitoring), a saturated aqueous solution of ammonium chloride was added and the mixture was stirred for 5 minutes. The organic layer was extracted with ethyl acetate (3×20 mL), washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified

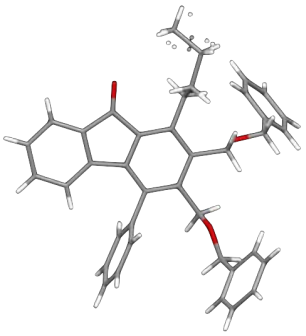
by flash chromatography on silica gel (Petroleum ether/Ethyl acetate gradient from 98/2 to 95/5) to afford compound **7** (232 mg, 98%) as a yellow solid. m.p. 124 – 126 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (d, J = 7.6 Hz, 1H), 7.72 – 7.57 (m, 3H), 7.55 – 7.39 (m, 4H), 7.36 – 7.29 (m, 1H), 4.86 (s, 2H), 4.57 (s, 2H), 3.52 (s, 3H), 3.48 (s, 3H), 3.21 (t, J = 7.5 Hz, 2H), 1.68 – 1.40 (m, 4H), 0.99 (t, J = 6.9 Hz, 3H).

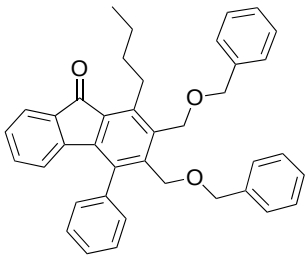
^{13}C NMR (75 MHz, $CDCl_3$) δ 193.9, 145.9, 145.3, 143.3, 138.1, 134.9, 134.7, 131.6, 131.0, 129.4, 129.1, 128.8, 123.9, 123.2, 123.1, 116.9, 97.8, 86.2, 69.5, 67.1, 59.0, 58.8, 33.6, 27.4, 23.5, 14.1.

HRMS (ESI^+): calcd. for $C_{29}H_{28}O_3Na$ $[M+Na]^+$: 447.1931, found 447.1930.

V. ORTEP diagram for the structure of compound 3h



CCDC 1487051



3h

Crystal data for **3h**. yellow prism-like crystals: $C_{39}H_{36}O_3$, monoclinic, *P* $2_1/n$, a = 15.9124(4), b = 10.2339(3), c = 19.2806(5) Å, β = 108.2530(10) °, V = 2981.78(14) $Å^3$, Z = 4, T = 200(2) K, m = 0.076 mm^{-1}, 33387 reflections measured, 8839 independent (R_{int}= 0.0329), 5842 observed [I≥2s(I)], 400 parameters, final R indices R_1 [I≥2s(I)] = 0.0468 and wR_2 (all data)= 0.1293, GOF on F^2 = 1.024, max/min residual electron density = 0.26/-0.20 e.$Å^{-3}$.

A single crystal of each compound was selected, mounted onto a cryoloop, and transferred in a cold nitrogen gas stream. Intensity data were collected with a BRUKER Kappa-APEXII diffractometer with graphite-monochromated Mo-Ka radiation (λ = 0.71073 Å). Data collection were performed with APEX2 suite (BRUKER). Unit-cell parameters refinement, integration and data reduction were carried out with SAINT program (BRUKER). SADABS (BRUKER) was used for scaling and multi-scan absorption corrections.

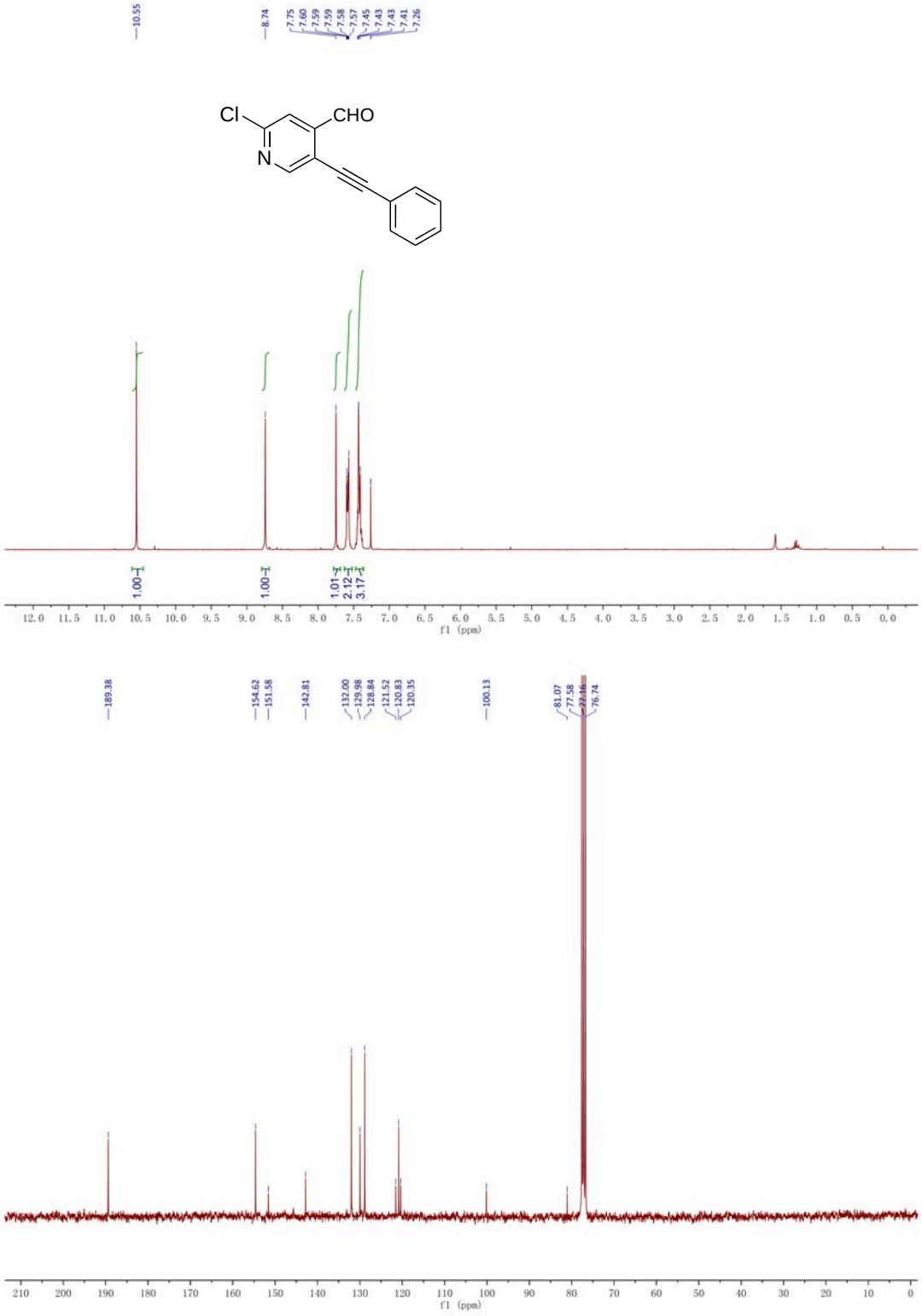
In the WinGX suite of programs,[14] the structure was solved with SHELXT program and refined by full-matrix least-squares methods using SHELXL-14.[15] All non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed at calculated positions and refined with a riding model.

CCDC 1487051 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

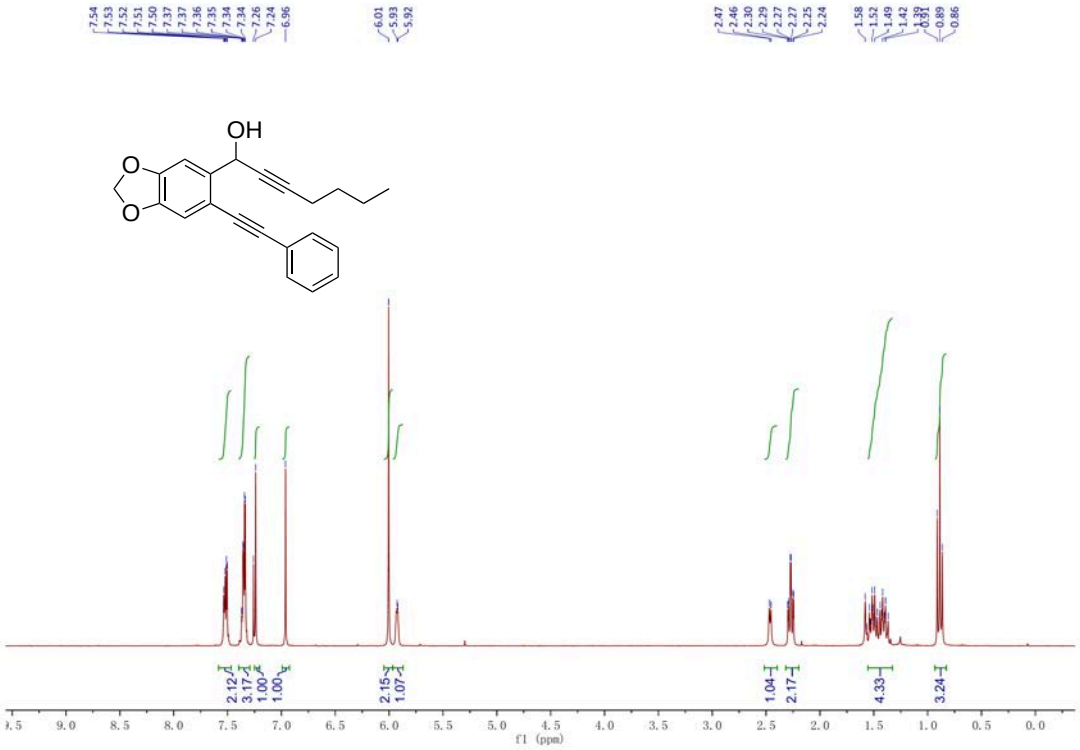
[14] Farrugia, L. J. *Journal of Applied Crystallography*, **1999**, *32*, 837.
[15] Sheldrick,G. M. *Acta Crystallographica Section A* **2015**, *71*, 3.

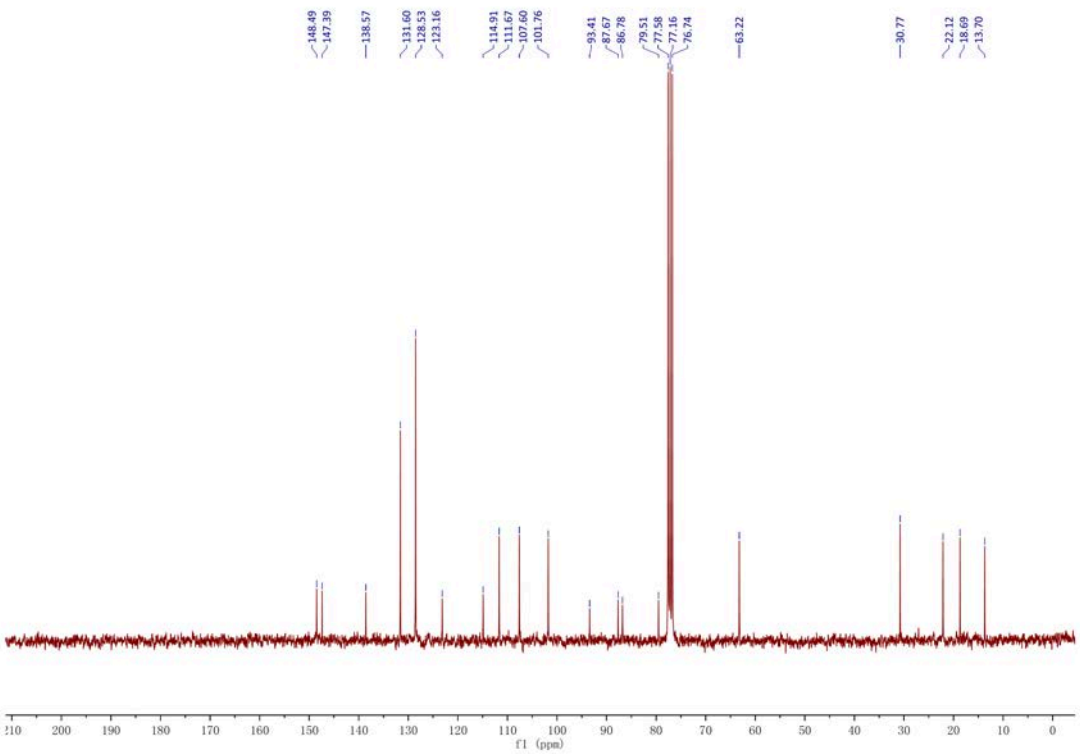
VI. NMR spectra for new compounds

S9



M5

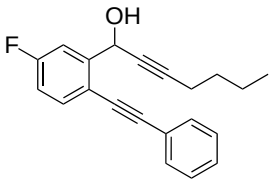


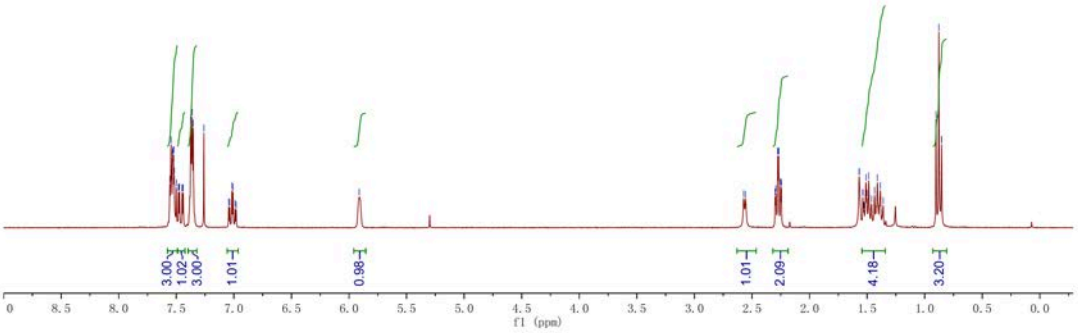


M6


7.56
7.55
7.53
7.53
7.52
7.52
7.50
7.48
7.47
7.45
7.44
7.37
7.36
7.35
7.26
7.04
7.04
7.02
7.01
6.99
6.98
5.91


2.57
2.56
2.28
2.27
2.25
2.25
1.57
1.51
1.49
1.43
1.41
1.38
0.90
0.88
0.85


OH
F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1.01
2.09
4.18
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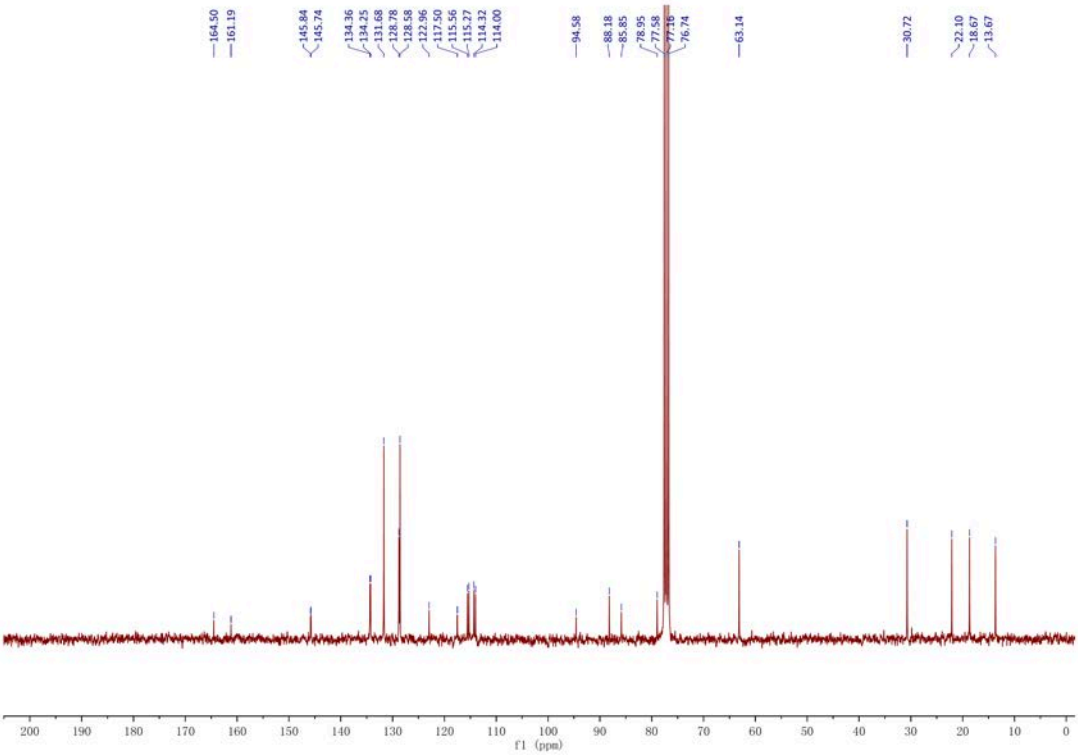
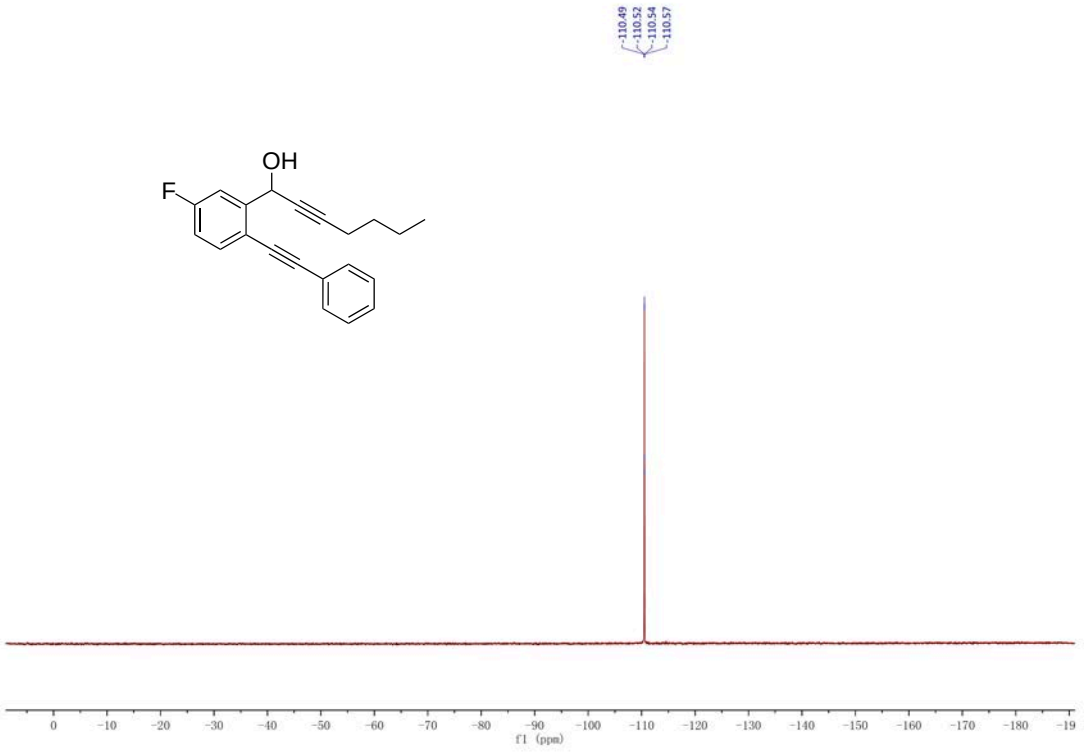
f1 (ppm)


164.50
161.19
145.84
145.74
134.36
134.25
131.68
128.78
128.58
122.96
117.50
115.56
115.27
114.32
114.00
94.58
88.18
85.85
78.95
77.58
77.16
76.74
63.14
30.72
22.10
18.67
13.67
f1 (ppm)

M6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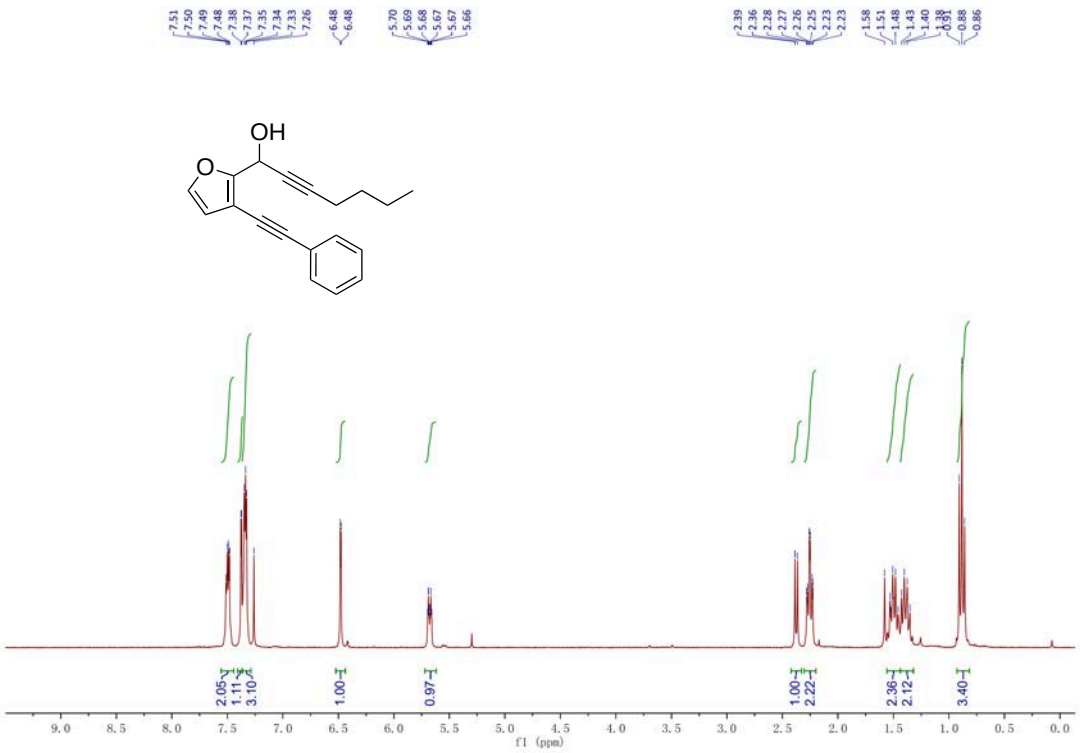
-110.52
-110.54
-110.57
OH
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-19
f1 (ppm)

M7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7.50
7.49
7.48
7.38
7.37
7.35
7.34
7.33
7.26
6.48
6.48
5.70
5.69
5.68
5.67
5.67
5.66
2.39
2.36
2.28
2.27
2.26
2.25
2.23
2.23
1.58
1.51
1.48
1.43
1.40
0.91
0.88
0.86
OH
O
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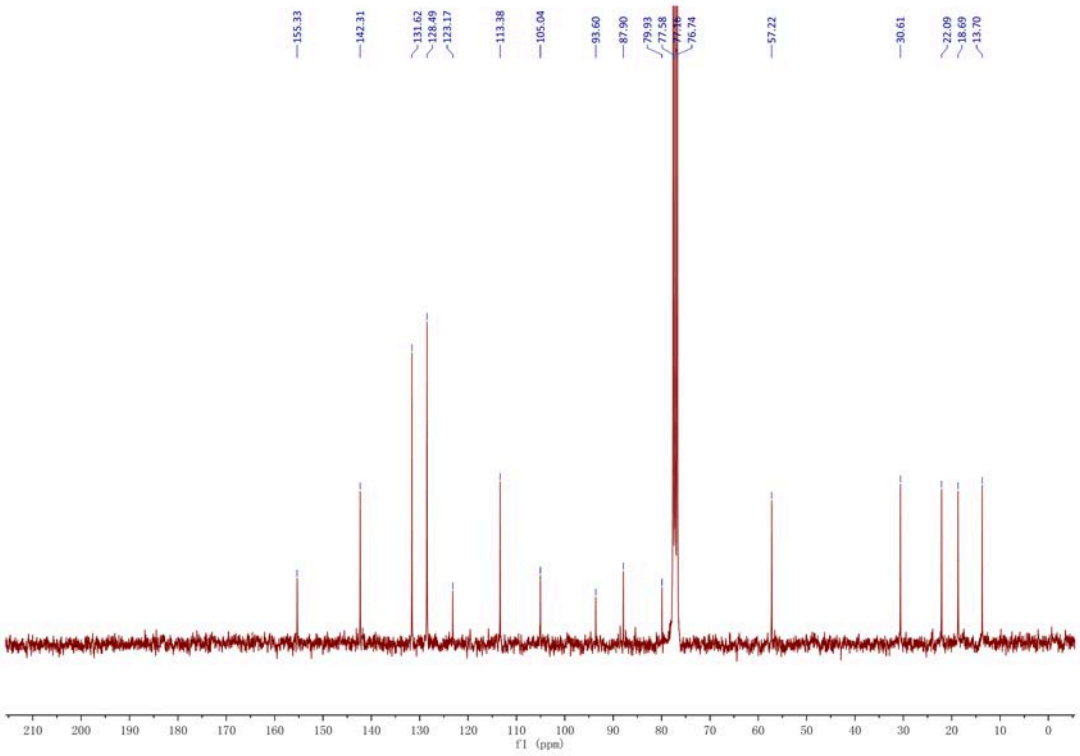
3.10
1.00
0.97
1.00
2.22
2.36
2.12
3.40
f1 (ppm)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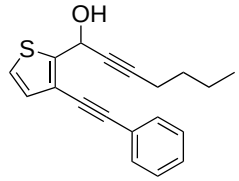
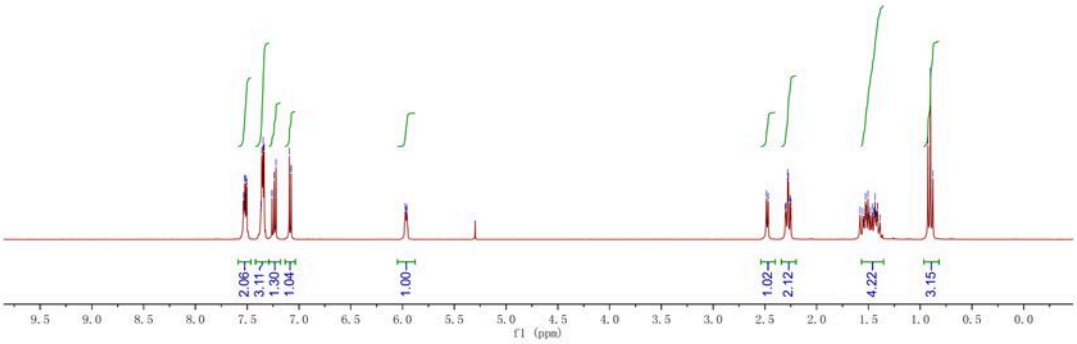
142.31
131.62
128.49
123.17
113.38
105.04
93.60
87.90
79.93
77.58
77.16
76.74
57.22
30.61
22.09
18.69
13.70
f1 (ppm)

M8


7.54
7.53
7.52
7.52
7.51
7.50
7.37
7.36
7.35
7.34
7.26
7.24
7.22
7.09
7.08
5.97
5.96
5.96
2.49
2.47
2.30
2.30
2.28
2.27
2.26
2.25
1.53
1.50
1.46
1.44
0.91
0.90
0.88


OH
S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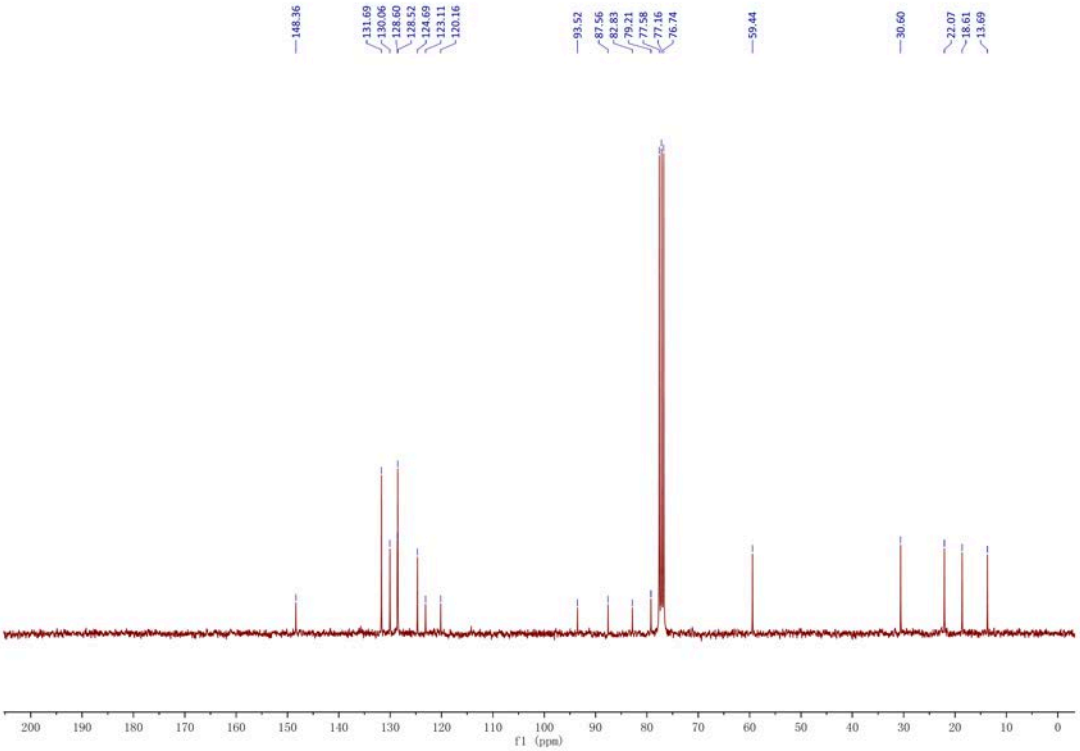
1.30
1.04
1.00
1.02
2.12
4.22
3.15
f1 (ppm)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128.60
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120.16
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87.56
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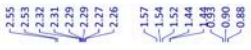
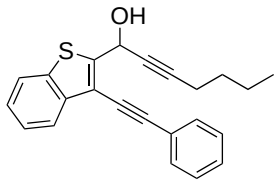
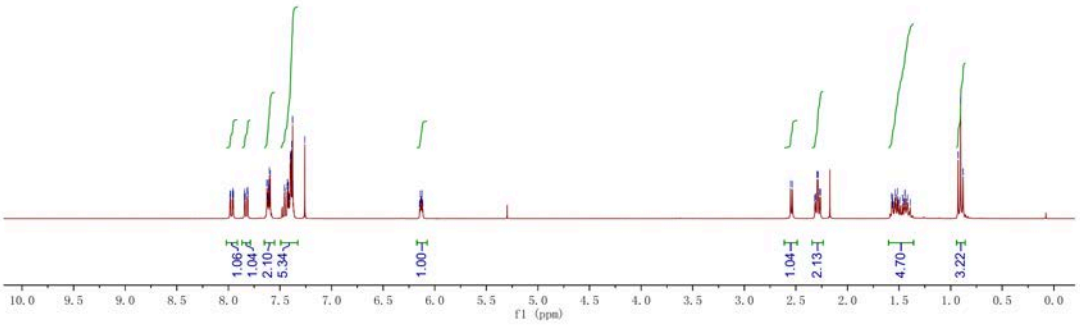
77.58
77.16
76.74
59.44
30.60
22.07
18.61
13.69
f1 (ppm)

M9




OH
S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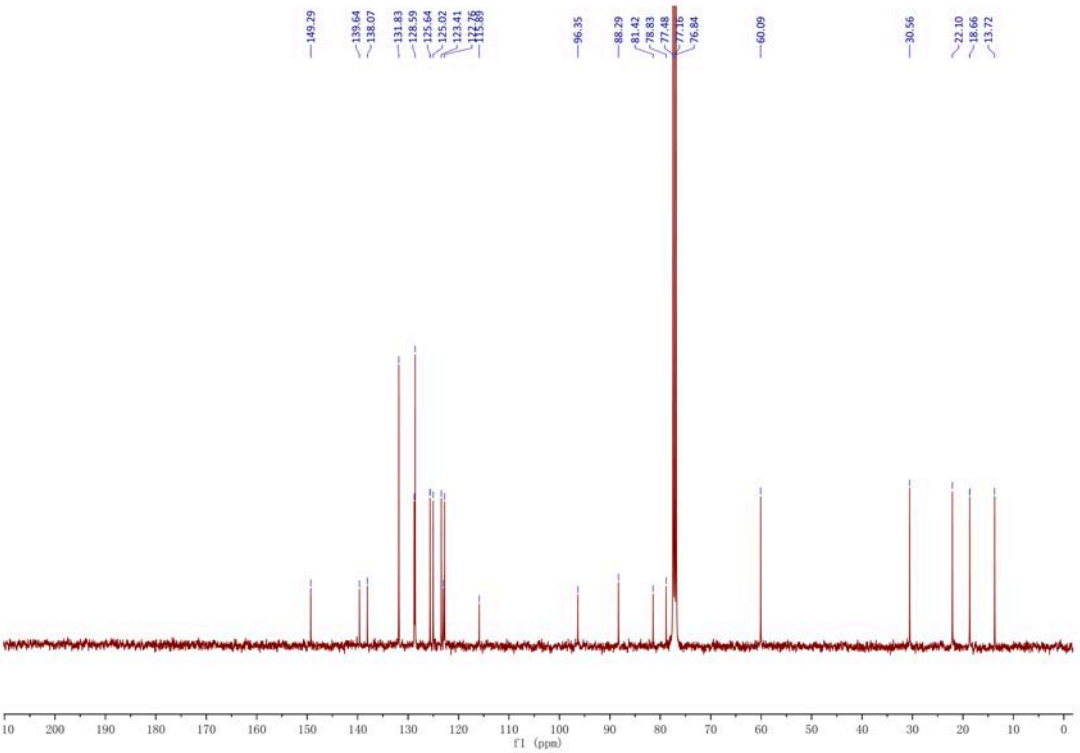
2.10
5.34
1.00
1.04
2.13
4.70
3.22
f1 (ppm)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139.64
138.07
131.83
128.59
125.64
125.02
123.41
122.76
115.88
96.35
88.29
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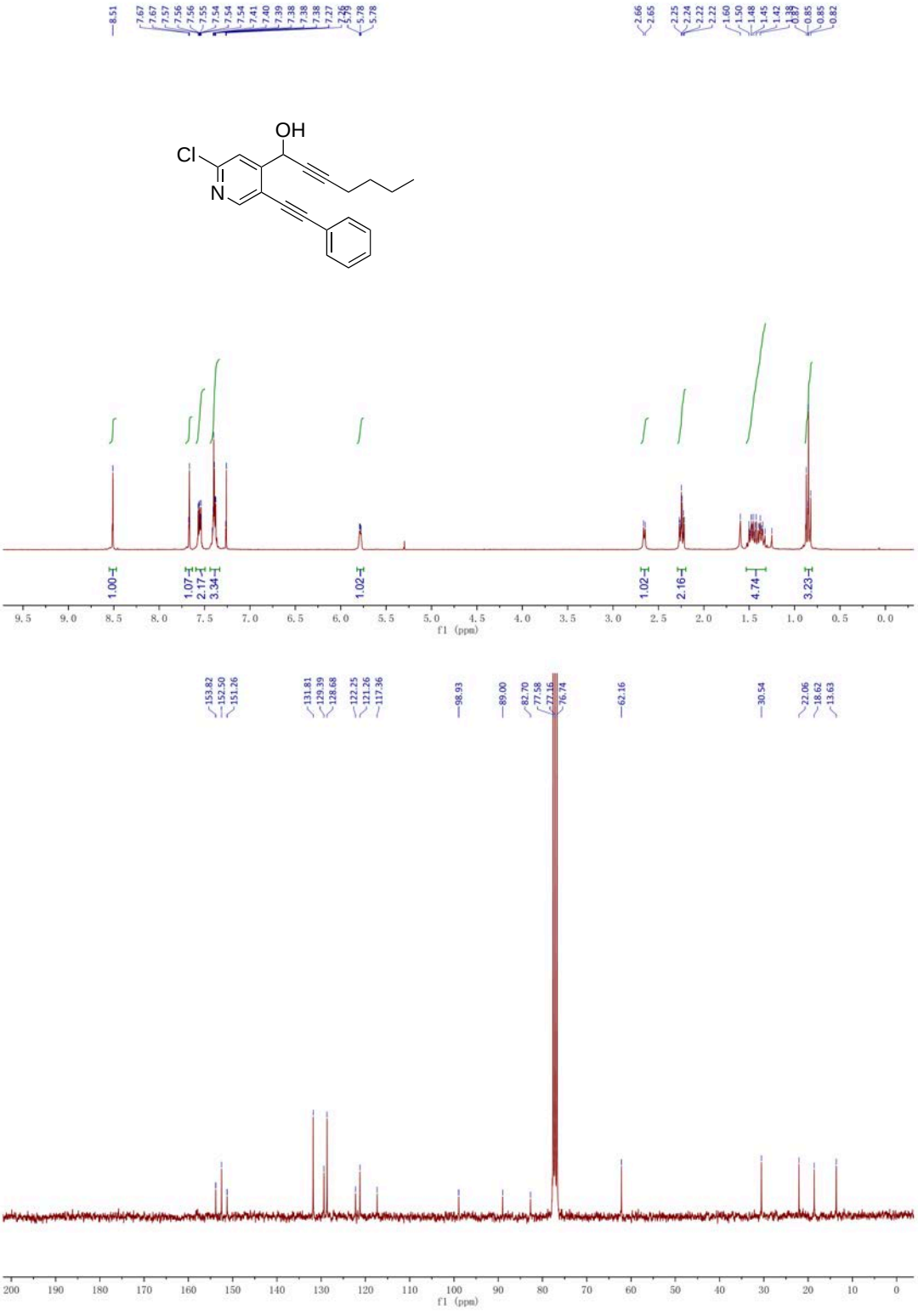
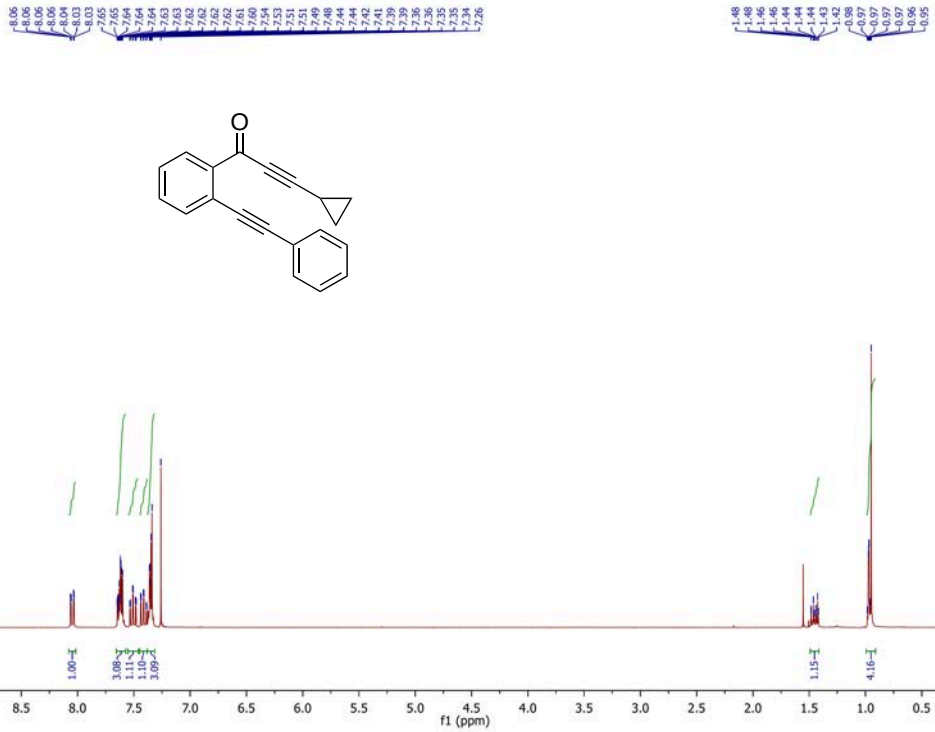
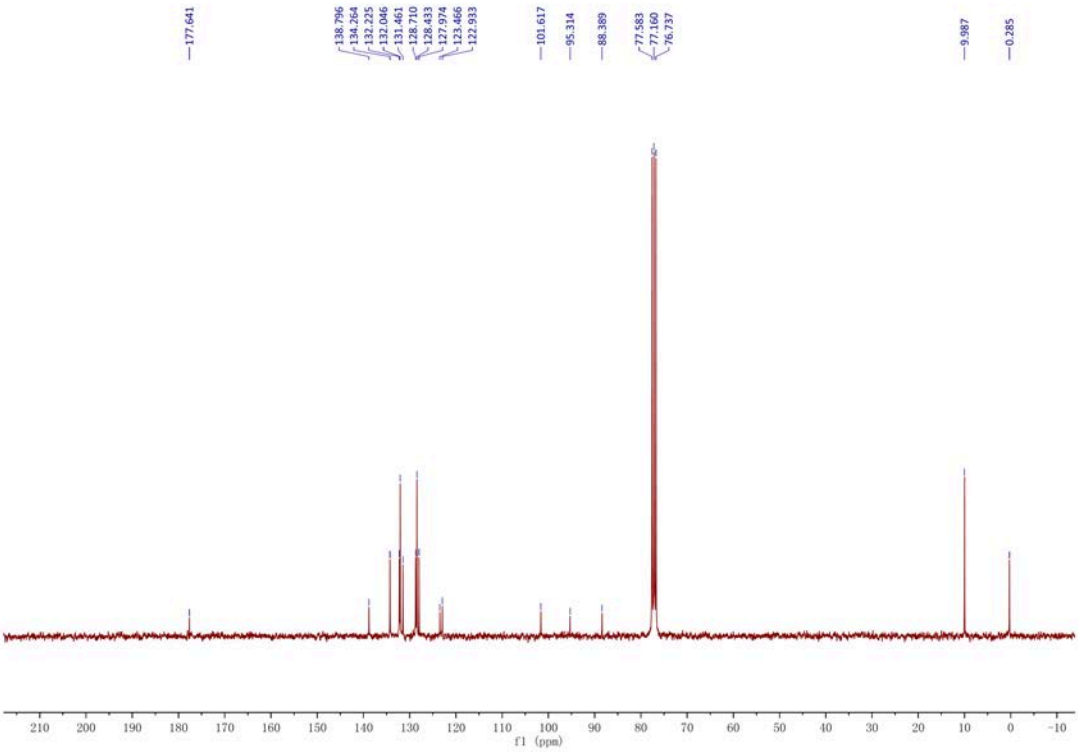
22.10
18.66
13.72
f1 (ppm)

M10

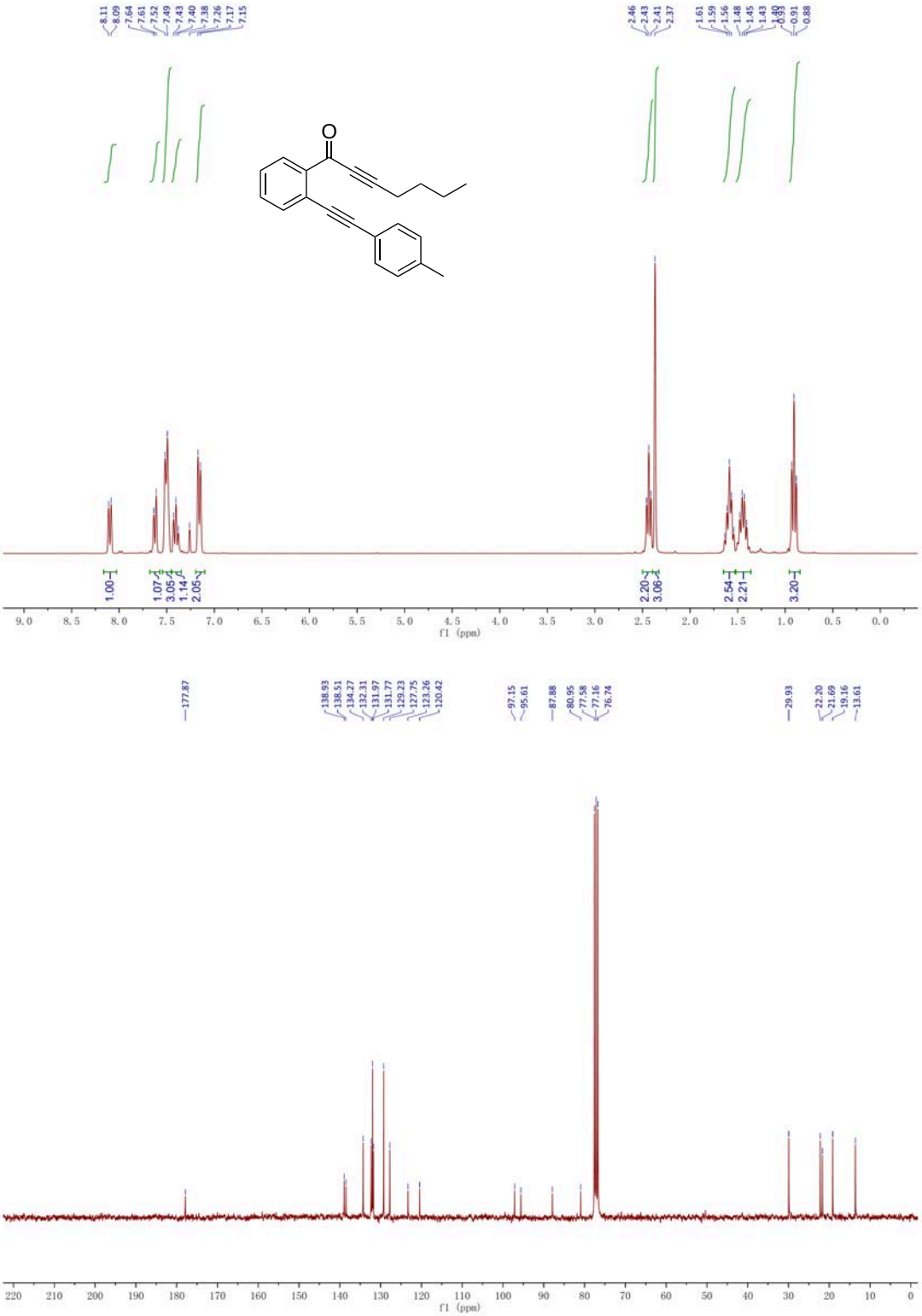


1b





1c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7.52
7.49
7.43
7.40
7.38
7.26
7.17
7.15
2.46
2.43
2.41
2.37
1.61
1.59
1.56
1.48
1.45
1.43
0.93
0.91
0.88
O
1.00
1.07
3.05
1.14
2.05
2.20
3.06
2.54
2.21
3.20
f1 (ppm)
177.87
138.93
138.51
134.27
132.31
131.97
131.77
129.23
127.75
123.26
120.42
97.15
95.61
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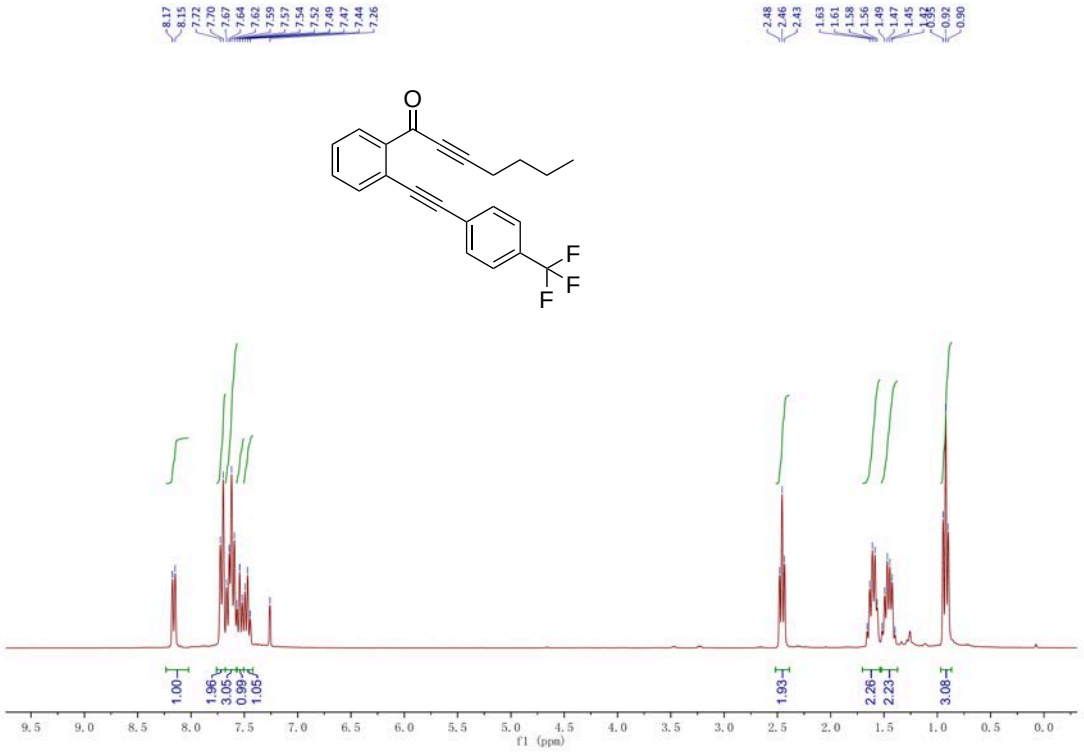
21.69
19.16
13.61
f1 (ppm)

1d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7.67
7.64
7.62
7.59
7.57
7.54
7.52
7.49
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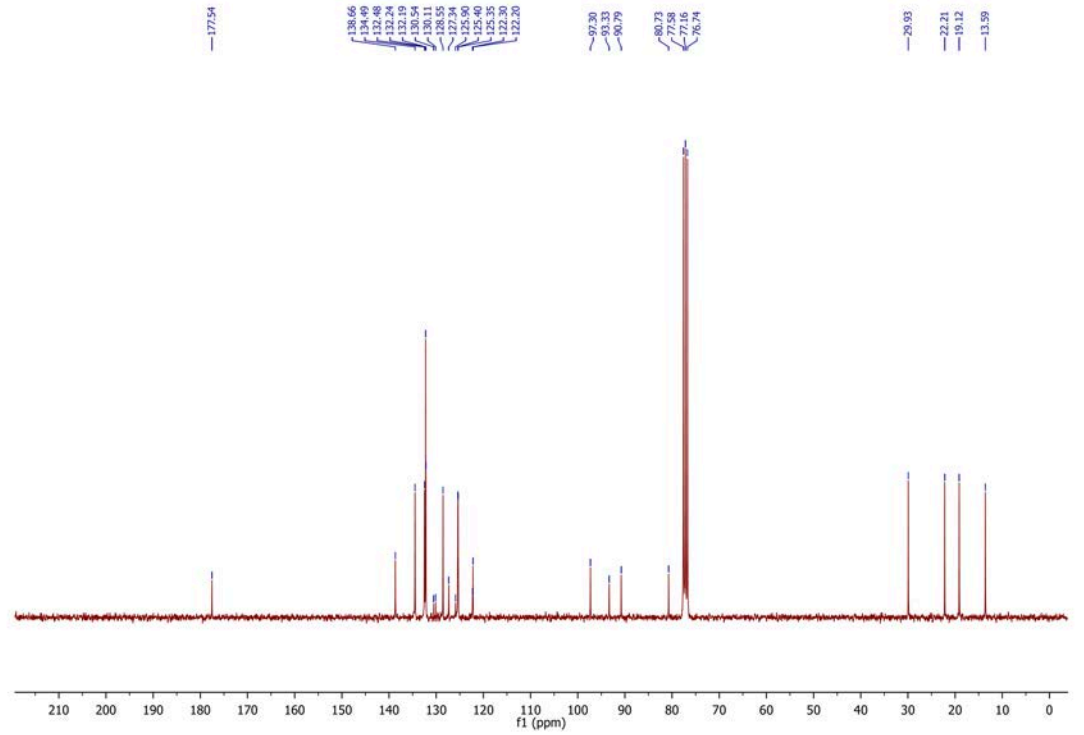
7.44
7.26
2.48
2.46
2.43
1.63
1.61
1.58
1.56
1.49
1.47
1.45
0.92
0.90
O
F
F
F
1.00
1.96
3.05
0.99
1.05
1.93
2.26
2.23
3.08
f1 (ppm)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125.90
125.40
123.35
122.30
122.20
97.30
93.33
90.79
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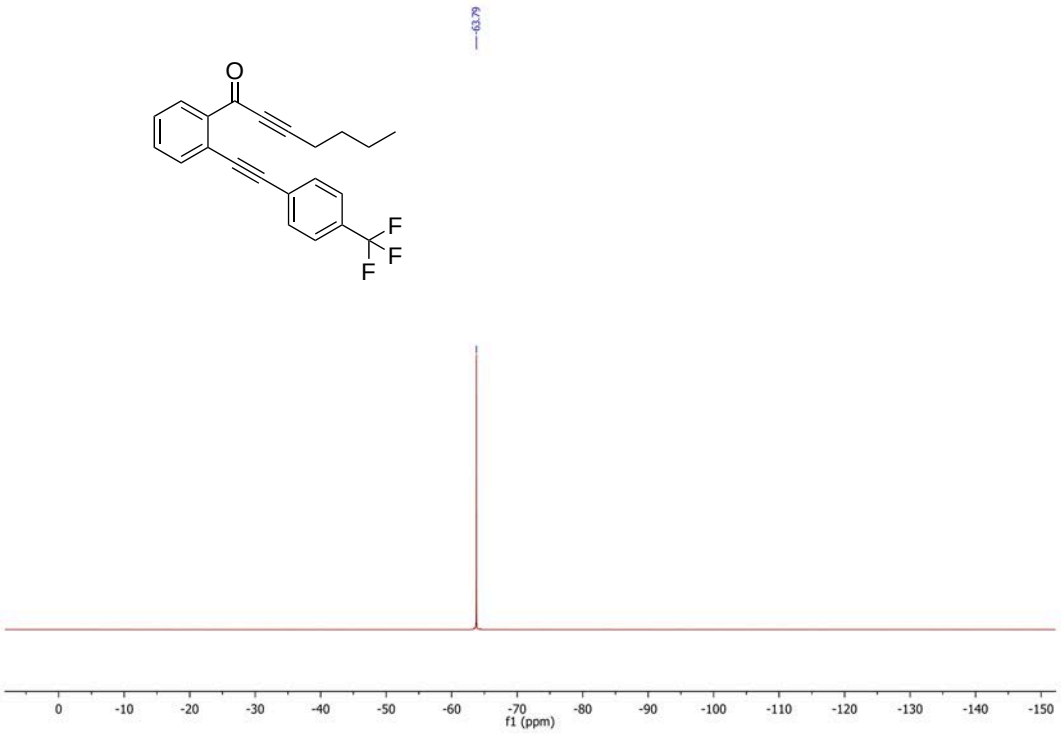
77.58
77.16
76.74
29.93
22.21
19.12
13.59
f1 (ppm)

1d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O
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F
F
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-10
-20
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-40
-50
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-70
-80
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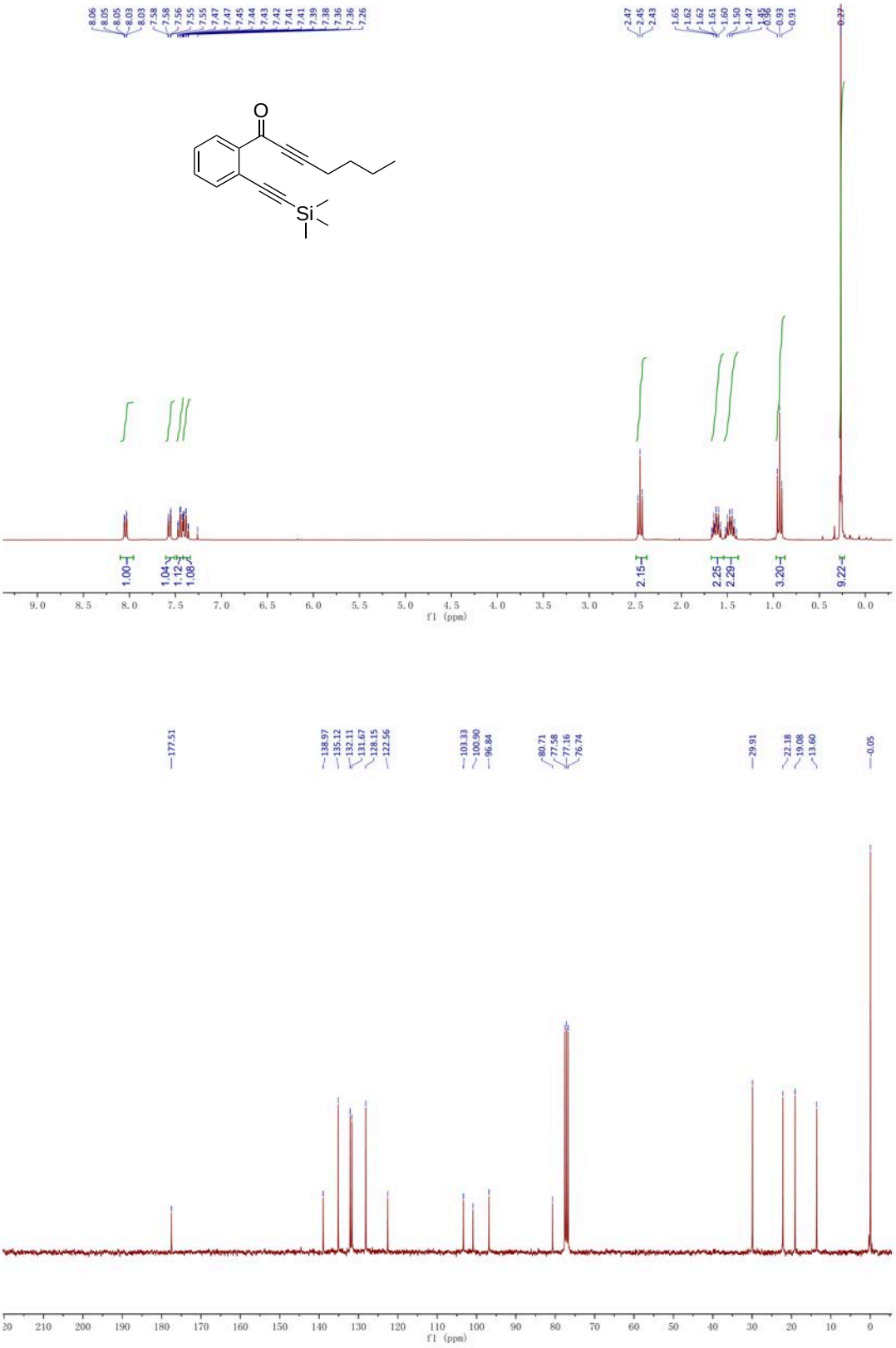
-120
-130
-140
-150
f1 (ppm)

1e



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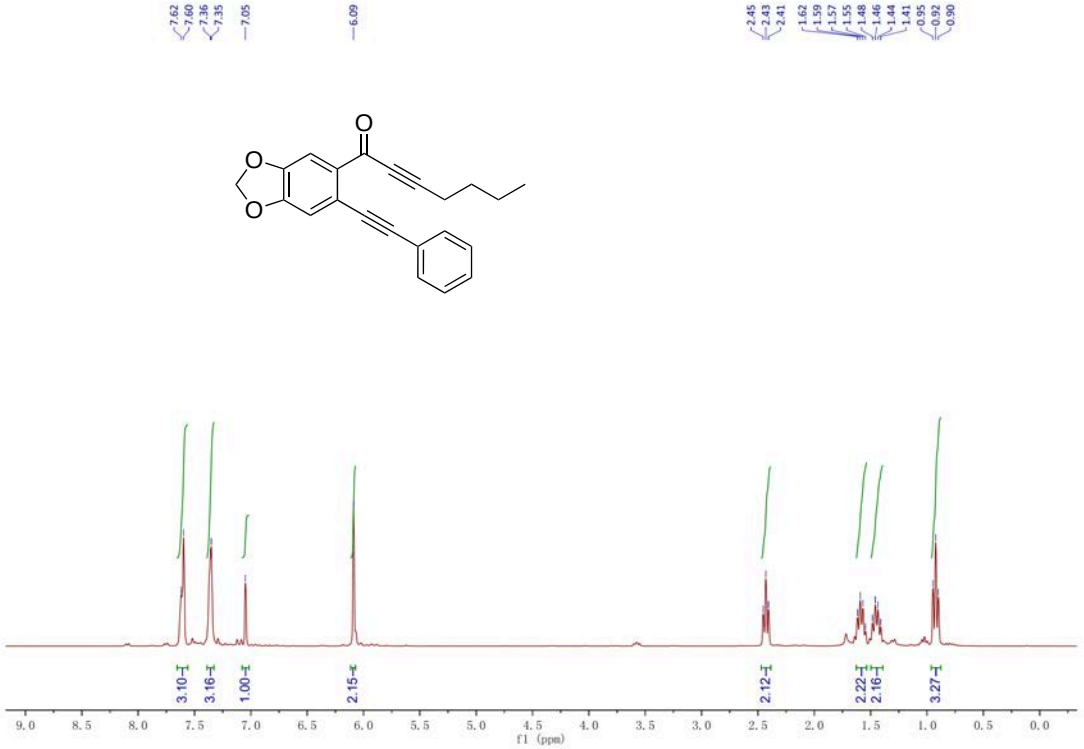
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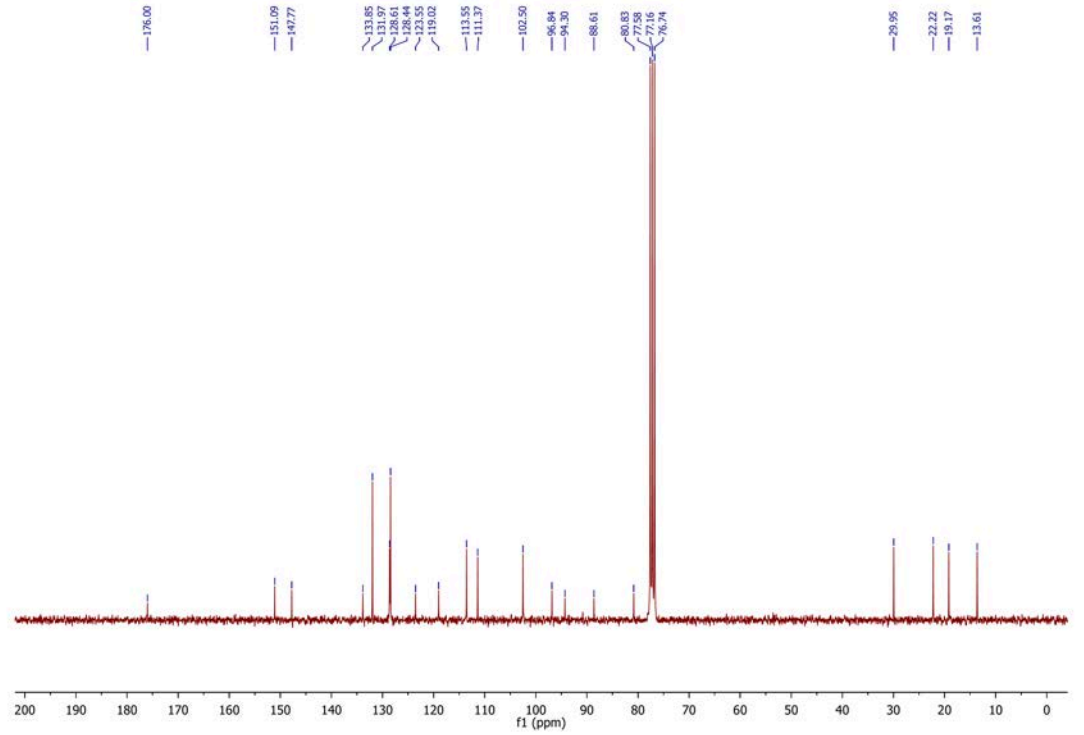
7.60
7.36
7.35
7.05
6.09
2.45
2.43
2.41
1.62
1.59
1.57
1.55
1.48
1.46
1.44
1.41
0.95
0.92
0.90
O
O
O
3.10
3.16
1.00
2.15
2.12
2.22
2.16
3.27
f1 (ppm)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131.97
128.61
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123.55
119.02
113.55
111.37
102.50
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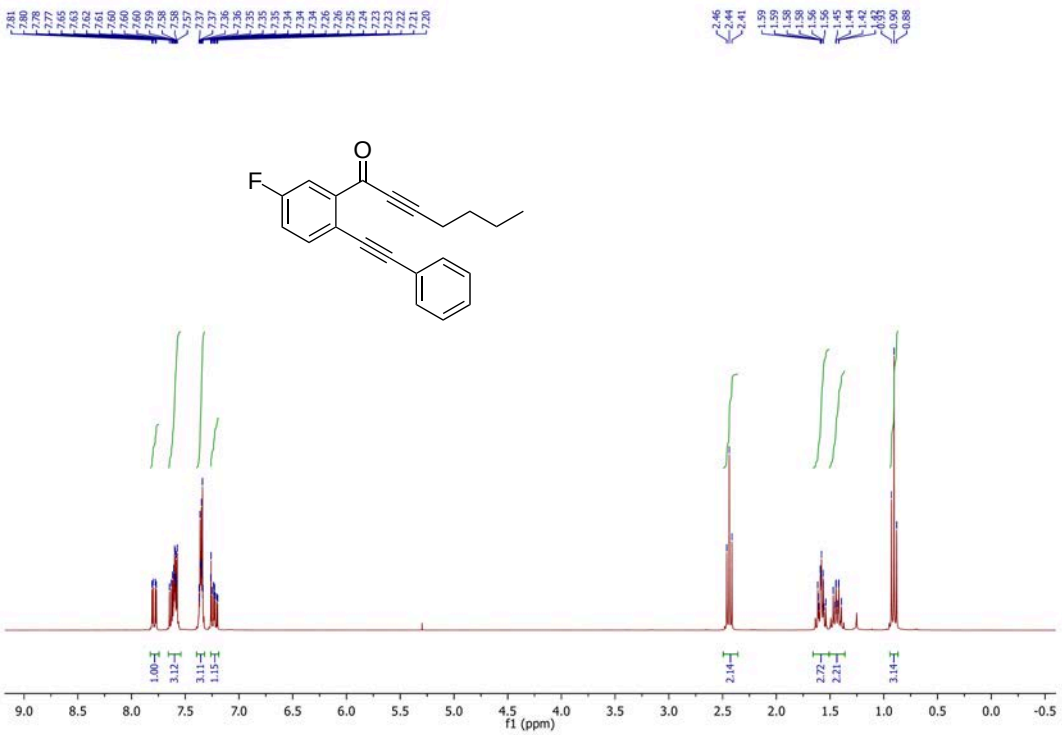
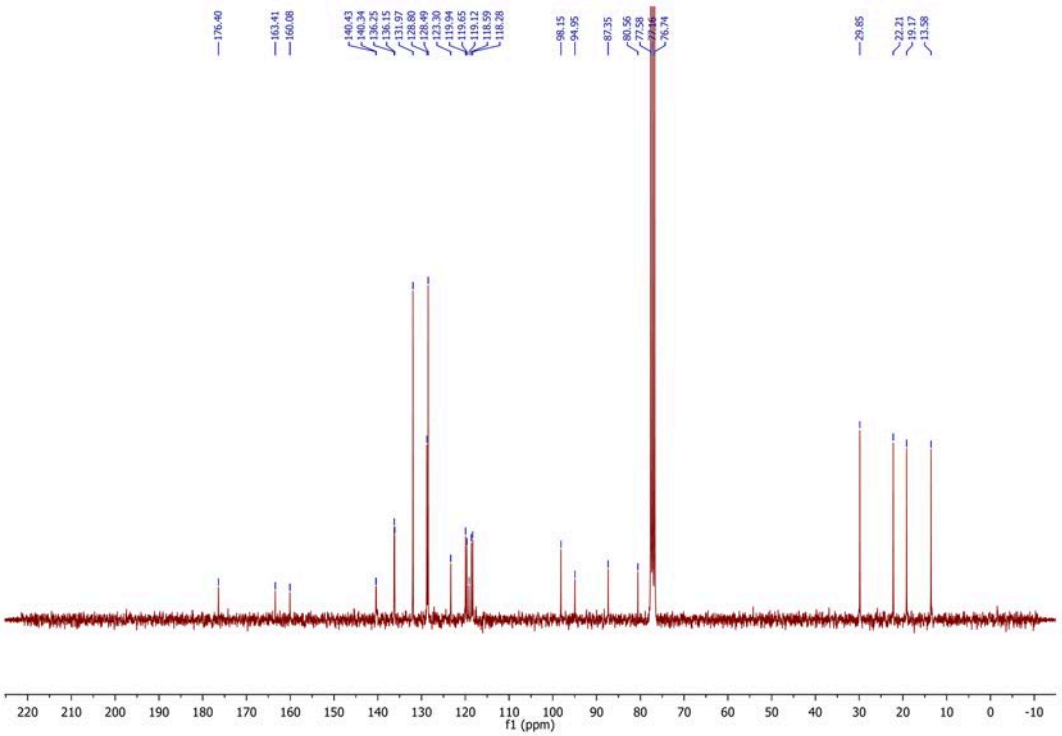
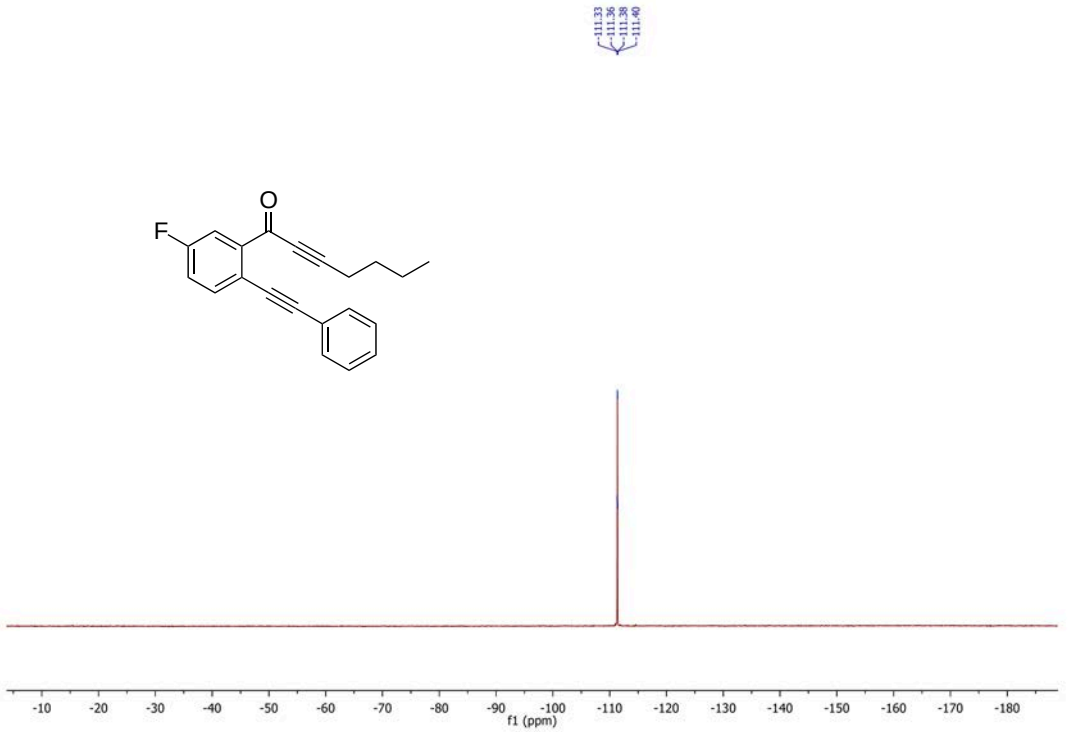
22.22
19.17
13.61
f1 (ppm)

1g

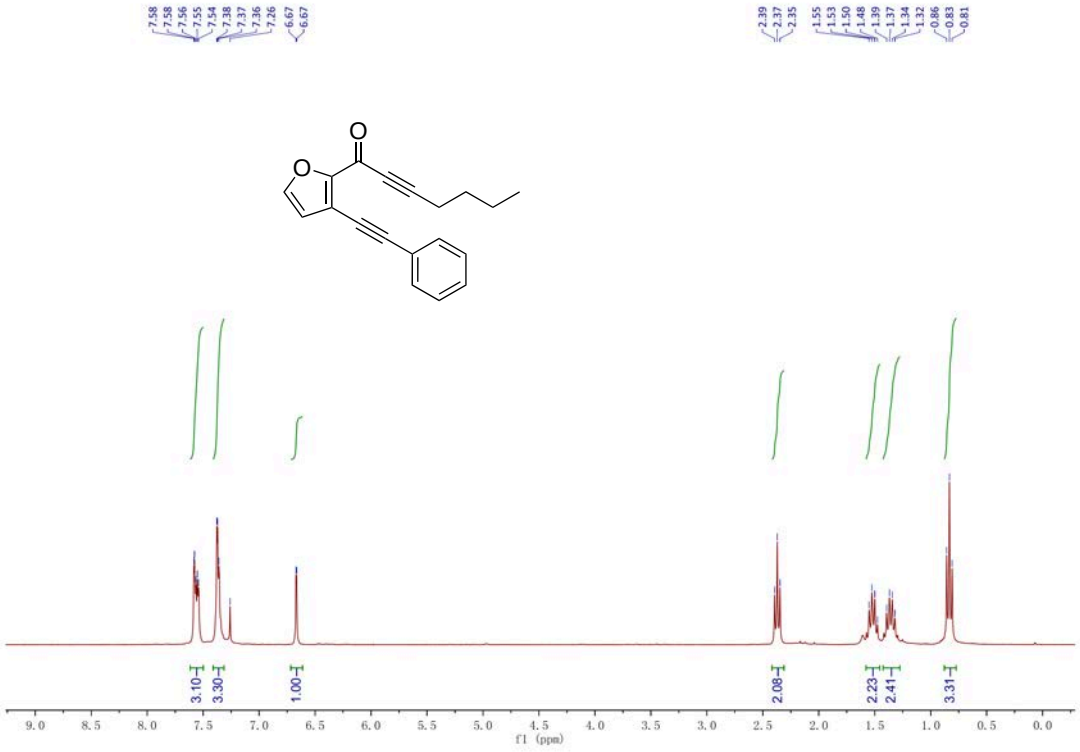


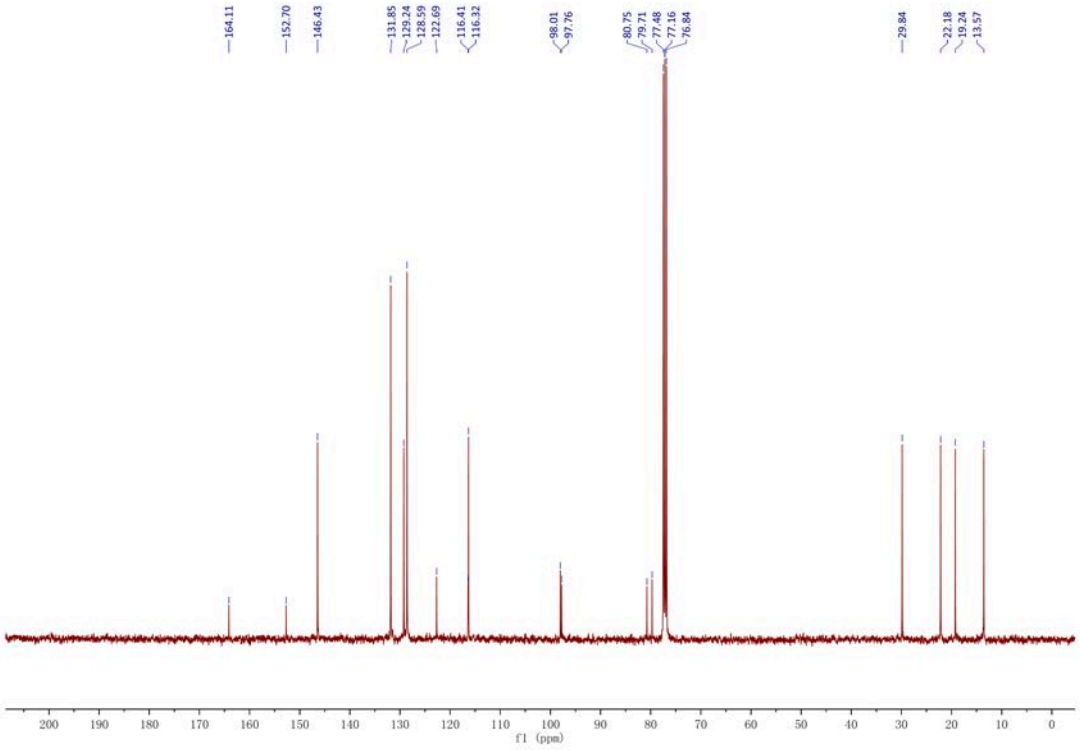


1g

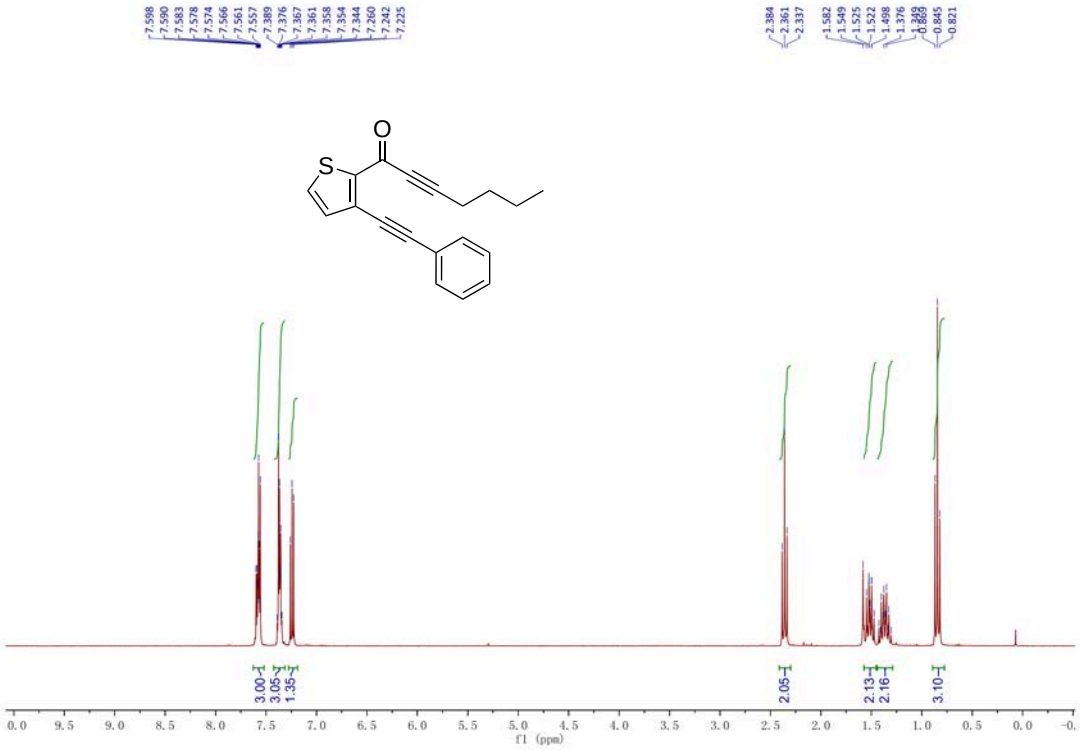

-111.33
-111.36
-111.38
-111.40
O
F
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

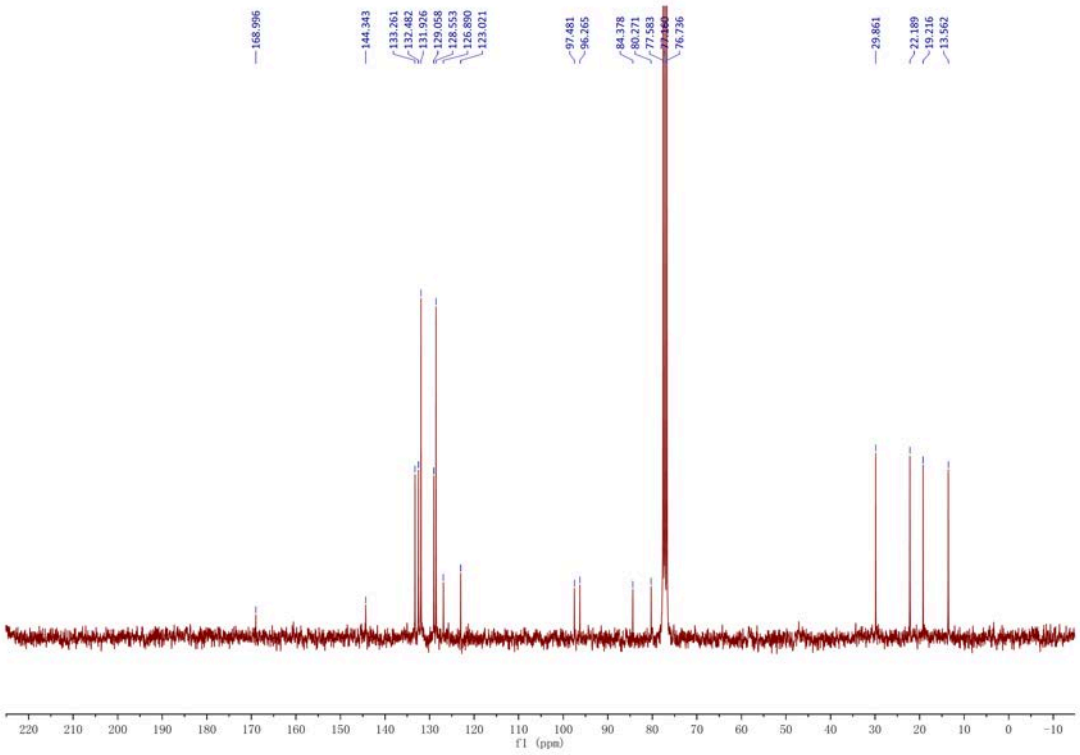
1h


7.58
7.58
7.56
7.55
7.54
7.38
7.37
7.36
7.26
6.67
6.67
2.39
2.37
2.35
1.55
1.53
1.50
1.48
1.39
1.37
1.34
1.32
0.86
0.83
0.81
O
O
3.10
3.30
1.00
2.08
2.23
2.41
3.31
f1 (ppm)

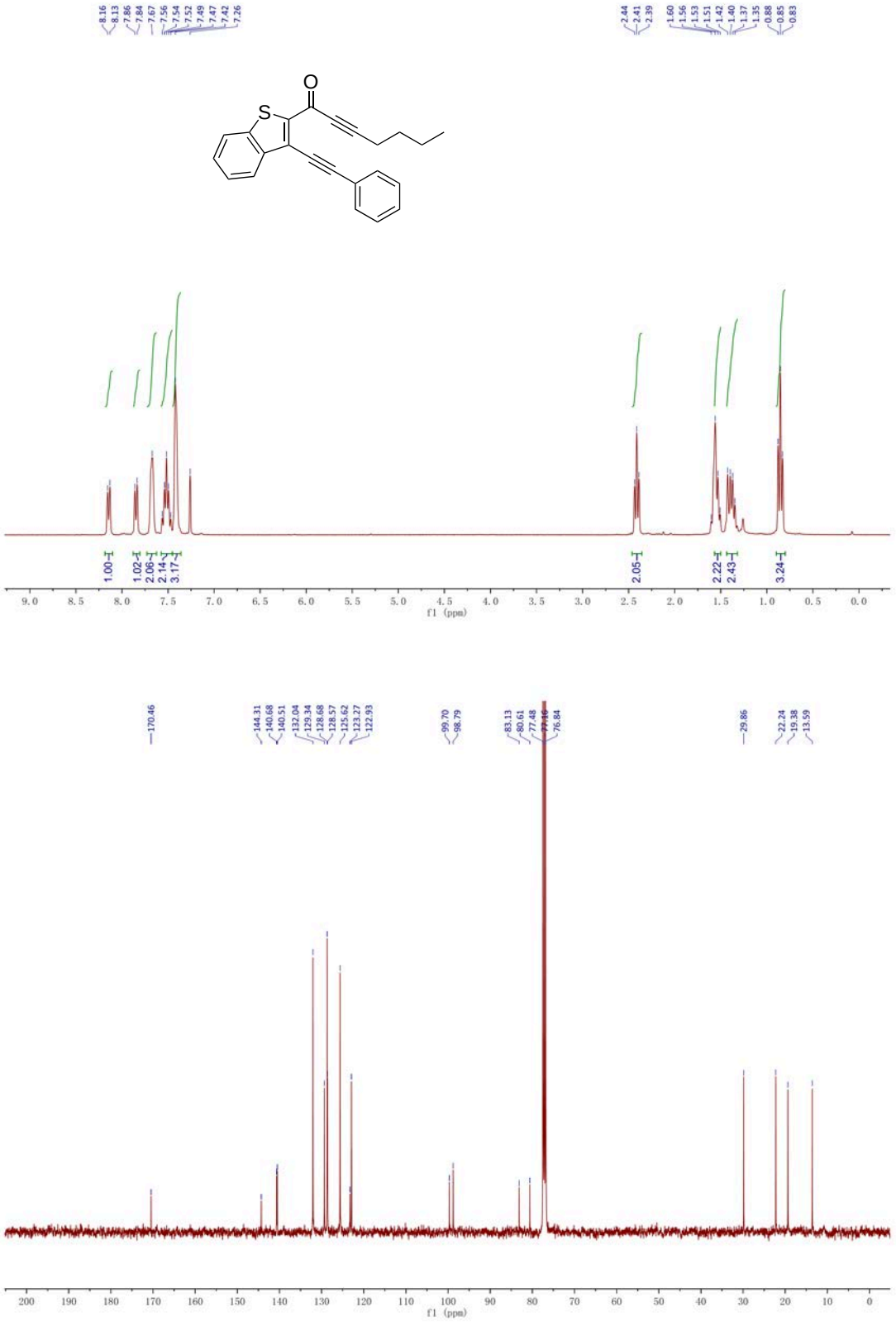

164.11
152.70
146.43
131.85
129.24
128.59
122.69
116.41
116.32
98.01
97.76
80.75
79.71
77.48
77.16
76.84
29.84
22.18
19.24
13.57
f1 (ppm)

1i

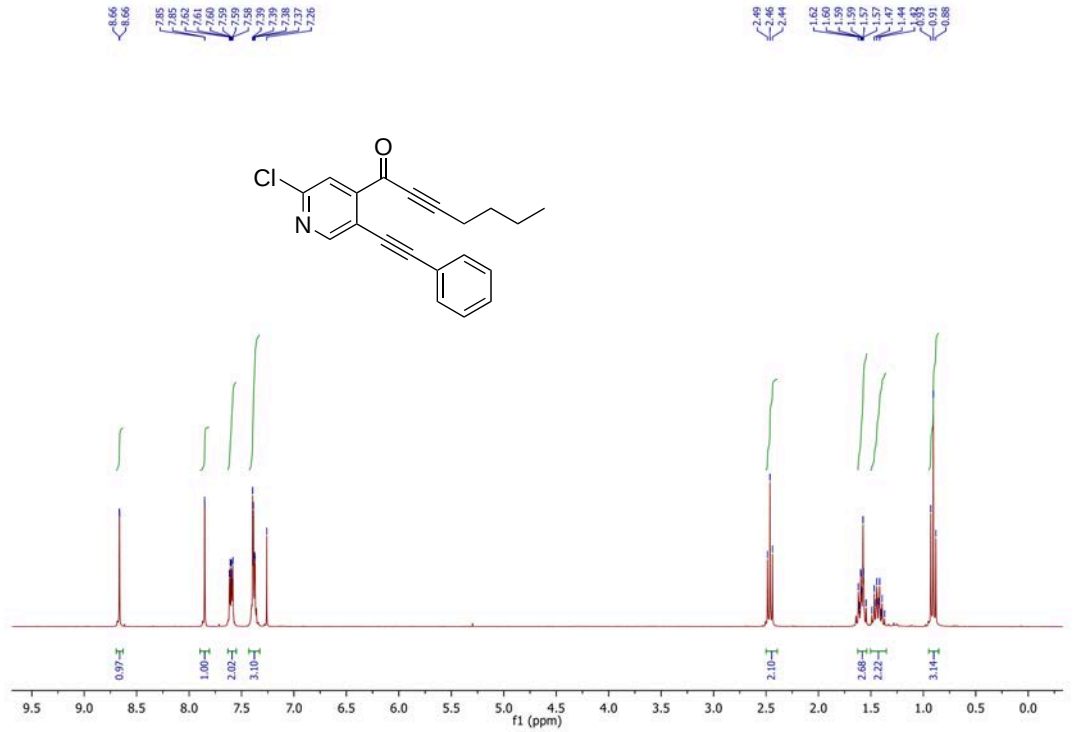

7.598
7.590
7.583
7.578
7.574
7.566
7.561
7.557
7.389
7.376
7.367
7.361
7.358
7.354
7.344
7.260
7.242
7.225
2.384
2.361
2.337
1.582
1.549
1.525
1.522
1.498
1.376
0.845
0.821
O
S
3.00
3.05
1.35
2.05
2.13
2.16
3.10
f1 (ppm)

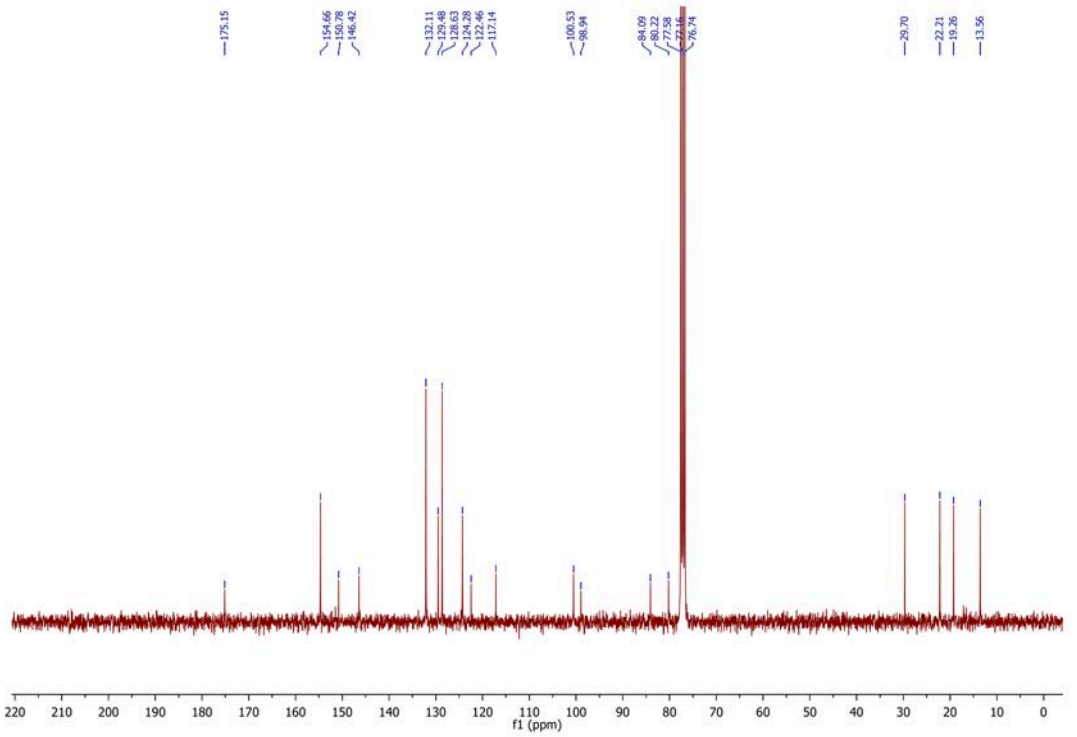

168.996
144.343
133.261
132.482
131.926
129.058
128.553
126.890
123.021
97.481
96.265
84.378
80.271
77.583
77.160
76.736
29.861
22.189
19.216
13.562
f1 (ppm)

1j

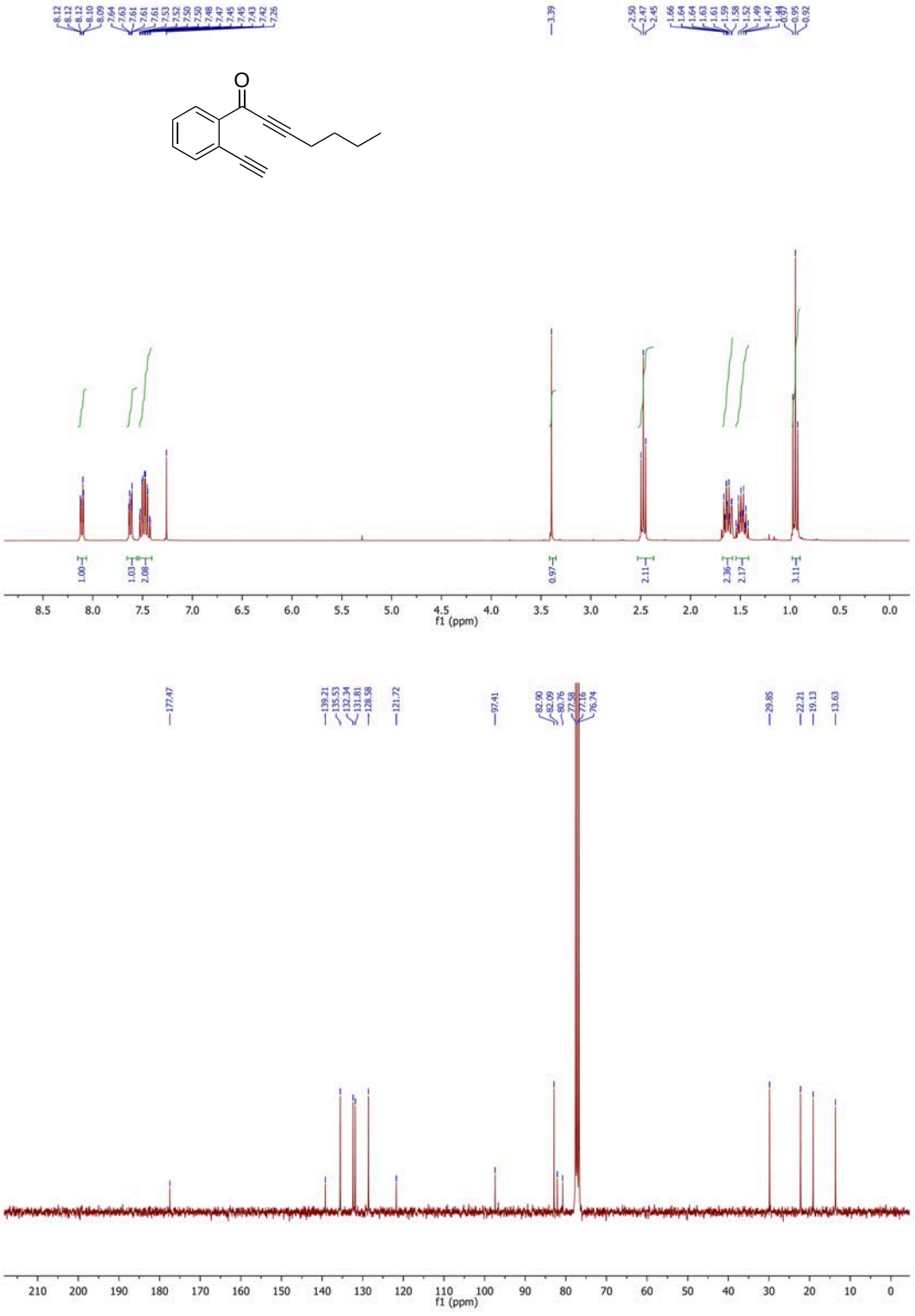

8.16
8.13
7.86
7.84
7.67
7.56
7.54
7.52
7.49
7.47
7.42
7.26
2.44
2.41
2.39
1.60
1.56
1.53
1.51
1.42
1.40
1.37
1.35
0.88
0.85
0.83
O
S
1.00
1.02
2.06
2.14
3.17
2.05
2.22
2.43
3.24
f1 (ppm)
170.46
144.31
140.68
140.51
132.04
129.34
128.68
128.57
125.62
123.27
122.93
99.70
98.79
83.13
80.61
77.48
77.16
76.84
29.86
22.24
19.38
13.59
f1 (ppm)

1k

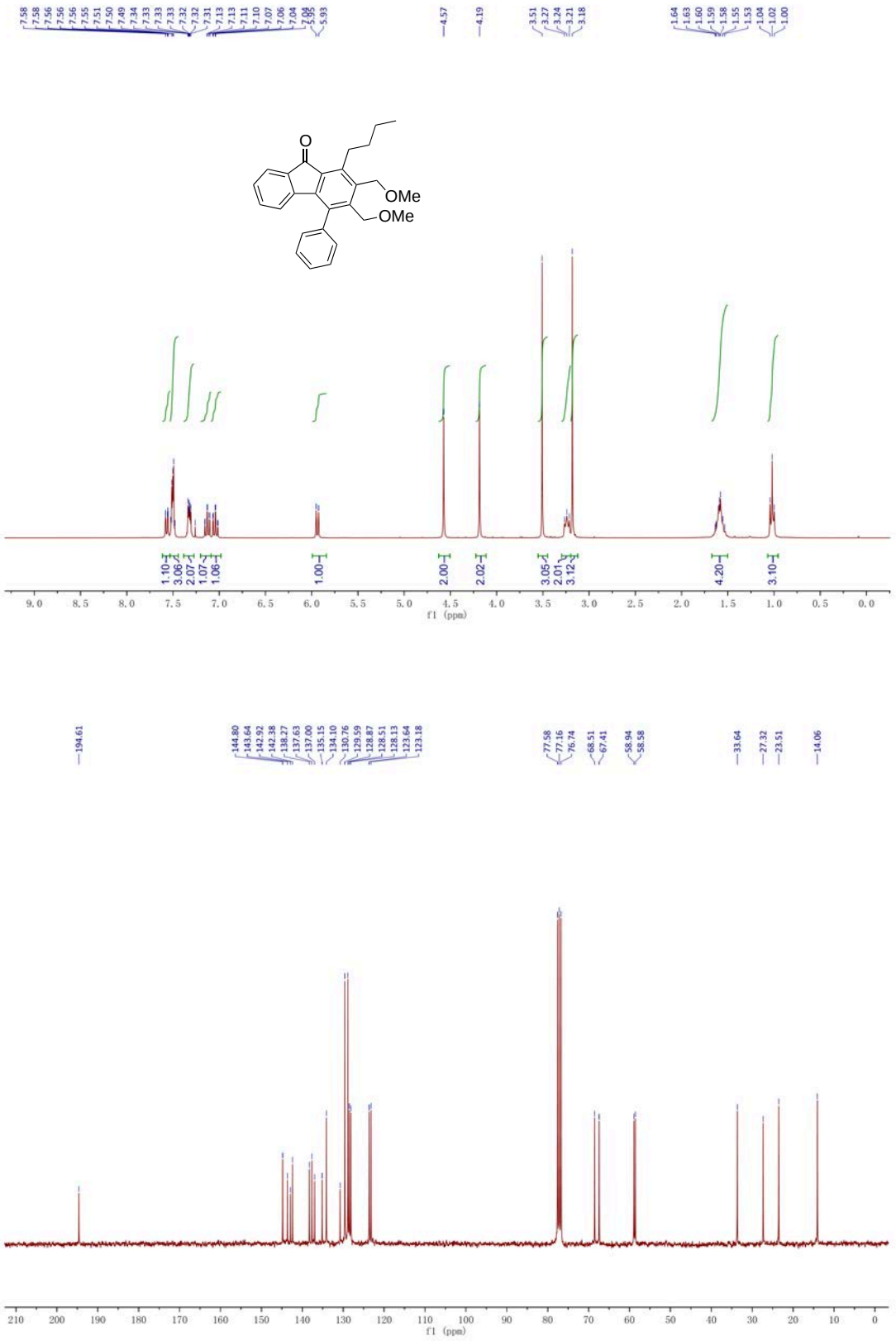

8.66
8.66
7.85
7.85
7.62
7.61
7.60
7.59
7.59
7.58
7.39
7.39
7.38
7.37
7.26
2.49
2.46
2.44
1.62
1.60
1.59
1.59
1.57
1.57
1.47
1.44
0.93
0.91
0.88
O
Cl
N
0.97
1.00
2.02
3.10
2.10
2.68
2.23
3.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


175.15
154.66
150.78
146.42
132.11
129.48
128.63
124.28
122.46
117.14
100.53
88.94
84.09
80.22
77.58
77.16
76.74
29.70
22.21
19.26
13.56
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

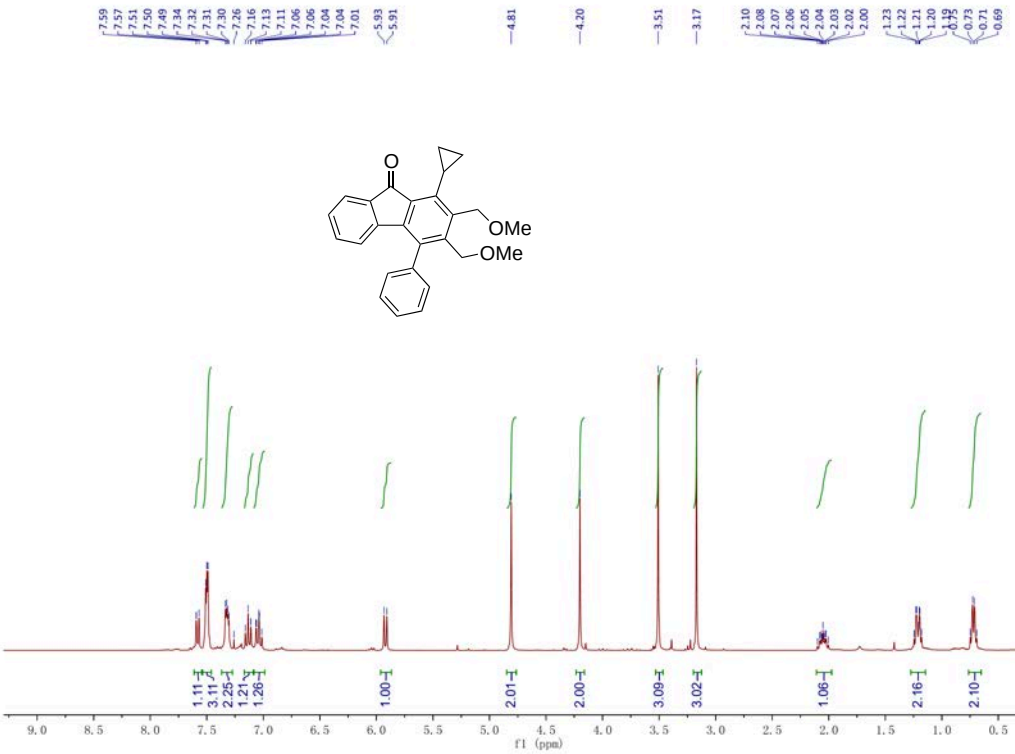
1l

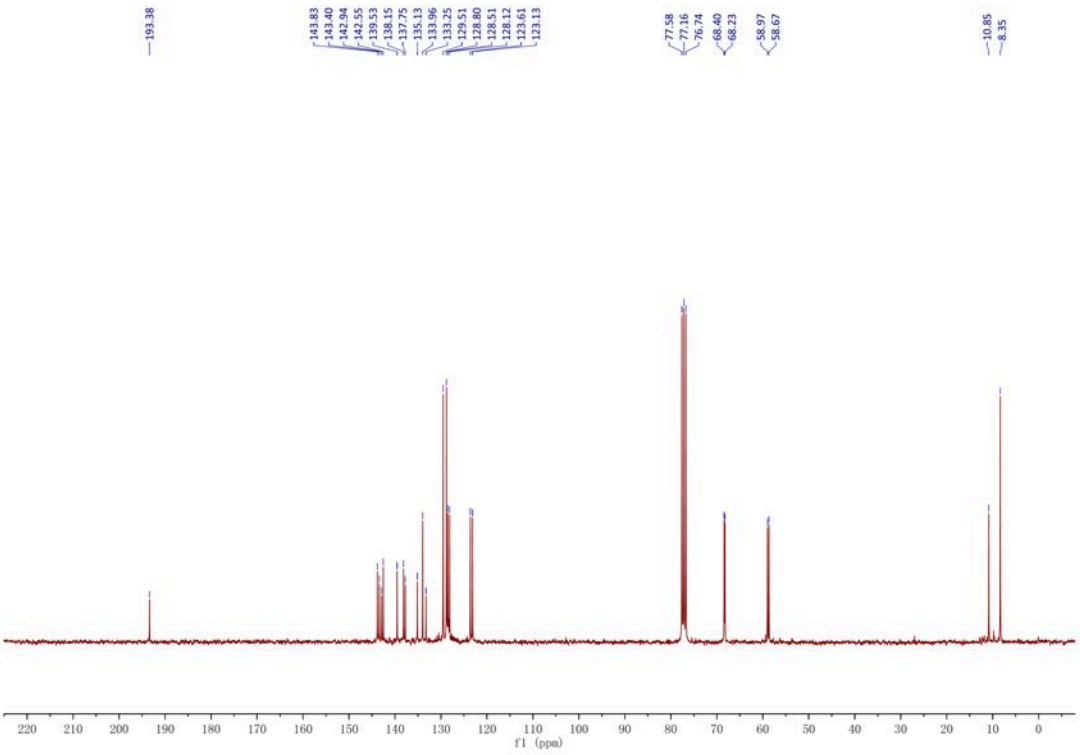


3a

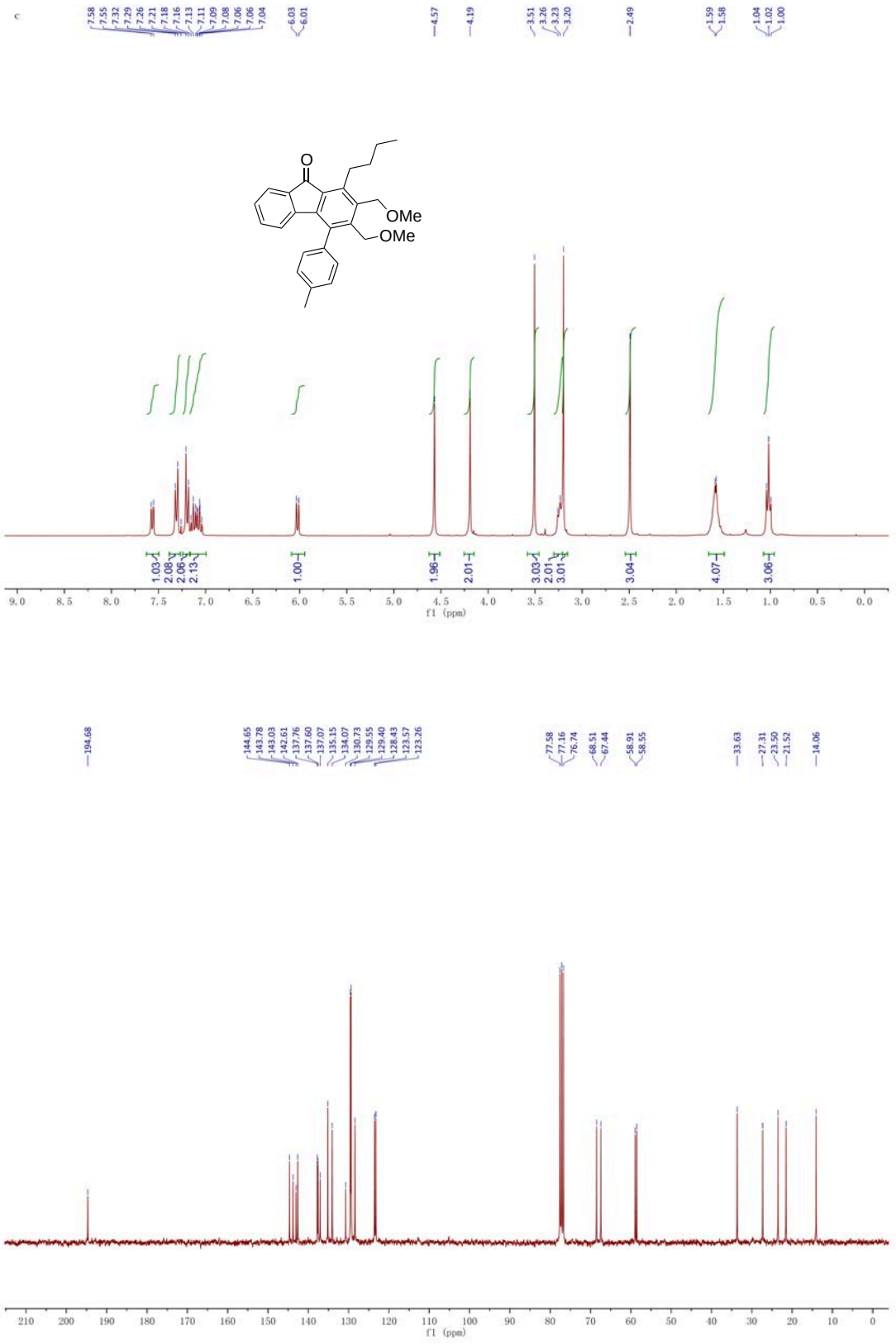


3b

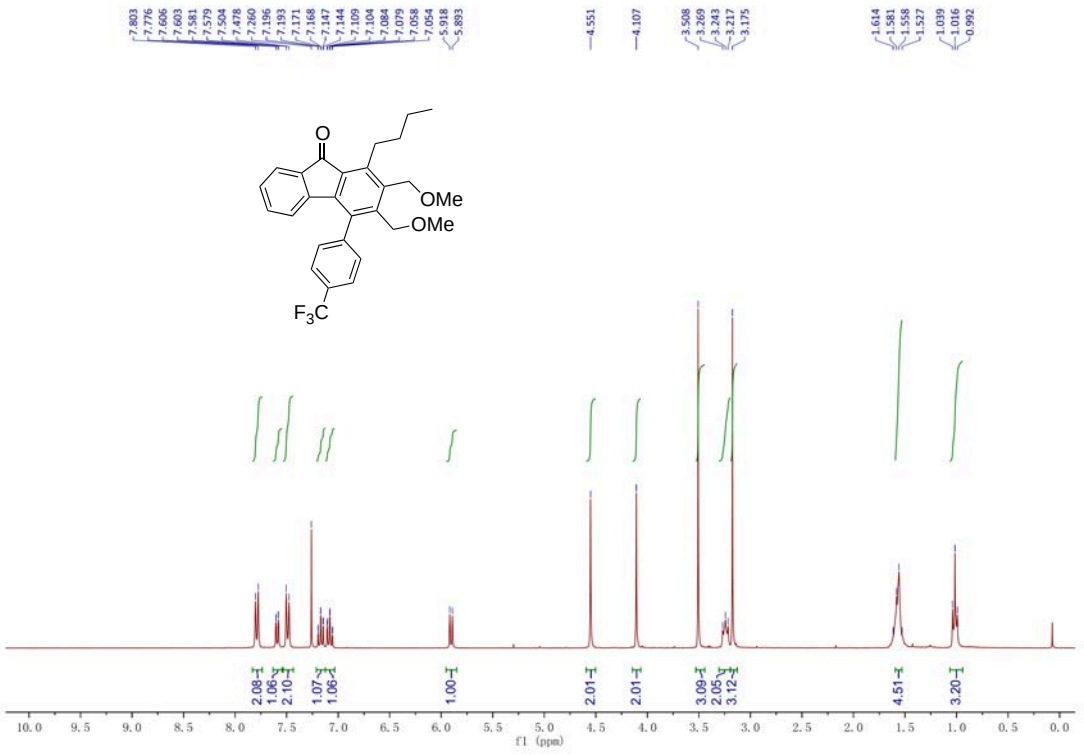

7.59
7.57
7.51
7.50
7.49
7.34
7.32
7.31
7.30
7.26
7.16
7.13
7.11
7.06
7.06
7.04
7.04
7.01
5.93
5.91
4.81
4.20
3.51
3.17
2.10
2.08
2.07
2.06
2.05
2.04
2.03
2.02
2.00
1.23
1.22
1.21
1.20
0.75
0.73
0.71
0.69
O
OMe
OMe
1.11
3.11
2.25
1.21
1.26
1.00
2.01
2.00
3.09
3.02
1.06
2.16
2.10
f1 (ppm)

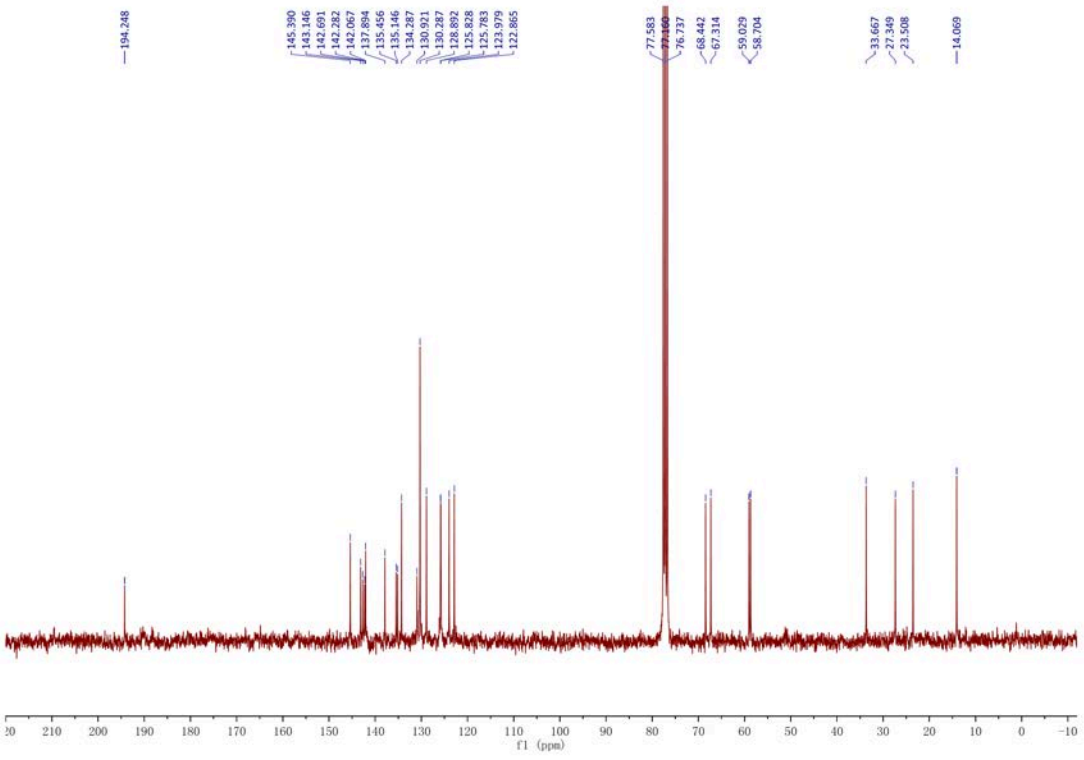

193.38
143.83
143.40
142.94
142.55
139.53
138.15
137.75
135.13
133.96
133.25
129.51
128.80
128.51
128.12
123.61
123.13
77.58
77.16
76.74
68.40
68.23
58.97
58.67
10.85
8.35
f1 (ppm)

3c

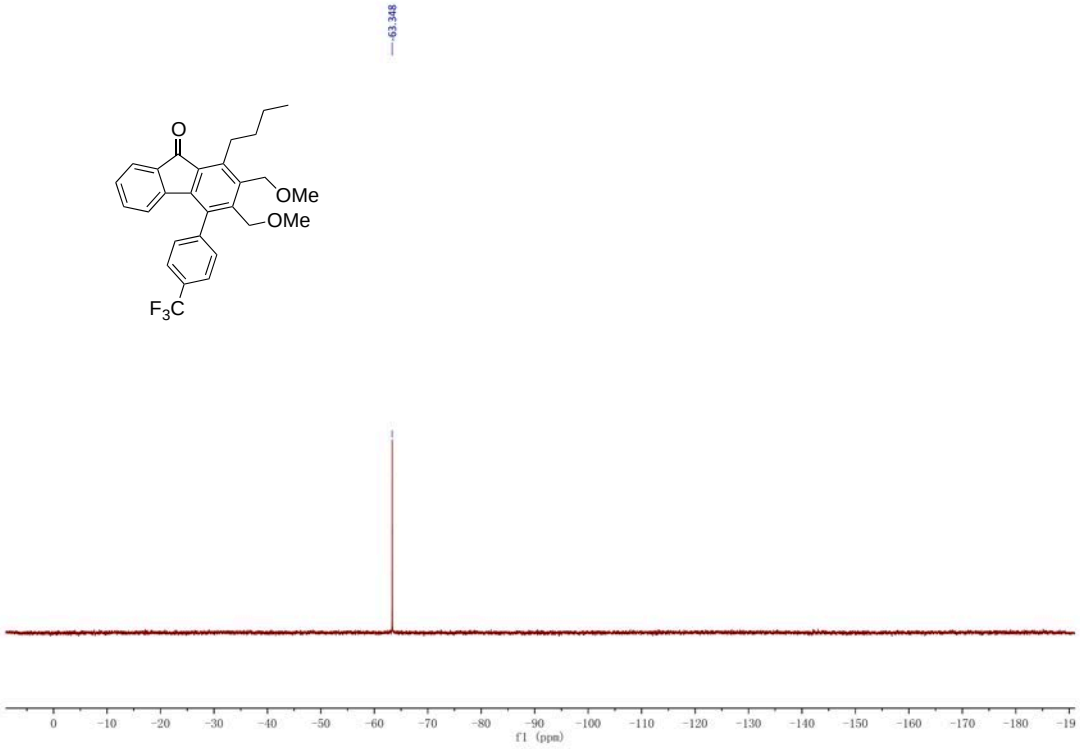

7.58
7.55
7.32
7.29
7.26
7.21
7.18
7.16
7.13
7.11
7.09
7.08
7.06
7.06
7.04
6.03
6.01
4.57
4.19
3.51
3.26
3.23
3.20
2.49
1.59
1.58
1.04
1.02
1.00
O
OMe
OMe
1.03
2.08
2.06
2.13
1.00
1.96
2.01
3.03
2.01
3.01
3.04
4.07
3.06
f1 (ppm)
194.68
144.65
143.78
143.03
142.61
137.76
137.60
137.07
135.15
134.07
130.73
129.55
129.40
128.43
123.57
123.26
77.58
77.16
76.74
68.51
67.44
58.91
58.55
33.63
27.31
23.50
21.52
14.06
f1 (ppm)

3**d**

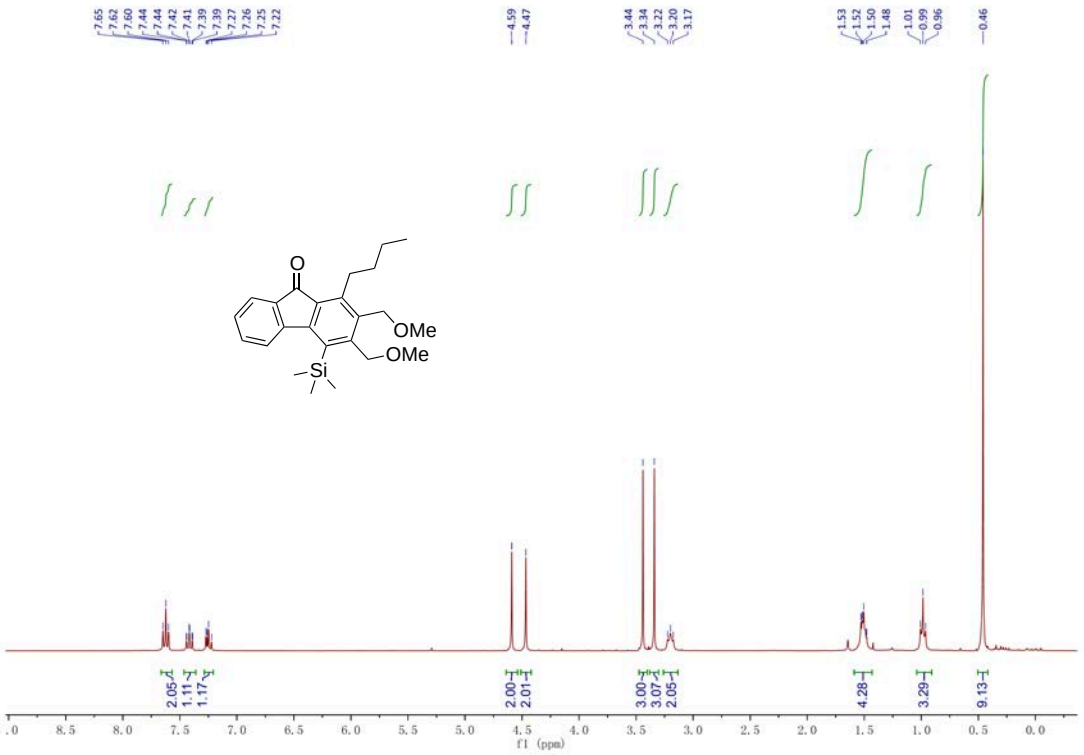

7.803
7.776
7.606
7.603
7.581
7.579
7.504
7.478
7.260
7.196
7.193
7.171
7.168
7.147
7.144
7.109
7.104
7.084
7.079
7.058
7.054
5.918
5.893
4.551
4.107
3.508
3.269
3.243
3.217
3.175
1.614
1.581
1.558
1.527
1.039
1.016
0.992
O
OMe
OMe
F3C
2.08
1.06
2.10
1.07
1.06
1.00
2.01
2.01
3.09
2.05
3.12
4.51
3.20
f1 (ppm)

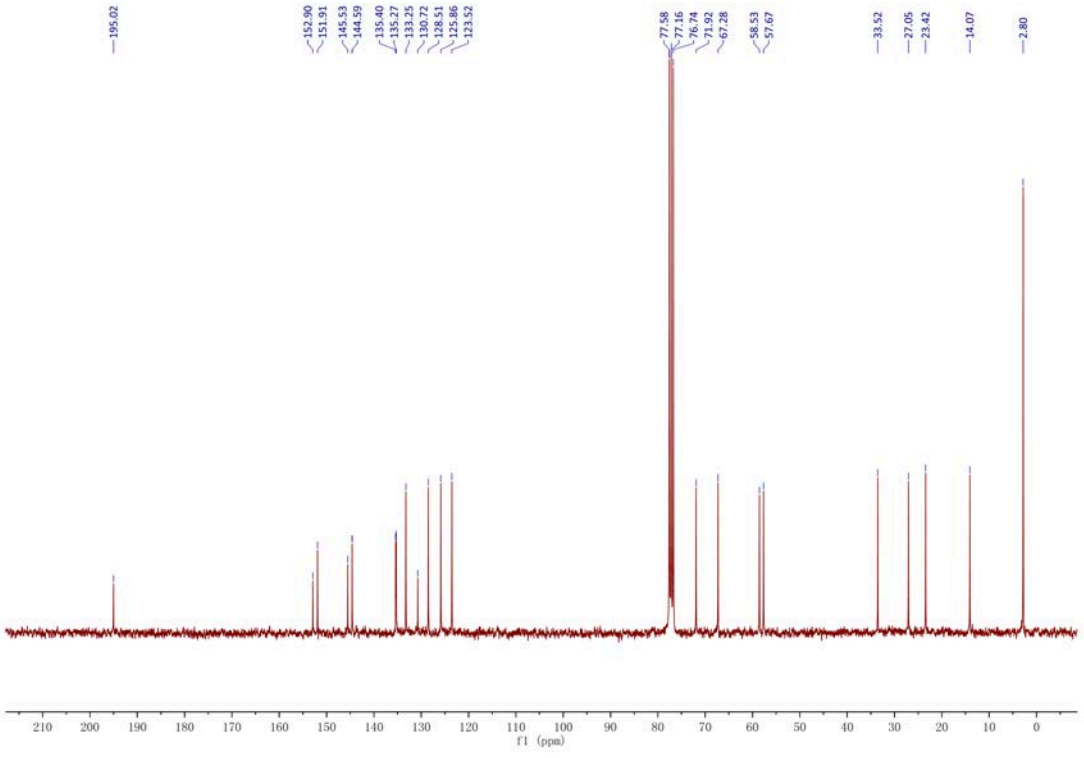

194.248
145.390
143.146
142.691
142.282
142.067
137.894
135.456
135.146
134.287
130.921
130.287
128.892
125.828
125.783
123.979
122.865
77.583
77.160
76.737
68.442
67.314
59.029
58.704
33.667
27.349
23.508
14.069
f1 (ppm)

3d

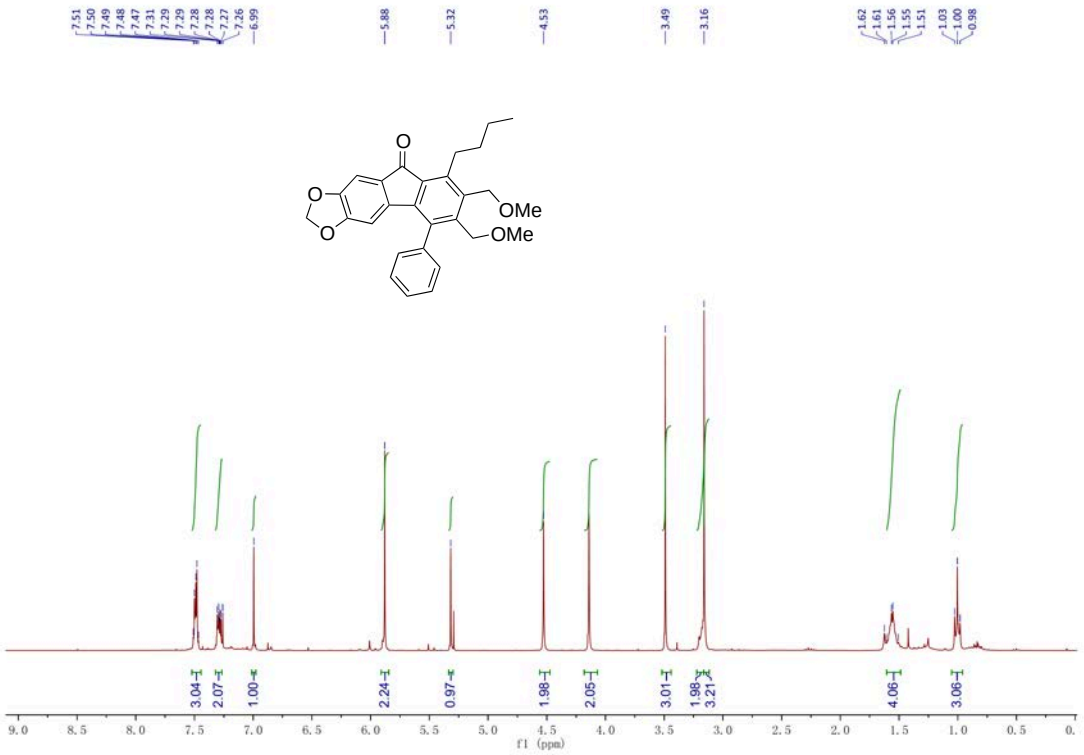

-63.348
O
OMe
OMe
F3C
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-19
f1 (ppm)

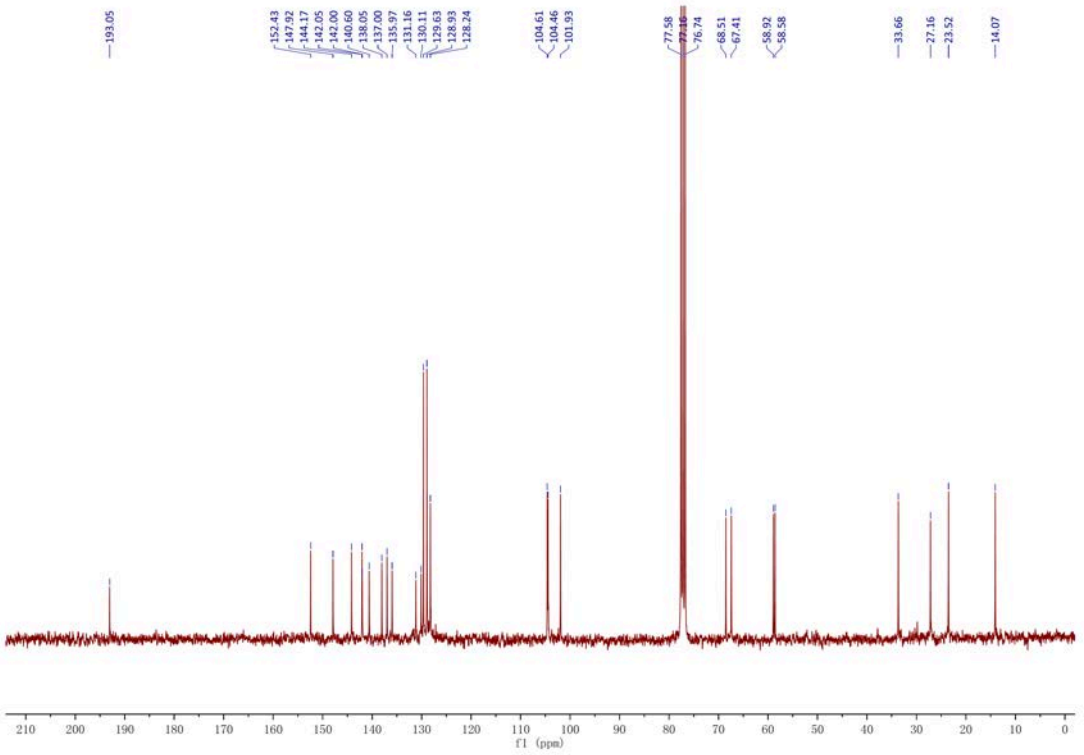
3e


7.65
7.62
7.60
7.44
7.42
7.41
7.39
7.39
7.27
7.26
7.25
7.22
4.59
4.47
3.44
3.34
3.22
3.20
3.17
1.53
1.52
1.50
1.48
1.01
0.99
0.96
0.46
O
OMe
OMe
Si
2.05
1.11
1.17
2.00
2.01
3.00
3.07
2.05
4.28
3.29
9.13
f1 (ppm)

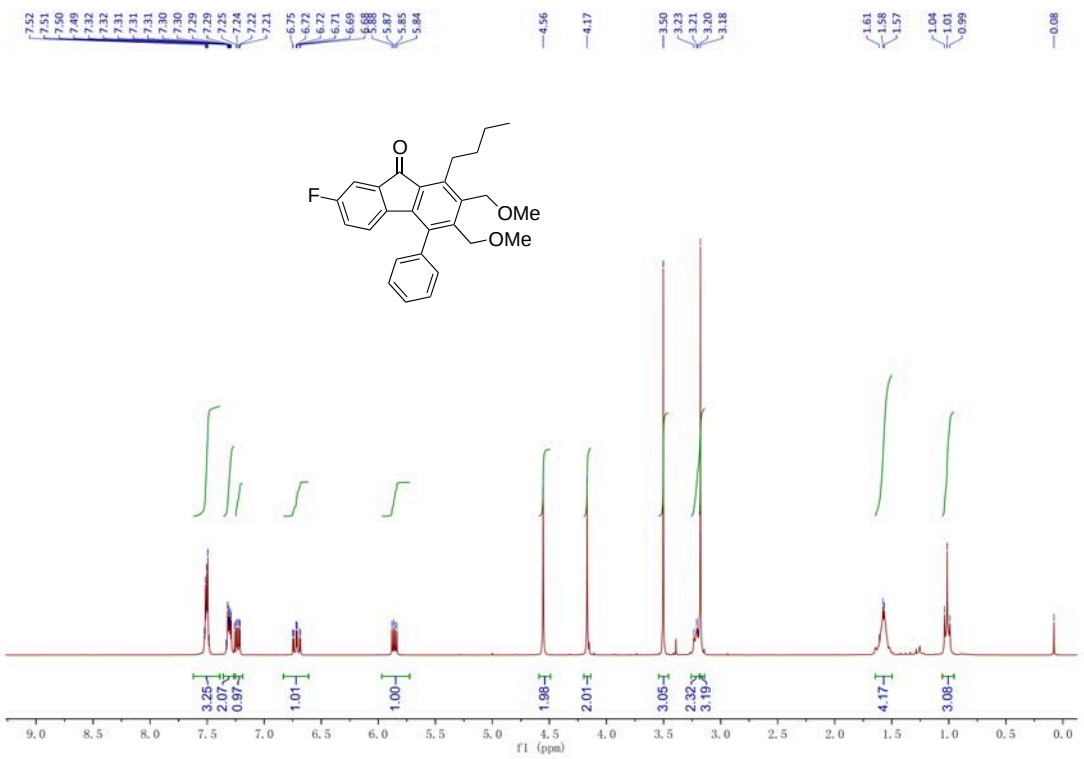

195.02
152.90
151.91
145.53
144.59
135.40
135.27
133.25
130.72
128.51
125.86
123.52
77.58
77.16
76.74
71.92
67.28
58.53
57.67
33.52
27.05
23.42
14.07
2.80
f1 (ppm)

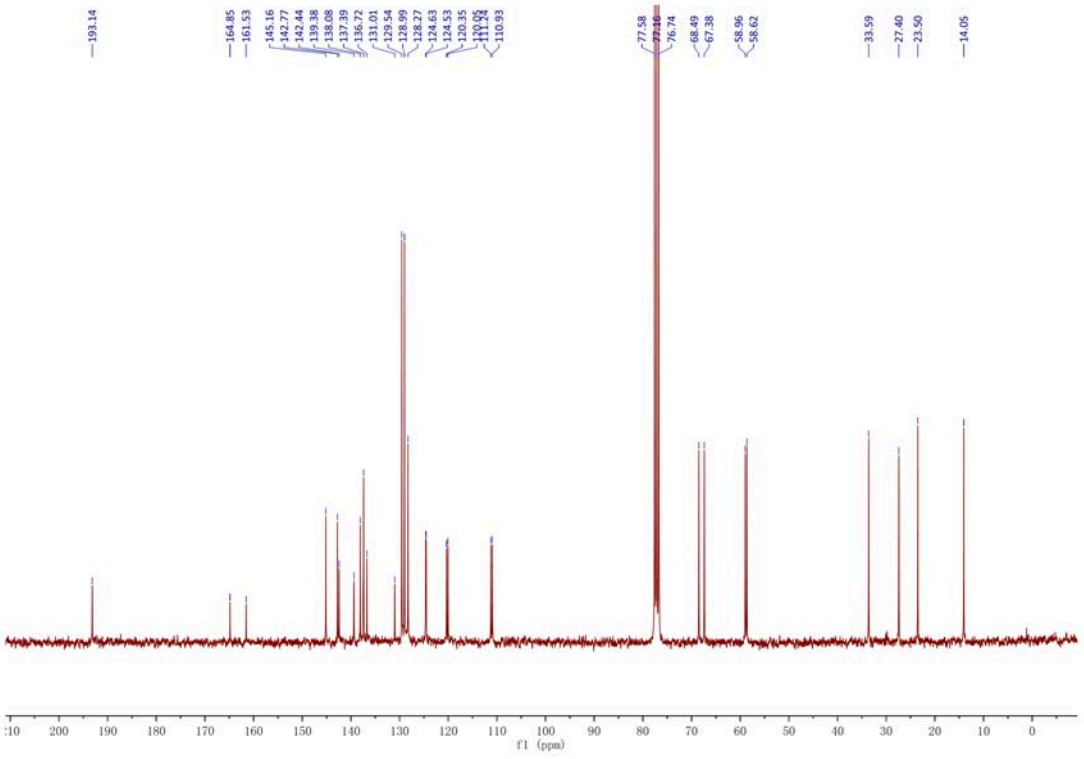
3f


7.51
7.50
7.49
7.48
7.47
7.31
7.29
7.29
7.28
7.28
7.27
7.26
6.99
5.88
5.32
4.53
3.49
3.16
1.62
1.61
1.56
1.55
1.51
1.03
1.00
0.98
O
O
O
OMe
OMe
3.04
2.07
1.00
2.24
0.97
1.98
2.05
3.01
1.98
3.21
4.06
3.06
f1 (ppm)

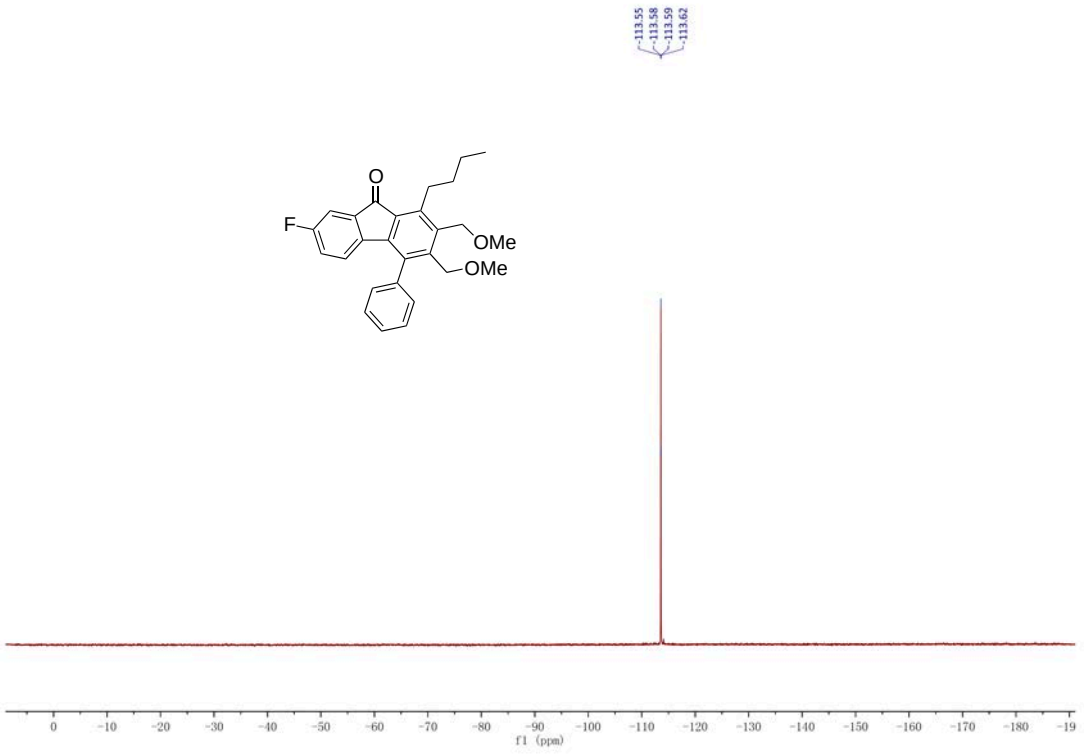

193.05
152.43
147.92
144.17
142.05
142.00
140.60
138.05
137.00
135.97
131.16
130.11
129.63
128.93
128.24
104.61
104.46
101.93
77.58
77.16
76.74
68.51
67.41
58.92
58.58
33.66
27.16
23.52
14.07
f1 (ppm)

3g

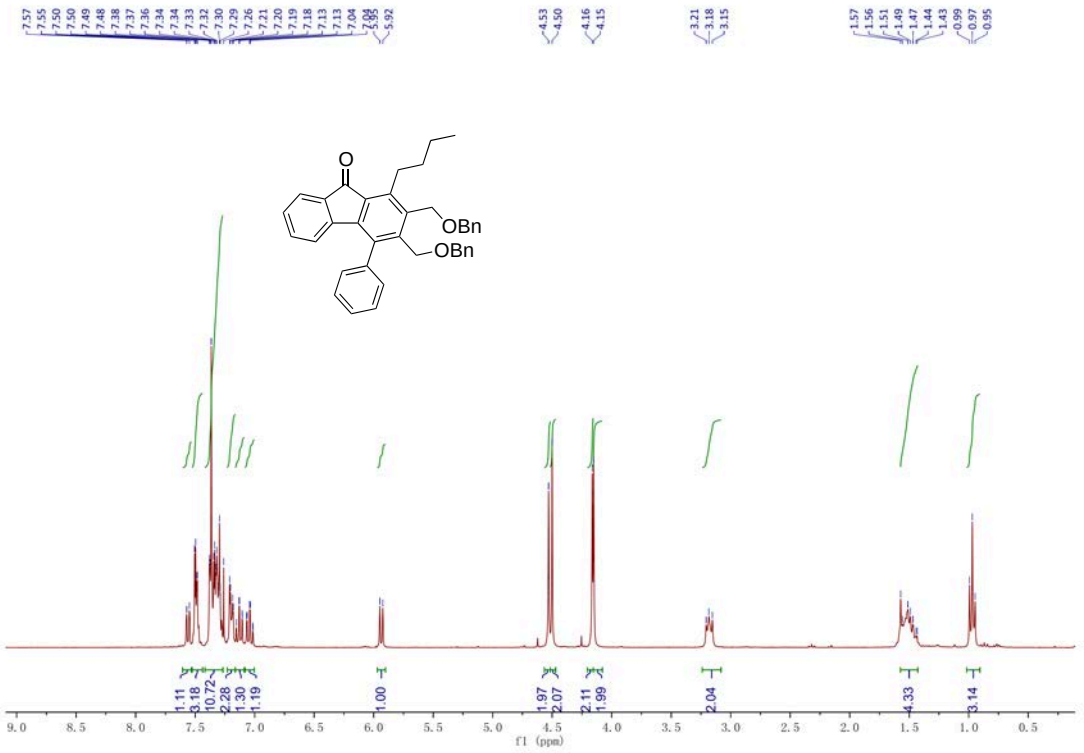

7.52
7.51
7.50
7.49
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.29
7.25
7.24
7.22
7.21
6.75
6.72
6.72
6.71
6.69
5.88
5.87
5.85
5.84
4.56
4.17
3.50
3.23
3.21
3.20
3.18
1.61
1.58
1.57
1.04
1.01
0.99
0.08
O
F
OMe
OMe
3.25
2.07
0.97
1.01
1.00
1.98
2.01
3.05
2.32
3.19
4.17
3.08
f1 (ppm)

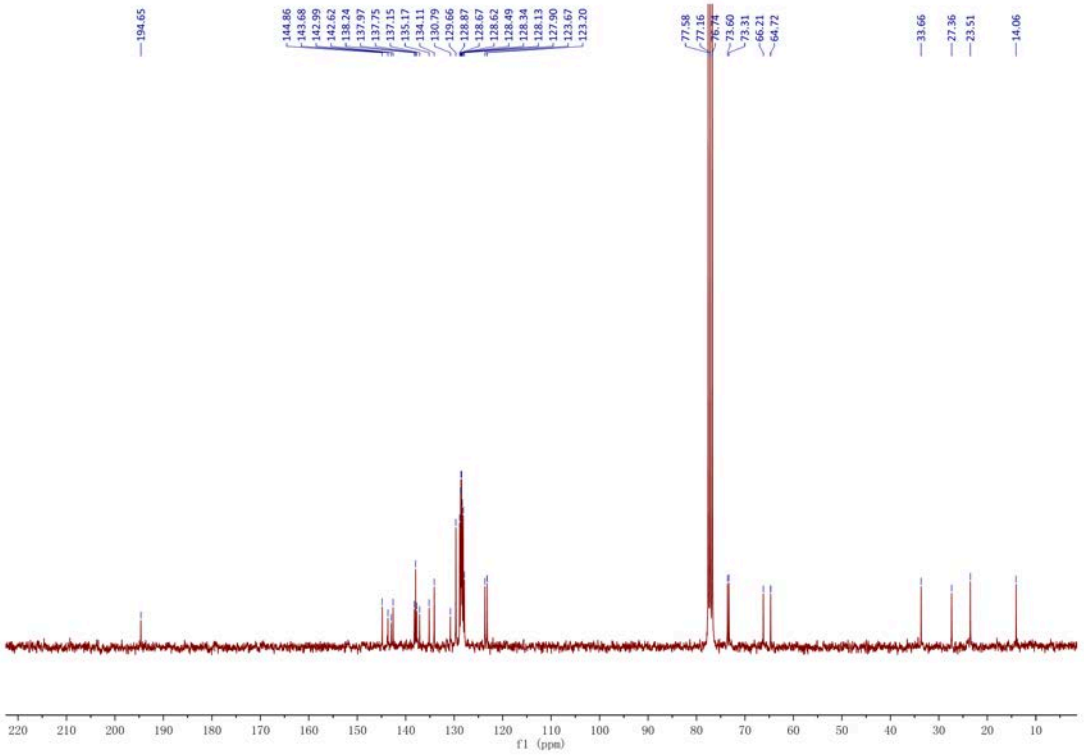

193.14
164.85
161.53
145.16
142.77
142.44
139.38
138.08
137.39
136.72
131.01
129.54
128.99
128.27
124.63
124.53
120.35
110.93
77.58
77.16
76.74
68.49
67.38
58.96
58.62
33.59
27.40
23.50
14.05
f1 (ppm)

3g

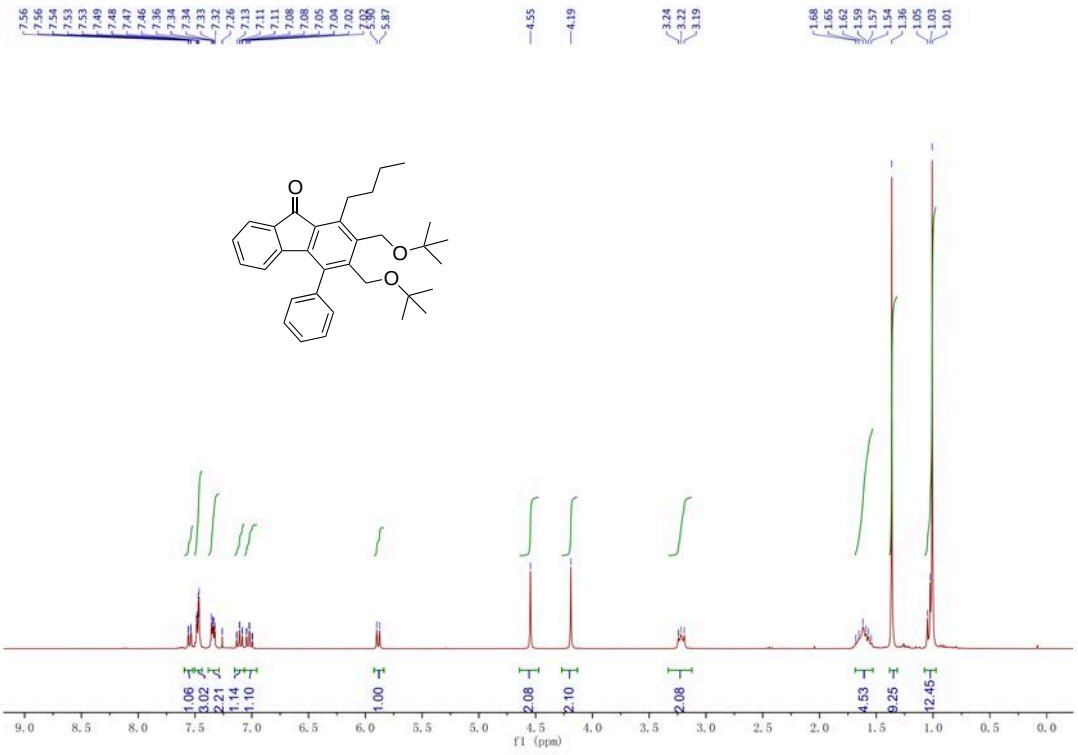

-113.55
-113.58
-113.59
-113.62
O
F
OMe
OMe
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-19
f1 (ppm)

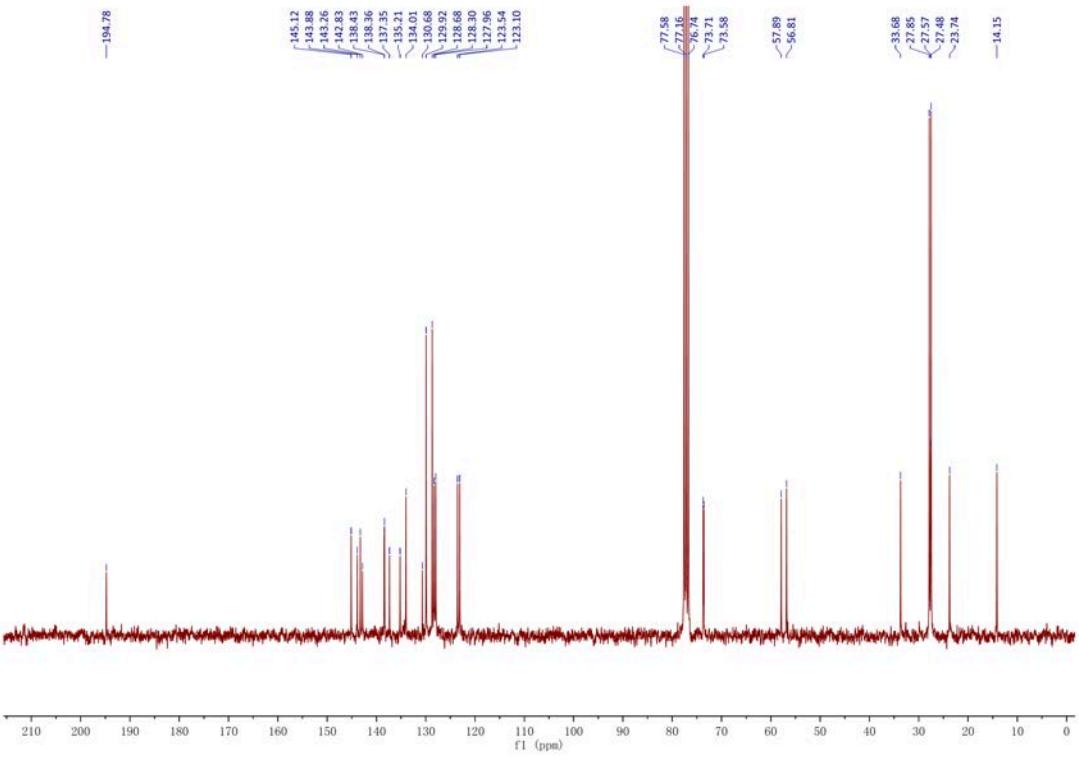
3h



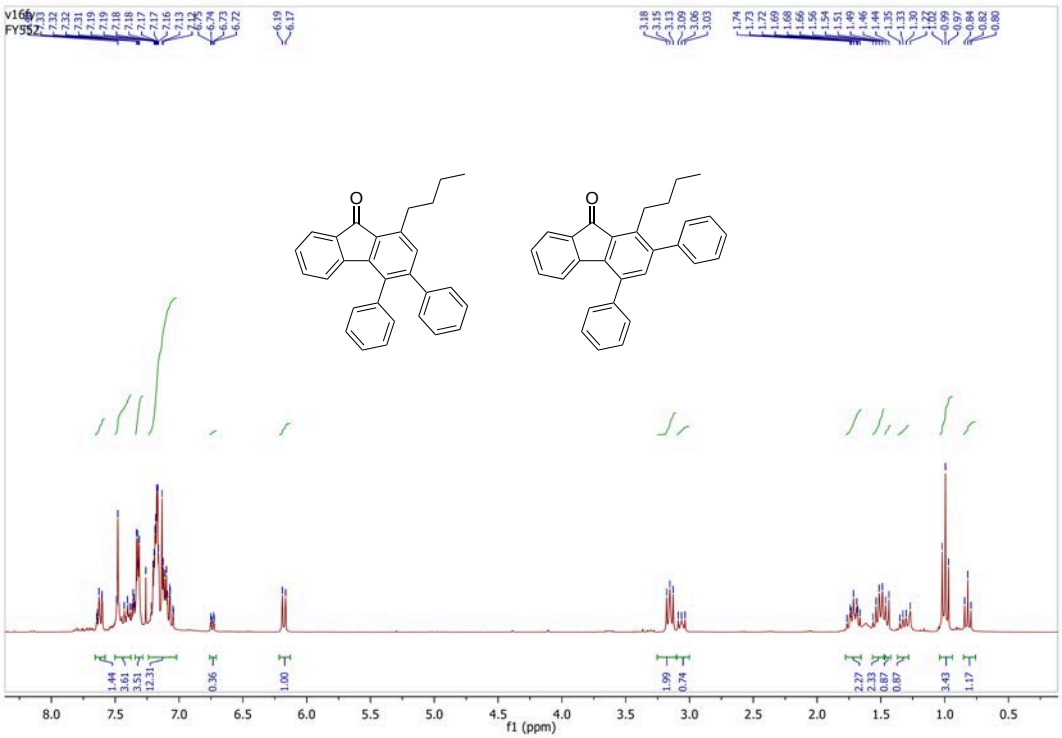


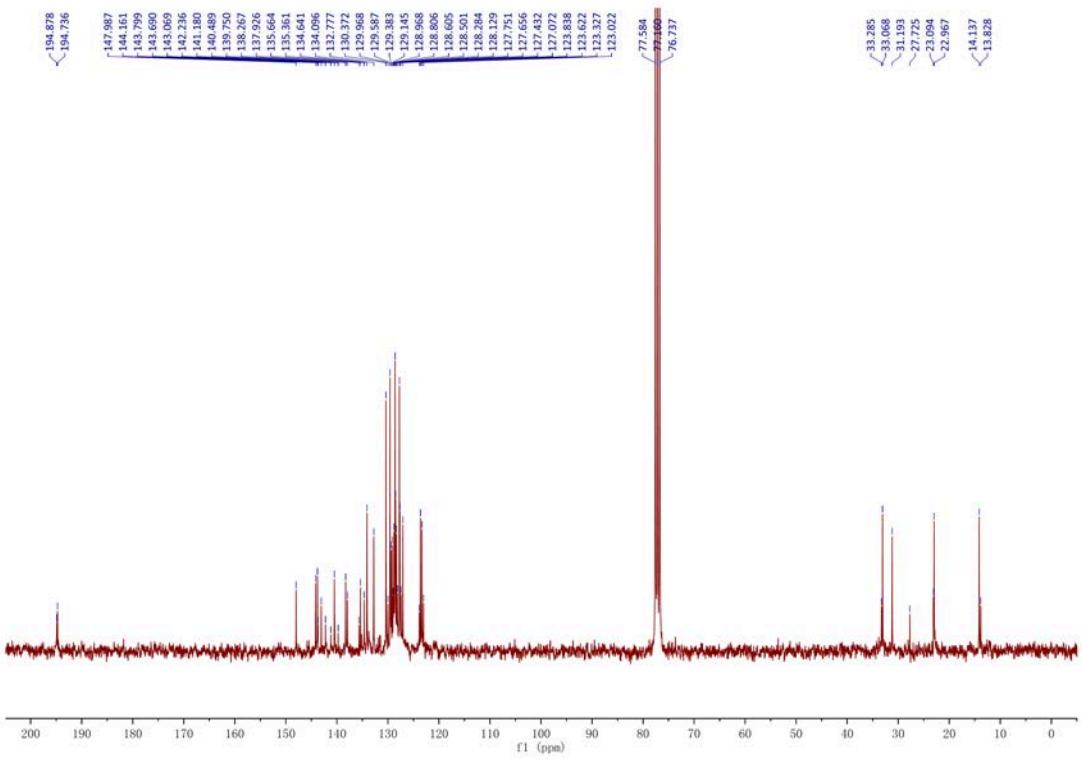
3i


7.56
7.56
7.54
7.53
7.53
7.49
7.48
7.47
7.46
7.36
7.34
7.34
7.33
7.32
7.26
7.13
7.11
7.11
7.08
7.08
7.05
7.04
7.02
5.90
5.87
4.55
4.19
3.24
3.22
3.19
1.68
1.65
1.62
1.59
1.57
1.54
1.36
1.05
1.03
1.01
O
O
O
1.06
3.02
2.21
1.14
1.10
1.00
2.08
2.10
2.08
4.53
9.25
12.45
f1 (ppm)

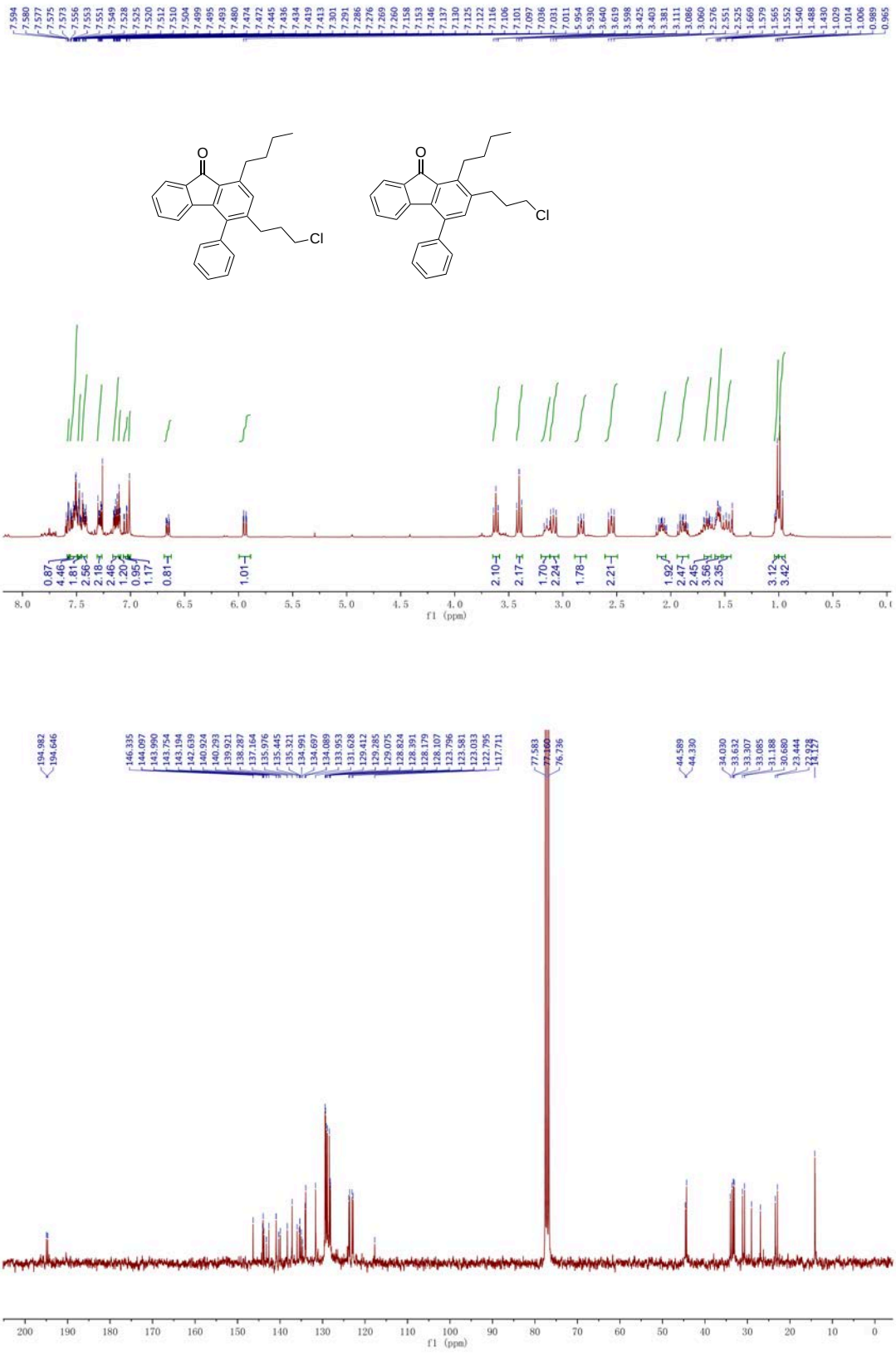

194.78
145.12
143.88
143.26
142.83
138.43
138.36
137.35
135.21
134.01
130.68
129.92
128.68
128.30
127.96
123.54
123.10
77.58
77.16
76.74
73.71
73.58
57.89
56.81
33.68
27.85
27.57
27.48
23.74
14.15
f1 (ppm)

3j





3k



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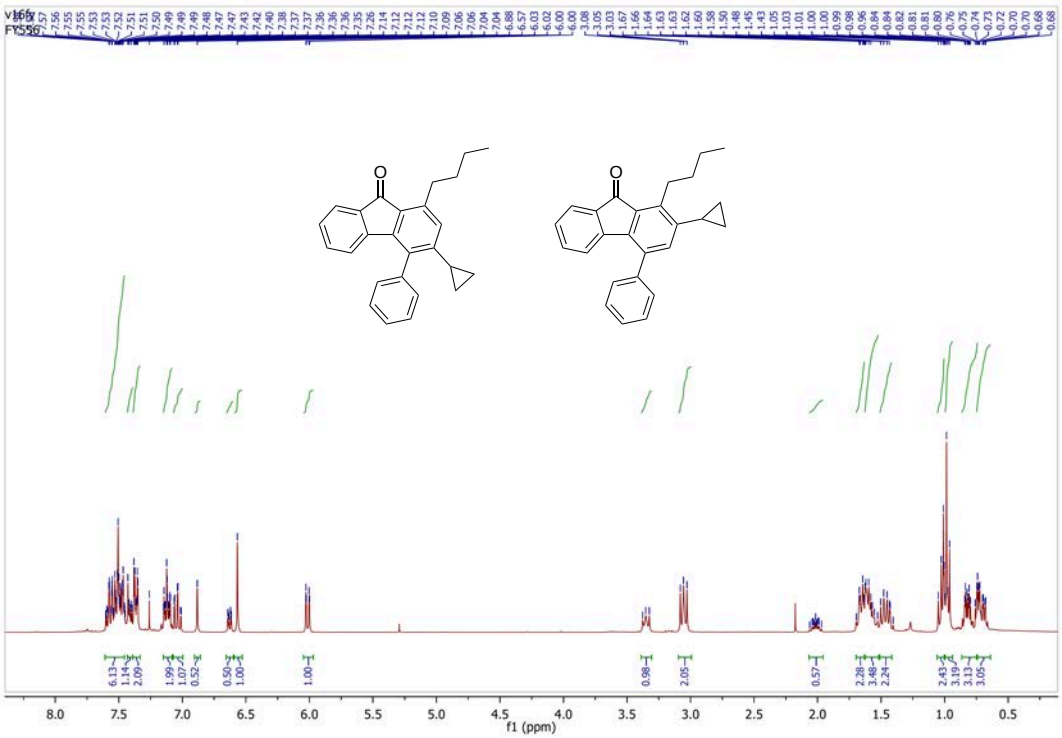
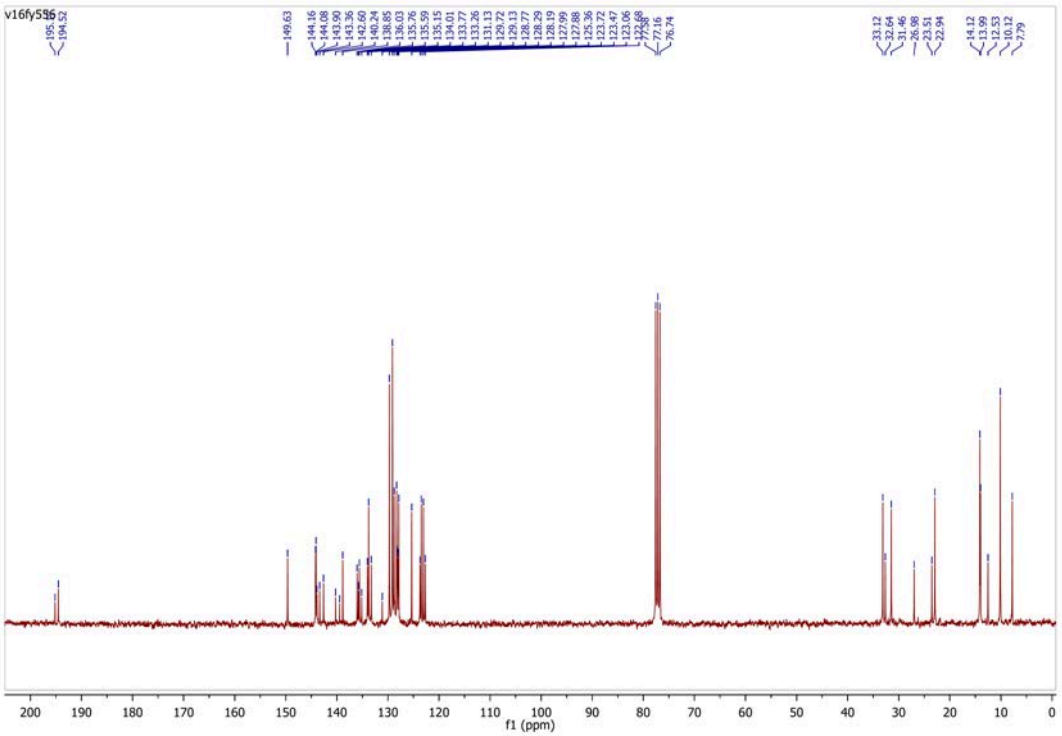
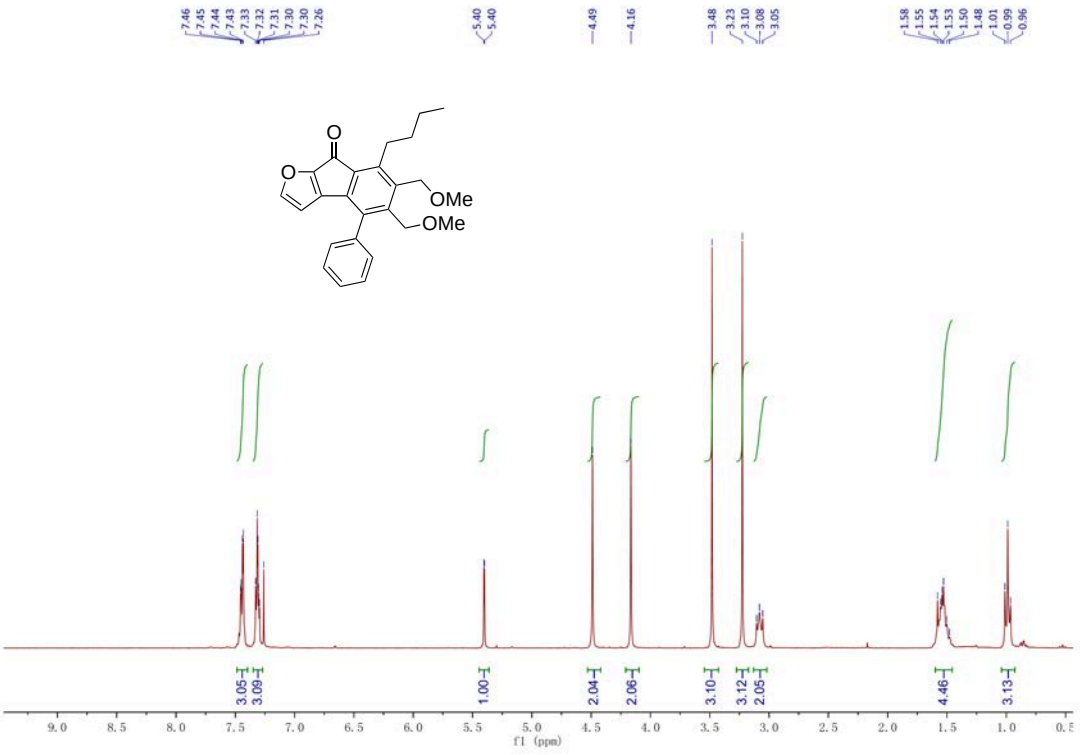




3m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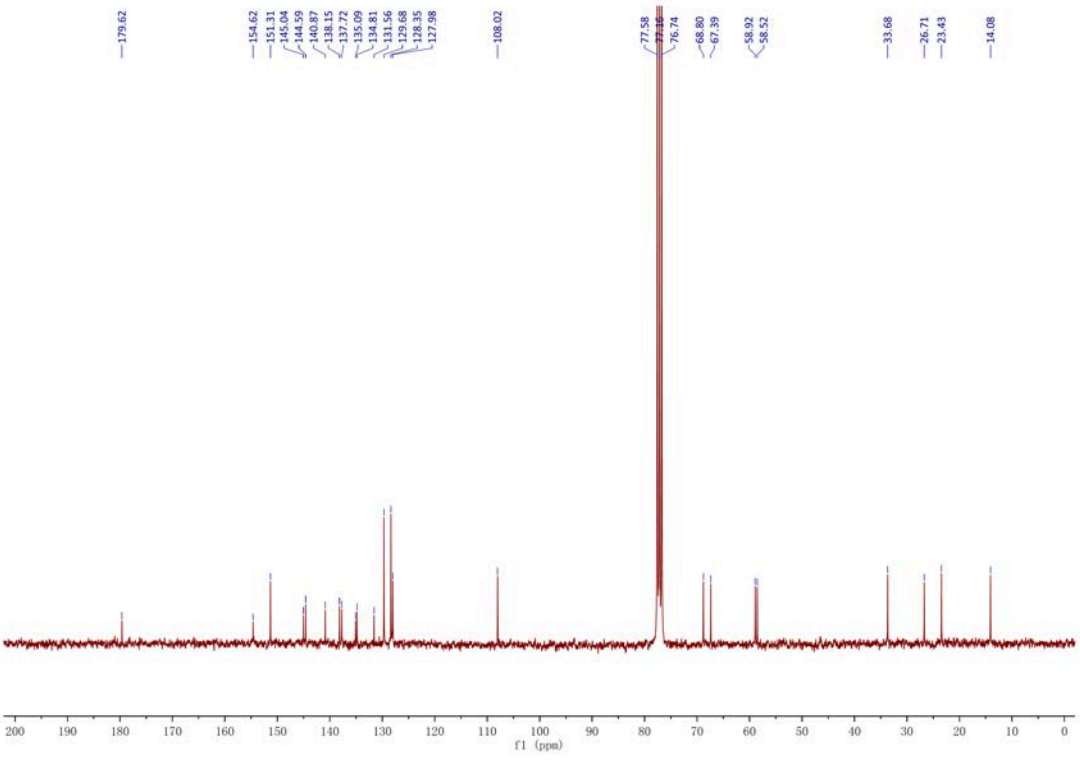
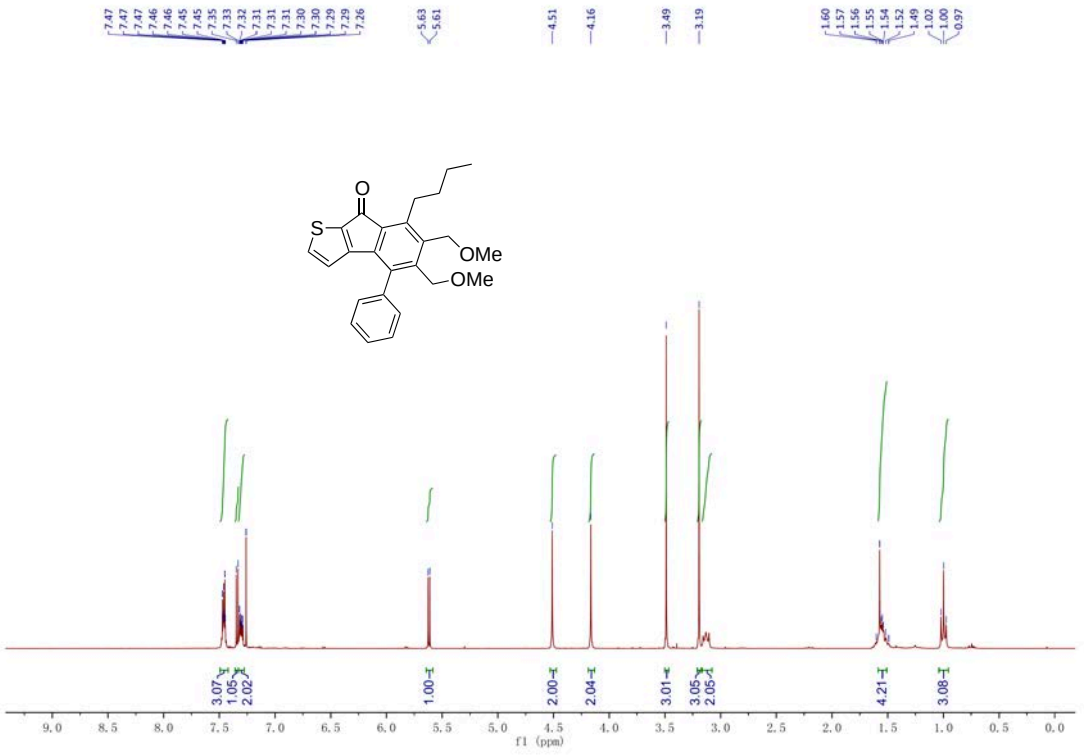
7.45
7.44
7.43
7.33
7.32
7.31
7.30
7.30
7.26
5.40
5.40
4.49
4.16
3.48
3.23
3.10
3.08
3.05
1.58
1.55
1.54
1.53
1.50
1.48
1.01
0.99
0.96
O
O
OMe
OMe
3.05
3.09
1.00
2.04
2.06
3.10
3.12
2.05
4.46
3.13
f1 (ppm)


179.62
154.62
151.31
145.04
144.59
140.87
138.15
137.72
135.09
134.81
131.56
129.68
128.35
127.98
108.02
77.58
77.16
76.74
68.80
67.39
58.92
58.52
33.68
26.71
23.43
14.08
f1 (ppm)

3n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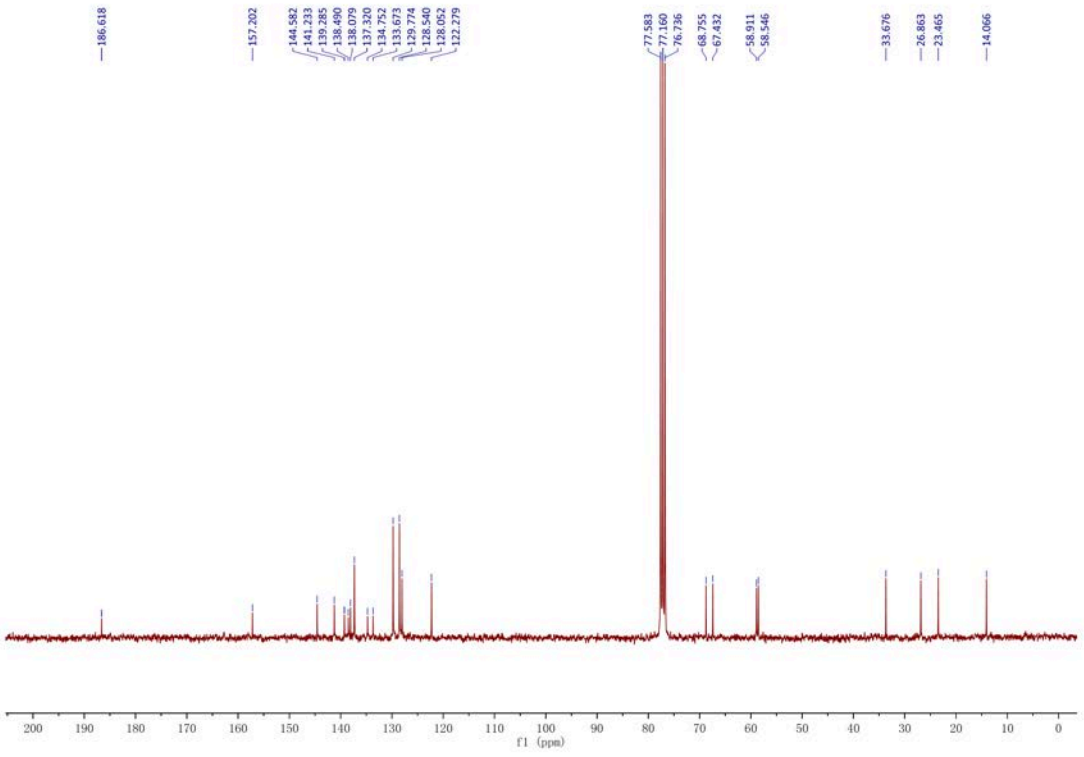
7.47
7.47
7.46
7.46
7.45
7.45
7.35
7.33
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.29
7.26
5.63
5.61
4.51
4.16
3.49
3.19
1.60
1.57
1.56
1.55
1.54
1.52
1.49
1.02
1.00
0.97
O
S
OMe
OMe
3.07
1.05
2.02
1.00
2.00
2.04
3.01
3.05
2.05
4.21
3.08
f1 (ppm)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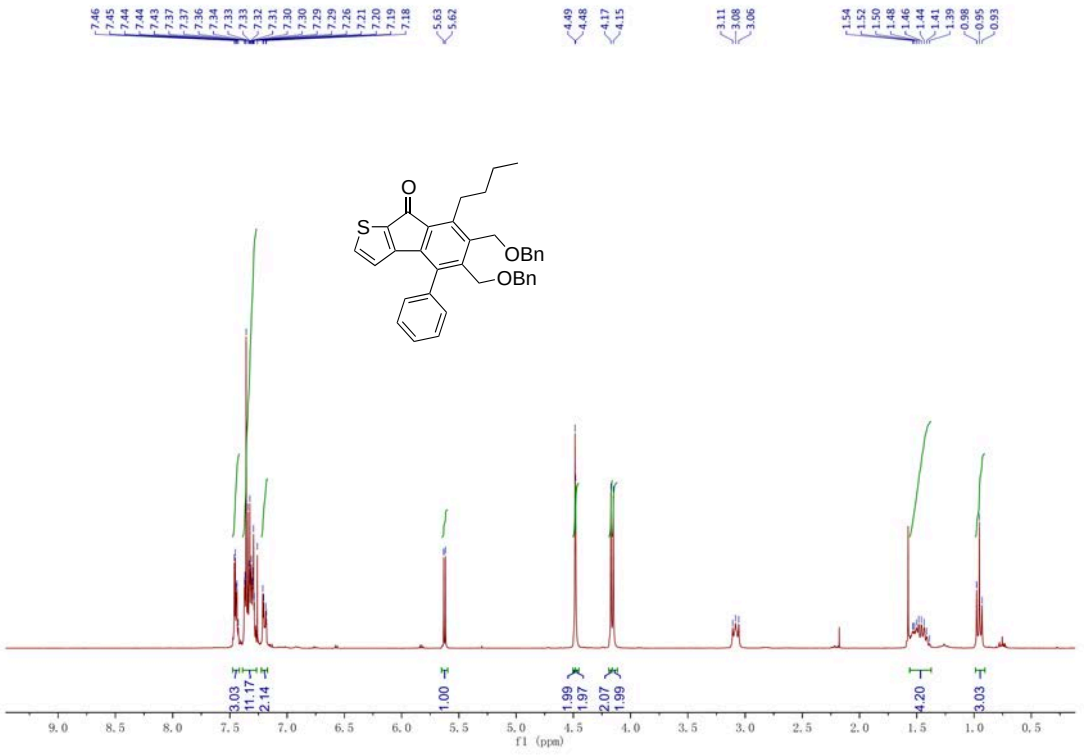
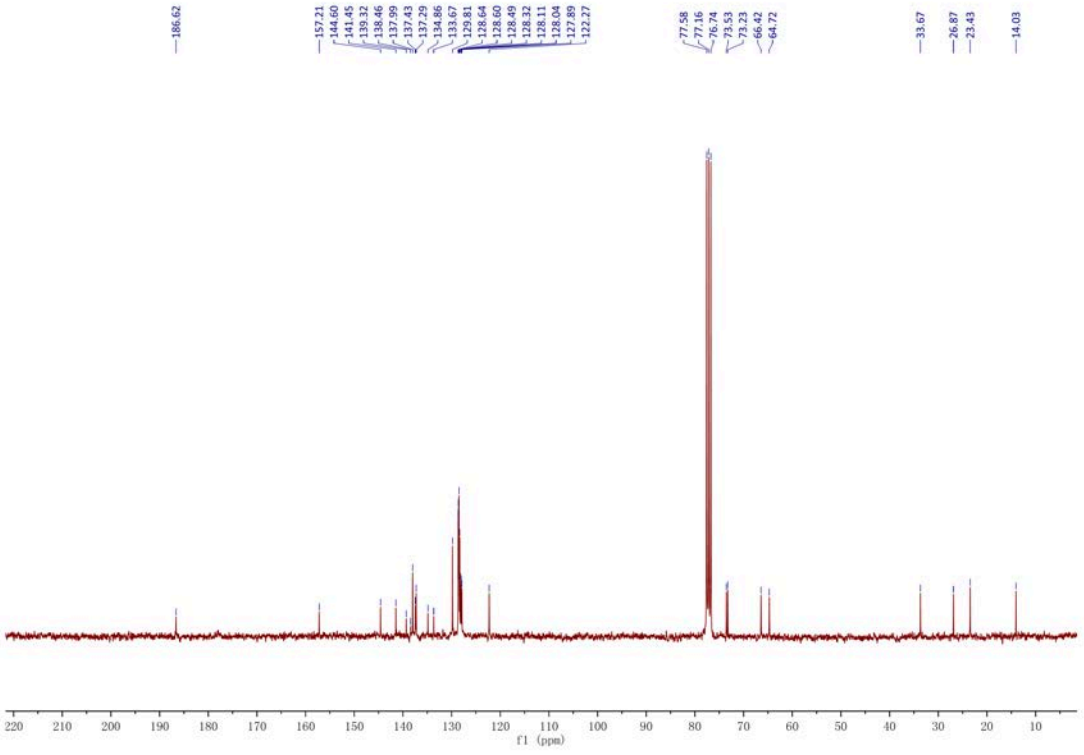
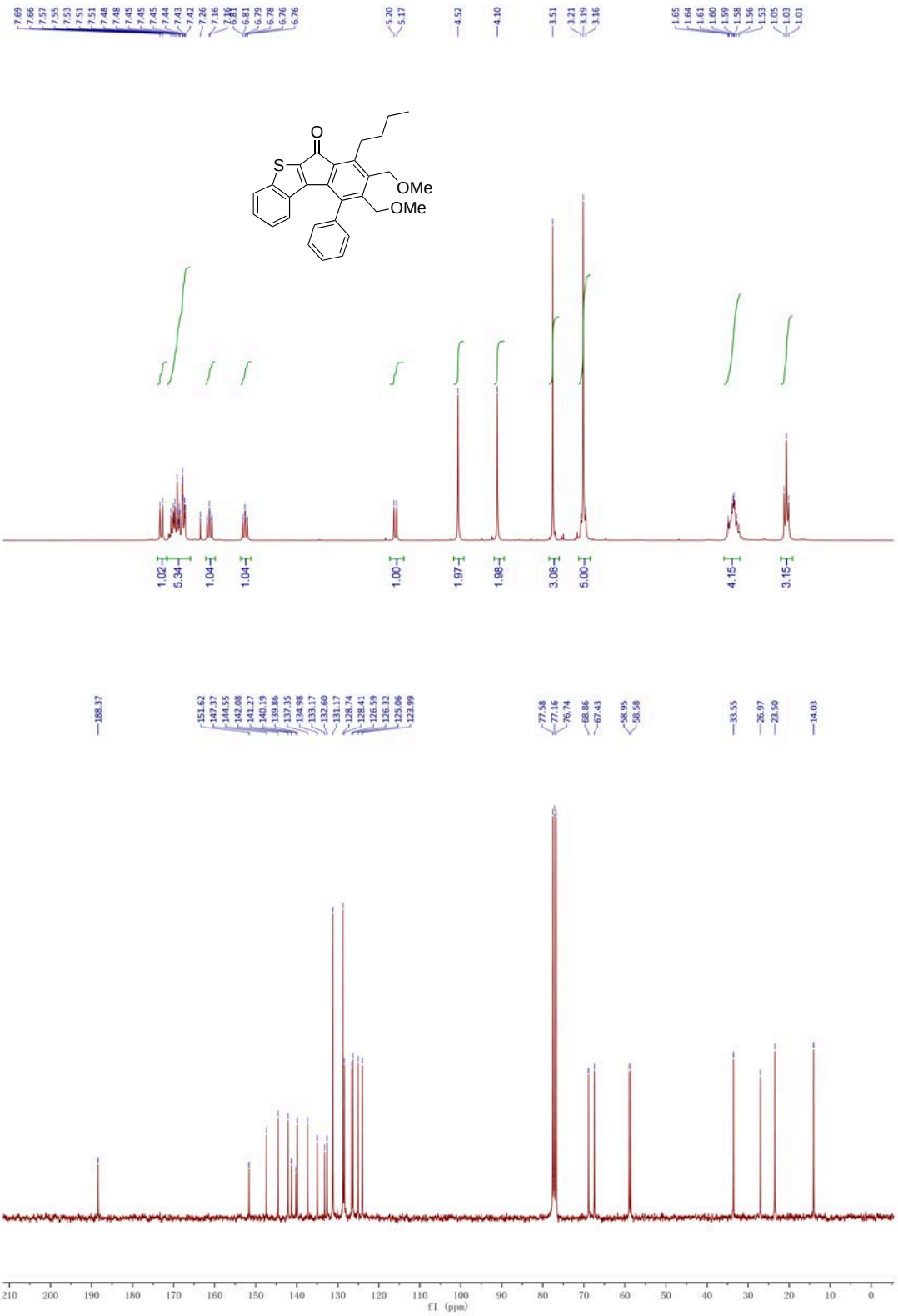
141.233
139.285
138.490
138.079
137.320
134.752
133.673
129.774
128.540
128.052
122.279
77.583
77.160
76.736
68.755
67.432
58.911
58.546
33.676
26.863
23.465
14.066
f1 (ppm)

3o

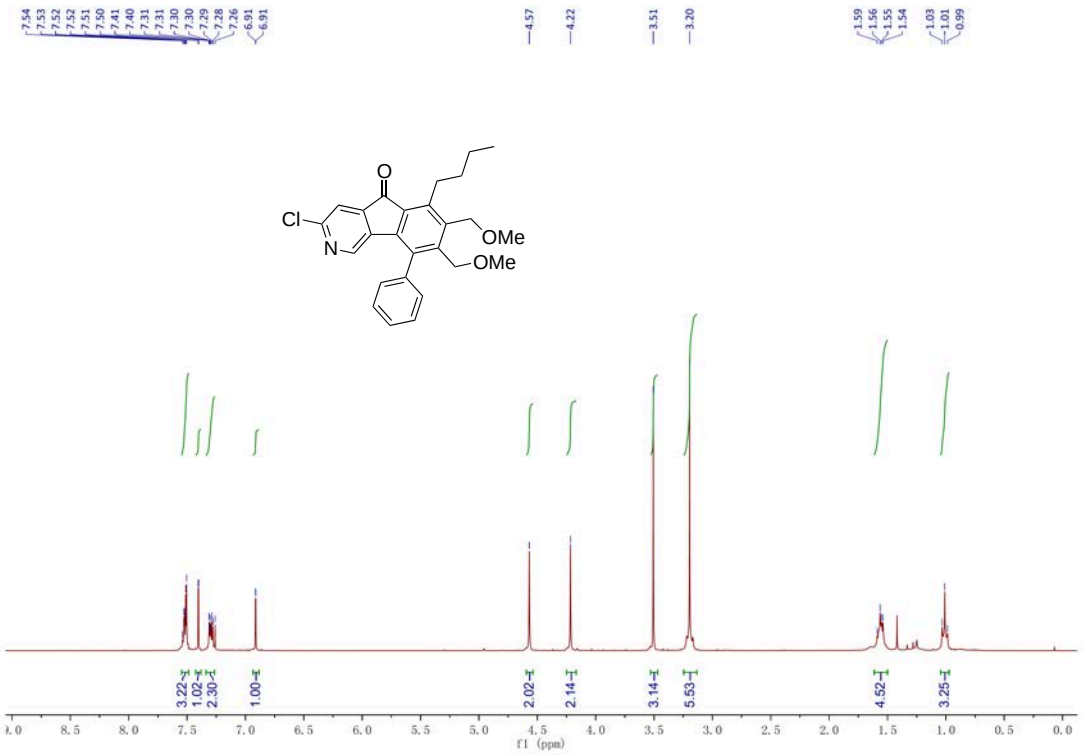

7.46
7.45
7.44
7.44
7.43
7.37
7.37
7.36
7.34
7.33
7.33
7.32
7.31
7.30
7.30
7.29
7.29
7.26
7.21
7.20
7.19
7.18
5.63
5.62
4.49
4.48
4.17
4.15
3.11
3.08
3.06
1.54
1.52
1.50
1.48
1.46
1.44
1.41
1.39
0.98
0.95
0.93
O
S
OBn
OBn
3.03
11.17
2.14
1.00
1.99
1.97
2.07
1.99
4.20
3.03
f1 (ppm)


186.62
157.21
144.60
141.45
139.32
138.46
137.99
137.43
137.29
134.86
133.67
129.81
128.64
128.60
128.49
128.32
128.11
128.04
127.89
122.27
77.58
77.16
76.74
73.53
73.23
66.42
64.72
33.67
26.87
23.43
14.03
f1 (ppm)

3p



3q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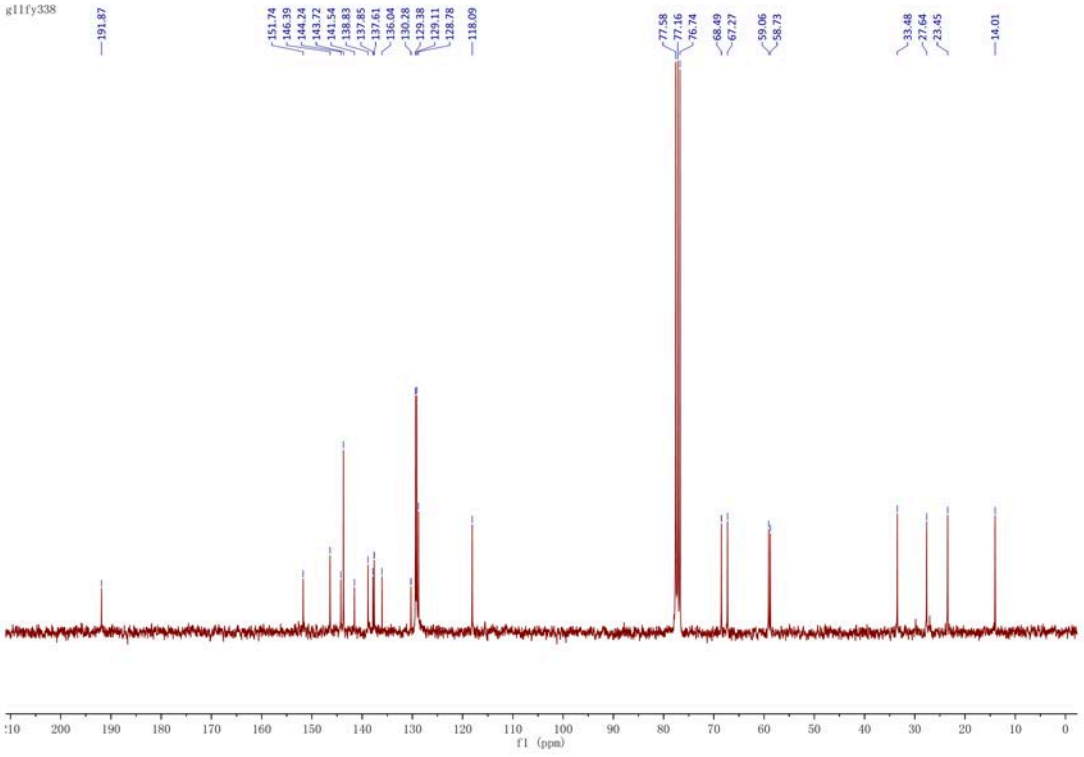
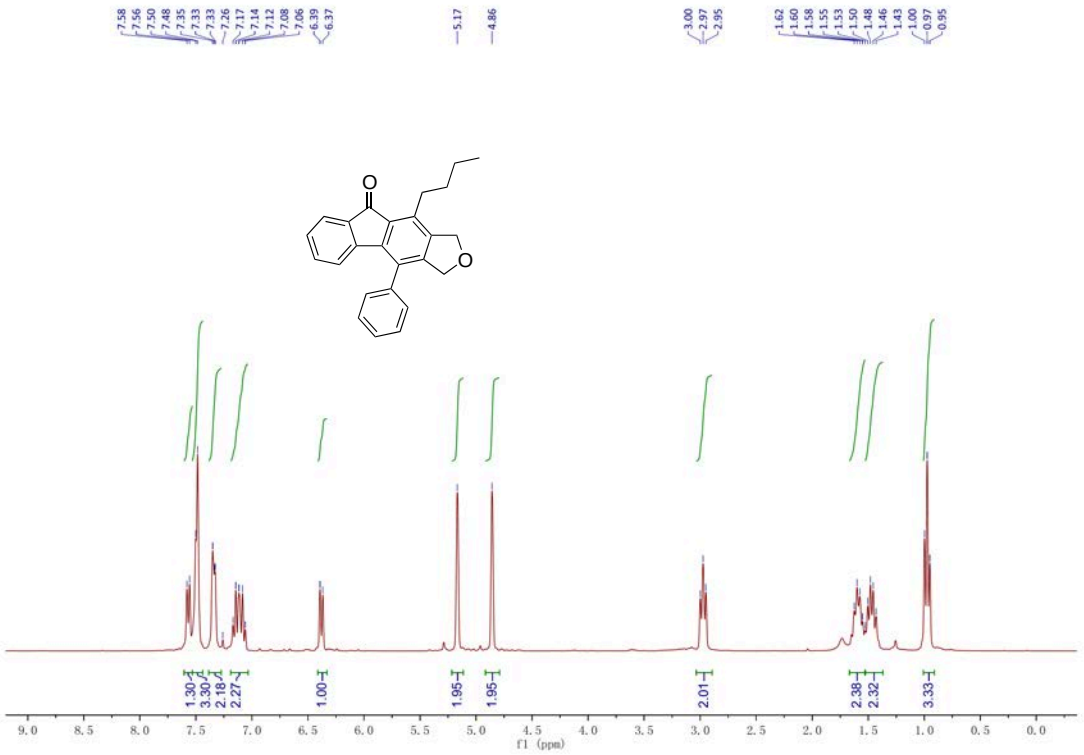
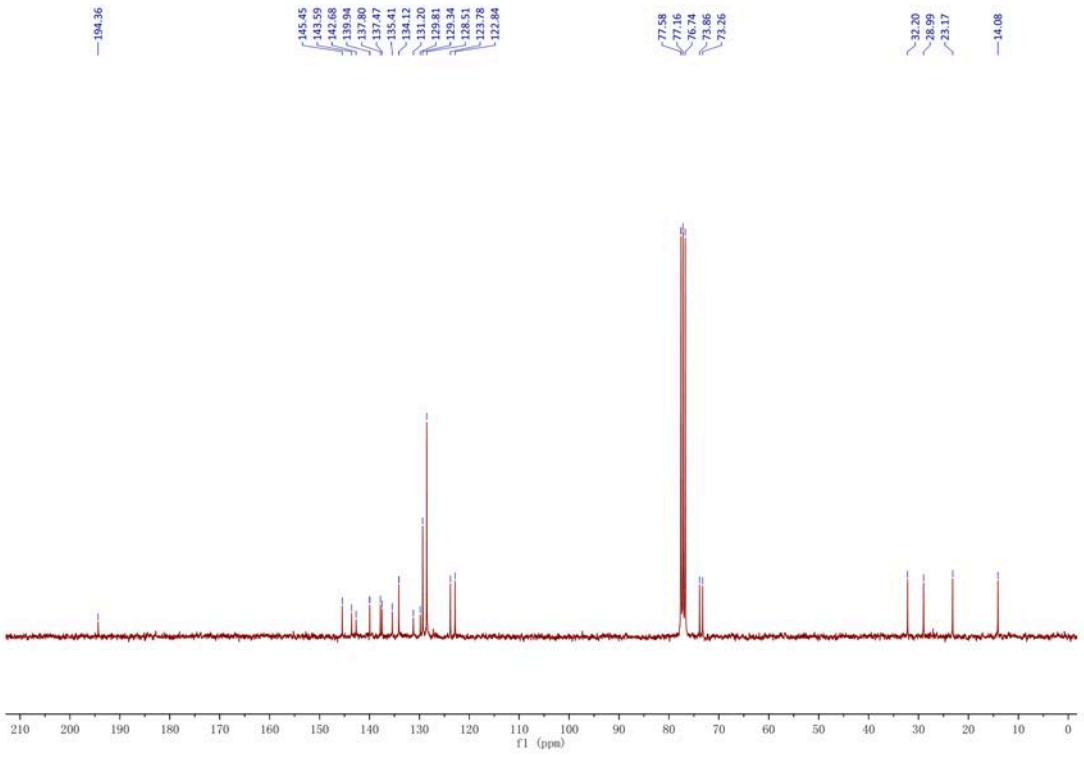
7.53
7.52
7.52
7.51
7.50
7.41
7.40
7.31
7.31
7.30
7.30
7.29
7.28
7.26
6.91
6.91
4.57
4.22
3.51
3.20
1.59
1.56
1.55
1.54
1.03
1.01
0.99
O
Cl
N
OMe
OMe
3.22
1.02
2.30
1.00
2.02
2.14
3.14
5.53
4.52
3.25
f1 (ppm)

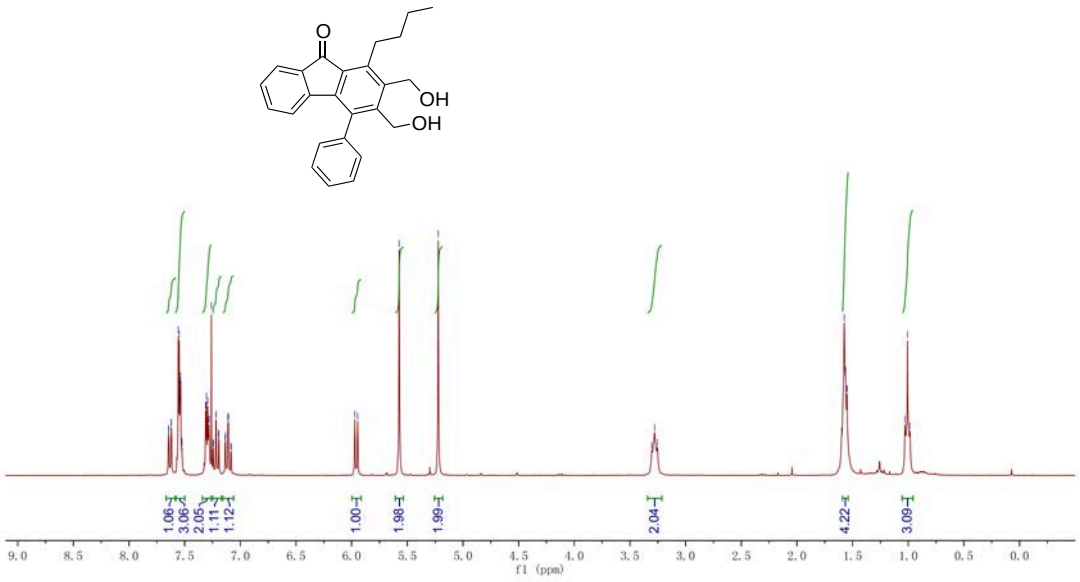

g11fy338
191.87
151.74
146.39
144.24
143.72
141.54
138.83
137.85
137.61
136.04
130.28
129.38
129.11
128.78
118.09
77.58
77.16
76.74
68.49
67.27
59.06
58.73
33.48
27.64
23.45
14.01
f1 (ppm)

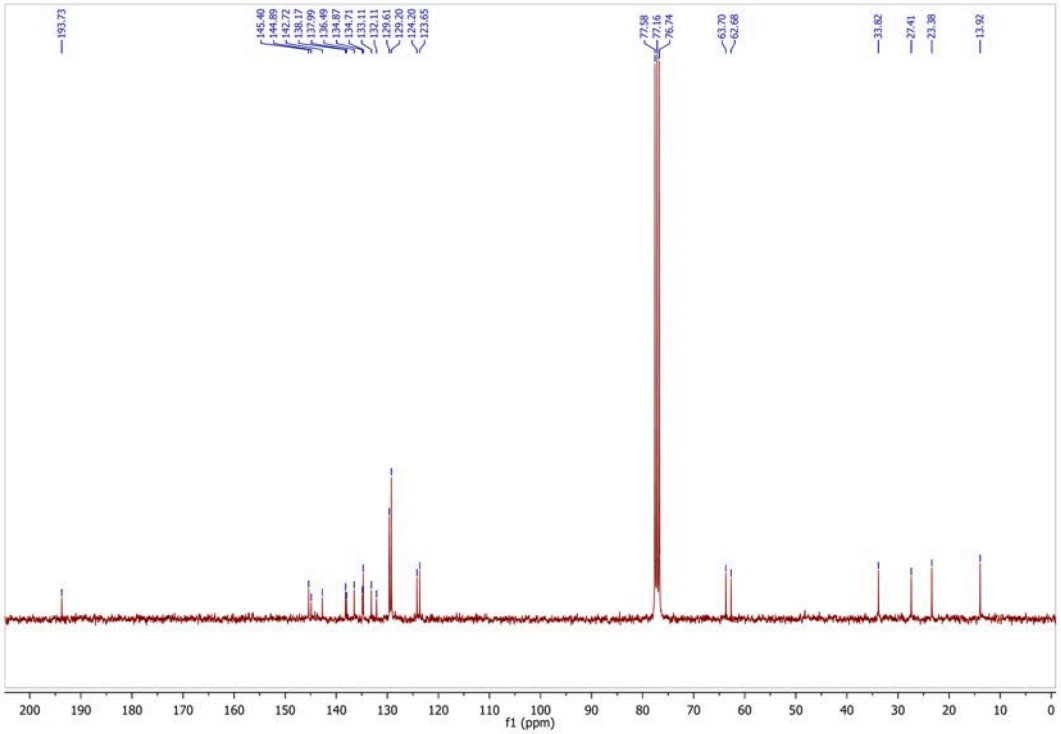
4


7.58
7.56
7.50
7.48
7.35
7.33
7.33
7.26
7.17
7.14
7.12
7.08
7.06
6.39
6.37
5.17
4.86
3.00
2.97
2.95
1.62
1.60
1.58
1.55
1.53
1.50
1.48
1.46
1.43
1.00
0.97
0.95
O
O
1.30
3.30
2.18
2.27
1.00
1.95
1.95
2.01
2.38
2.32
3.33
f1 (ppm)


194.36
145.45
143.59
142.68
139.94
137.80
137.47
135.41
134.12
131.20
129.81
129.34
128.51
123.78
122.84
77.58
77.16
76.74
73.86
73.26
32.20
28.99
23.17
14.08
f1 (ppm)

5


O
OH
OH
1.06
3.06
2.05
1.11
1.12
1.00
1.98
1.99
2.04
4.22
3.09
f1 (ppm)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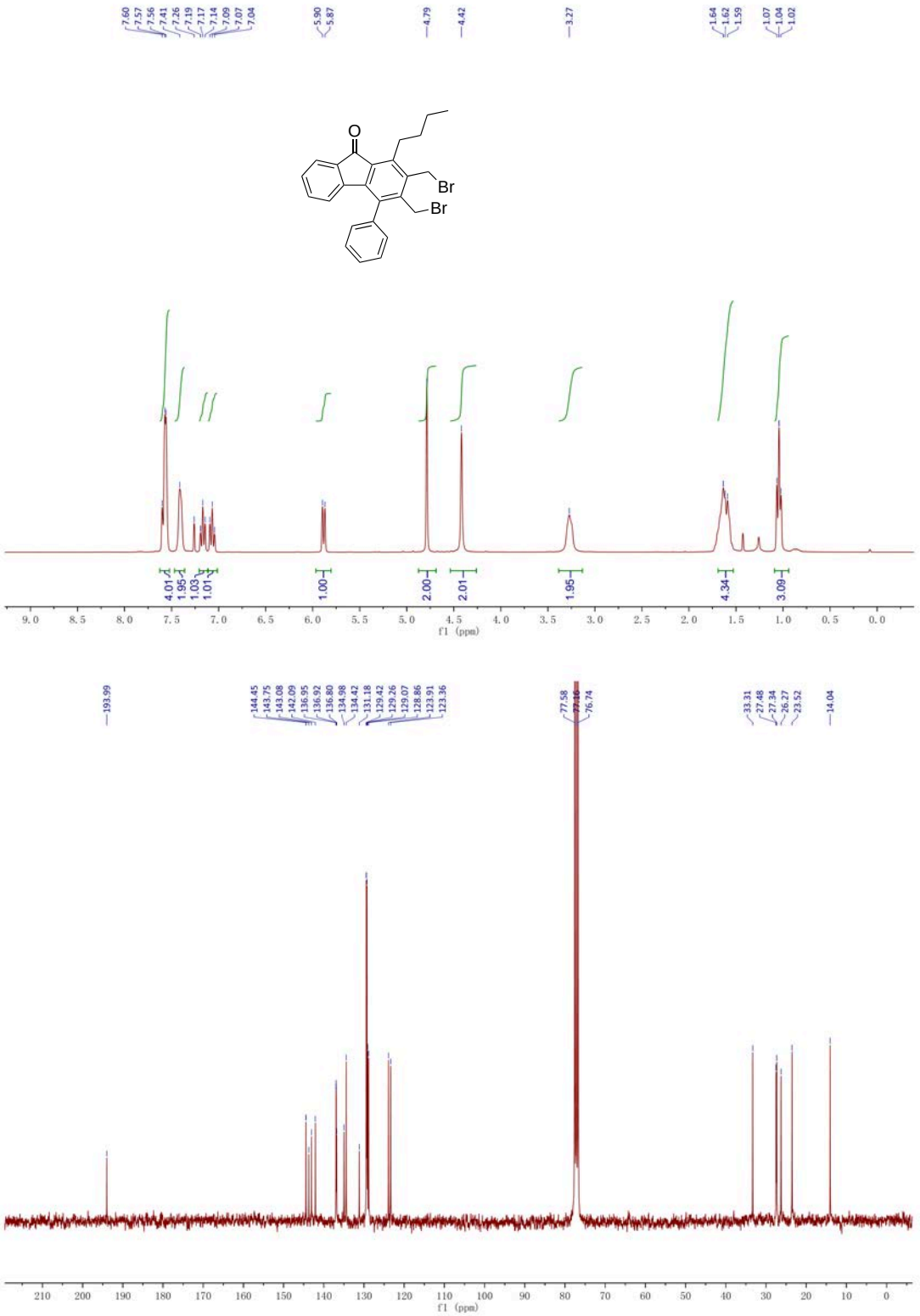
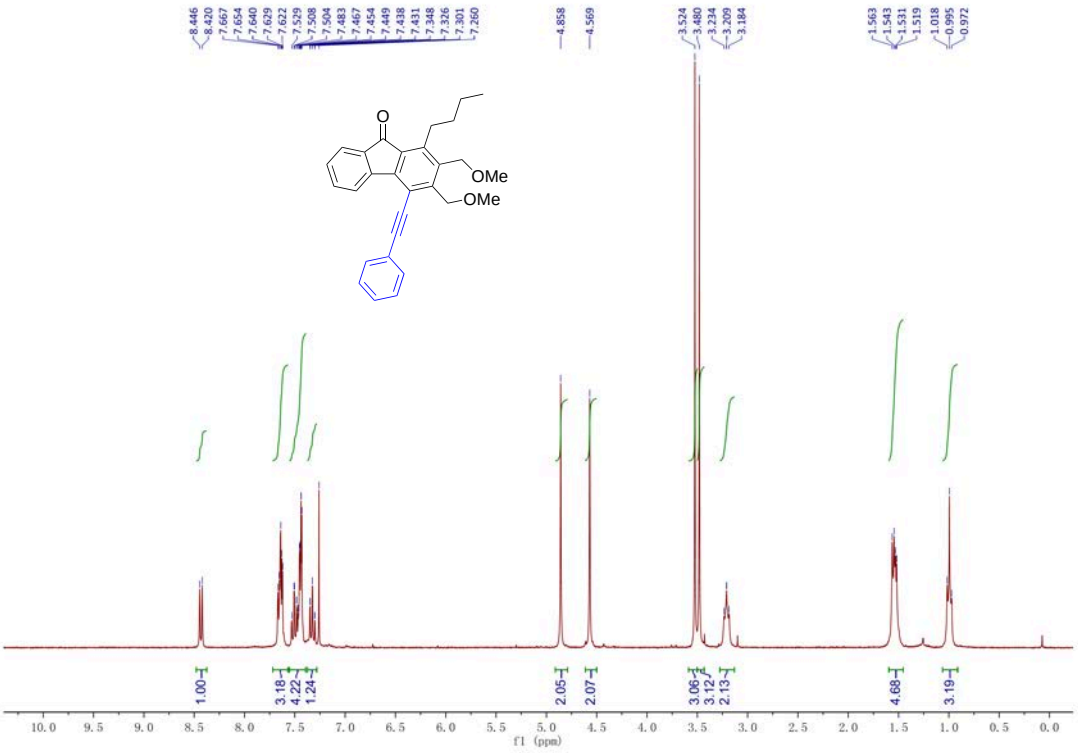
144.89
142.72
138.17
137.99
136.49
134.87
134.71
133.11
132.11
129.61
129.20
124.20
123.65
77.58
77.16
76.74
63.70
62.68
33.82
27.41
23.38
13.92
f1 (ppm)

6


7.60
7.57
7.56
7.41
7.26
7.19
7.17
7.14
7.09
7.07
7.04
5.90
5.87
4.79
4.42
3.27
1.64
1.62
1.59
1.07
1.04
1.02
O
Br
Br
4.01
1.95
1.03
1.01
1.00
2.00
2.01
1.95
4.34
3.09
f1 (ppm)
193.99
144.45
143.75
143.08
142.09
136.95
136.92
136.80
134.98
134.42
131.18
129.42
129.26
129.07
128.86
123.91
123.36
77.58
77.16
76.74
33.31
27.48
27.34
26.27
23.52
14.04
f1 (ppm)

7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7.629
7.622
7.529
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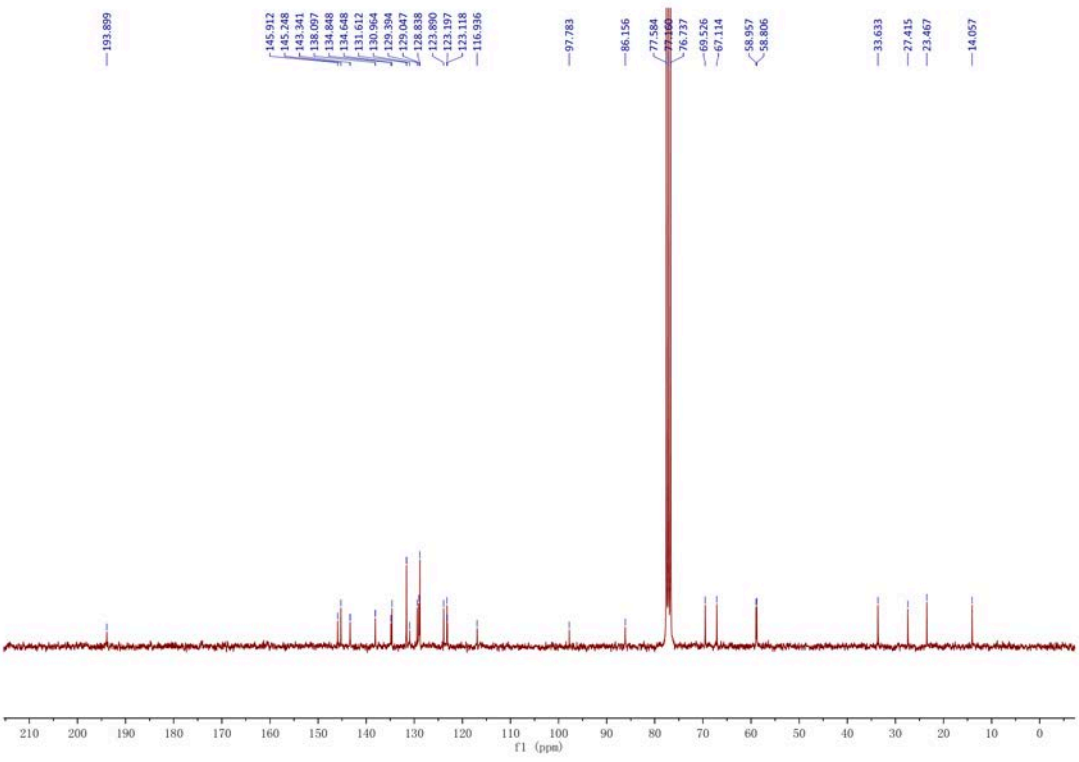
7.504
7.483
7.467
7.454
7.449
7.438
7.431
7.348
7.326
7.301
7.260
4.858
4.569
3.524
3.480
3.234
3.209
3.184
1.563
1.543
1.531
1.519
1.018
0.995
0.972
O
OMe
OMe
1.00
3.18
4.22
1.24
2.05
2.07
3.06
3.12
2.13
4.68
3.19
f1 (ppm)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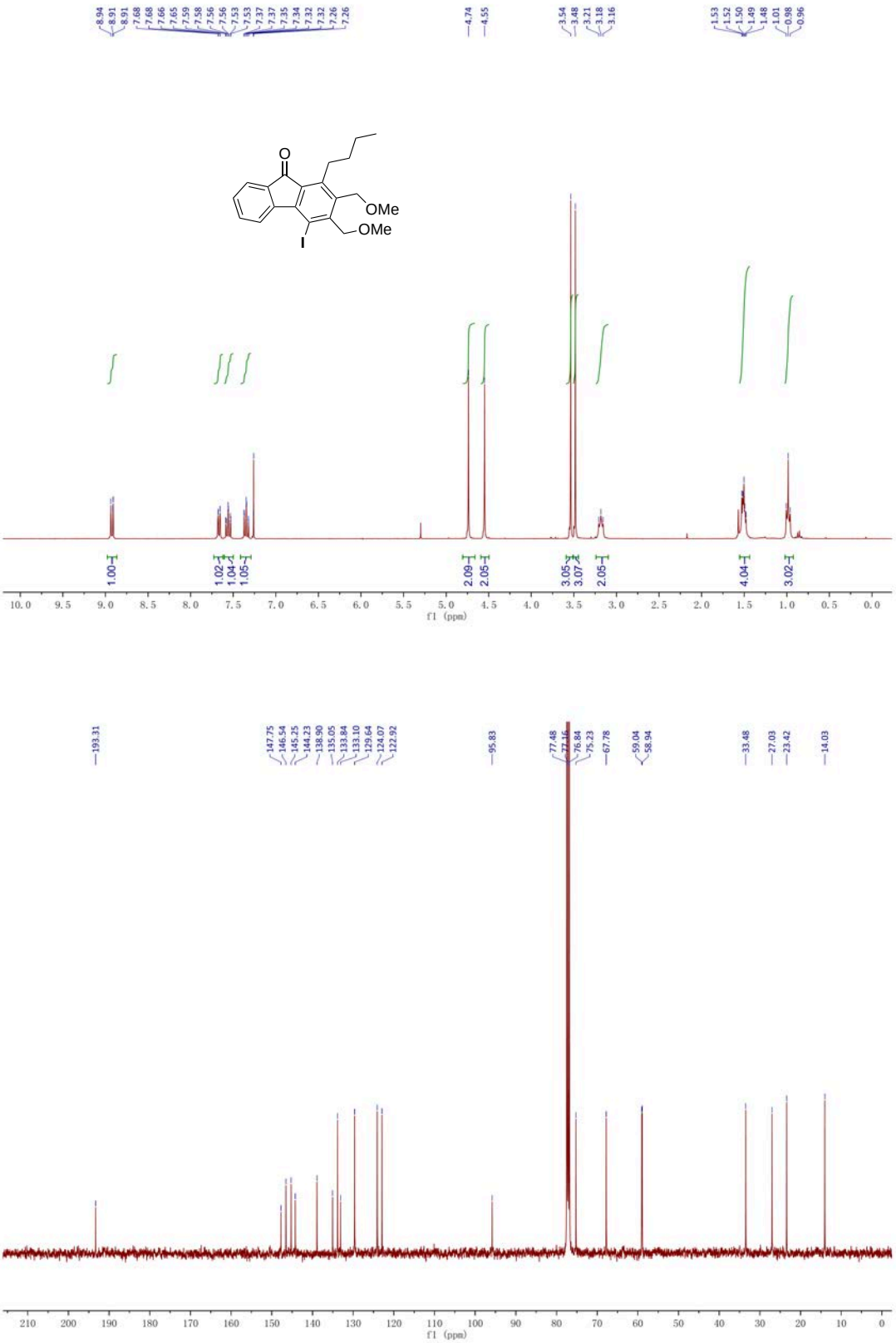
145.248
143.341
138.097
134.848
134.648
131.612
130.964
129.394
129.047
128.838
123.890
123.197
123.118
116.936
97.783
86.156
77.584
77.160
76.737
69.526
67.114
58.957
58.806
33.633
27.415
23.467
14.057
f1 (ppm)

8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8.91
7.68
7.68
7.66
7.65
7.59
7.58
7.56
7.56
7.53
7.53
7.37
7.37
7.35
7.34
7.32
7.32
7.26
7.26
4.74
4.55
3.54
3.48
3.21
3.18
3.16
1.53
1.52
1.50
1.49
1.48
1.01
0.98
0.96
O
OMe
OMe
I
1.00
1.02
1.04
1.05
2.09
2.05
3.05
3.07
2.05
4.04
3.02
f1 (ppm)
193.31
147.75
146.54
145.25
144.23
138.90
135.05
133.84
133.10
129.64
124.07
122.92
95.83
77.48
77.16
76.84
75.23
67.78
59.04
58.94
33.48
27.03
23.42
14.03
f1 (ppm)