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Palladium-Catalyzed Multi-component Heck Alkynylcarbonylation of Unactivated Alkenes for Synthesis of β,γ -Alkynoates

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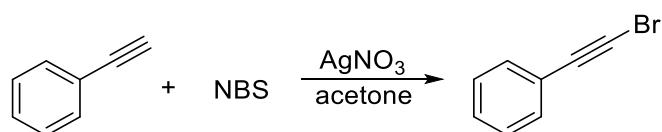
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1. General information

Chemicals and solvents were purchased from commercial suppliers and used as received unless noted. Bromoalkynes and chloroalkynes were prepared according to literature procedures. All products were purified by flash chromatography on silica gel. All reactions were heated by metal sand bath (WATTCAS, LAB-500, <http://www.wattcas.com/>). The chemical yields referred are isolated products. ^1H NMR and ^{13}C NMR spectra were recorded on 400 MHz, 500MHz and 600MHz Bruker spectrometers. Chemical shifts of ^1H were reported in part per million relative to the CDCl_3 residual peak (δ 7.260). Chemical shifts of ^{13}C NMR were reported relative to CDCl_3 (δ 77.00). The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), quart (quartet), quint (quintet), m (multiplet), br (broad). Structural assignments were made with additional information from NOE and HMBC experiments. Multiplets which arise from accidental equality of coupling constants of magnetically non-equivalent protons are marked as virtual (virt.). High resolution mass spectra (HRMS) data were measured on an ESI-microTOF II. The crystal data were collected by a diffractometer Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu $K\alpha$ radiation (1.54178 Å) by using a ω scan mode. ICP-OES/MS were measured on a Agilent ICPMS 7700. Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates and compounds were visualized with a UV light at 254 nm or 365 nm.

2. Synthesis of substrates

2.1 General methods for the synthesis of haloalkynes^[1]

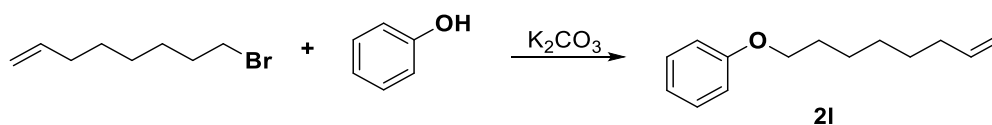


A mixture of phenylacetylene (2.0 mmol, 204 mg) was dissolved in acetone (15 mL), then NBS (427 mg, 2.4 mmol, 1.2 equiv), silver nitrate (20 mg, 0.12 mmol, 0.06 equiv.) was added successively in 25 mL round bottom flask. The Schlenk tube was then insert in metal sand bath at 30 °C stirring for 4h. Afterwards, filtered and concentrated under vacuum. The residue was purified by flash chromatography (petroleum ether) on silica gel to afford the corresponding (bromoethynyl)benzene as a pale yellow liquid (324 mg, 90% yield).

2.2 General methods for the synthesis of alkenes

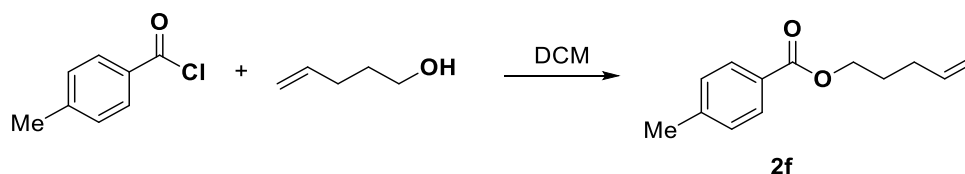
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2.2.1 Synthesis of (oct-7-en-1-yloxy)benzene^[2]



A mixture of 8-bromooct-1-ene (1.0 mmol, 190 mg) was dissolved in DMF (4 mL), then phenol (103 mg, 1.1 mmol, 1.1 equiv), K_2CO_3 (424 mg, 3 mmol, 2 equiv.) under a N_2 atmosphere were added to successively in 25 mL round bottom flask. The Schlenk tube was then insert in metal sand bath at 30 °C stirring for 12h. Afterwards, filtered and concentrated under vacuum. The residue was purified by flash chromatography (petroleum ether) on silica gel to afford the oct-7-en-1-yloxy benzene as a pale yellow liquid (184 mg, 90% yield).

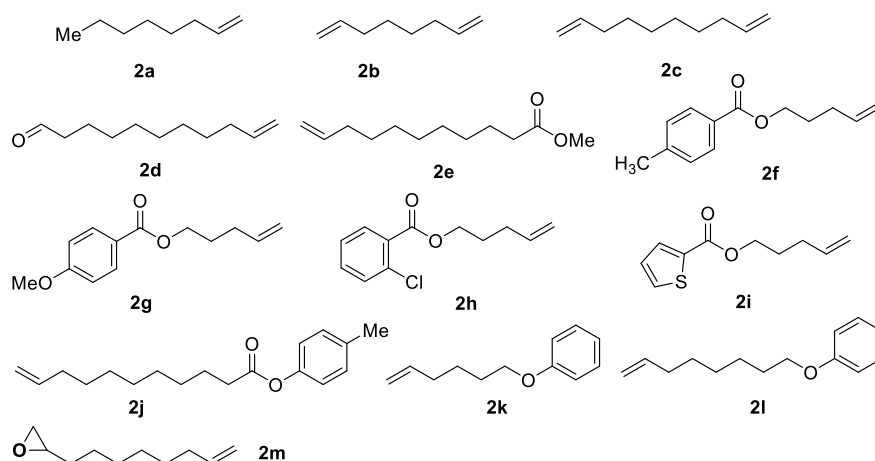
2.2.2 Synthesis of pent-4-en-1-yl benzoate^[3]



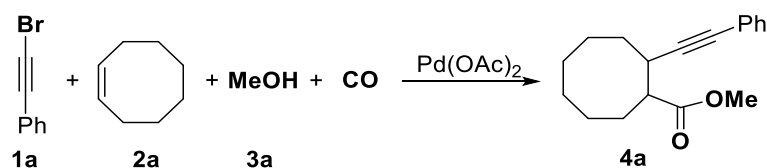
A mixture of 4-methylbenzoyl chloride (1.0 mmol, 154 mg) was dissolved in DCM (6 mL), then pent-4-en-1-ol (103 mg, 1.2 mmol, 1.2 equiv), was added successively in 25 mL round bottom flask. The Schlenk tube was then insert in metal sand bath at 40 °C stirring for 12h. Afterwards, filtered and concentrated under vacuum. The residue was purified by flash chromatography (petroleum ether) on silica gel to afford the corresponding pent-4-en-1-yl 4-methylbenzoate **2f** as a pale yellow liquid (173 mg, 85% yield).

Scheme S1. Alkene substrates

Substrates of terminal alkenes



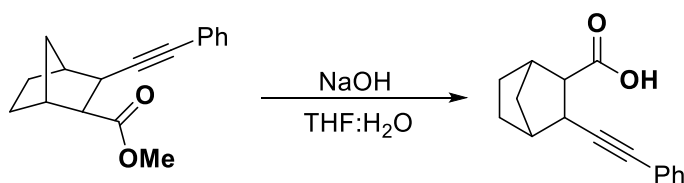
3. Pd-catalyzed alkynylcarbonylation of alkenes



A mixture of Pd(OAc)₂ (5 mol%), (bromoethynyl)benzene (0.5 mmol, 90 mg) and cyclooctene (0.75 mmol, 83 mg), DPPE (5 mol%), CO (1 atm) and CH₃OH (0.3 mL) was added successively in a 20 mL Schlenk tube. After stirring for 14h at 40 °C, then quenched with 30 mL of brine and extracted with ethyl acetate (3×20 mL). The combined organic layer was dried over Na₂SO₄, filtered and concentrated under vacuum. The residue was purified by flash chromatography (Hexane/EtOAc = 50:1, R_f = 0.5) on silica gel, which furnished **4a** (104 mg, 77% yield) as a pale yellow oil.

4. Synthetic applications

4.1. synthesis of 3-(phenylethynyl)bicyclo[2.2.1]heptane-2-carboxylic acid

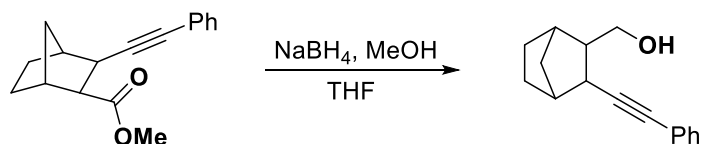


The methyl-3-(phenylethynyl)bicyclo[2.2.1]heptane-2-carboxylate (51 mg) was dissolved with THF/H₂O (1:1, 2 mL), and NaOH (24 mg, 3.0 mmol, 3.0 equiv.) was added to the solution in sequence. The mixture was allowed to react at 80 °C for overnight. After that, the reaction was cooled down to room temperature, HCl (10%, 5 mL) was added to the mixture and extracted with ethyl acetate (3×10 mL). The combined organic phase was washed with brine (20.0 mL) and dried over Na₂SO₄. The residue was purified by flash chromatography (petroleum ether/EtOAc = 2:1, R_f = 0.4) on silica gel, which furnished **7a** (28 mg, 58%).

3-(phenylethynyl)bicyclo[2.2.1]heptane-2-carboxylic acid (7a): ¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.29 (m, 2H), 7.24 – 7.22 (m, 3H), 2.99 – 2.49 (m, 4H), 2.12 – 2.05 (m, 1H), 1.67 – 1.48 (m, 2H), 1.32 – 1.12 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 177.8, 131.5 (2C), 128.0 (2C), 127.6, 123.5, 89.7, 83.1, 52.0, 43.4, 38.9, 36.2, 28.6, 27.9. HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₆H₁₇O₂, 241.1223, found: 241.1233.

4.2. Synthesis of (3-(phenylethynyl)bicyclo[2.2.1]heptan-2-yl)methanol^[4]

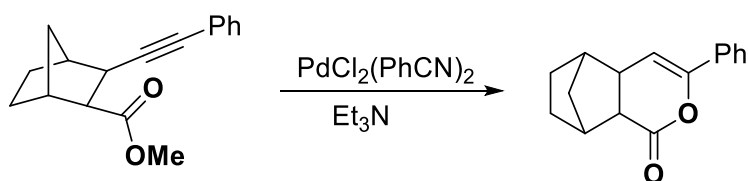
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The methyl-3-(phenylethynyl)bicyclo[2.2.1]heptane-2-carboxylate was dissolved with THF (2 mL) and MeOH (1 mL) was added to the solution in sequence. The mixture was allowed to react at 70 °C for 2 hours. After that, the reaction was cooled down to room temperature, extracted with ethyl acetate (3×10 mL). The combined organic phase was washed with brine (20.0 mL) and dried over Na₂SO₄. The residue was purified by flash chromatography (petroleum ether/EtOAc = 10:1, R_f = 0.4) on silica gel, which furnished **7b** (40 mg, 89%).

(3-(phenylethynyl)bicyclo[2.2.1]heptan-2-yl)methanol (7b): ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.26 (m, 5H), 3.81 – 3.65 (m, 3H), 2.46 (s, 1H), 2.11 (d, *J* = 3.1 Hz, 1H), 1.93 – 1.73 (m, 2H), 1.61 – 1.54 (m, 2H), 1.30 – 1.23 (m, 3H), 1.23 – 1.16 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 131.5 (2C), 128.2 (2C), 127.8, 123.3, 90.9, 82.6, 64.9, 48.7, 44.4, 38.7, 37.3, 34.7, 29.7, 28.2. HRMS (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₁₆H₁₉O, 227.1430, found: 227.1426.

4.3. Synthesis of 3-phenyl-4a,5,6,7,8,8a-hexahydro-1H-5,8-methanoisochromen-1-one^[5]

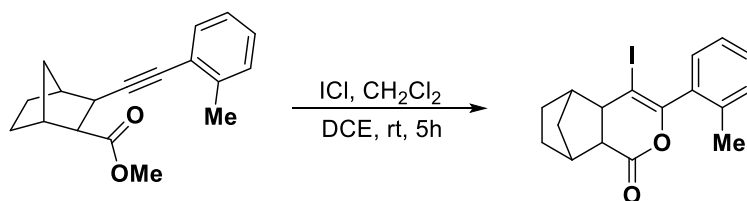


A mixture of 3-(phenylethynyl)bicyclo[2.2.1]heptane-2-carboxylic acid (0.2 mmol, 48 mg) and PdCl₂(PhCN)₂ (0.14 mmol, 54 mg), and Et₃N (0.43 mmol, 43 mg) in MeCN (2 mL) was refluxed for 5 h and concentrated. The residue was purified by flash chromatography (Petroleum ether/EtOAc = 5:1, R_f = 0.4) on silica gel, which furnished **7c** (36 mg, 75%).

3-phenyl-4a,5,6,7,8,8a-hexahydro-1H-5,8-methanoisochromen-1-one (7c): ¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.19 (m, 5H), 5.56 (s, 1H), 3.05 – 2.51 (m, 4H), 1.66 – 1.56 (m, 2H), 1.40 – 1.33 (m, 2H), 1.32 – 1.24 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 176.8, 152.4, 134.1, 128.4 (2C), 128.2 (2C), 126.6, 104.7, 47.4, 46.8, 44.7, 40.7, 33.9, 28.0, 27.0. HRMS (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₁₆H₁₇O₂, 241.1223, found: 241.1219.

4.4. Synthesis of 4-iodo-3-(o-tolyl)-4a,5,6,7,8,8a-hexahydro-1H-5,8-methanoisochromen-1-one^[6]

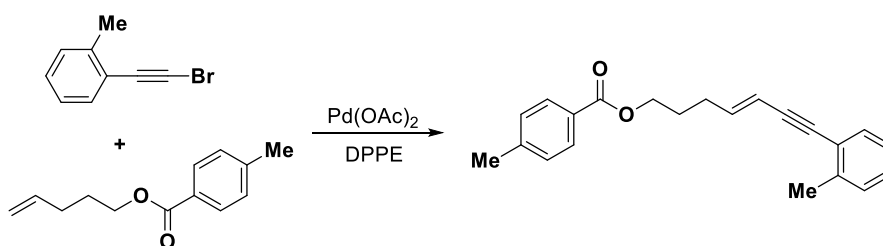
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Under N₂ atmosphere condition, a mixture of methyl-3-(o-tolyethynyl)bicyclo[2.2.1]heptane-2-carboxylate (0.5 mmol, 134 mg) and ICl (0.6 mmol, 1.0mol/L in dichloromethane) and the mixture was stirred in the dark at room temperature until completion of the reaction. It was then poured into a 10 % aqueous NaHCO₃ solution (10 mL) and extracted with CH₂Cl₂ (2×20 mL). The organic extract was washed with a 10% aqueous Na₂S₂O₃ solution (10 mL) and brine (10 mL), dried over Na₂SO₄. The residue was purified by flash chromatography (Petroleum ether/EtOAc = 10:1, R_f = 0.4) on silica gel, which furnished **7d** (123.5 mg, 65%).

4-iodo-3-(o-tolyl)-4a,5,6,7,8,8a-hexahydro-1H-5,8-methanoisochromen-1-one (7d): ¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.22 (m, 4H), 3.02 – 2.76 (m, 4H), 2.33 (s, 3H), 1.79 – 1.63 (m, 3H), 1.56 – 1.47 (m, 1H), 1.46 – 1.32 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 198.2, 178.7, 140.1, 133.6, 132.6, 132.5, 128.8, 125.9, 84.1, 48.1, 45.7, 42.5, 40.9, 33.9, 27.6, 27.5, 21.4. HRMS (ESI-TOF) m/z: [M+H]⁺ calcd for C₁₇H₁₈IO₂, 381.0346, found: 381.0337.

5. Mechanistic studies

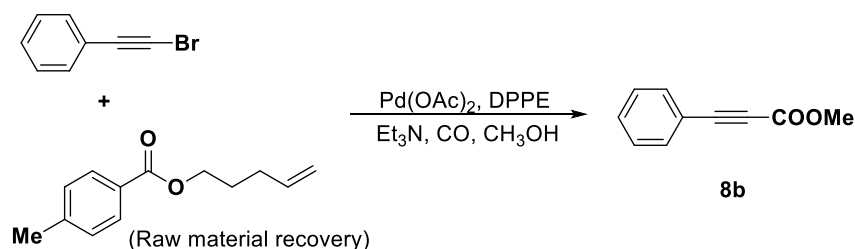


A mixture of Pd(OAc)₂ (5 mol%), 1-(bromoethynyl)-2-methylbenzene (0.5 mmol, 98 mg) and pent-4-en-1-yl 4-methylbenzoate (0.75 mmol, 153 mg), DPPE (5 mol%) and CH₃OH (2 mL) was added successively in a 20 mL Schlenk tube. After stirring for 14 h at 40 °C, then quenched with 30 mL of brine and extracted with ethyl acetate (3×30 mL). The combined organic layer was dried over Na₂SO₄, filtered and concentrated under vacuum. The residue was purified by flash chromatography (Hexane /EtOAc = 50:1, R_f = 0.5) on silica gel, which furnished **8a** (116 mg, 73%) as a pale yellow oil.

7-(o-tolyl)hept-4-en-6-yn-1-yl 4-methylbenzoate (8a): Yellow liquid (116 mg, 73% yield), R_f = 0.5 (Hexane/EtOAc = 50:1); ¹H NMR (500 MHz, CDCl₃) δ 7.94 – 7.33 (m, 3H), 7.26 – 7.10 (m, 5H),

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5.46 – 4.38 (m, 4H), 2.48 – 2.10 (m, 10H). ^{13}C NMR (125 MHz, CDCl_3) δ 166.6, 143.5, 140.0, 131.8, (2C) 130.6 (2C), 129.5, 129.4, 129.0, 128.2, 125.5, 121.6, 93.2, 88.5, 63.8, 33.9, 27.3, 21.6, 20.7. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{23}\text{O}_2$, 319.1693, found: 319.1689.



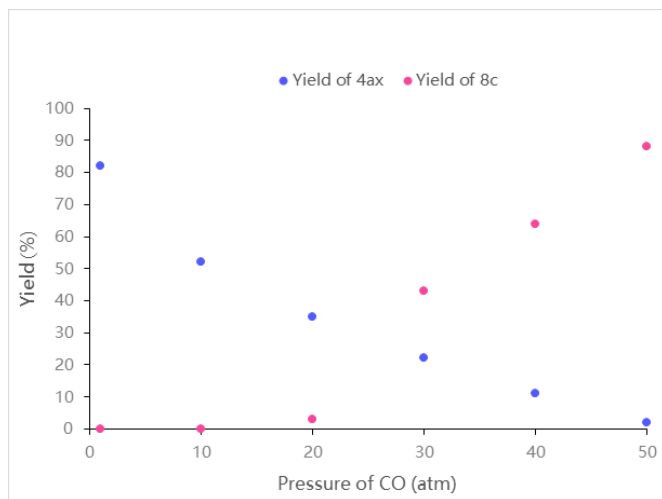
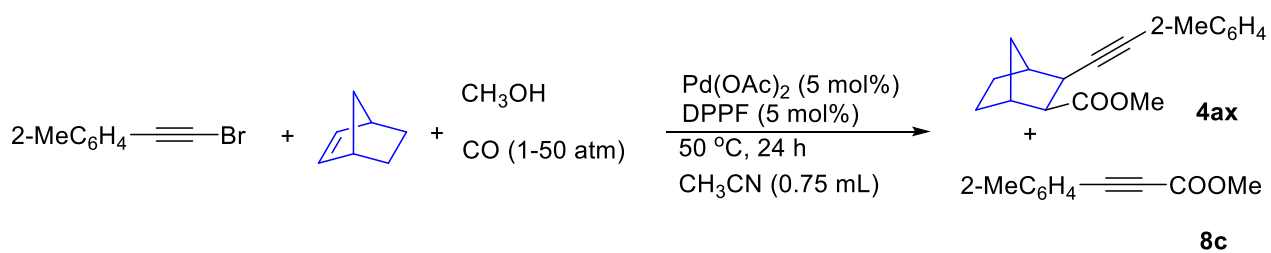
A mixture of $\text{Pd}(\text{OAc})_2$ (5 mol%), (bromoethynyl)benzene (0.5 mmol, 90 mg) and pent-4-en-1-yl 4-methylbenzoate (0.75 mmol, 153 mg), DPPE (5 mol%), CO (1 atm), Et_3N (1 mL) and CH_3OH (1 mL) was added successively in a 20 mL Schlenk tube. After stirring for 14 h at 40 °C, then quenched with 30 mL of brine and extracted with ethyl acetate (3×30 mL). The combined organic layer was dried over Na_2SO_4 , filtered and concentrated under vacuum. The residue was purified by flash chromatography (Hexane /EtOAc = 50:1, R_f = 0.5) on silica gel, which furnished **8b** (74 g, 92%) as a pale yellow oil.

methyl 3-phenylpropiolate (8b):^[7] Yellow liquid (74 mg, 92% yield), R_f = 0.5 (Hexane/EtOAc = 50:1); ^1H NMR (500 MHz, CDCl_3) δ 7.61 – 7.56 (m, 2H), 7.49 – 7.42 (m, 1H), 7.41 – 7.34 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 154.4, 132.9 (2C), 130.6, 128.5 (2C), 119.5, 86.4, 80.3, 52.79.

The influence of CO pressure

1-(bromoethynyl)-2-methylbenzene (97 mg, 0.5 mmol), $\text{Pd}(\text{OAc})_2$ (5 mol%), bicyclo[2.2.1]hept-2-ene (71 mg, 0.75 mmol), DPPE (5 mol%) and CH_3OH (0.3 mL) and a stirring bar were added into a vial (5 mL). Then, the vial was then transferred into an autoclave (50 mL). At 40 °C, the autoclave was flushed with CO gas three times and pressurized with CO gas to 2 atm, 10 atm, 20 atm, 30 atm, 40 atm, 50 atm. After 14 h, the CO gas was released, and then quenched with 30 mL of brine and extracted with ethyl acetate (3×30 mL). The combined organic layer was dried over Na_2SO_4 , filtered and concentrated under vacuum. The residue was purified by flash chromatography (Hexane/EtOAc = 50:1, R_f = 0.5) on silica gel, which furnished **4ax** as a pale yellow oil. The results was summarized in Scheme S2.

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Scheme S2. The influence of CO pressure.

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6. Crystal structure of **4ab**

Experimental: Single crystals of $C_{25}H_{21}O_2$ (Methyl-3-((4-(phenylethynyl)phenyl)ethynyl)bicyclo[2.2.1]heptane-2-carboxylate **4ab**) were generated in the mixed solution of dichloromethane and n-hexane. A suitable crystal was selected and analyzed it on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 149.99(10) K during data collection. The X-ray crystallographic structures for **4ab**. ORTEP representation with 50% probability thermal ellipsoids. Crystal data have been deposited to CCDC, number 2094034.

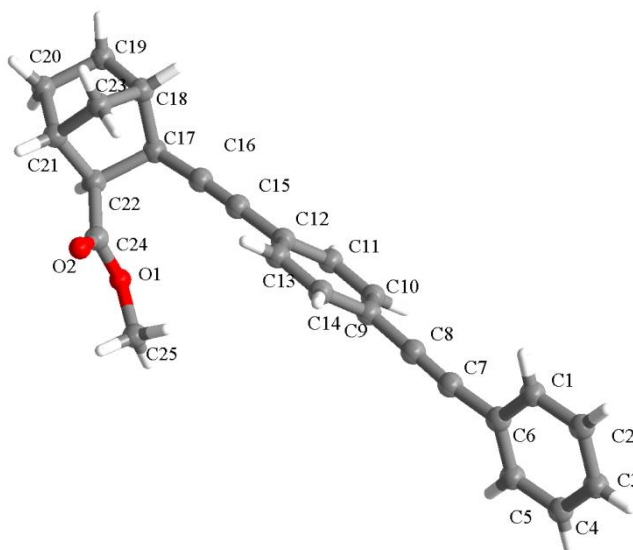


Figure S1. X-ray crystallographic structures of **4ab** with thermal ellipsoids at 50% probability.

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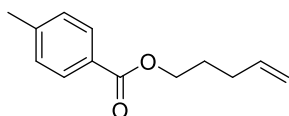
Table S1. Crystal Structure of 4ab

Identification code	4ab
Empirical formula	C ₂₅ H ₂₂ O ₂
Formula weight	354.43
Temperature	273 K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	Pna2 ₁
Unit cell dimensions	a = 7.2816(11) Å a = 90 ° b = 42.358(6) Å b = 90 ° c = 6.3202(9) Å g = 90 °
Volume	1949.4(5) Å ³
Z	4
Density (calculated)	1.208 Mg/m ³
Absorption coefficient	0.589 mm ⁻¹
F(000)	752
Crystal size	0.120 x 0.100 x 0.080 mm ³
Theta range for data collection	4.175 to 68.524 °
Index ranges	-8 ≤ h ≤ 7, -48 ≤ k ≤ 51, -7 ≤ l ≤ 6
Reflections collected	14015
Independent reflections	3324 [R(int) = 0.1289]
Completeness to theta = 24.980 °	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3324 / 15 / 222
Goodness-of-fit on F ²	0.959
Final R indices [I > 2σ(I)]	R1 = 0.1005, wR2 = 0.2502
R indices (all data)	R1 = 0.1599, wR2 = 0.2979
Absolute structure parameter	-0.3(5)
Extinction coefficient	0.023(4)
Largest diff. peak and hole	0.409 and -0.269 e.Å ⁻³

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7. Analytical data of all products

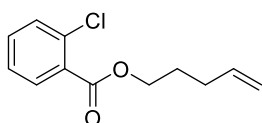
Pent-4-en-1-yl 4-methylbenzoate (2f)^[3]



Yellow liquid (173 mg, 85% yield), $R_f = 0.5$ (Hexane/EtOAc = 50:1); ^1H

NMR (500 MHz, CDCl_3) δ 7.97 – 7.91 (m, 2H), 7.23 (s, 2H), 5.85 – 4.32 (m, 5H), 2.40 (s, 3H), 2.26 – 2.18 (m, 2H), 1.90 – 1.82 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.6, 143.4, 137.5, 129.5, 129.0 (2C), 127.7 (2C), 115.3, 64.1, 30.2, 27.9, 21.6.

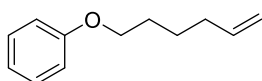
Pent-4-en-1-yl 2-chlorobenzoate (2h)^[15]



Yellow liquid (186 mg, 83% yield), $R_f = 0.5$ (Hexane/EtOAc = 50:1); ^1H

NMR (400 MHz, CDCl_3) δ 7.81 – 7.31 (m, 4H), 5.84 – 4.35 (m, 5H), 2.27 – 2.18 (m, 2H), 1.93 – 1.82 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 137.3, 133.5, 132.3, 131.2, 130.9, 130.4, 126.51 115.4, 64.9, 30.0, 27.7.

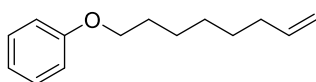
Hex-5-en-1-yloxy)benzene (2k)^[16]



Yellow liquid (151 mg, 86% yield), $R_f = 0.5$ (Hexane/EtOAc = 50:1); ^1H

NMR (500 MHz, CDCl_3) δ 7.31 – 7.19 (m, 2H), 7.07 – 6.75 (m, 3H), 5.84 – 4.95 (m, 3H), 3.95 (s, 2H), 2.13 – 1.81 (m, 4H), 1.63 – 1.53 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.0, 138.5, 129.3 (2C), 120.4, 114.5, 114.4 (2C), 67.6, 33.4, 28.7, 25.3.

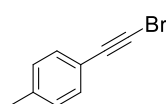
Oct-7-en-1-yloxy)benzene (2l)^[2]



Pale yellow liquid (184 mg, 90% yield), $R_f = 0.5$ (Hexane/EtOAc = 50:1);

^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.28 (m, 2H), 7.01 – 6.92 (m, 3H), 5.87 (m, 1H), 5.10 – 4.97 (m, 2H), 3.99 – 2.12 (m, 4H), 1.94 – 1.78 (m, 2H), 1.57 – 1.34 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 159.0, 138.9, 129.3 (2C), 120.4, 114.4, 114.2 (2C), 67.7, 33.6, 29.2, 28.8, 28.1, 25.8.

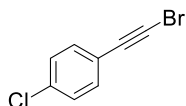
1-(Bromoethynyl)-4-methylbenzene^[17]



Yellow liquid (91 mg, 95% yield), $R_f = 0.8$ (Hexane/EtOAc = 100:1); ^1H NMR (500

MHz, CDCl_3) δ 7.38 – 7.34 (m, 2H), 7.22 – 7.08 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 138.8, 131.8 (2C), 129.0 (2C), 119.5, 80.1, 48.7, 21.4.

1-(Bromoethynyl)-4-chlorobenzene^[18]



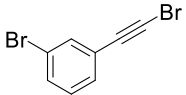
Yellow liquid (106 mg, 99% yield), $R_f = 0.8$ (Hexane/EtOAc = 100:1); ^1H NMR

(500 MHz, CDCl_3) δ 7.40 – 7.25 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 134.7,

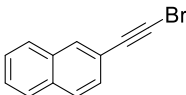
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133.1 (2C), 128.6 (2C), 121.1, 78.9, 51.0.

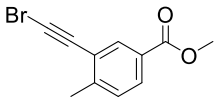
1-Bromo-3-(bromoethynyl)benzene^[17]

 Yellow liquid (125 mg, 98% yield), $R_f = 0.8$ (Hexane/EtOAc = 100:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.62 – 7.59 (m, 1H), 7.48 – 7.44 (m, 1H), 7.39 – 7.34 (m, 1H), 7.17 (m, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 134.7, 131.8, 130.5, 129.7, 124.5, 122.0, 78.5, 51.6.

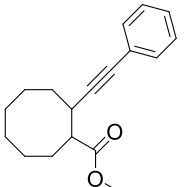
2-(Bromoethynyl)naphthalene^[17]

 Yellow solid (111 mg, 97% yield), $R_f = 0.8$ (Hexane/EtOAc = 100:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.99 – 7.80 (m, 4H), 7.58 – 7.46 (m, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 132.9, 132.8, 132.1, 128.4, 128.0, 127.8, 127.7, 126.9, 126.6, 119.9, 80.4, 50.0.

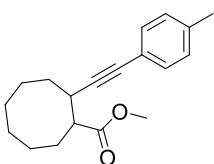
Methyl 3-(bromoethynyl)-4-methylbenzoate

 Yellow liquid (124 mg, 99% yield), $R_f = 0.5$ (Hexane/EtOAc = 100:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.09 – 8.07 (m, 1H), 7.29 – 7.24 (m, 2H), 3.90 (s, 3H), 2.48 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 166.3, 146.0, 133.6, 129.5, 127.8, 122.8, 78.1, 54.0, 52.1, 20.8. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{10}\text{BrO}_2$, 252.9859, found: 252.9860.

Methyl 2-(phenylethynyl)cyclooctane-1-carboxylate (4a)

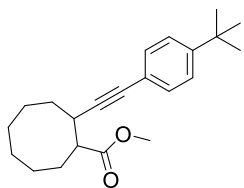
 Yellow liquid (103 mg, 76% yield), $R_f = 0.5$ (Hexane/EtOAc = 50:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.37 – 7.20 (m, 5H), 3.71 (s, 3H), 3.35 – 2.81 (m, 2H), 2.08 – 1.98 (m, 3H), 1.87 – 1.67 (m, 2H), 1.63 – 1.48 (m, 7H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 175.4, 131.6 (2C), 128.0 (2C), 127.5, 123.7, 90.7, 82.7, 51.8, 45.3, 33.3, 31.3, 27.7, 26.2, 25.3, 25.1, 24.3. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{23}\text{O}_2$, 271.1693, found: 271.1689.

methyl 2-(p-tolyethynyl)cyclooctane-1-carboxylate (4b)

 Yellow liquid (72 mg, 51% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.29 – 7.24 (m, 2H), 7.07 – 7.04 (m, 2H), 3.34 – 3.29 (m, 1H), 3.71 (s, 3H), 2.80 – 2.74 (m, 1H), 2.32 (s, 3H), 2.12 – 1.89 (m, 1H), 1.87 – 1.72 (m, 3H), 1.63 – 1.49 (m, 8H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 175.5, 137.5, 131.4 (2C), 128.8 (2C), 120.6, 89.9, 82.7, 51.8, 45.3, 33.3, 31.3, 27.7, 26.2, 25.3, 25.1, 24.3, 21.3. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{25}\text{O}_2$, 285.1849, found: 258.1855.

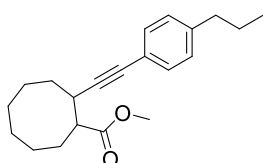
Methyl 2-((4-(tert-butyl)phenyl)ethynyl)cyclooctane-1-carboxylate (4c)

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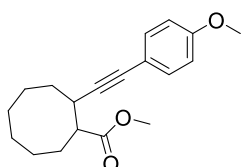
Yellow liquid (89 mg, 55% yield), $R_f = 0.5$ (Hexane/EtOAc=50:1); ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.24 (m, 4H), 3.71 (s, 3H), 3.34 – 2.80 (m, 2H), 2.11 – 2.03 (m, 1H), 2.02 – 1.93 (m, 2H), 1.85 – 1.71 (m, 2H), 1.64 – 1.48 (m, 7H), 1.34 – 1.29 (m, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.5, 150.7, 131.3 (2C), 125.0 (2C), 120.7, 89.9, 82.7, 51.8, 45.4, 34.6, 33.3, 31.3, 31.1 (3C), 27.7, 26.2, 25.3, 25.1, 24.3. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{31}\text{O}_2$, 327.2319, found: 327.2324.

Methyl 2-((4-propylphenyl)ethynyl)cyclooctane-1-carboxylate (4d)



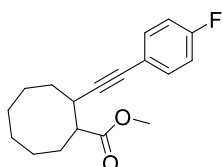
Yellow liquid (90 mg, 58% yield), $R_f = 0.5$ (Hexane/EtOAc = 50:1); ^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.26 (m, 2H), 7.07 – 6.80 (m, 2H), 3.71 (s, 3H), 3.34 – 2.80 (m, 2H), 2.55 – 2.07 (m, 3H), 2.02 – 1.89 (m, 3H), 1.86 – 1.71 (m, 2H), 1.47 – 1.64 (m, 7H), 1.35 – 1.27 (m, 1H), 0.91 – 0.87 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.5, 142.4, 131.5 (2C), 128.3 (2C), 120.9, 89.9, 82.8, 51.9, 45.4, 37.9, 33.4, 31.4, 27.8, 26.2, 25.4, 25.1, 24.4, 24.3, 13.7. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{29}\text{O}_2$, 313.2162, found: 313.2162.

methyl 2-((4-methoxyphenyl)ethynyl)cyclooctane-1-carboxylate (4e)



Yellow liquid (56 mg, 37% yield), $R_f = 0.4$ (Hexane/EtOAc = 10:1) ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.22 (m, 2H), 6.89 – 6.79 (m, 2H), 3.85 (s, 3H), 3.71 (s, 3H), 3.41 – 2.81 (m, 2H), 2.13 – 1.91 (m, 4H), 1.90 – 1.74 (m, 2H), 1.64 – 1.48 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.4, 159.9, 133.6 (2C), 113.0, 110.7 (2C), 94.9, 78.8, 55.7, 51.8, 45.5, 33.5, 31.4, 27.7, 26.2, 25.4, 25.2, 24.3. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{25}\text{O}_3$, 301.1798, found: 301.1789.

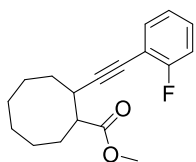
Methyl 2-((4-fluorophenyl)ethynyl)cyclooctane-1-carboxylate (4f)



Yellow liquid (80 mg, 56% yield), $R_f = 0.5$ (Hexane/EtOAc = 50:1); ^1H NMR (500 MHz, CDCl_3) δ 7.38 – 7.31 (m, 2H), 6.99 – 6.91 (m, 2H), 3.71 (s, 3H), 3.33 – 2.07 (m, 3H), 1.98 – 1.92 (m, 3H), 1.86 – 1.67 (m, 2H), 1.60 – 1.49 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.5, 162.1 (d, $J = 246.8$ Hz, 1C), 133.4 (d, $J = 8.1$ Hz, 2C), 119.8 (d, $J = 4.6$ Hz, 1C), 115.3 (d, $J = 21.9$ Hz, 2C), 90.4, 81.6, 51.9, 45.2, 33.3, 31.3, 27.8, 26.2, 25.2, 24.3. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{FO}_2$, 289.1598, found: 289.1598.

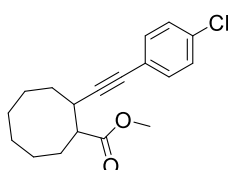
methyl 2-((2-fluorophenyl)ethynyl)cyclooctane-1-carboxylate (4g)

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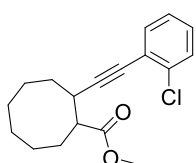
Yellow liquid (119 mg, 83% yield), $R_f = 0.5$ (Hexane/EtOAc = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.69 – 6.80 (m, 4H), 3.63 (s, 3H), 2.95 – 2.42 (m, 2H), 1.98 – 1.08 (m, 12H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 175.4, 162.8 (d, $J = 249.1$ Hz, 1C), 133.6 (d, $J = 1.1$ Hz, 1C), 129.2 (d, $J = 7.7$ Hz, 1C), 123.7 (d, $J = 3.8$ Hz, 1C), 115.2 (d, $J = 21.0$ Hz, 1C), 96.3 (d, $J = 3.4$ Hz, 1C), 76.0, 51.9, 45.4, 33.5, 31.3, 27.7, 26.2, 25.4, 25.2, 24.3. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{FO}_2$, 289.1598, found: 289.1591.

Methyl 2-((4-chlorophenyl)ethynyl)cyclooctane-1-carboxylate (4h)



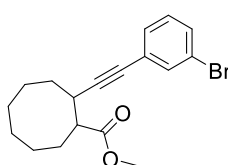
Yellow liquid (99 mg, 65% yield), $R_f = 0.5$ (Hexane/EtOAc = 50:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.30 – 7.28 (m, 2H), 7.26 – 7.20 (m, 2H), 3.71 (s, 3H), 3.33 – 2.07 (m, 3H), 1.97 – 1.92 (m, 3H), 1.78 – 1.51 (m, 8H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 175.4, 133.5, 132.8 (2C), 128.4 (2C), 122.2, 91.9, 81.6, 51.9, 45.2, 33.3, 31.2, 27.8, 26.2, 25.3, 25.2, 24.3. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{ClO}_2$, 305.1303, found: 305.1297.

methyl 2-((2-chlorophenyl)ethynyl)cyclooctane-1-carboxylate (4i)



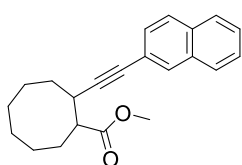
Yellow liquid (129 mg, 85% yield), $R_f = 0.5$ (Hexane/EtOAc = 50:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.30 – 7.28 (m, 2H), 7.26 – 7.20 (m, 2H), 3.71 (s, 3H), 3.33 – 2.07 (m, 3H), 1.97 – 1.92 (m, 3H), 1.78 (m, 2H), 1.63 – 1.51 (m, 6H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 175.4, 136.0, 133.5, 132.8, 128.8, 127.5, 124.2, 91.9, 81.6, 51.9, 45.2, 33.3, 31.2, 27.8, 26.2, 25.3, 25.2, 24.3. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{ClO}_2$, 305.1303, found: 305.1297.

methyl 2-((3-bromophenyl)ethynyl)cyclooctane-1-carboxylate (4j)



Yellow liquid (104 mg, 54% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.51 – 7.39 (m, 2H), 7.29 – 7.13 (m, 2H), 3.71 (s, 3H), 3.34 – 2.07 (m, 3H), 1.93 – 1.92 (m, 5H), 1.58 – 1.48 (m, 6H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 175.3, 134.3, 130.7, 130.2, 125.7, 121.9, 92.3, 81.2, 51.9, 45.1, 33.3, 31.2, 27.7, 26.1, 25.3, 25.2, 24.2. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{BrO}_2$, 349.0798, found: 349.0791.

methyl 2-((naphthalen-2-yl)ethynyl)cyclooctane-1-carboxylate (4k)

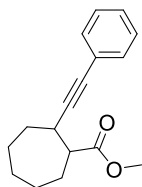


Yellow liquid (79 mg, 52% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.29 – 7.24 (m, 4H), 7.18 – 7.05 (m, 3H), 3.71 (s, 3H), 3.34 – 2.80 (m, 2H), 2.32 (s, 1H), 2.07 – .96 (m, 4H), 1.86 – 1.71 (m, 3H), 1.55 – 1.32 (m, 4H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 175.5, 132.9, 132.5, 131.1, 128.7, 127.7, 127.6,

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127.5, 126.3, 126.2, 121.0, 89.9, 82.7, 51.8, 45.3, 33.4, 31.3, 27.7, 26.2, 25.3, 25.1, 24.3. HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $C_{22}H_{25}O_2$, 321.1849, found: 321.1856.

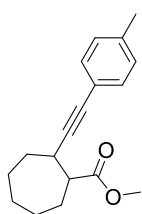
Methyl 2-(phenylethynyl)cycloheptane-1-carboxylate (4l)



Yellow liquid (83 mg, 65% yield), $R_f = 0.5$ (Hexane/EtOAc=50:1); 1H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 2H), 7.34 – 7.22 (m, 3H), 3.71 (s, 3H), 3.49 – 2.65 (m, 2H), 2.11 – 1.93 (m, 3H), 1.83 – 1.48 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 131.5 (2C), 128.1 (2C), 127.5, 123.8, 90.1, 83.6, 51.7, 48.9, 33.5, 33.0, 27.3, 26.4, 25.8, 24.8.

HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $C_{17}H_{21}O_2$, 257.1536, found: 257.1533.

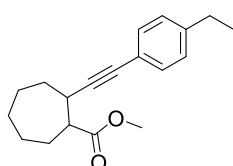
methyl 2-(p-tolyethynyl)cycloheptane-1-carboxylate (4m)



Yellow liquid (69 mg, 51 % yield), 1H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 2H), 7.14 – 7.08 (m, 2H), 3.70 (s, 3H), 3.47 – 2.64 (m, 2H), 2.32 (s, 3H), 2.11 – 1.90 (m, 3H), 1.82 (m, 3H), 1.70 – 1.58 (m, 3H), 1.55 – 1.41 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0, 137.5, 131.4 (2C), 128.8 (2C), 120.7, 89.3, 83.6, 51.7, 48.9, 33.5, 33.0, 27.4,

26.4, 25.9, 24.8, 21.4. HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $C_{18}H_{23}O_2$, 271.1693, found: 271.1689.

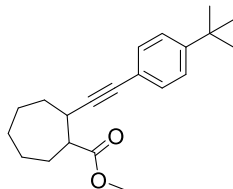
methyl 2-((4-ethylphenyl)ethynyl)cycloheptane-1-carboxylate (4n)



Yellow liquid (83 mg, 58% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); 1H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.24 – 7.10 (m, 2H), 3.70 (s, 3H), 3.47 – 2.56 (m, 4H), 2.04 – 1.93 (m, 2H), 1.79 – 1.61 (m, 7H), 1.54 – 1.41 (m,

1H), 1.21 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ 175.0, 143.9, 131.5 (2C), 127.6(2C), 120.9, 89.3, 83.6, 51.7, 48.9, 33.5, 33.0, 28.7, 27.3, 26.4, 25.8, 24.7, 15.4. HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $C_{19}H_{25}O_2$, 285.1849, found: 285.1843.

Methyl 2-((4-(tert-butyl)phenyl)ethynyl)cycloheptane-1-carboxylate (4o)

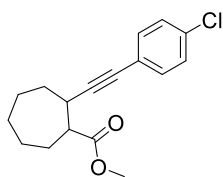


Yellow liquid (84 mg, 54% yield), $R_f = 0.5$ (Hexane/EtOAc=50:1); 1H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 4H), 3.70 (s, 3H), 3.48 – 2.64 (m, 2H), 2.05 – 1.90 (m, 2H), 1.89 – 1.73 (m, 3H), 1.71 – 1.40 (m, 5H), 1.35 – 1.29 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0, 150.7, 131.2 (2C), 125.1 (2C), 120.8,

89.3, 83.6, 50.3, 48.9, 34.6, 33.5, 33.0, 31.1 (3C), 27.3, 26.4, 25.8, 24.7. HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $C_{21}H_{29}O_2$, 313.2162, found: 313.2161.

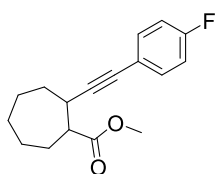
Methyl 2-((4-chlorophenyl)ethynyl)cycloheptane-1-carboxylate (4p)

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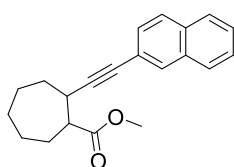
Yellow liquid (68 mg, 47% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.28 (m, 2H), 7.28 – 7.21 (m, 2H), 3.70 (s, 3H), 3.47 – 2.65 (m, 2H), 2.10 – 1.89 (m, 5H), 1.62 – 1.49 (m, 5H). ^{13}C NMR (125 MHz, CDCl_3) δ 174.9, 133.5, 132.8 (2C), 128.4 (2C), 122.2, 91.3, 82.5, 51.8, 48.7, 33.5, 32.9, 27.3, 26.4, 25.8, 24.8. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{20}\text{ClO}_2$, 291.1146, found: 291.1142.

Methyl 2-((4-fluorophenyl)ethynyl)cycloheptane-1-carboxylate (4q)



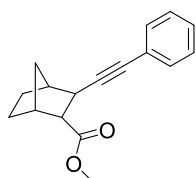
Yellow liquid (68.5 mg, 50% yield), $R_f = 0.5$ (Hexane/EtOAc=50:1); ^1H NMR (500 MHz, CDCl_3) δ 7.39 – 7.32 (m, 2H), 7.00 – 6.92 (m, 2H), 3.70 (s, 3H), 3.46 – 2.65 (m, 2H), 2.06 – 1.91 (m, 3H), 1.80 – 1.50 (m, 7H). ^{13}C NMR (125 MHz, CDCl_3) δ 174.9, 162.1 (d, $J = 308.6$ Hz, 1C), 133.3 (d, $J = 10.3$ Hz, 2C), 131.0 (d, $J = 10.3$ Hz, 1C), 119.8 (d, $J = 3.5$ Hz, 1C), 115.3 (d, $J = 27.4$ Hz, 2C), 89.8, 82.5, 51.8, 48.8, 33.5, 33.0, 27.4, 26.5, 25.9, 24.8. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{20}\text{FO}_2$, 275.1442, found: 275.1436.

methyl 2-(naphthalen-2-ylethynyl)cycloheptane-1-carboxylate (4r)



Yellow liquid (77 mg, 52% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.81 – 7.71 (m, 4H), 7.56 – 7.41 (m, 3H), 3.73 (s, 3H), 3.54 – 2.69 (m, 2H), 2.09 – 1.99 (m, 2H), 1.94 – 1.76 (m, 3H), 1.75 – 1.47 (m, 5H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.0, 132.9, 132.5, 131.0, 128.7, 127.7, 127.6, 127.5, 126.3, 126.2, 121.1, 90.5, 83.9, 51.8, 48.9, 33.6, 33.1, 27.4, 26.5, 25.9, 24.8. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{23}\text{O}_2$, 307.1693, found: 307.1688.

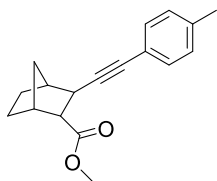
Methyl-3-(phenylethynyl)bicyclo[2.2.1]heptane-2-carboxylate (4s)



Yellow liquid (72 mg, 57% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.35 (m, 2H), 7.23-7.27 (m, 3H), 3.65 (s, 3H), 2.97 – 2.67 (m, 3H), 2.59 (d, $J = 3.7$ Hz, 1H), 2.47 – 2.10 (m, 3H), 1.67 – 1.22 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.3, 131.4 (2C), 128.1 (2C), 127.6, 123.5, 90.2, 82.6, 52.3, 51.4, 43.4, 39.0, 38.2, 36.3, 28.6, 28.0. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{19}\text{O}_2$, 255.1380, found: 255.1387.

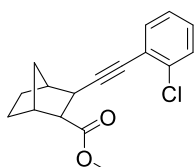
Methyl-3-(p-tolyethynyl)bicyclo[2.2.1]heptane-2-carboxylate (4t)

SUPPORTING INFORMATION



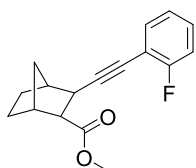
Yellow liquid (96 mg, 72% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.22 – 7.06 (m, 4H), 3.65 (s, 3H), 2.95 – 2.67 (m 2H), 2.60 – 2.46 (m, 2H), 2.32 (s, 3H), 1.65 – 1.49 (m, 1 H), 1.33 – 1.15 (m, 5H). ^{13}C NMR (125 MHz, CDCl_3) δ 173.3, 137.6, 131.3 (2C), 128.8 (2C), 120.4, 89.4, 82.6, 52.3, 51.4, 43.4, 39.0, 38.7, 36.2, 28.6, 27.9, 21.3. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{21}\text{O}_2$, 269.1536, found: 269.1538.

methyl-3-((2-chlorophenyl)ethynyl)bicyclo[2.2.1]heptane-2-carboxylate (4u)



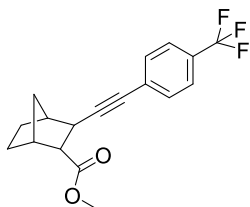
Yellow liquid (125 mg, 87% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.48 – 7.31 (m, 4H), 3.65 (s, 3H), 3.26 – 2.67 (m, 3H), 2.60 – 2.56 (m, 1H), 2.46 – 2.32 (m, 3H), 1.65 – 1.33 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 171.9, 136.0, 133.6, 132.6, 128.8, 127.5, 123.7, 89.3, 81.7, 52.0, 51.7, 41.5, 39.1, 36.2, 33.2, 28.0, 27.1. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{18}\text{ClO}_2$, 289.0990, found: 289.0983.

methyl-3-((2-fluorophenyl)ethynyl)bicyclo[2.2.1]heptane-2-carboxylate (4v)



Yellow liquid (115 mg, 85% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.56 (m, 1H), 7.46 (m, 1H), 7.22 (m, 2H), 3.65 (s, 3H), 3.26 (m, 1H), 2.67 (m, 2H), 2.60 – 2.56 (m, 1H), 2.46 (m, 1H), 2.32 (m, 2H), 1.65 – 1.49 (m, 1 H), 1.33 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.2, 162.3 (d, $J = 248.8$ Hz, 1C), 133.6, 129.2 (d, $J = 7.8$ Hz, 1C), 123.7 (d, $J = 3.6$ Hz, 1C), 115.4 (d, $J = 20.9$ Hz, 1C), 112.0 (d, $J = 15.8$ Hz, 1C), 95.5 (d, $J = 3.4$ Hz, 1C), 75.9, 52.2, 51.3 (d, $J = 1.7$ Hz, 1C), 43.6, 39.2, 38.9, 36.3, 28.6, 28.0. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{18}\text{FO}_2$, 273.1285, found: 273.1294.

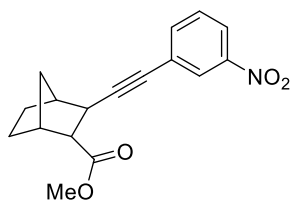
Methyl-3-((4-(trifluoromethyl)phenyl)ethynyl)bicyclo[2.2.1]heptane-2-carboxylate (4w)



Yellow liquid (80 mg, 54% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.60 – 7.34 (m, 4H), 3.62 (s, 3H), 3.02 (m, 1H), 2.71 – 2.47 (m, 3H), 2.10 – 1.59 (m, 4H), 1.36 – 1.16 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 173.1, 134.1 (2C), 131.2, 127.4 (2C), 125.7 (q, $J = 10.1, 5.3$ Hz, 1C), 122.3 (q, $J = 217.6, 110.6$ Hz, 1C), 96.3, 78.6, 52.1, 51.4, 43.5, 39.2, 38.9, 36.3, 28.7, 28.0. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{18}\text{F}_3\text{O}_2$, 323.1253, found: 323.1247.6666

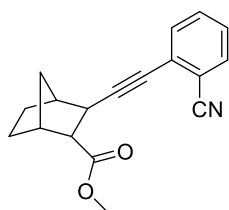
Methyl-3-((3-nitrophenyl)ethynyl)bicyclo[2.2.1]heptane-2-carboxylate (4x)

SUPPORTING INFORMATION



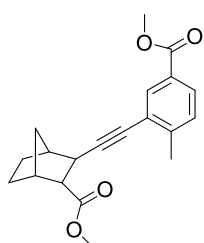
Yellow liquid (94 mg, 64% yield), $R_f = 0.6$ (Hexane/EtOAc = 5:1) ^1H NMR (400 MHz, CDCl_3) δ 8.26 – 8.02 (m, 2H), 7.63 – 7.44 (m, 2H), 3.66 (s, 3H), 2.98 – 2.08 (m, 5H), 1.70 – 1.50 (m, 2H), 1.37 (m, 1H), 1.32 – 1.14 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.1, 148.0, 137.2, 129.1, 126.2, 125.3, 122.4, 93.3, 80.4, 52.1, 51.4, 43.4, 39.7, 38.9, 36.3, 28.5, 28.0. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_4$, 300.1230, found: 300.1239.

methyl (1R,2R,4S)-3-((2-cyanophenyl)ethynyl)bicyclo[2.2.1]heptane-2-carboxylate (4y)



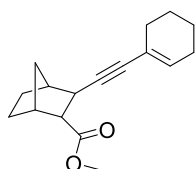
Yellow liquid (122 mg, 88% yield), $R_f = 0.2$ (Hexane/EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.59 – 7.33 (m, 4H), 3.66 (s, 3H), 3.05 – 2.58 (m, 4H), 2.17 – 2.10 (m, 1H), 1.63 – 1.55 (m, 2H), 1.44 – 1.34 (m, 1H), 1.34 – 1.16 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.1, 132.4, 132.42, 132.2, 127.8, 117.4, 115.0, 97.5, 78.9, 52.1, 51.4, 43.6, 39.1, 38.9, 36.4, 28.6, 27.9. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{18}\text{NO}_2$, 280.1332, found: 280.1333.

Methyl-3-((5-(methoxycarbonyl)-2-methylphenyl)ethynyl)bicyclo[2.2.1]heptane-2-carboxylate (4z)



Yellow liquid (132 mg, 81% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.97 – 7.81 (m, 2H), 7.28 – 7.20 (m, 1H), 3.88 (s, 3H), 3.61 (s, 3H), 3.03 – 2.48 (m, 4H), 2.42 (s, 3H), 2.26 – 1.55 (m, 3H), 1.36 – 1.25 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 173.2, 166.6, 145.3, 133.0, 130.9, 127.6, 121.3, 95.1, 80.5, 52.5, 52.0, 51.3, 43.7, 39.2, 38.2, 36.3, 28.6, 27.9, 20.9. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{23}\text{O}_4$, 327.1591, found: 327.1583.

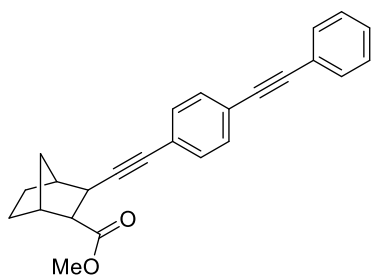
Methyl-3-(cyclohex-1-en-1-ylethynyl)bicyclo[2.2.1]heptane-2-carboxylate (4aa)



Yellow liquid (82 mg, 64% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 5.98 – 5.94 (m, 1H), 3.66 (s, 3H), 2.85 – 2.35 (m, 4H), 2.05 – 1.98 (m, 5H), 1.62 – 1.45 (m, 6H), 1.28 – 1.26 (m, 1H), 1.22 – 1.11 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 173.3, 133.5, 120.6, 85.7, 84.4, 52.2, 51.2, 43.5, 38.9, 38.7, 36.1, 29.4, 28.6, 27.9, 25.5, 22.2, 21.5. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{23}\text{O}_2$, 259.1693, found: 259.1688.

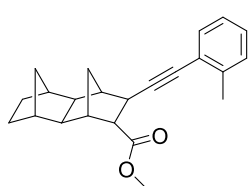
Methyl-3-((4-(phenylethynyl)phenyl)ethynyl)bicyclo[2.2.1]heptane-2-carboxylate (4ab)

SUPPORTING INFORMATION



Yellow solid (103 mg, 58% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.54 – 7.49 (m, 2H), 7.45 – 7.40 (m, 2H), 7.39 – 7.27 (m, 5H), 3.65 (s, 3H), 2.98 – 2.69 (m, 2H), 2.60 – 2.10 (m, 2H), 1.67 – 1.51 (m, 4H), 1.24 – 1.16 (m, 2H); $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 173.3, 131.6 (2C), 131.4 (2C), 131.4 (2C), 128.4, 128.3 (2C), 123.4, 123.0, 92.3, 89.1, 82.4, 52.3, 51.4, 43.4, 39.14 38.8, 36.3, 28.6, 28.0. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{23}\text{O}_2$, 355.1693, found: 355.1684.

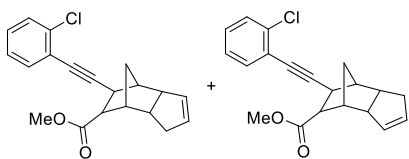
3-(*o*-tolylethynyl)decahydro-1,4:5,8-dimethanonaphthalene-2-carboxylate (4ac)



Yellow liquid (125 mg, 76% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.30 – 7.28 (m, 1H), 7.19 – 7.13 (m, 2H), 7.08 – 7.05 (m, 1H), 3.60 (s, 3H), 3.38 – 3.07 (m, 2H), 2.63 – 2.59 (m, 1H), 2.48 – 2.36 (m, 1H), 2.37 (s, 3H), 2.23 (s, 1H), 2.13 – 1.78 (m, 4H), 1.52 – 1.41 (m, 4H), 1.07 – 1.00 (m, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 173.6, 139.9, 131.8, 129.2, 127.6, 125.3, 123.3, 94.8, 81.2, 51.3, 49.7, 48.8, 48.4, 46.8, 43.2, 40.0, 36.2, 36.1, 34.9, 33.8, 31.2, 31.1, 20.6. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{27}\text{O}_2$, 335.2006, found: 335.1998.

methyl-5-((2-chlorophenyl)ethynyl)-3a,4,5,6,7,7a-hexahydro-1H-4,7-methanoindene-6-carboxylate (4ad-1);

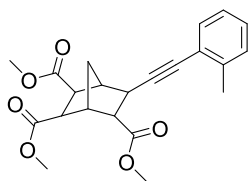
methyl-6-((2-chlorophenyl)ethynyl)-3a,4,5,6,7,7a-hexahydro-1H-4,7-methanoindene-5-carboxylate (4ad-2)



Yellow liquid (141.8 mg, 87% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.39 – 7.31 (m, 4H), 7.16 (td, $J = 6.9, 1.7$ Hz, 4H), 5.73 (td, $J = 6.0, 2.1$ Hz, 2H), 5.62 (dd, $J = 5.6, 2.2$ Hz, 1H), 5.50 (dd, $J = 5.5, 2.3$ Hz, 1H), 3.63 (d, $J = 4.4$ Hz, 6H), 3.19 – 3.07 (m, 4H), 2.85 (dd, $J = 9.6, 1.7$ Hz, 1H), 2.70 – 2.56 (m, 5H), 2.52 (d, $J = 4.3$ Hz, 1H), 2.45 (d, $J = 4.5$ Hz, 1H), 2.38 – 2.21 (m, 5H), 2.14 – 2.06 (m, 1H), 1.65 – 1.56 (m, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 173.6, 173.3, 135.6 (2C), 133.4, 133.3, 132.0, 131.8, 131.6, 131.5, 129.1 (2C), 128.6 (2C), 126.2 (2C), 123.4 (2C), 96.5, 96.3, 79.2, 79.0, 52.3, 52.0, 51.5, 51.4, 48.3, 47.5, 46.6, 44.9, 43.1, 41.8, 41.6, 41.4, 39.6, 39.1, 34.8, 32.2, 32.1 (2C). HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{20}\text{ClO}_2$, 327.1146, found: 327.1141.

Trimethyl-6-(*o*-tolylethynyl)bicyclo[2.2.1]heptane-2,3,5-tricarboxylate (4ae)

SUPPORTING INFORMATION

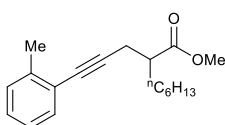


Yellow liquid (119 mg, 62% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.31 (m, 1H), 7.21 – 7.12 (m, 3H), 3.70 (s, 3H), 3.64 – 3.19 (m, 9H), 2.97 – 2.76 (m, 3H), 2.38 – 2.35 (m, 4H), 1.53 – 1.24 (m, 1H).

^{13}C NMR (125 MHz, CDCl_3) δ 173.3, 172.1, 170.9, 139.9, 131.9, 129.3, 127.8,

125.3, 122.9, 93.2, 81.9, 51.8, 51.6, 51.5, 47.2, 46.2, 45.9, 45.5, 41.6, 37.6, 34.1, 20.6. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{25}\text{O}_6$, 385.1646, found: 385.1650.

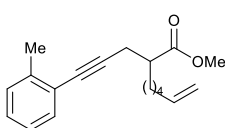
Methyl 2-(3-(o-tolyl)prop-2-yn-1-yl)octanoate (4af)



Yellow liquid (88 mg, 62% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.34 (m, 1H), 7.24 – 7.15 (m, 2H), 7.14 – 7.06 (m, 1H), 3.72 (s, 3H), 2.76 – 2.57 (m, 3H), 2.39 (s, 3H), 1.72 – 1.65 (m, 2H), 1.33 – 1.22

(m, 8H), 0.91 – 0.87 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.2, 140.0, 131.8, 129.2, 127.7, 125.3, 123.3, 91.0, 80.7, 51.7, 44.9, 31.6, 31.4, 29.1, 26.9, 22.5, 22.3, 20.6, 14.0. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{27}\text{O}_2$, 287.2006, found: 287.2000.

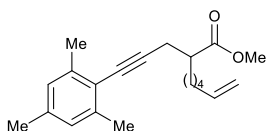
Methyl 2-(3-(o-tolyl)prop-2-yn-1-yl)oct-7-enoate (4ag)



Yellow liquid (122 mg, 86% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.37 – 7.32 (m, 2H), 7.17 – 7.10 (m, 2H), 5.79 – 5.63 (m, 1H), 5.04 – 4.88 (m, 2H), 3.72 (s, 3H), 2.81 – 2.59 (m, 3H), 2.39 (s, 3H), 2.10 –

1.98 – 1.74 (m, 4H), 1.57 – 1.27 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.1, 140.0, 138.6, 131.8, 129.2, 127.7, 125.4, 123.3, 114.4, 90.9, 80.8, 51.7, 44.8, 33.4, 31.2, 28.6, 26.4, 22.3, 20.6. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{25}\text{O}_2$, 285.1849, found: 285.1856.

Methyl 2-(3-(2-mesityl)prop-2-yn-1-yl)oct-7-enoate (4ah)

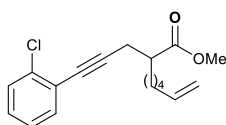


Yellow liquid (114 mg, 73% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 6.83 (s, 2H), 5.79 – 4.99 (m, 4H), 3.71 (s, 3H), 2.84 – 2.75 (m, 1H), 2.74 – 2.59 (m, 1H), 2.34 (s, 3H), 2.26 (s, 6H), 2.10 –

1.97 (m, 2H), 1.82 – 1.66 (m, 2H), 1.52 – 1.29 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.2, 139.9 (2C), 138.6, 137.0, 127.4 (2C), 120.2, 114.4, 94.4, 79.5, 51.6, 45.0, 33.5, 31.2, 28.6, 26.4, 22.4, 21.2, 20.9 (2C). HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{29}\text{O}_2$, 313.2162, found: 313.2155.

Methyl 2-(3-(2-chlorophenyl)prop-2-yn-1-yl)oct-7-enoate (4ai)

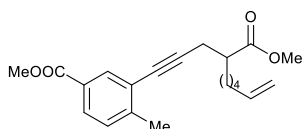
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Yellow liquid (98 mg, 71% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.38 – 7.19 (m, 4H), 5.80 – 4.91 (m, 3H), 3.72 (s, 3H), 2.12 – 2.02 (m, 3H), 1.76 – 1.59 (m, 4H), 1.55 – 1.29 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.0, 138.7, 135.7, 133.3, 129.1, 128.7, 126.3, 123.3, 114.4, 92.6, 78.8, 51.7, 44.5, 33.4,

31.1, 28.6, 26.3, 22.2. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{22}\text{ClO}_2$, 305.1303, found: 305.1297.

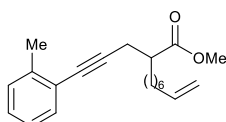
Methyl 3-(4-(methoxycarbonyl)dec-9-en-1-yn-1-yl)-4-methylbenzoate (4aj)



Yellow liquid (130 mg, 76% yield), $R_f = 0.3$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 8.01 (d, $J = 1.9$ Hz, 1H), 7.83 (m, 1H), 7.24 (d, $J = 8.0$ Hz, 1H), 5.79 – 4.91 (m, 2H), 3.89 (s, 3H), 3.72 (s, 3H), 2.83 – 2.72

(m, 1H), 2.72 – 2.59 (m, 2H), 2.43 (s, 3H), 2.11 – 2.05 (m, 2H), 1.82 – 1.61 (m, 2H), 1.52 – 1.30 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.0, 166.6, 145.3, 138.64 133.0, 129.4, 128.7, 127.6, 123.6, 114.5, 91.9, 79.9, 52.0, 51.7, 44.7, 33.4, 31.2, 28.6, 26.4, 22.2, 20.9. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{27}\text{O}_4$, 343.1904, found: 343.1905.

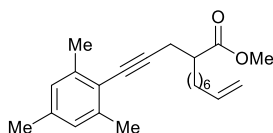
Methyl 2-(3-(o-tolyl)prop-2-yn-1-yl)dec-9-enoate (4ak)



Yellow liquid (126 mg, 81% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.28 (m, 1H), 7.19 – 7.15 (m, 2H), 7.10 – 7.06 (m, 1H), 5.80 – 4.92 (m, 3H), 3.72 (s, 3H), 2.79 – 2.58 (m, 3H), 2.39 (s, 3H), 2.07 –

1.99 (m, 2H), 1.79 – 1.67 (m, 2H), 1.42 – 1.21 (m, 8H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.2, 140.0, 139.0, 131.8, 129.2, 127.7, 125.4, 123.3, 114.2, 80.9, 80.8, 51.7, 44.9, 33.7, 31.4, 29.2, 28.8, 28.7, 26.9, 22.3, 20.6. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{29}\text{O}_2$, 313.2162, found: 313.2155.

Methyl 2-(3-mesitylprop-2-yn-1-yl)dec-9-enoate (4al)

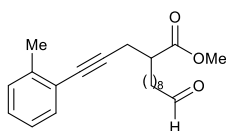


Yellow liquid (113 mg, 67% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 6.83 (s, 2H), 5.86 – 5.74 (m, 1H), 5.00 – 4.97 (m, 2H), 3.71 (s, 3H), 2.86 – 2.75 (m, 1H), 2.75 – 2.58 (m, 2H), 2.30 – 2.23 (m,

9H), 2.16 – 1.95 (m, 4H), 1.61 – 1.28 (m, 8H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.3, 139.9 (2C), 139.0, 137.0, 127.4 (2C), 123.3, 114.1, 94.5, 79.5, 51.6, 45.1, 33.7, 31.4, 29.3, 28.8, 28.7, 26.9, 22.5, 21.2, 20.9 (2C). HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{33}\text{O}_2$, 341.2475, found: 341.2465.

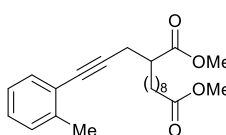
Methyl 10-oxo-2-(3-(o-tolyl)prop-2-yn-1-yl)decanoate (4am)

SUPPORTING INFORMATION



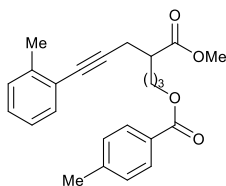
Yellow liquid (125 mg, 73% yield), $R_f = 0.3$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 9.75 – 7.16 (m, 4H), 7.14 – 7.06 (m, 1H), 3.72 (s, 3H), 2.80 – 2.60 (m, 3H), 2.43 – 2.39 (m, 1H), 2.39 (s, 3H), 1.77 – 1.56 (m, 5H), 1.32 – 1.25 (m, 10H). ^{13}C NMR (125 MHz, CDCl_3) δ 202.9, 175.2, 140.0, 131.8, 129.2, 127.7, 125.4, 123.3, 90.9, 80.8, 51.7, 44.8, 43.8, 31.4, 29.3, 29.2, 29.1, 29.0, 26.9, 22.3, 22.0, 20.6. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{31}\text{O}_3$, 343.2268, found: 343.2260.

Dimethyl 2-(3-(o-tolyl)prop-2-yn-1-yl)dodecanedioate (4an)



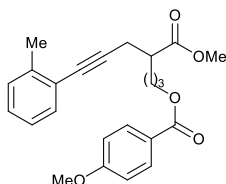
Yellow liquid (143 mg, 77% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.34 – 7.28 (m, 1H), 7.21 – 7.15 (m, 2H), 7.10 – 7.05 (m, 1H), 3.72 (s, 3H), 3.66 (s, 3H), 2.80 – 2.69 (m, 3H), 2.39 (s, 3H), 2.29 – 1.72 (m, 4H), 1.64 – 1.55 (m, 2H), 1.51 – 1.29 (m, 10H). ^{13}C NMR (125 MHz, CDCl_3) δ 175.2, 174.3, 140.0, 131.8, 129.2, 127.7, 125.4, 123.3, 90.9, 80.8, 51.5, 44.9, 34.0, 31.4, 29.3, 29.2, 29.1, 29.0, 28.6, 26.9, 24.9, 22.3, 20.6. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{33}\text{O}_4$, 373.2373, found: 373.2368.

4-(Methoxycarbonyl)-7-(o-tolyl)hept-6-yn-1-yl 4-methylbenzoate (4ao)



Yellow liquid (122 mg, 65% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.91 – 7.32 (m, 3H), 7.17 – 7.08 (m, 5H), 4.40 – 4.30 (m, 2H), 3.73 (s, 3H), 2.80 – 2.75 (m, 3H), 2.38 (m, 6H), 2.04 – 1.67 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 174.7, 166.6, 143.5, 140.0, 131.8, 129.5 (2C), 129.2, 129.0 (2C), 127.7, 127.4, 125.3, 123.1, 90.3, 81.1, 64.2, 51.8, 44.3, 27.7, 26.2, 22.3, 21.6, 20.6. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{27}\text{O}_4$, 379.1904, found: 379.1896.

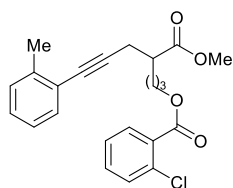
4-(Methoxycarbonyl)-7-(o-tolyl)hept-6-yn-1-yl 4-methoxybenzoate (4ap)



Yellow liquid (141 mg, 72% yield), $R_f = 0.2$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.97 – 7.86 (m, 2H), 7.38 – 7.30 (m, 1H), 7.21 – 7.13 (m, 3H), 6.94 – 6.81 (m, 2H), 4.31 – 4.25 (m, 2H), 3.83 (s, 3H), 3.73 (s, 3H), 2.86 – 2.64 (m, 3H), 2.37 (s, 3H), 1.99 – 1.65 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 174.7, 166.3, 163.2, 140.0, 131.8, 131.5 (2C), 129.2, 127.7 (2C), 125.4, 123.1, 122.6, 113.5, 90.4, 81.14, 64.1, 55.3, 51.8, 44.3, 27.7, 26.2, 22.3, 20.6. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{27}\text{O}_5$, 395.1853, found: 395.1854

4-(Methoxycarbonyl)-7-(o-tolyl)hept-6-yn-1-yl 2-chlorobenzoate (4aq)

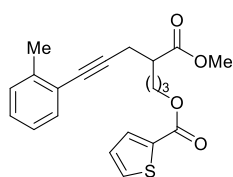
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Yellow liquid (121 mg, 61% yield), $R_f = 0.4$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.80 – .42 (m, 3H), 7.34 – 7.28 (m, 1H), 7.27 – 7.22 (m, 1H), 7.19 – 7.08 (m, 3H), 4.36 – 4.28 (m, 2H), 3.73 (s, 3H), 2.86 – 2.64 (m, 3H), 2.36 (s, 3H), 2.03 – 1.76 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 174.6, 165.7,

139.9, 133.6, 132.4, 131.8, 131.3, 131.1, 130.0, 129.2, 127.8, 126.5, 125.4, 123.1, 90.3, 81.1, 65.0, 51.8, 44.3, 27.7, 26.1, 22.3, 20.6. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{24}\text{ClO}_4$, 399.1358, found: 399.1350.

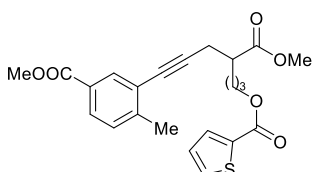
4-(Methoxycarbonyl)-7-(o-tolyl)hept-6-yn-1-yl thiophene-2-carboxylate (4ar)



Yellow liquid (107 mg, 58% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.78 – 7.75 (m, 1H), 7.51 (s, 1H), 7.36 – 7.30 (m, 1H), 7.19 – 7.10 (m, 4H), 4.32 – 4.27 (m, 2H), 3.73 (s, 3H), 2.88 – 2.63 (m, 3H), 2.37 (s, 3H), 1.97 – 1.72 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 174.6, 162.1, 140.0,

133.7, 133.3, 132.3, 131.8, 129.2, 127.8, 127.6, 125.4, 123.1, 90.3, 81.1, 64.6, 51.8, 44.3, 27.7, 26.2, 22.3, 20.6. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{23}\text{O}_4\text{S}$, 371.1312, found: 371.1302.

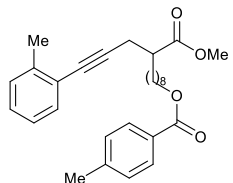
(Methoxycarbonyl)-8-(5-(methoxycarbonyl)-2-methylphenyl)oct-7-yn-1-yl thiophene-2-carboxylate (4as)



Yellow liquid (139 mg, 65% yield), $R_f = 0.3$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 8.01 – 7.77 (m, 3H), 7.28 – 7.20 (m, 2H), 7.06 – 7.01 (m, 1H), 4.32 (m, 2H), 3.89 (m, 3H), 3.74 (s, 3H), 2.87 – 2.64 (m, 3H), 2.41 (s, 3H), 1.95 – 1.74 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3) δ 174.5, 166.5, 162.1, 145.3,

133.6, 133.3, 133.0, 132.3, 129.4, 128.7, 127.7, 127.6, 123.5, 91.38, 80.2, 64.5, 52.0, 51.9, 44.1, 27.7, 26.2, 22.2, 20.9. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{25}\text{O}_6\text{S}$, 429.1366, found: 429.1360.

9-(2-Methoxy-2-oxoethyl)-11-(o-tolyl)undec-10-yn-1-yl 4-methylbenzoate (4at)

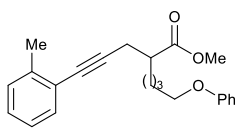


Yellow liquid (151 mg, 72% yield), $R_f = 0.3$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.95 – 7.90 (m, 2H), 7.23 (d, $J = 7.9$ Hz, 1H), 7.19 – 7.14 (m, 2H), 7.09 (m, 3H), 4.29 (d, $J = 5.6$ Hz, 2H), 3.71 (s, 3H), 2.80 – 2.59 (m, 3H), 2.41 – 2.36 (m, 6H), 1.79 – 1.68 (m, 4H), 1.37 – 1.24 (m, 10H). ^{13}C NMR (125

MHz, CDCl_3) δ 175.2, 166.7, 143.4, 139.9, 131.8, 129.5 (2C), 129.2, 129.0 (2C), 127.7, 127.4, 125.3, 123.3, 90.9, 80.8, 64.8, 51.7, 44.9, 31.4, 29.3, 29.2, 29.1, 28.6, 26.9, 25.9, 22.3, 21.6, 20.6. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{37}\text{O}_4$, 449.2686, found: 449.2680.

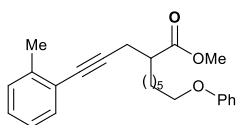
SUPPORTING INFORMATION

Methyl 8-phenoxy-2-(3-(*o*-tolyl)prop-2-yn-1-yl)octanoate (4au)



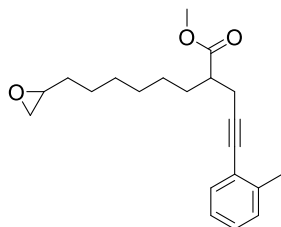
Yellow liquid (113 mg, 65% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.33 – 7.30 (m, 1H), 7.25 – 7.21 (m, 2H), 7.17 – 7.11 (m, 2H), 7.07 – 7.01 (m, 1H), 6.93 – 6.83 (m, 3H), 3.93 – 3.87 (m, 2H), 3.69 (s, 3H), 2.79 – 2.60 (m, 3H), 2.36 (s, 3H), 1.87 – 1.72 (m, 4H), 1.51 (m, 2H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 175.0, 158.9, 139.9, 131.8, 129.3 (2C), 129.2, 127.7, 125.4, 123.2, 120.5, 114.4 (2C), 90.7, 80.9, 67.3, 51.7, 44.7, 31.1, 29.1, 23.6, 22.3, 20.6. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{27}\text{O}_3$, 351.1955, found: 351.1945.

Methyl 2-(2-phenoxyethyl)-5-(*o*-tolyl)pent-4-ynoate (4av)



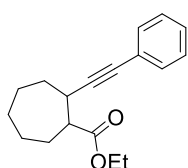
Yellow liquid (109 mg, 68% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.34 – 7.24 (m, 3H), 7.21 – 7.15 (m, 2H), 7.14 – 7.06 (m, 3H), 6.96 – 6.86 (m, 1H), 3.94 – 3.85 (m, 2H), 3.72 (s, 3H), 2.81 – 2.70 (m, 3H), 2.39 (s, 3H), 1.76 – 1.62 (m, 4H), 1.51 – 1.42 (m, 2H), 1.38 – 1.24 (m, 4H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 175.2, 159.0, 140.0, 131.8, 129.4 (2C), 129.3, 127.7, 125.4, 123.3, 120.5, 114.4 (2C), 90.9, 80.8, 67.7, 51.7, 44.9, 31.3, 29.3, 29.2, 26.9, 25.9, 22.3, 20.7. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{31}\text{O}_3$, 379.2268, found: 379.2268.

methyl 8-(oxiran-2-yl)-2-(3-(*o*-tolyl)prop-2-yn-1-yl)octanoate (4aw)



Yellow liquid (85 mg, 52% yield), $R_f = 0.5$ (Hexane/EtOAc = 2:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.34 – 7.17 (m, 3H), 7.10 – 7.05 (m, 1H), 3.76 – 3.72 (m, 1H), 3.72 (s, 3H), 3.53 – 3.37 (m, 2H), 2.78 – 2.59 (m, 2H), 2.54 – 2.51 (m, 1H), 2.39 (s, 3H), 1.78 – 1.65 (m, 2H), 1.62 – 1.45 (m, 4H), 1.42 – 1.28 (m, 6H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 172.1, 139.9, 131.8, 129.2, 127.7, 125.4, 123.2, 95.3, 80.9, 71.0, 51.7, 44.8, 40.7, 40.2, 35.0, 34.6, 29.1, 27.1, 25.5, 22.3, 20.6. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{29}\text{O}_3$, 328.2111, found: 328.2119.

Ethyl 2-(phenylethynyl)cycloheptane-1-carboxylate (6a)

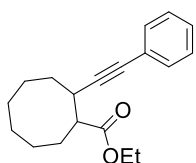


Yellow liquid (73 mg, 54% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.42 – 7.30 (m, 3H), 7.30 – 7.23 (m, 2H), 4.23 – 4.10 (m, 2H), 3.49 – 3.46 (m, 1H), 2.62 – 3.58 (m, 2H), 2.10 – 1.91 (m, 3H), 1.90 – 1.73 (m, 1H), 1.72

SUPPORTING INFORMATION

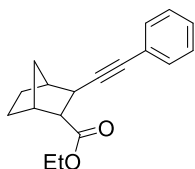
– 1.55 (m, 3H), 1.49 – 1.26 (m, 5H). ^{13}C NMR (125 MHz, CDCl_3) δ 174.5, 131.5 (2C), 128.1 (2C), 127.5, 123.8, 90.2, 83.5, 60.4, 48.9, 33.5, 33.0, 27.4, 26.3, 25.9, 24.7, 14.2. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{23}\text{O}_2$, 271.1693, found: 271.1693.

Ethyl 2-(phenylethynyl)cyclooctane-1-carboxylate (6b)



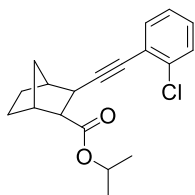
Yellow liquid (74 mg, 52% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.37 – 7.28 (m, 2H), 7.26 – 7.16 (m, 2H), 4.26 – 4.10 (m, 2H), 3.36 – 2.79 (m, 2H), 2.14 – 1.96 (m, 1H), 1.96 (m, 3H), 1.80 – 1.27 (m, 11H). ^{13}C NMR (125 MHz, CDCl_3) δ 174.9, 131.6 (2C), 128.0 (2C), 127.5, 123.8, 90.8, 82.5, 60.5, 45.3, 33.4, 31.2, 27.7, 26.2, 25.3, 25.0, 24.3, 14.2. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{25}\text{O}_2$, 285.1849, found: 285.1842.

Ethyl-3-(phenylethynyl)bicyclo[2.2.1]heptane-2-carboxylate (6c)



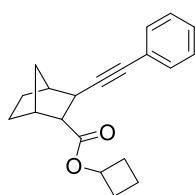
Yellow liquid (75 mg, 56% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.36 – 7.29 (m, 2H), 7.27 – 7.22 (m, 3H), 4.19 – 4.02 (m, 2H), 2.98 – 2.95 (m, 1H), 2.72 – 2.33 (m, 4H), 2.11 (m, 2H), 1.70 – 1.12 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 172.9, 133.7 (2C), 127.6 (2C), 127.5, 122.2, 90.3, 82.5, 60.2, 52.1, 43.5, 39.0, 38.8, 36.3, 28.6, 28.0, 14.3. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{21}\text{O}_2$, 269.1536, found: 269.1532.

Isopropyl 3-((2-chlorophenyl)ethynyl)bicyclo[2.2.1]heptane-2-carboxylate (6d)



Yellow liquid (113 mg, 72% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.36 – 7.29 (m, 2H), 7.27 – 7.22 (m, 2H), 5.06 – 5.01 (m, 1H), 3.29 – 3.22 (m, 1H), 2.95 – 2.51 (m, 2H), 2.49 – 2.22 (m, 1H), 2.10 – 1.57 (m, 6H), 1.44 – 1.23 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 172.9, 136.0, 133.7, 132.6, 128.8, 127.6, 127.5, 122.2, 90.3, 82.5, 60.2, 52.1, 43.5, 39.5, 36.2, 33.4, 28.0, 27.1, 21.6. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{22}\text{ClO}_2$, 317.1303, found: 317.1294.

Cyclobutyl-3-(phenylethynyl)bicyclo[2.2.1]heptane-2-carboxylate (6e)

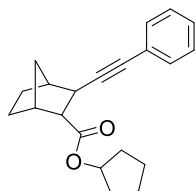


Yellow liquid (74 mg, 53% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.31 (m, 2H), 7.28 – 7.23 (m, 3H), 4.95 (s, 1H), 2.97 (m, 1H), 2.58 – 2.54 (m, 2H), 2.46 (d, $J = 4.3$ Hz, 2H), 2.33 – 2.13 (m, 4H), 1.72 – 1.54 (m, 2H), 1.54 – 1.33 (m, 3H), 1.28 – 1.19 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ

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172.2, 131.5 (2C), 128.0 (2C), 127.6, 123.6, 90.3, 82.6, 68.5, 51.8, 43.6, 39.0, 38.9, 36.3, 30.4, 30.3, 28.7, 28.0, 13.5. HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $C_{20}H_{23}O_2$, 295.1693, found: 295.1695.

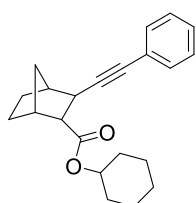
Cyclopentyl-3-(phenylethynyl)bicyclo[2.2.1]heptane-2-carboxylate (6f)



Yellow liquid (85 mg, 55% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); 1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.26 – 7.22 (m, 3H), 5.13 – 2.98 (m, 2H), 2.61 – 2.54 (m, 2H), 2.45 (d, $J = 4.3$ Hz, 2H), 1.77 – 1.58 (m, 7H), 1.57 – 1.39 (m, 3H), 1.33 – 1.14 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 131.5 (2C), 128.0 (2C),

127.5, 123.7, 90.4, 82.5, 76.9, 52.0, 43.6, 39.1, 39.0, 36.9, 32.7, 32.5, 28.7, 28.0, 23.8, 23.7. HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $C_{21}H_{25}O_2$, 309.1849, found: 309.1849.

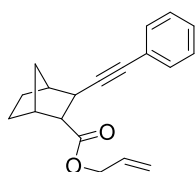
Cyclohexyl-3-(phenylethynyl)bicyclo[2.2.1]heptane-2-carboxylate (6g)



Yellow liquid (101 mg, 63% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); 1H NMR (500 MHz, $CDCl_3$) δ 7.32 (m, 2H), 7.27 – 7.21 (m, 3H), 4.73 – 2.99 (m, 2H), 2.64 – 2.55 (m, 2H), 2.46 – 2.13 (m, 2H), 1.82 – 1.71 (m, 3H), 1.68 – 1.48 (m, 6H), 1.47 – 1.14 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 131.4 (2C), 128.0 (2C), 127.5,

123.7, 90.5, 82.4, 72.4, 52.1, 43.6, 39.1, 39.0, 31.7 (2C), 31.6, 28.7, 28.0, 23.6 (2C), 23.5. HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $C_{22}H_{27}O_2$, 323.2006, found: 323.2005.

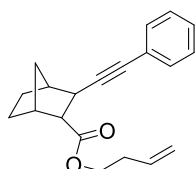
Allyl-3-(phenylethynyl)bicyclo[2.2.1]heptane-2-carboxylate (6h)



Yellow liquid (94 mg, 67% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); 1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.30 – 7.22 (m, 3H), 5.88 – 4.50 (m, 5H), 2.99 – 2.12 (m, 6H), 1.67 – 1.50 (m, 1H), 1.35 – 1.16 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 132.4, 131.5 (2C), 128.1 (2C), 127.6, 123.5, 118.1, 90.2, 82.7,

65.15, 52.2, 43.5, 39.0, 38.8, 36.3, 28.6, 28.0. HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $C_{19}H_{21}O_2$, 281.1536, found: 281.1532.

But-3-en-1-yl-3-(phenylethynyl)bicyclo[2.2.1]heptane-2-carboxylate (6i)

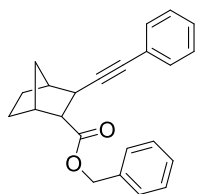


Yellow liquid (74 mg, 51% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); 1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.26 – 7.23 (m, 3H), 5.06 – 4.96 (m, 1H), 4.13 – 4.04 (m, 4H), 2.98 – 2.47 (m, 6H), 2.34 – 2.33 (m, 1H), 1.64 – 1.34 (m, 2H), 1.30 – 1.15 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 134.1, 131.4 (2C),

128.1 (2C), 127.6, 123.6, 113.5, 90.3, 82.6, 63.4, 52.2, 43.5, 38.9, 38.8, 36.3, 33.0, 28.6, 28.0. HRMS (ESI-TOF) m/z : $[M+H]^+$ calcd for $C_{20}H_{23}O_2$, 295.1693, found: 295.1695.

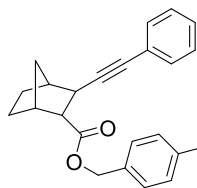
SUPPORTING INFORMATION

Benzyl-3-(phenylethynyl)bicyclo[2.2.1]heptane-2-carboxylate (6j)



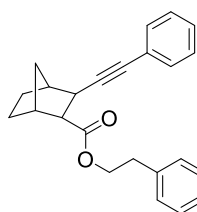
Yellow liquid (100 mg, 58% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.36 – 7.27 (m, 6H), 7.25 – 7.21 (m, 4H), 5.15 – 5.08 (m, 1H), 4.98 – 3.00 (m, 2H), 2.73 – 2.15 (m, 4H), 1.62 – 1.61 (m, 2H), 1.36 – 1.15 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 172.8, 135.9, 131.5 (2C), 128.4 (2C), 128.3 (2C), 128.1 (2C), 128.0, 127.3, 123.5, 90.4, 82.7, 66.3, 52.3, 43.5, 39.1, 38.9, 36.4, 28.7, 28.0. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{23}\text{O}_2$, 331.1693, found: 331.1688.

4-Methylbenzyl-3-(phenylethynyl)bicyclo[2.2.1]heptane-2-carboxylate (6k)



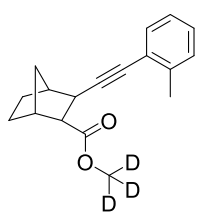
Yellow liquid (109 mg, 61% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.39 – 7.29 (m, 2H), 7.25 – 7.09 (m, 7H), 5.11 – 4.94 (m, 2H), 2.99 – 2.48 (m, 4H), 2.31 (s, 3H), 2.14 – 1.49 (m, 3H), 1.3 – 1.22 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 172.8, 137.8, 132.9, 131.5 (2C), 129.1 (2C), 128.4 (2C), 128.1 (2C), 127.6, 123.5, 90.4, 82.7, 66.2, 52.3, 43.5, 39.1, 38.8, 36.3, 28.6, 27.9, 21.1. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{25}\text{O}_2$, 345.1849, found: 345.1844.

phenethyl-3-(phenylethynyl)bicyclo[2.2.1]heptane-2-carboxylate (6l)



Yellow liquid (116 mg, 68% yield), $R_f = 0.5$ (Hexane/EtOAc = 10:1); ^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.13 (m, 10H), 4.31 – 4.23 (m, 2H), 2.99 – 2.11 (m, 7H), 1.66 – 1.50 (m, 2H), 1.34 – 1.15 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 172.85, 137.91, 131.47 (2C), 128.84 (2C), 128.34 (2C), 128.17 (2C), 127.6, 126.3, 123.5, 90.3, 82.6, 64.8, 52.2, 43.5, 39.0, 38.8, 36.3, 35.1, 28.6, 27.9. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{25}\text{O}_2$, 345.1849, found: 345.1844.

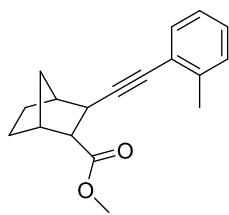
methyl-d₃-3-(phenylethynyl)bicyclo[2.2.1]heptane-2-carboxylate (6m)



Yellow liquid (86 mg, 67% yield), $R_f = 0.6$ (Hexane/EtOAc = 10:1); ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.29 (m, 1H), 7.16 – 7.13 (m, 2H), 7.10 – 7.02 (m, 1H), 3.01 – 2.60 (m, 3H), 2.55 – 2.45 (m, 1H), 2.38 (s, 3H), 2.13 – 2.06 (m, 1H), 1.69 – 1.49 (m, 2H), 1.36 – 1.24 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 173.4, 140.0, 131.8, 129.2, 127.7, 125.3, 123.3, 94.2, 81.4, 52.3, 43.8, 39.3, 38.9, 36.3, 28.7, 28.0, 20.7. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{18}\text{D}_3\text{O}_2$, 272.1724, found: 272.1715.

methyl-3-(o-tolyethynyl)bicyclo[2.2.1]heptane-2-carboxylate (4ax)

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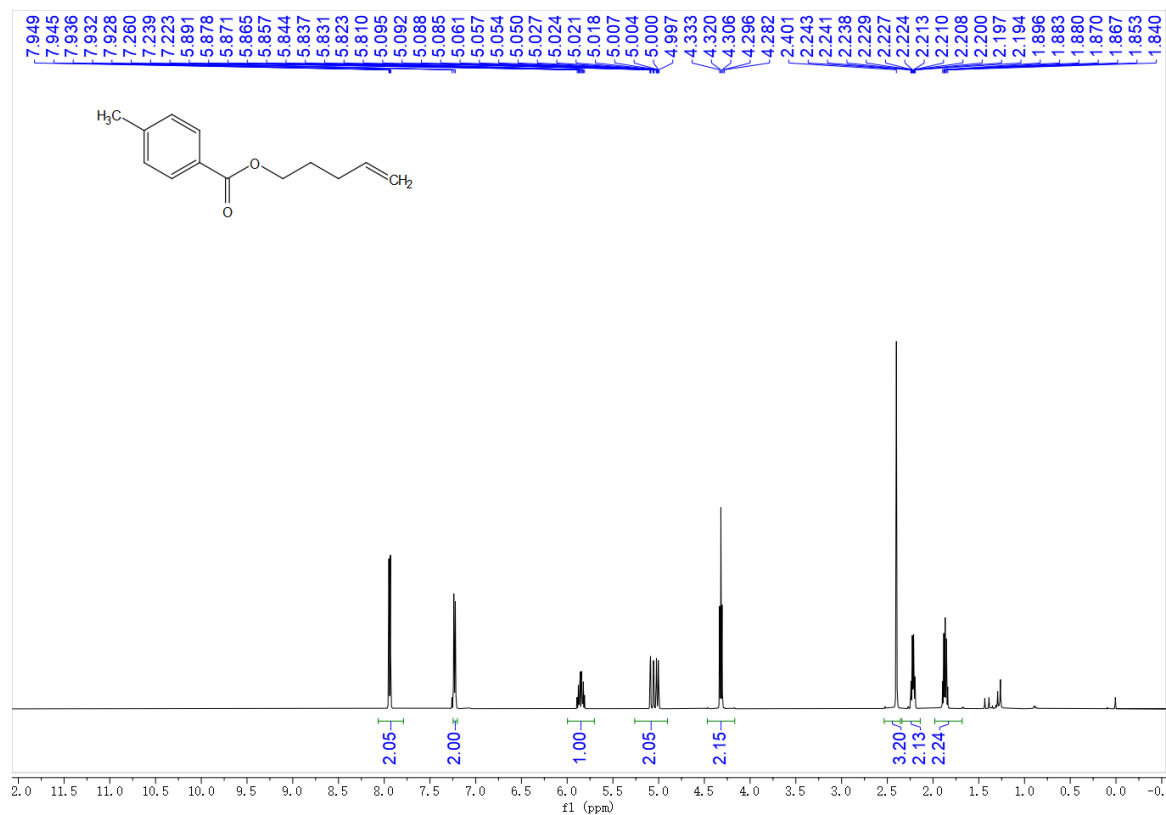


Yellow liquid (111 mg, 82% yield), $R_f = 0.5$ (Hexane/EtOAc=50:1); ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.22 (m, 1H), 7.18 – 7.08 (m, 3H), 3.62 (s, 3H), 3.02 – 2.45 (m, 4H), 2.38 (s, 3H), 2.13 – 2.06 (m, 1H), 1.69 – 1.49 (m, 2H), 1.40 – 1.15 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 173.3, 139.9, 131.8, 129.2, 127.6, 125.3, 123.3, 94.1, 81.4, 52.3, 51.3, 43.7, 39.3, 38.8, 36.3, 28.6, 27.9, 20.6. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{21}\text{O}_2$, 269.1536, found: 269.1544.

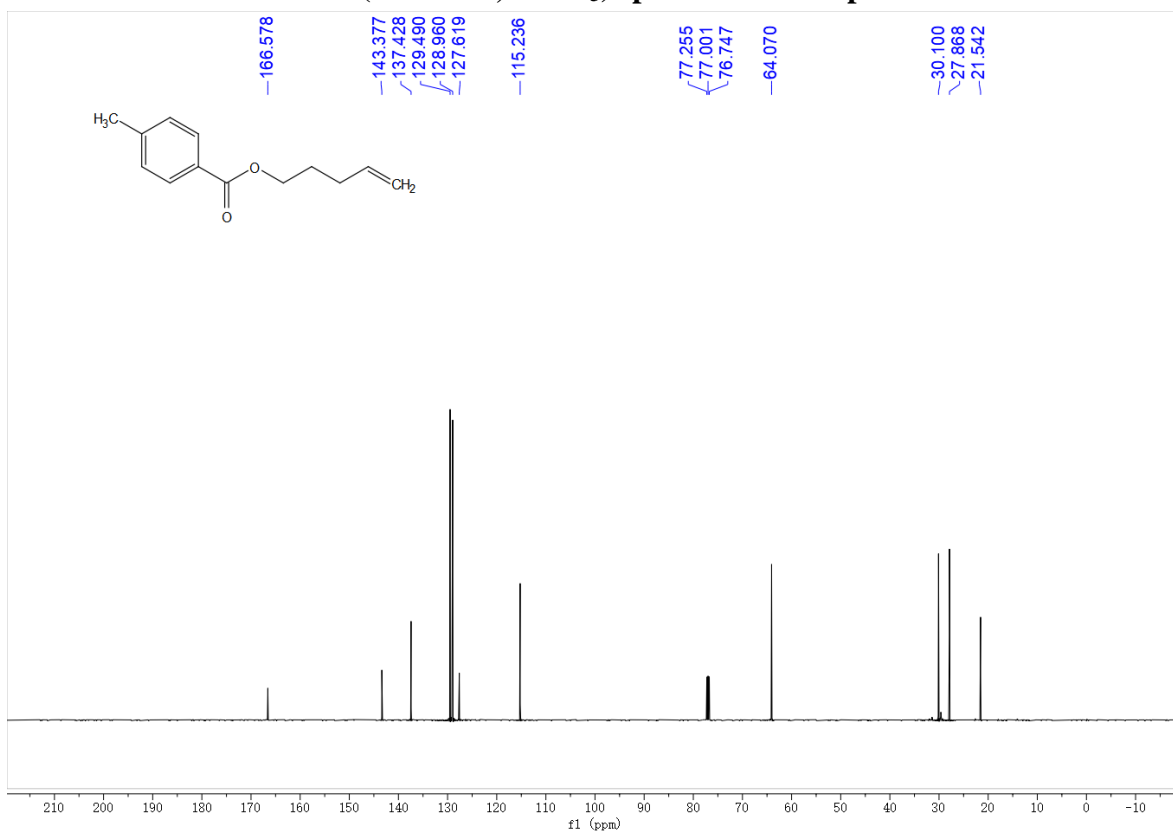
SUPPORTING INFORMATION

8. ^1H NMR and ^{13}C NMR Spectra for Products

^1H NMR (500 MHz, CDCl_3) spectrum of compound 2f

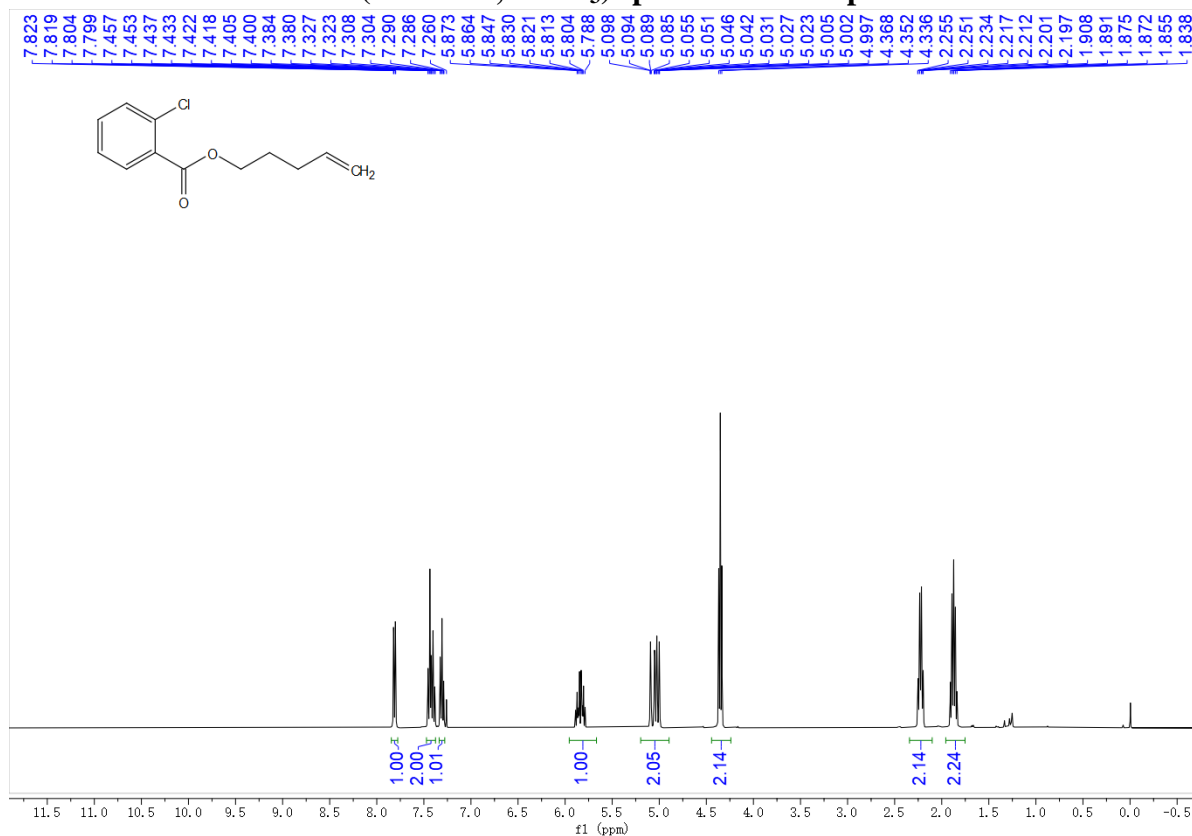


^{13}C NMR (125 MHz, CDCl_3) spectrum of compound 2f

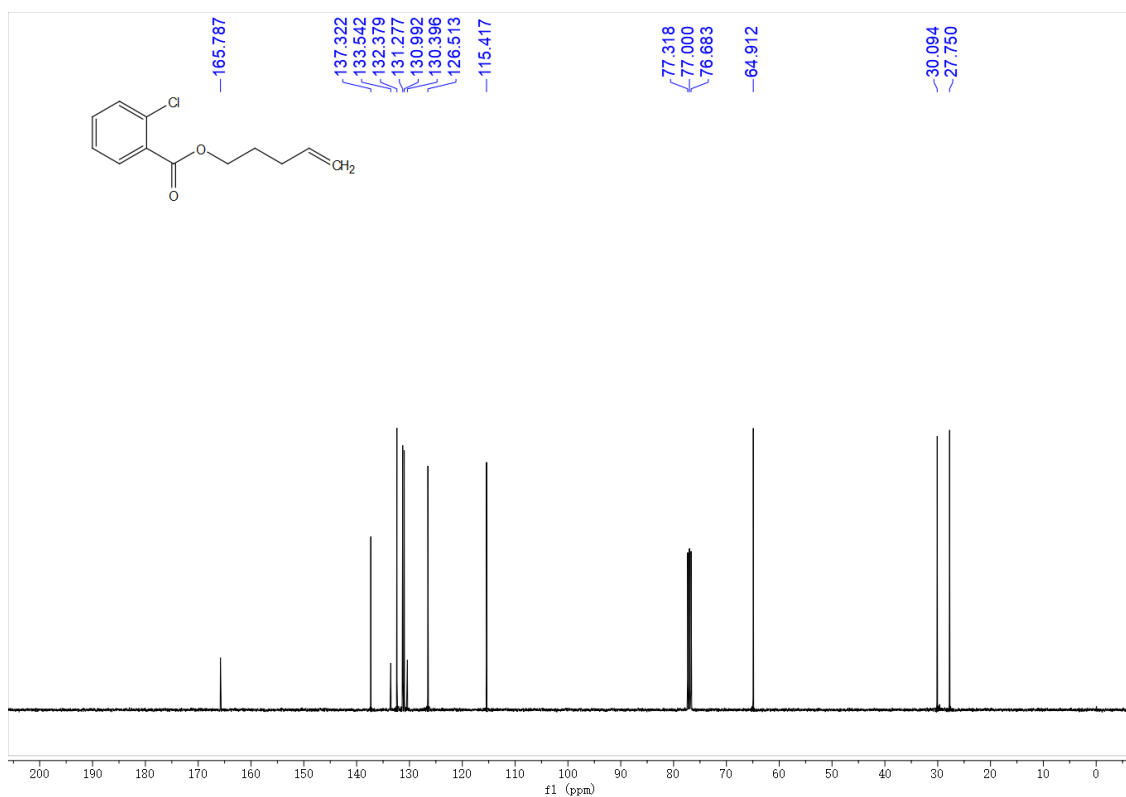


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¹H NMR (400 MHz, CDCl₃) spectrum of compound 2h

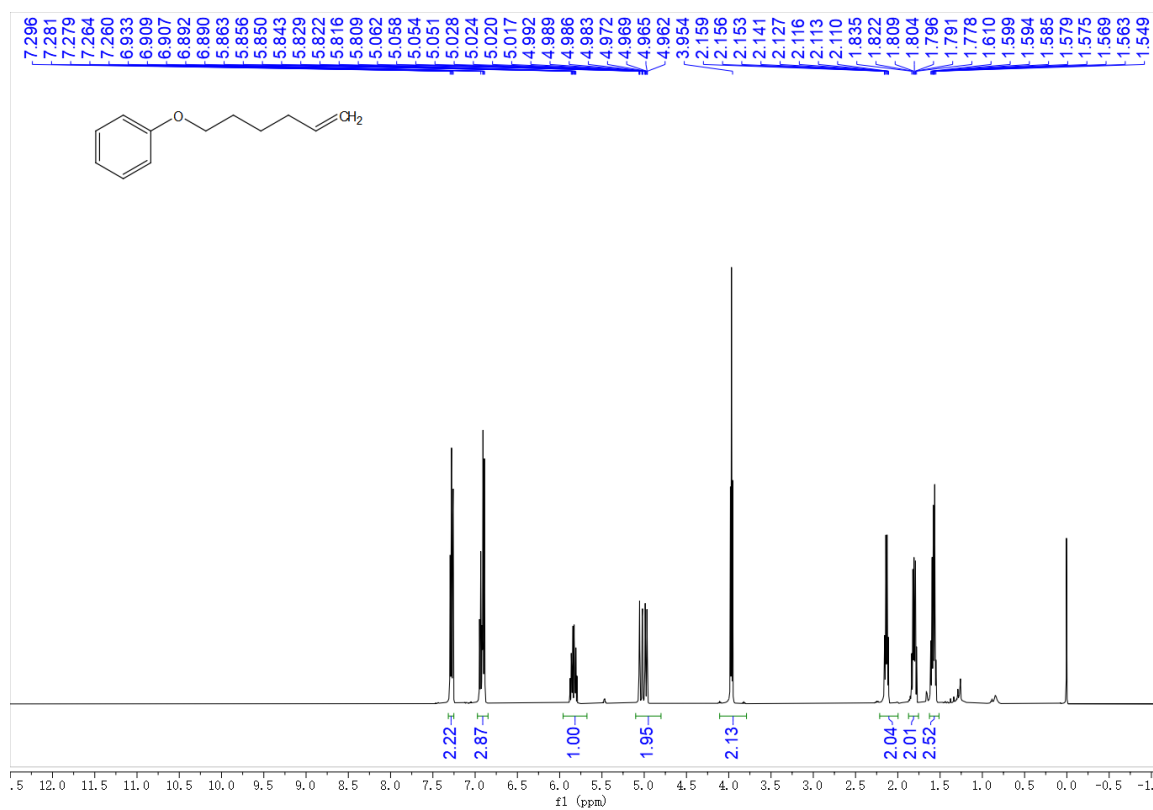


¹³C NMR (100 MHz, CDCl₃) spectrum of compound 2h

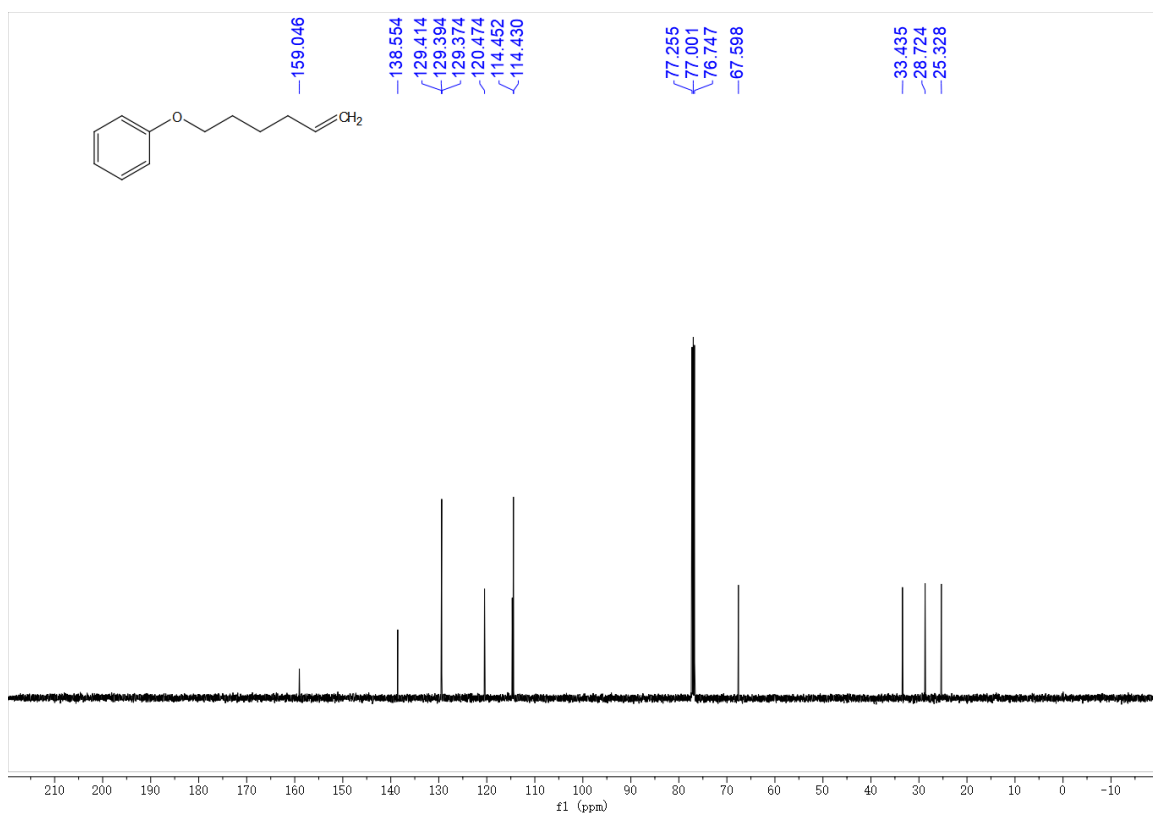


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 2k

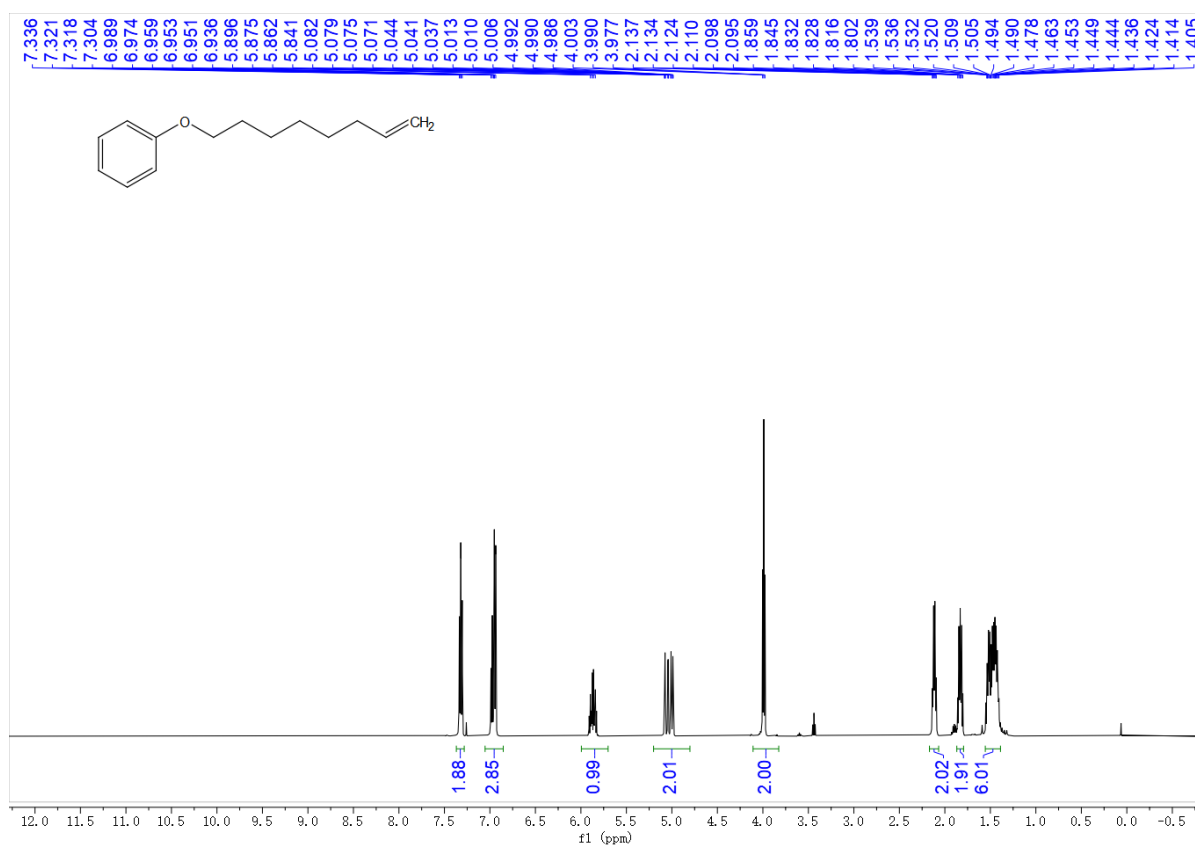


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 2k

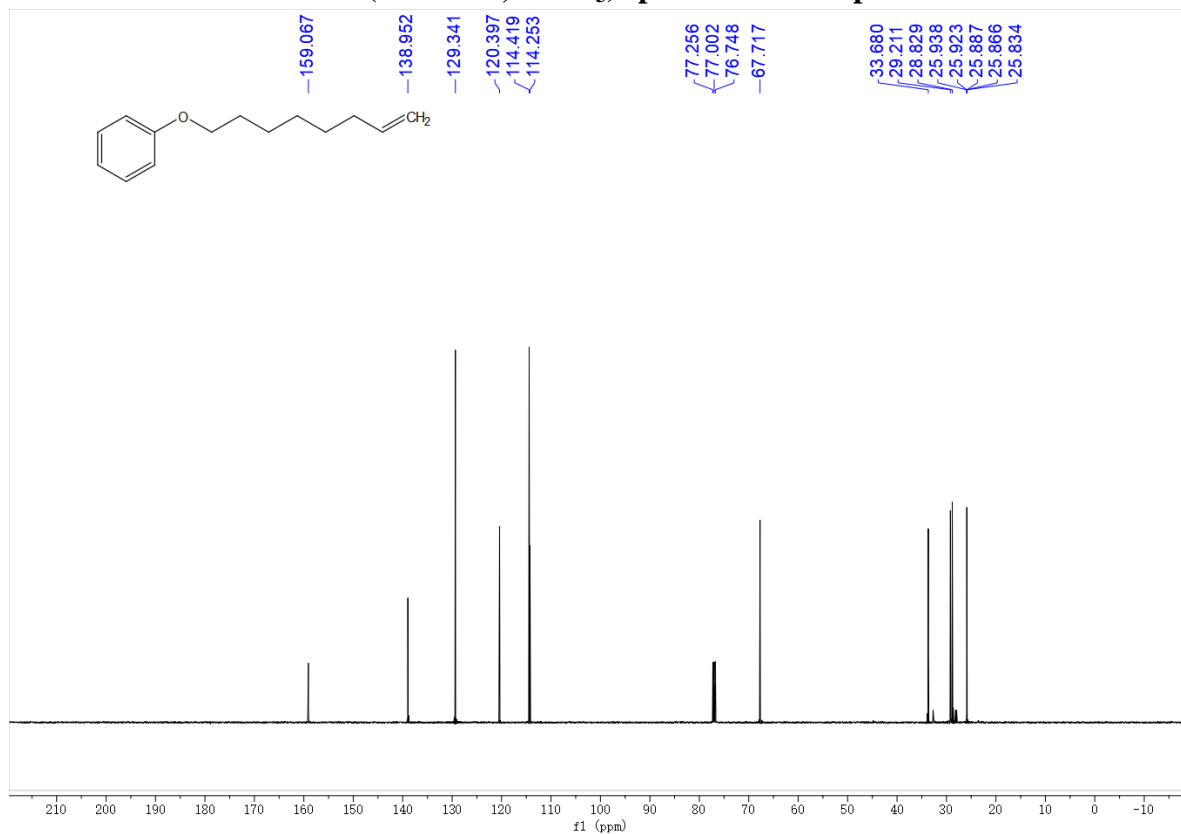


SUPPORTING INFORMATION

^1H NMR (500 MHz, CDCl_3) spectrum of compound 21

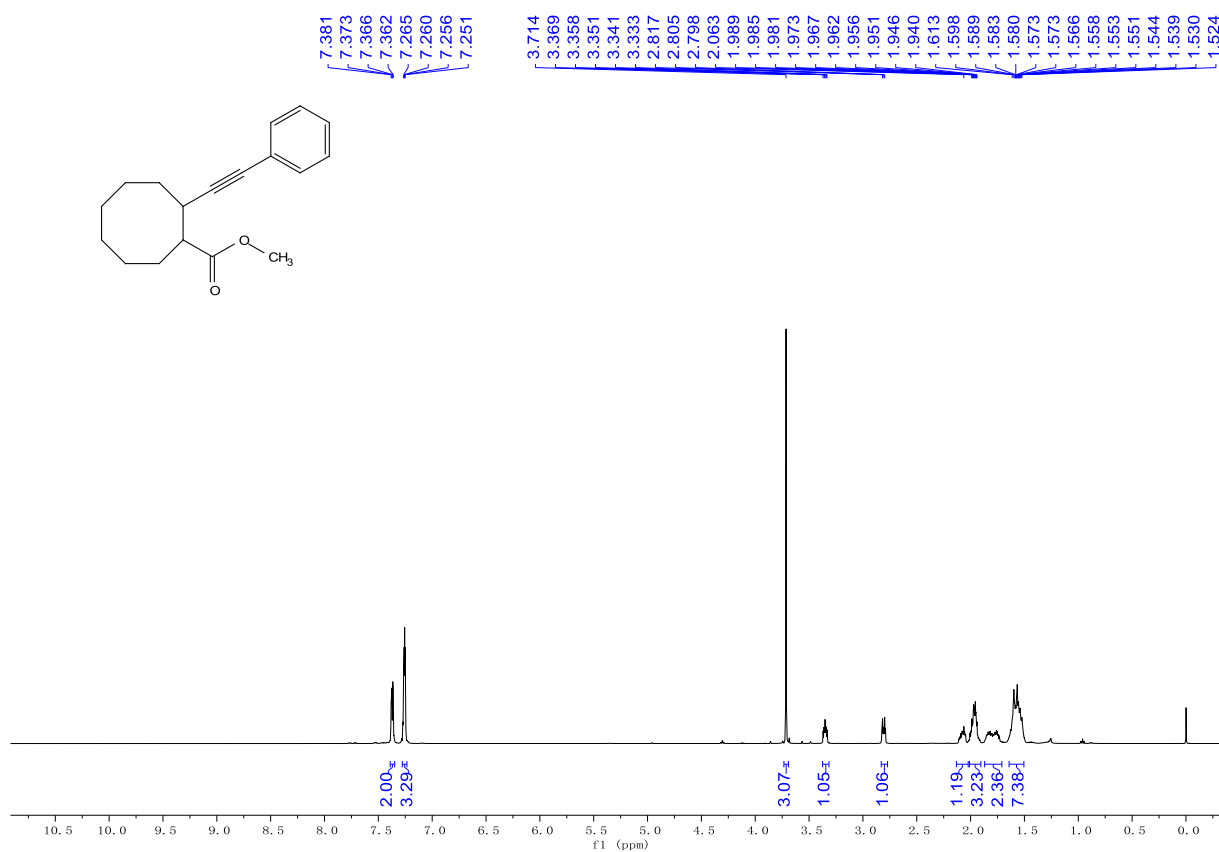


^{13}C NMR (125 MHz, CDCl_3) spectrum of compound 21

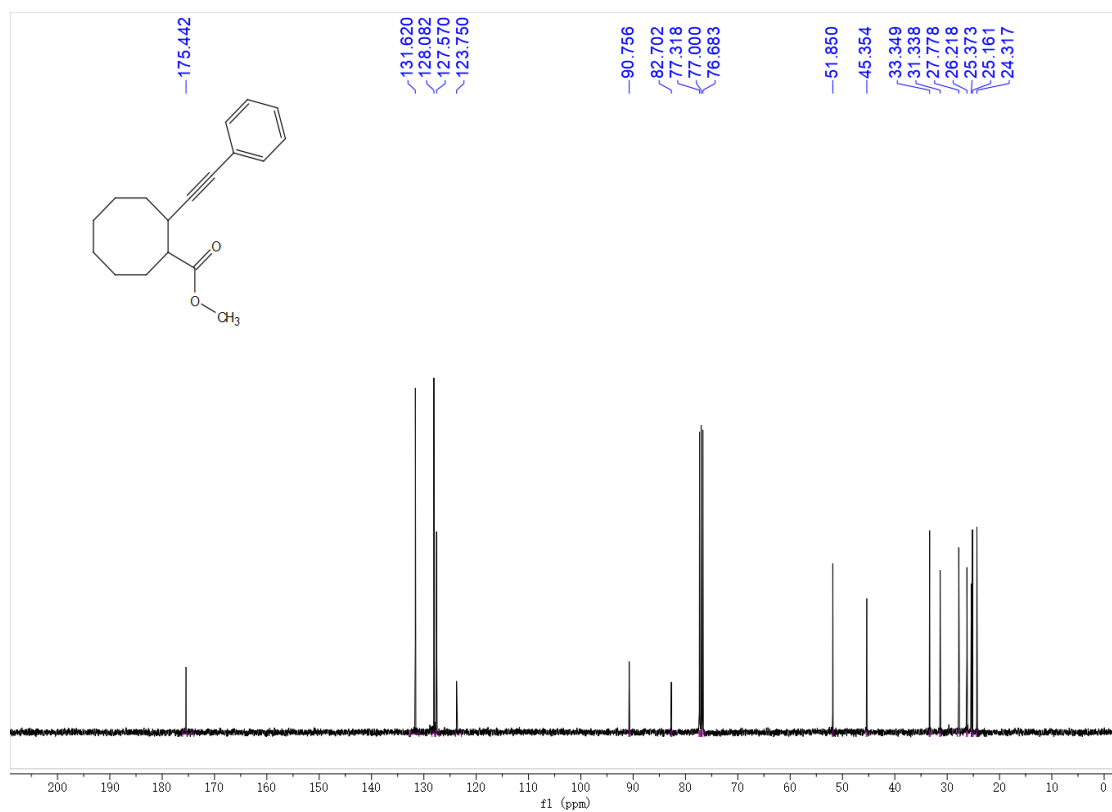


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¹H NMR (500 MHz, CDCl₃) spectrum of compound 4a

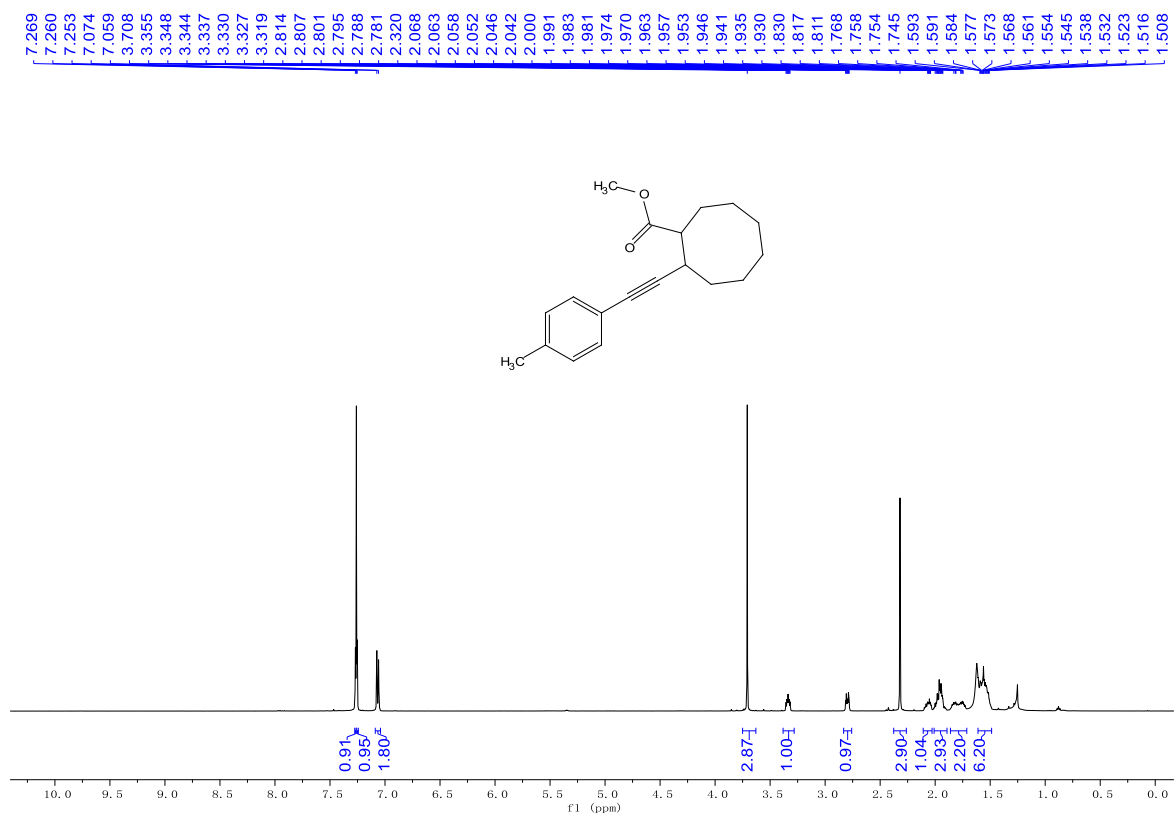


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4a

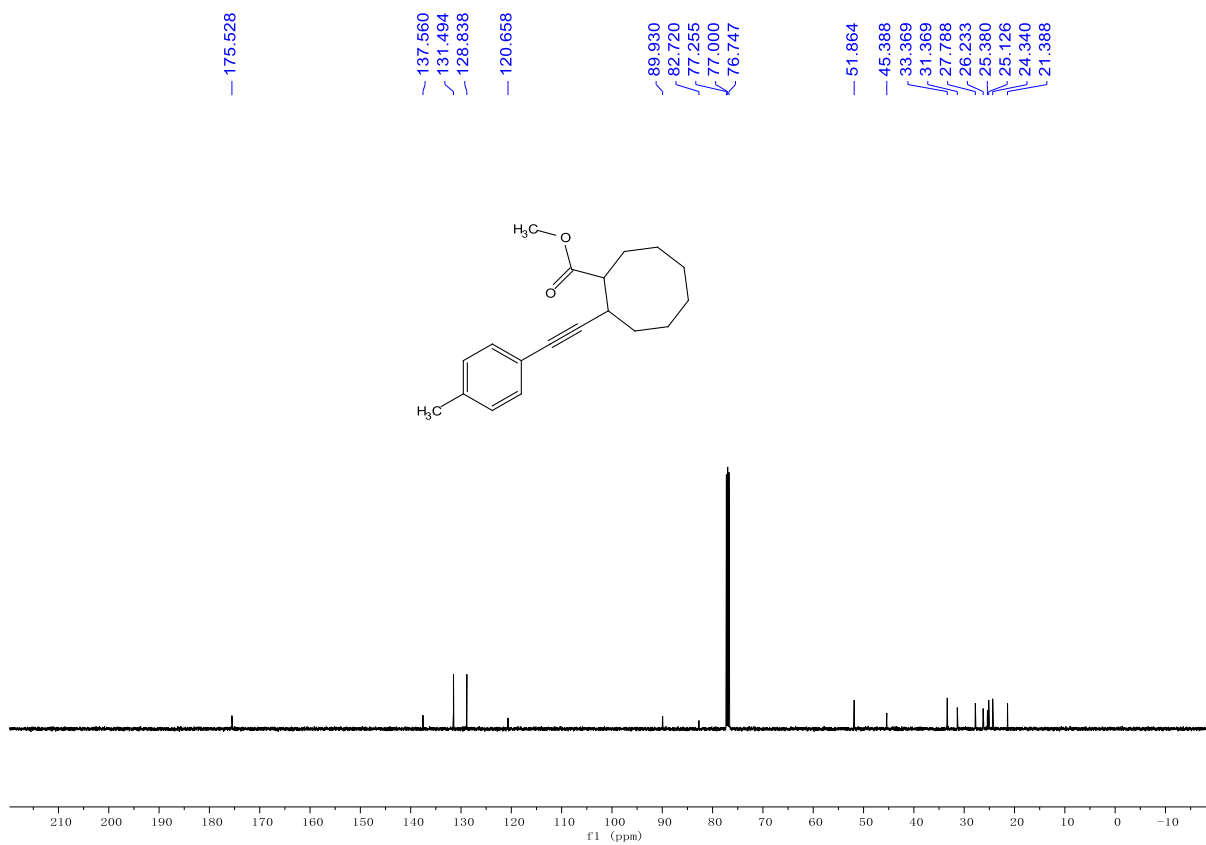


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4b

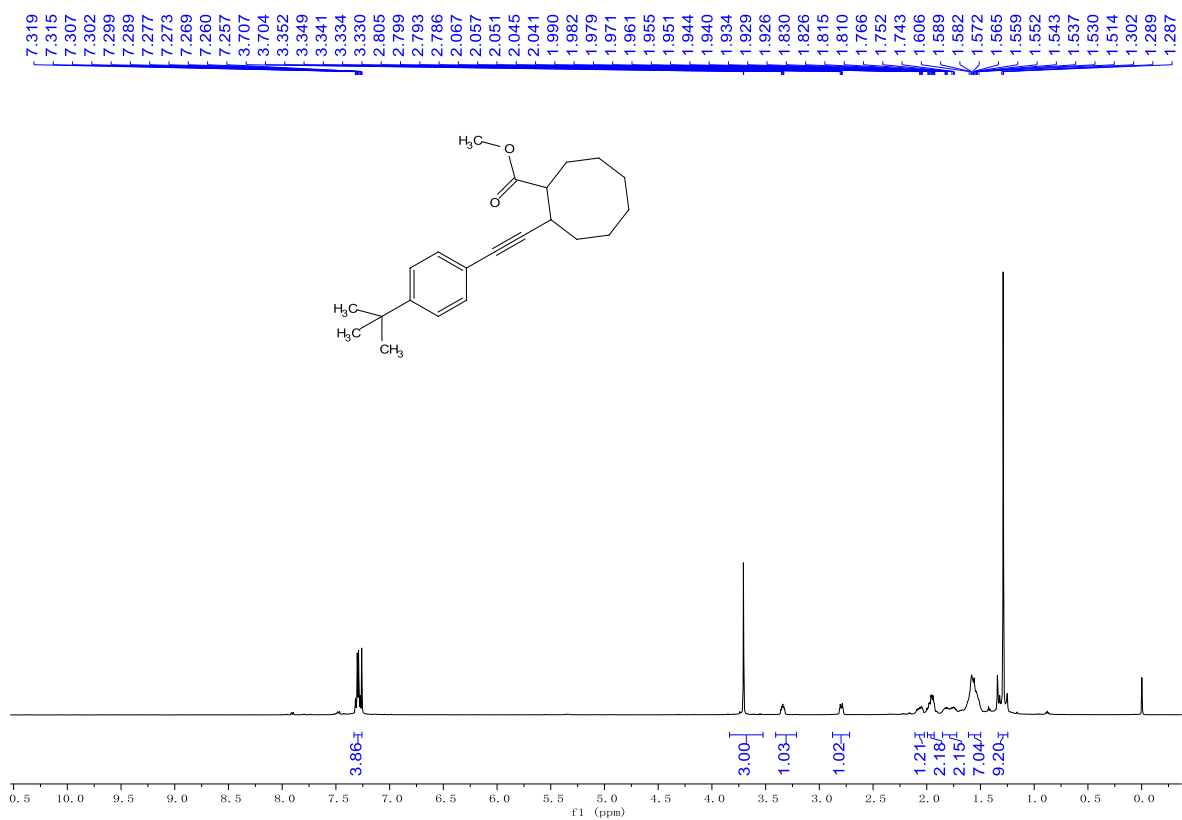


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4b

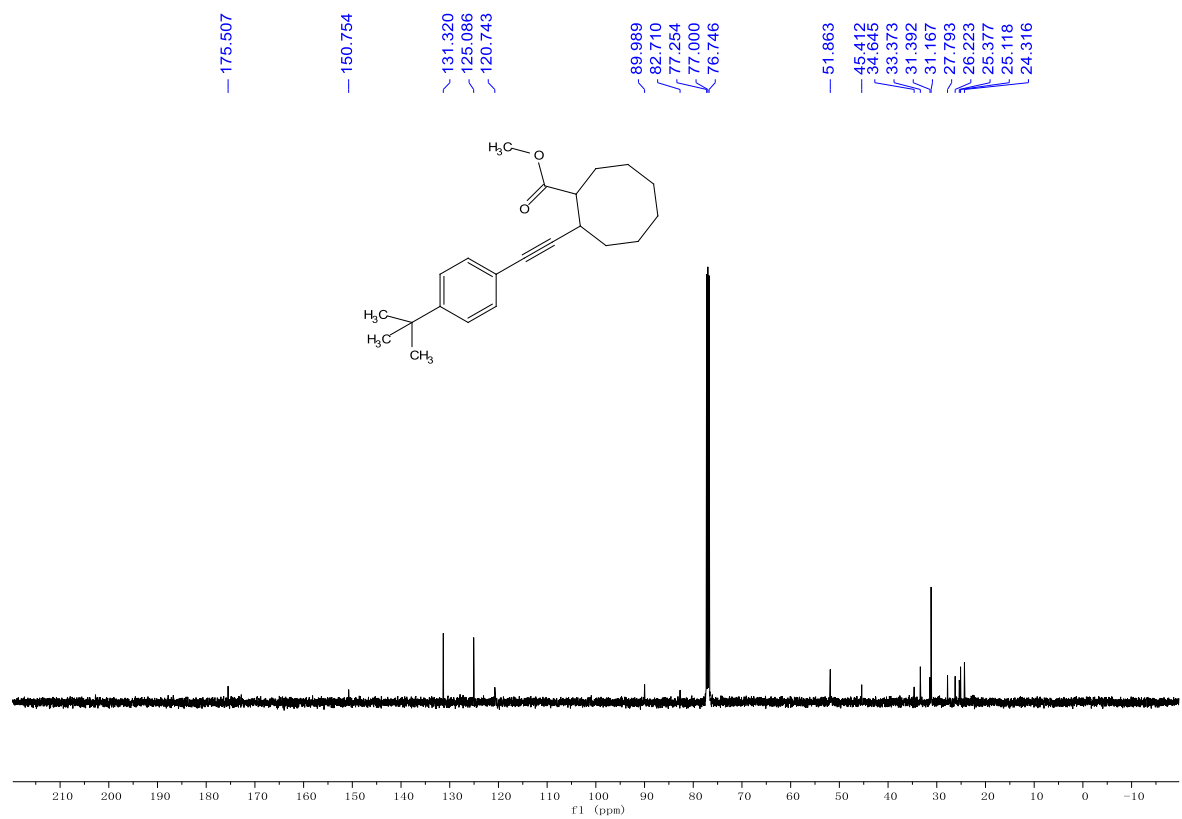


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4c

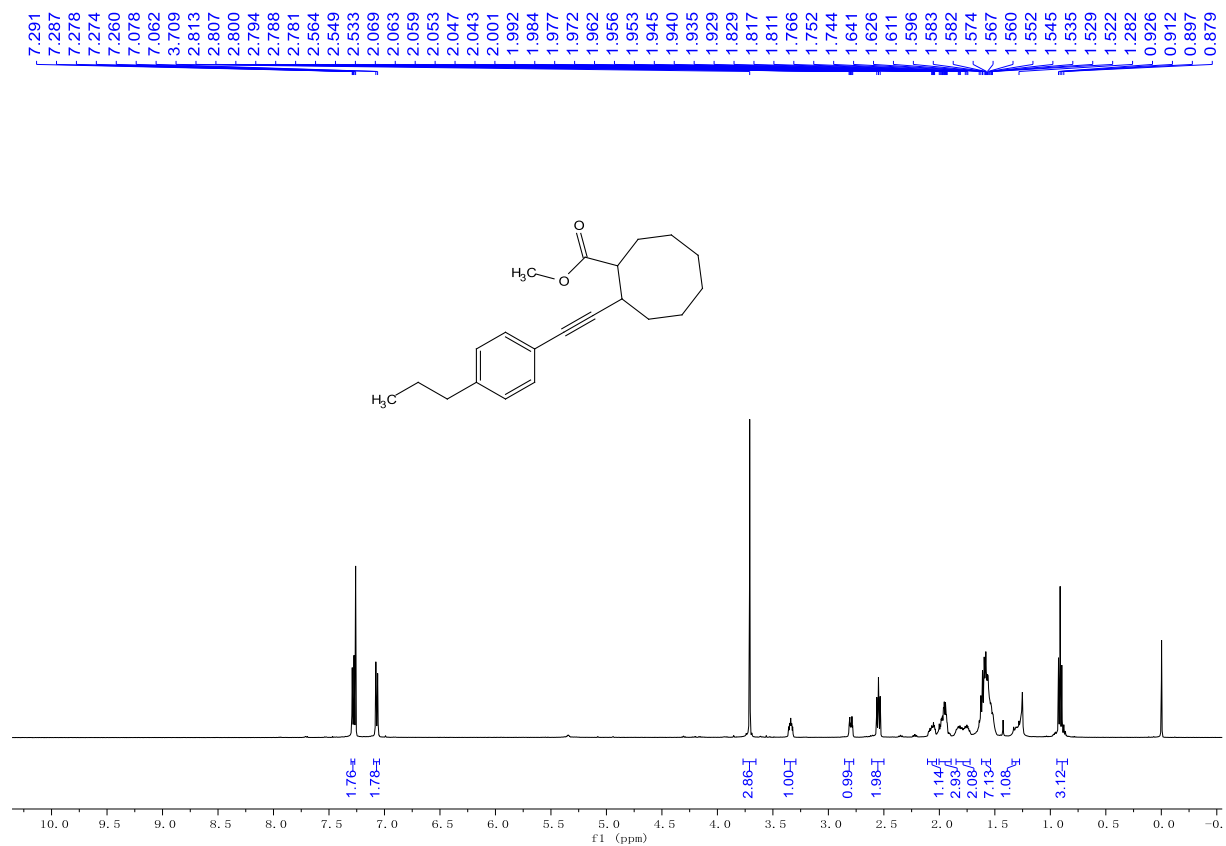


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4c

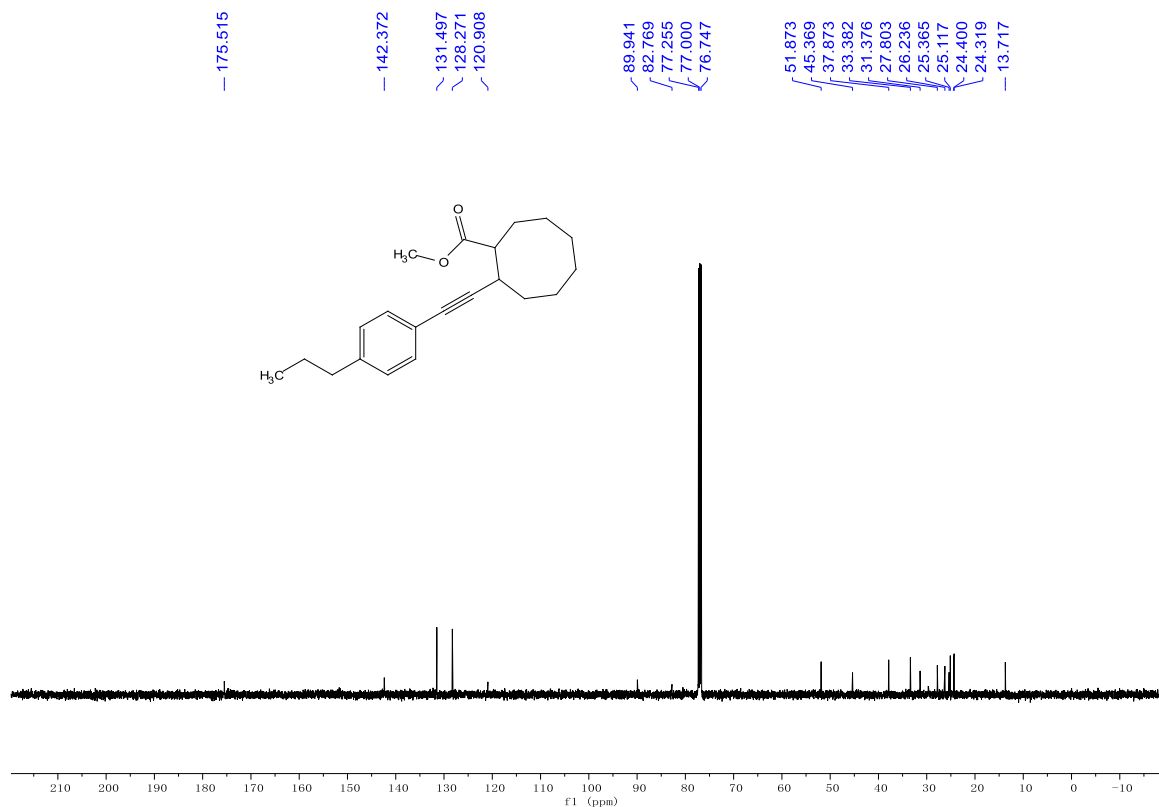


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4d

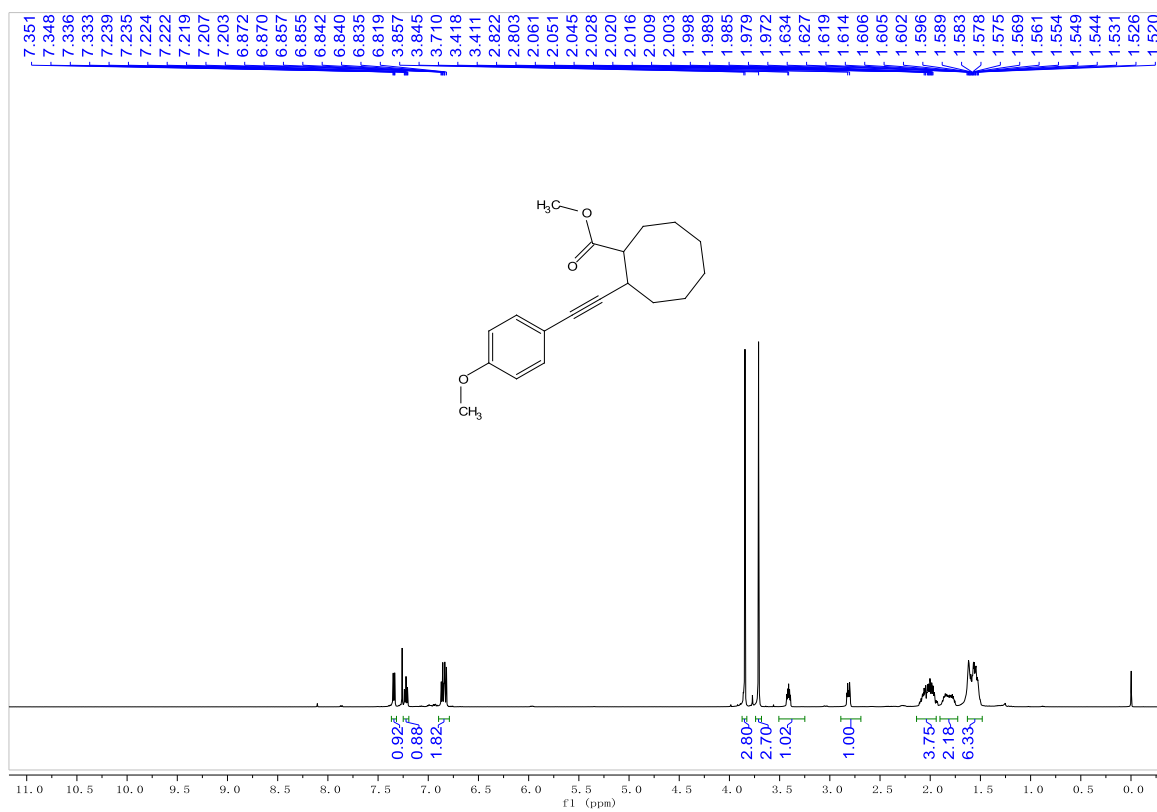


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4d

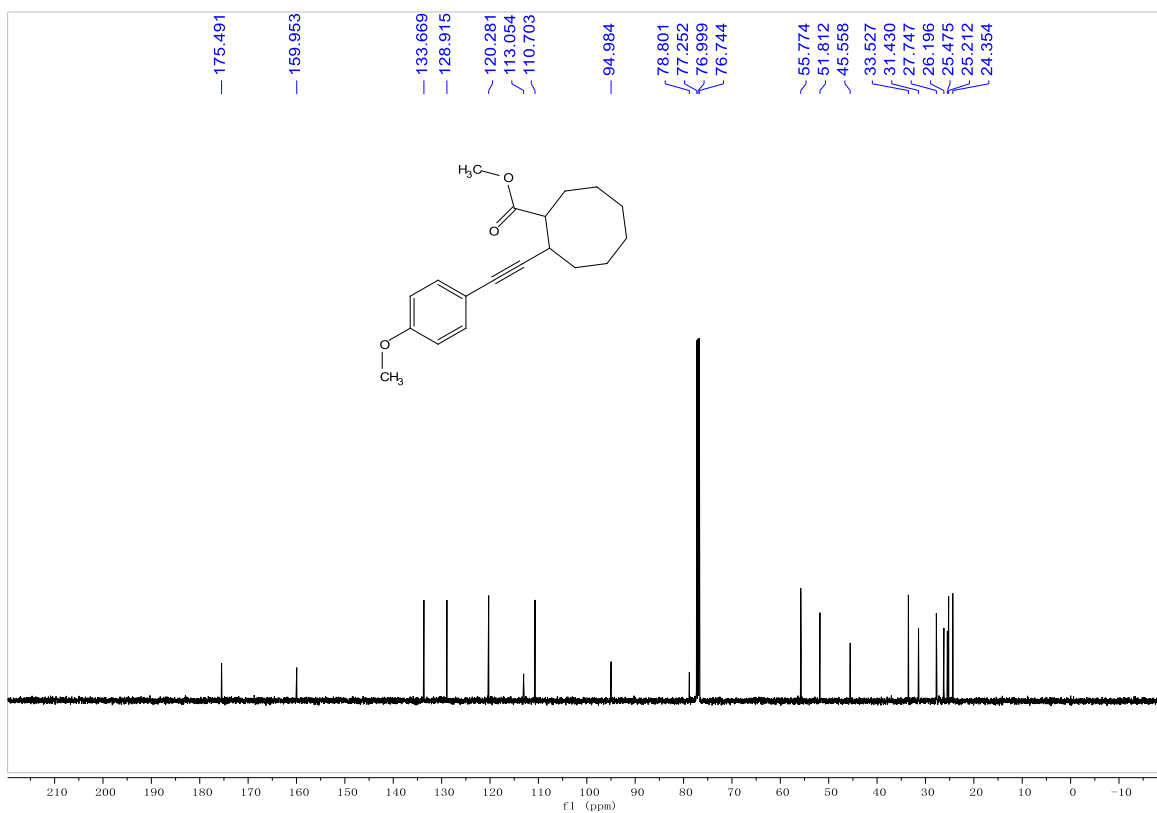


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4e

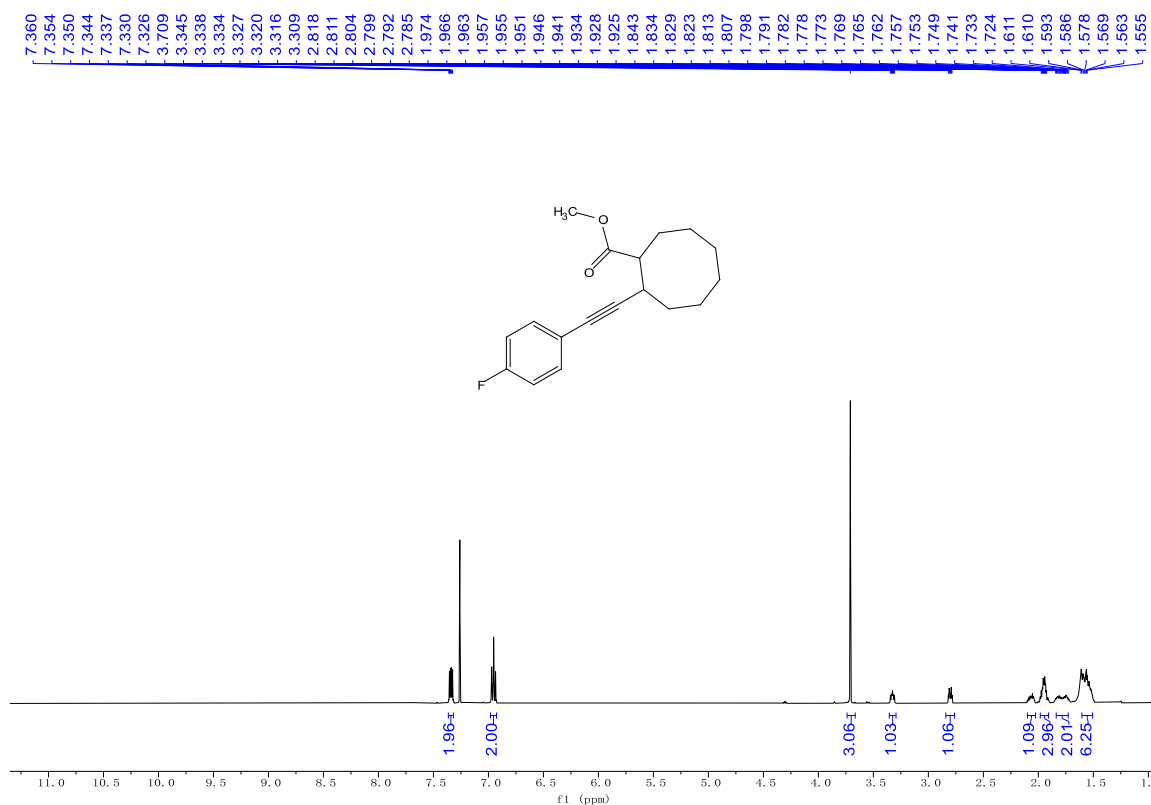


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4e

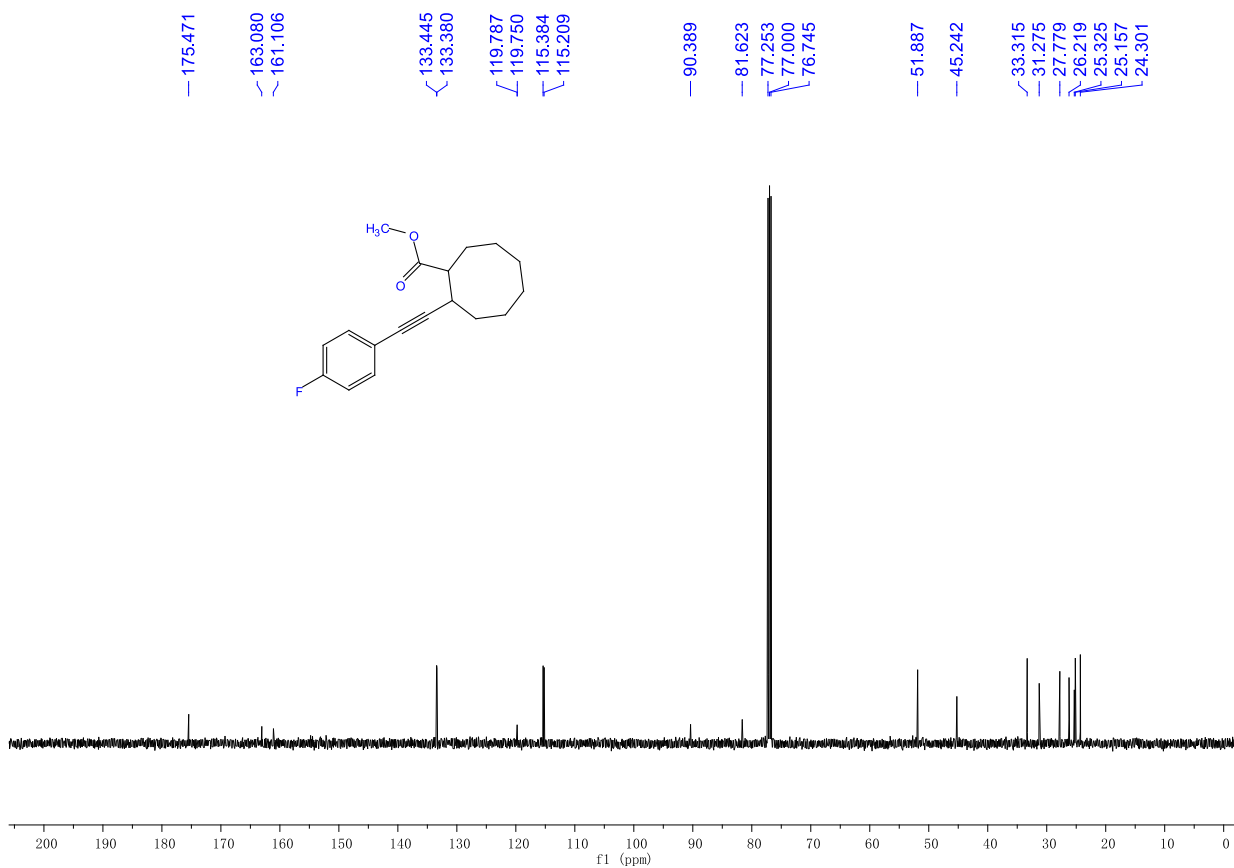


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4f

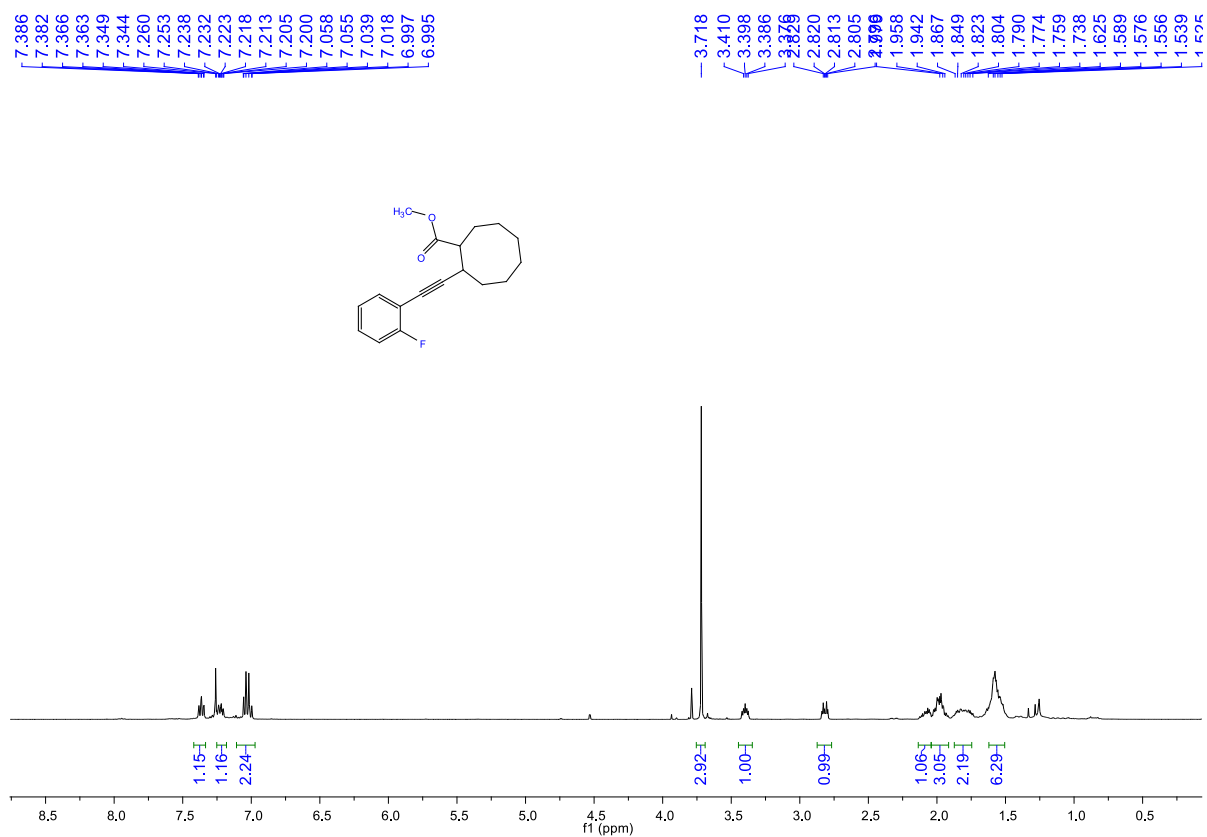


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4f

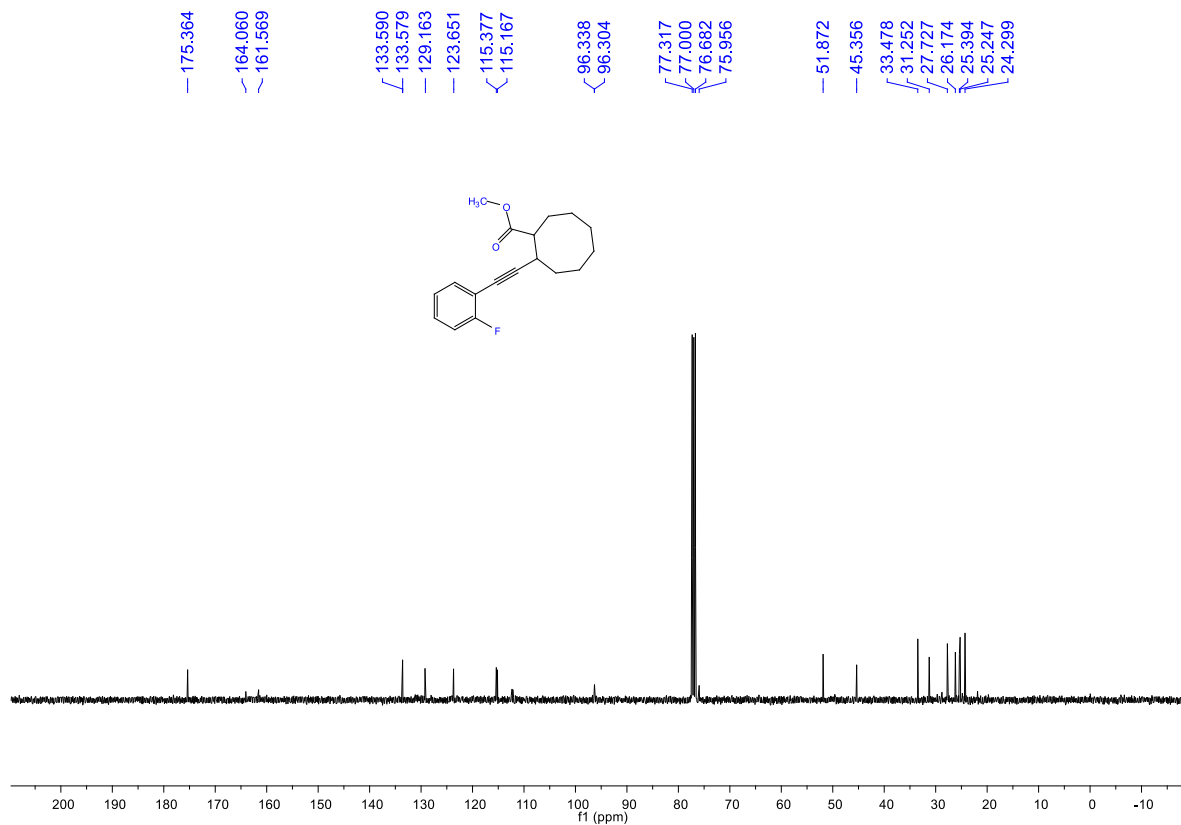


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4g

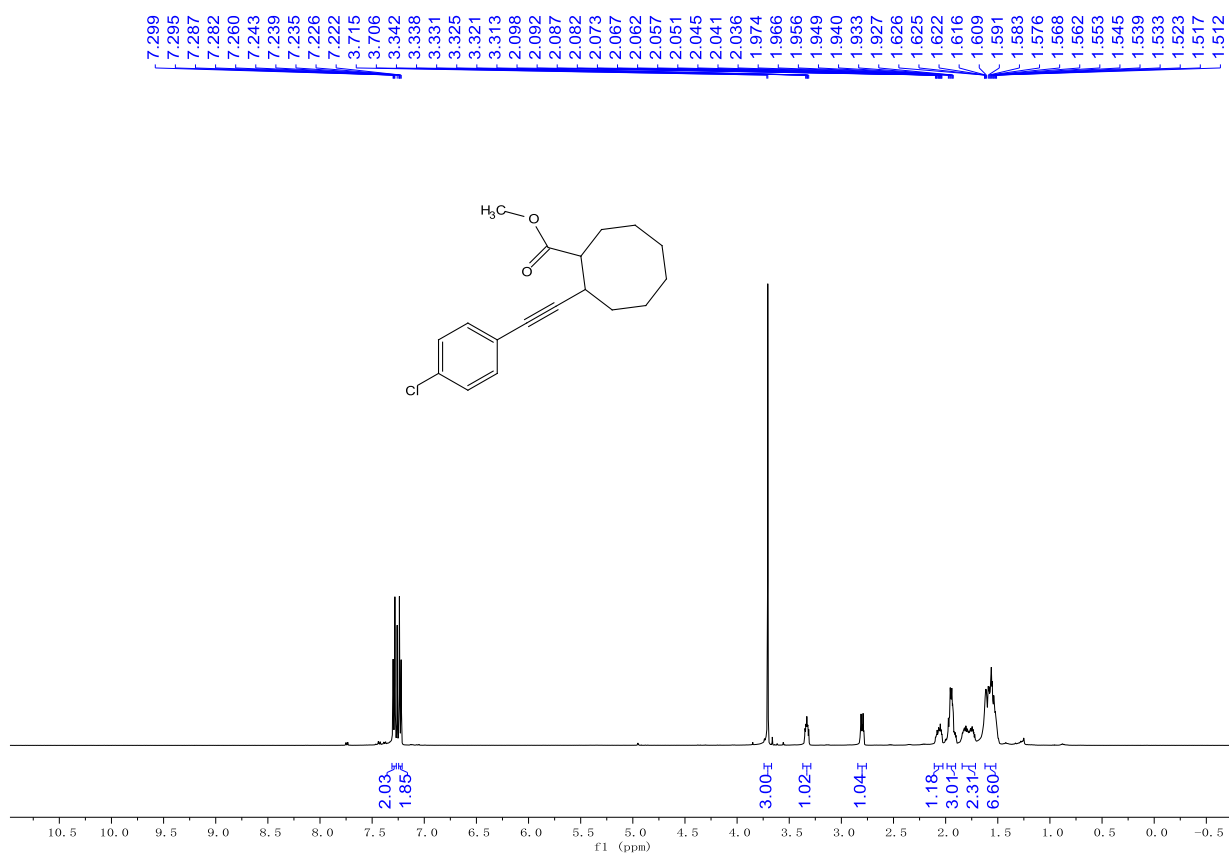


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4g

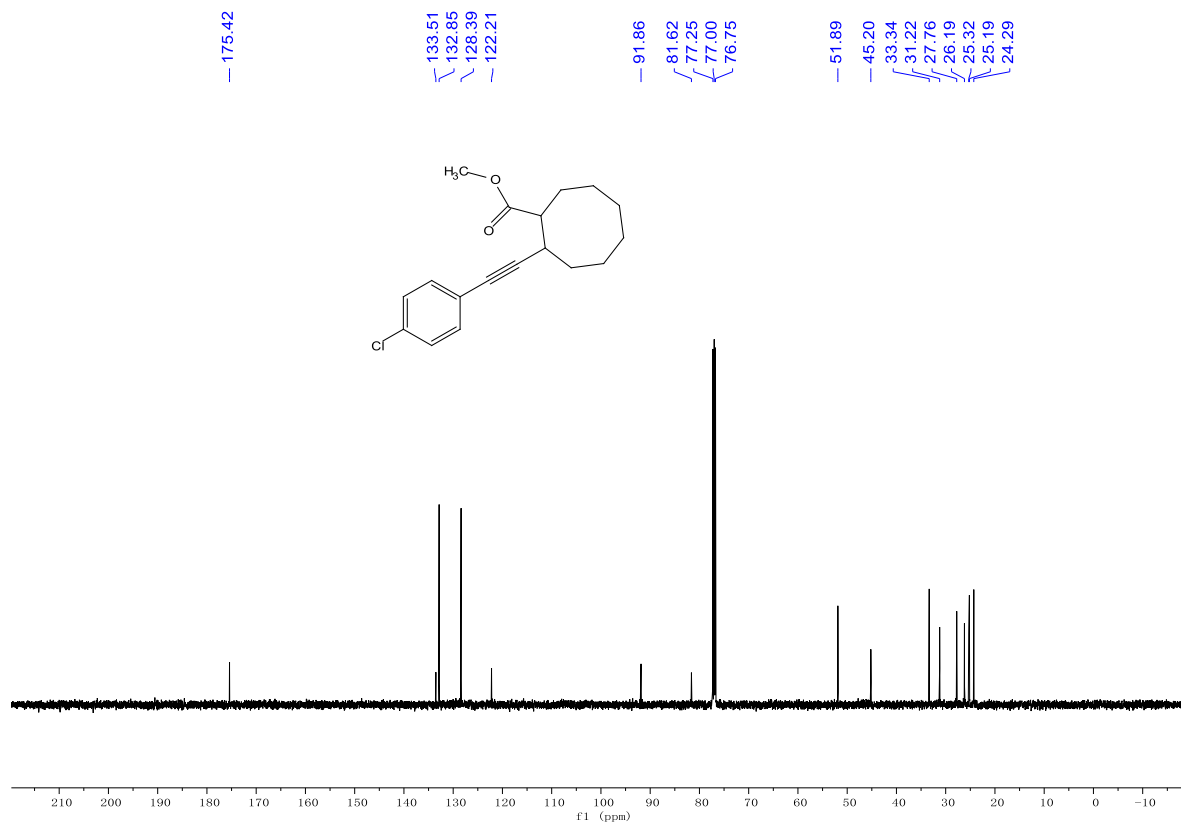


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4h

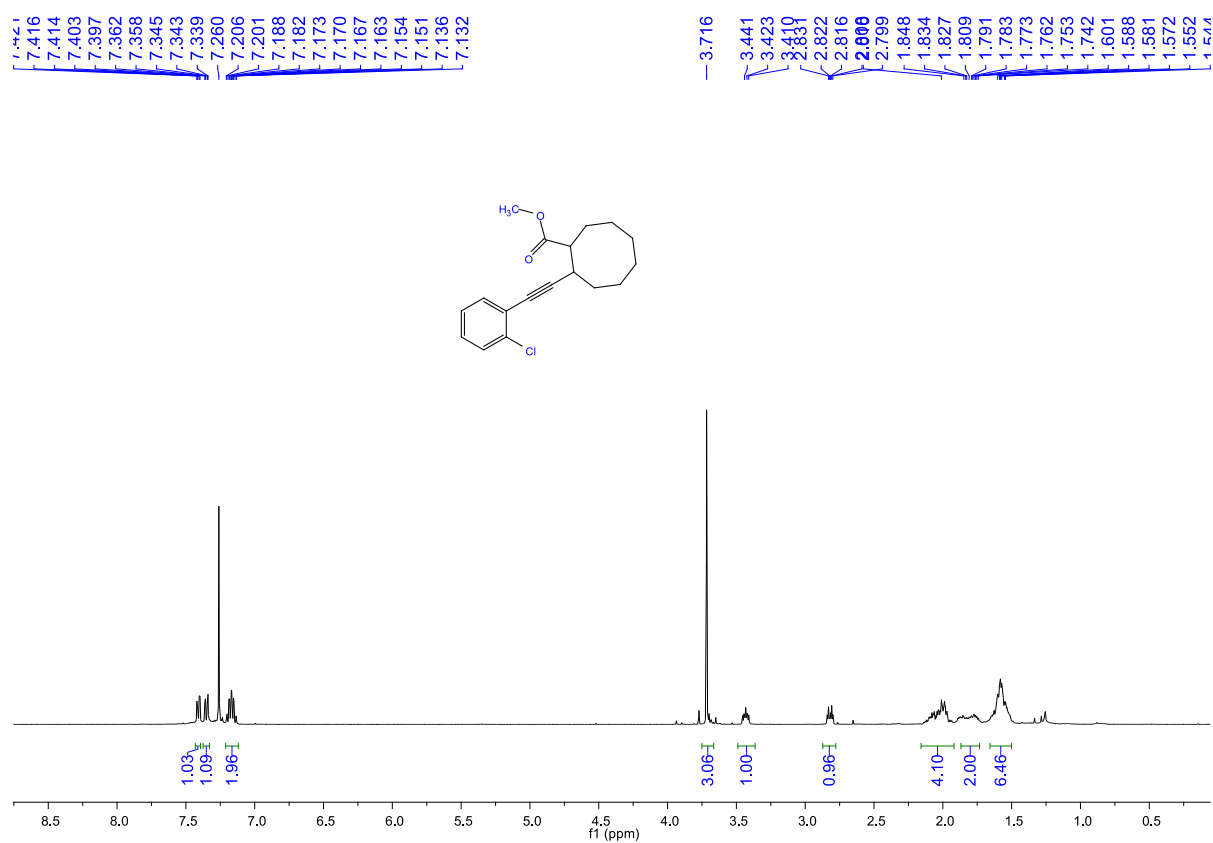


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4h

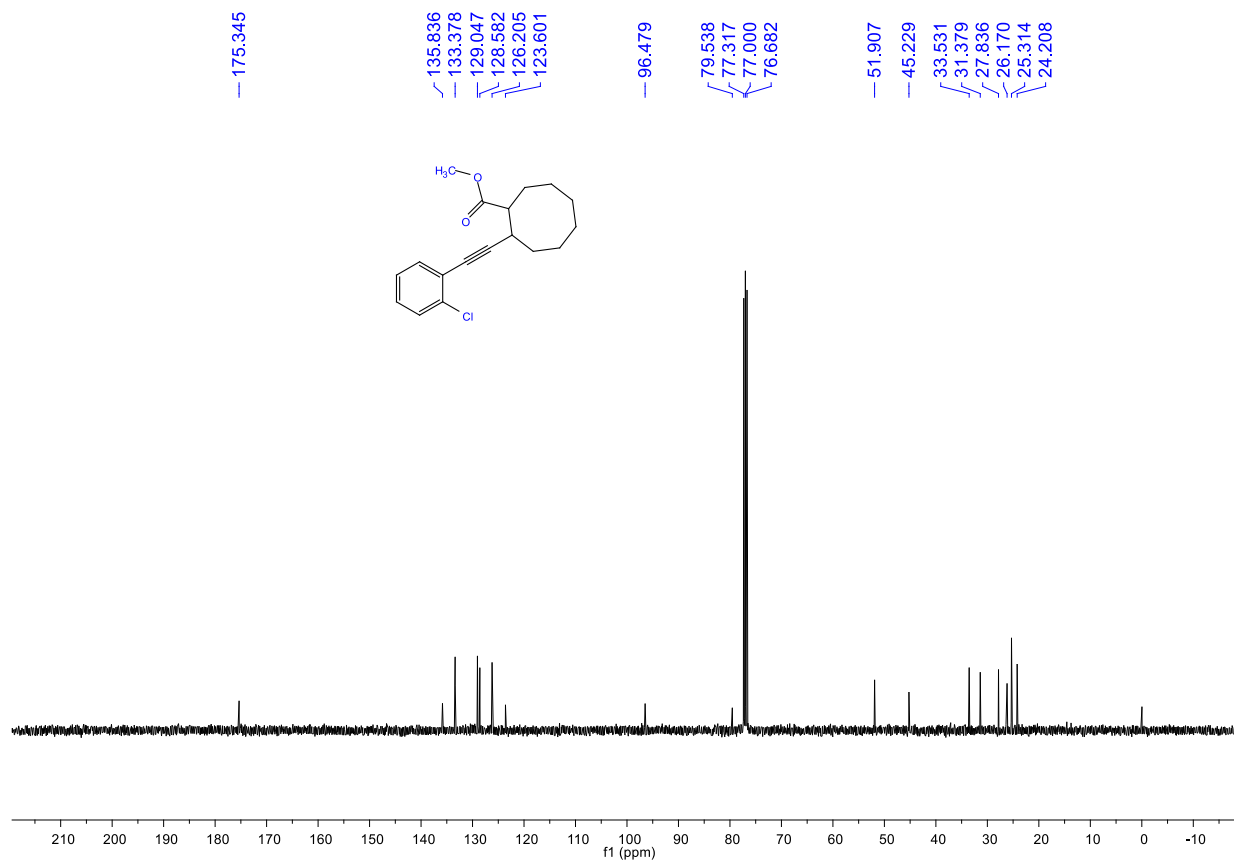


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4i

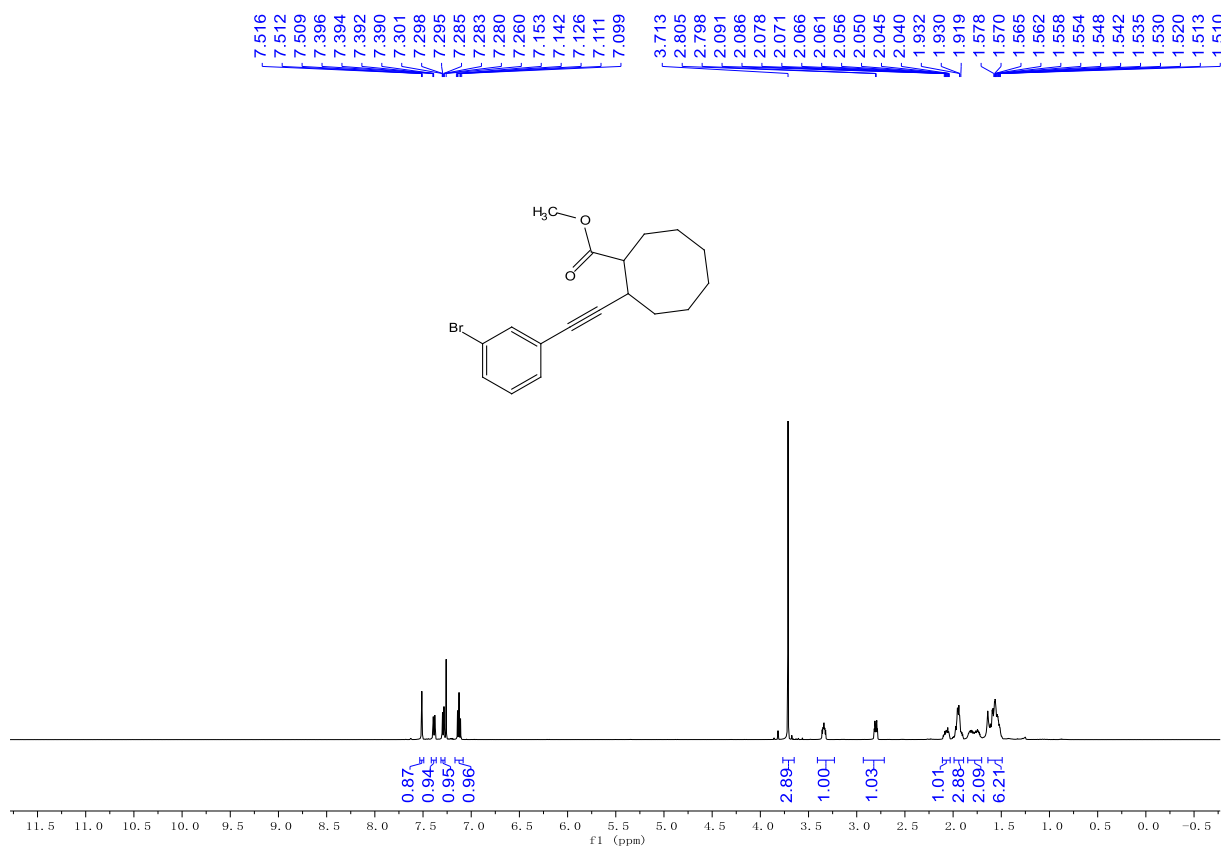


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4i

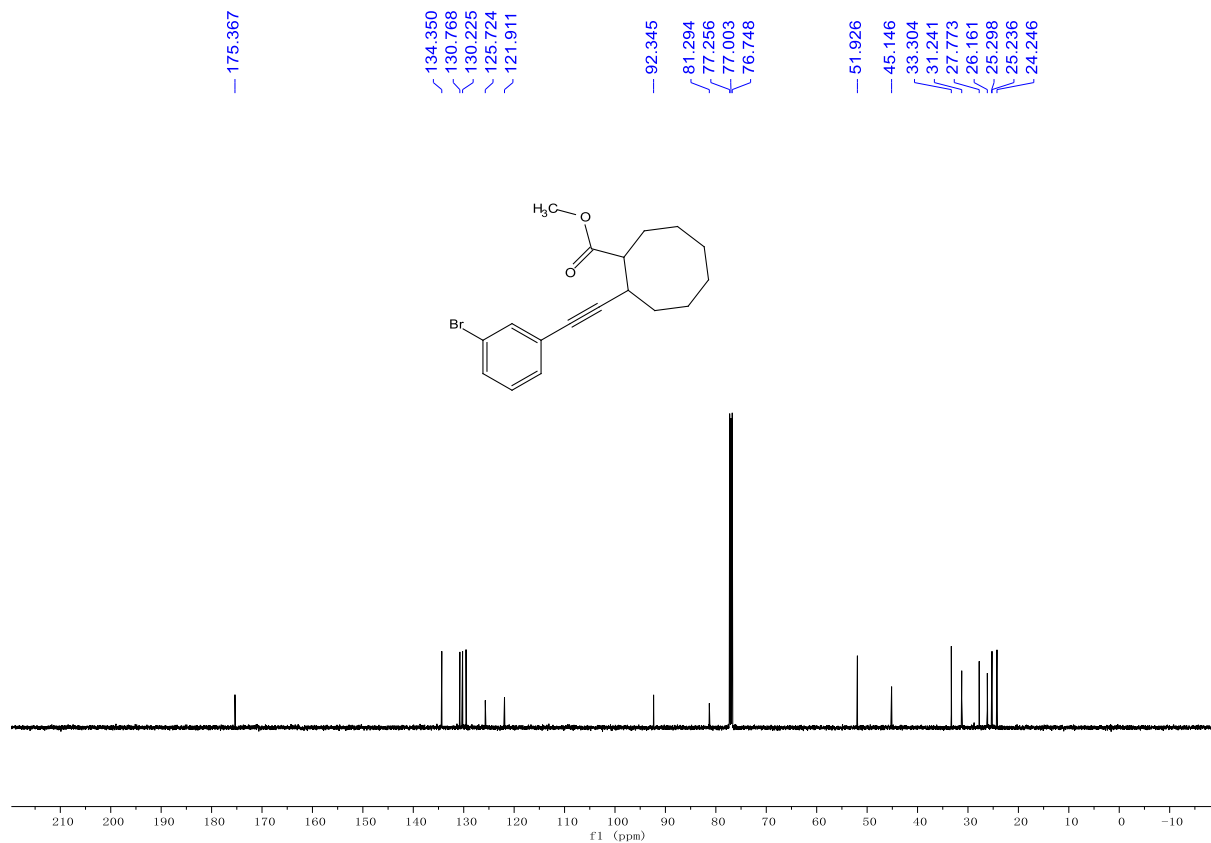


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4j

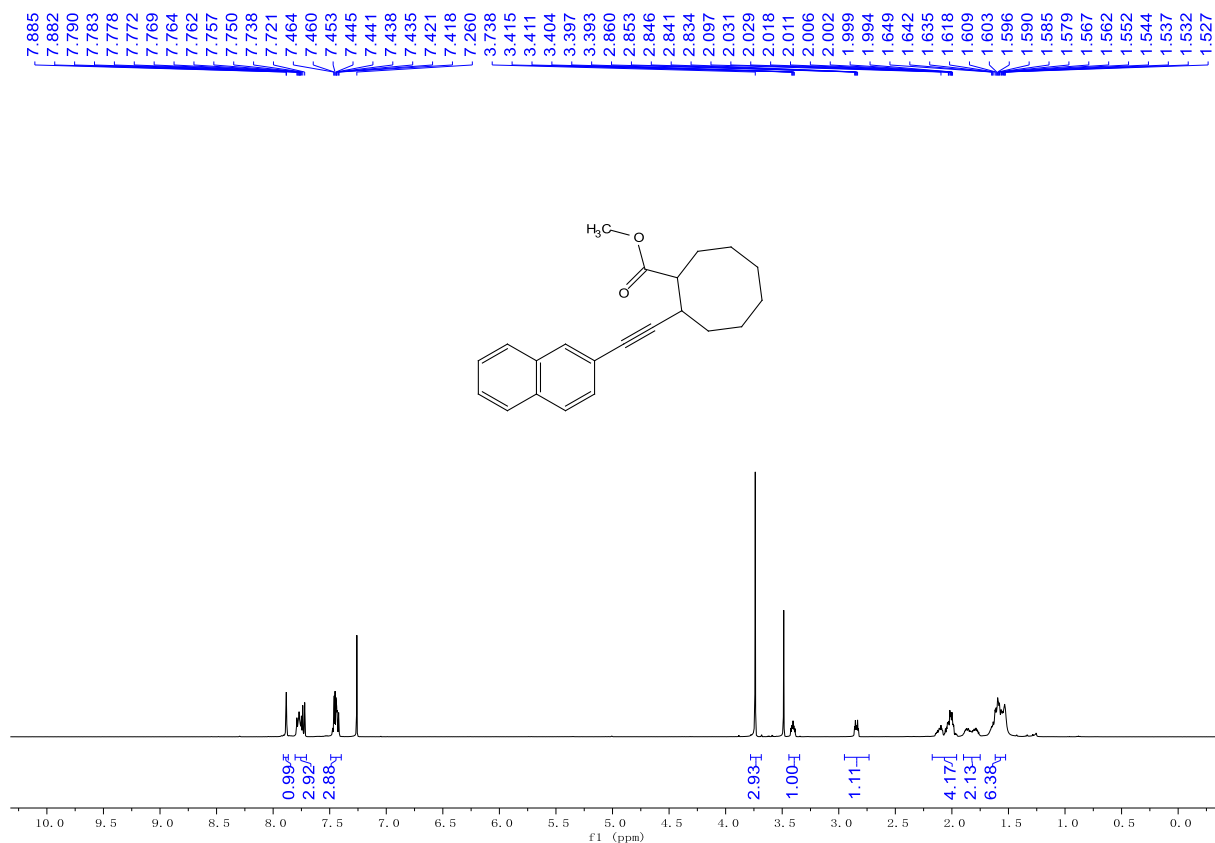


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4j

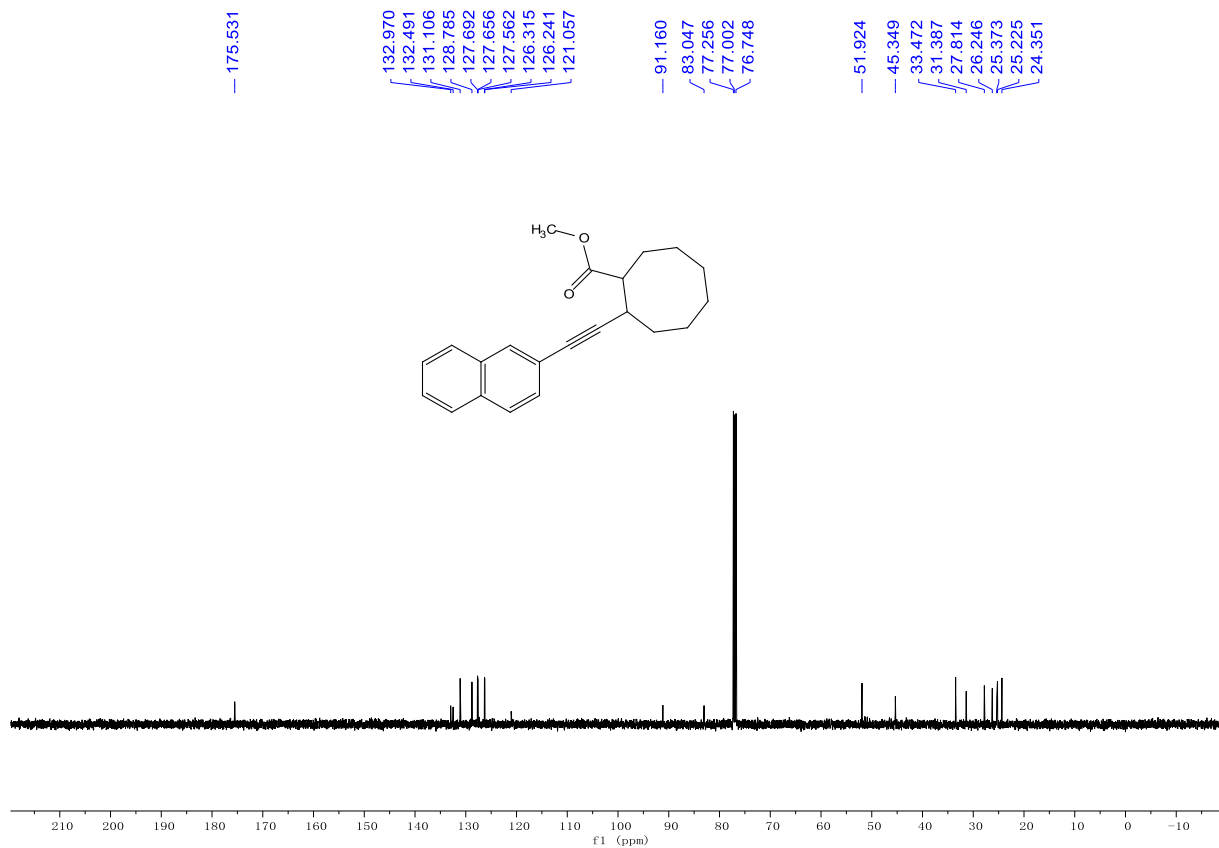


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4k



¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4k

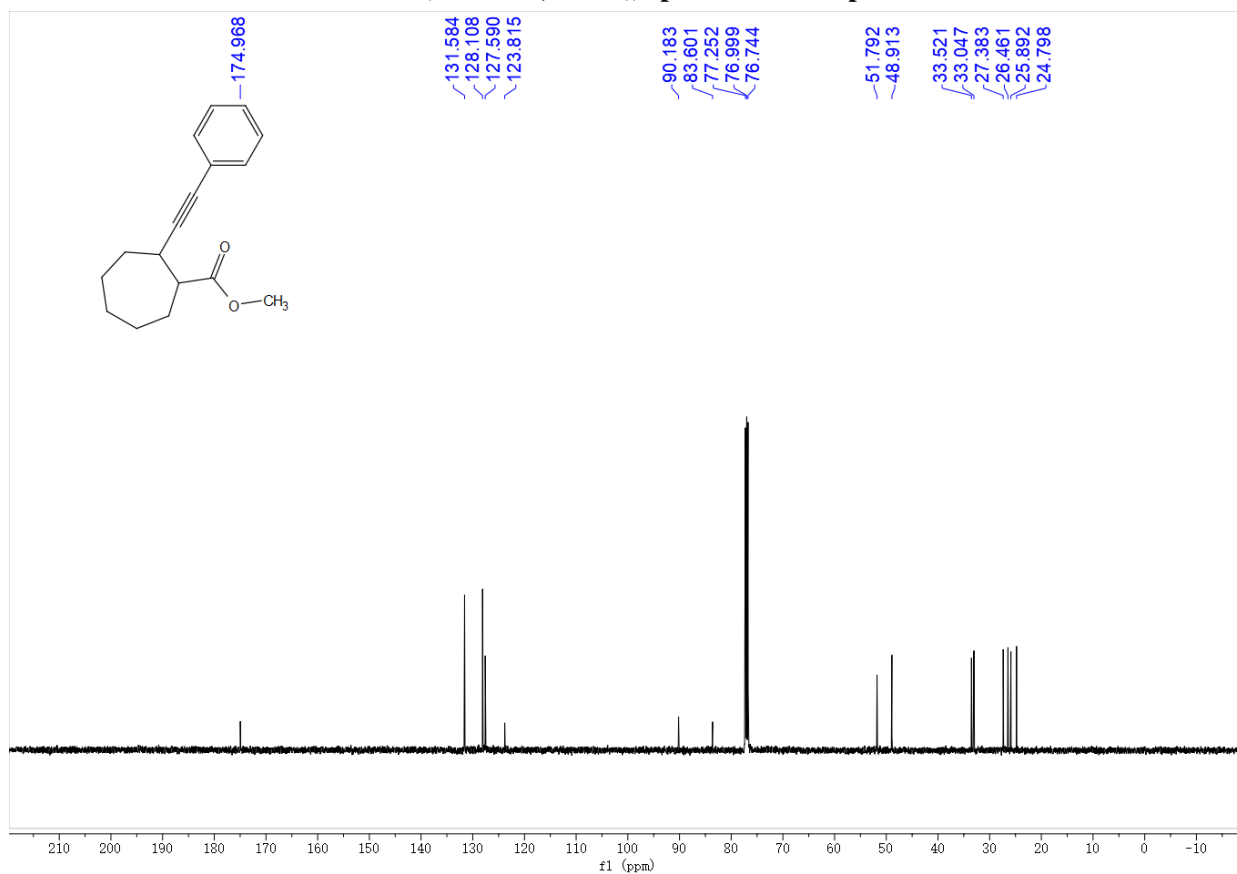


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 41

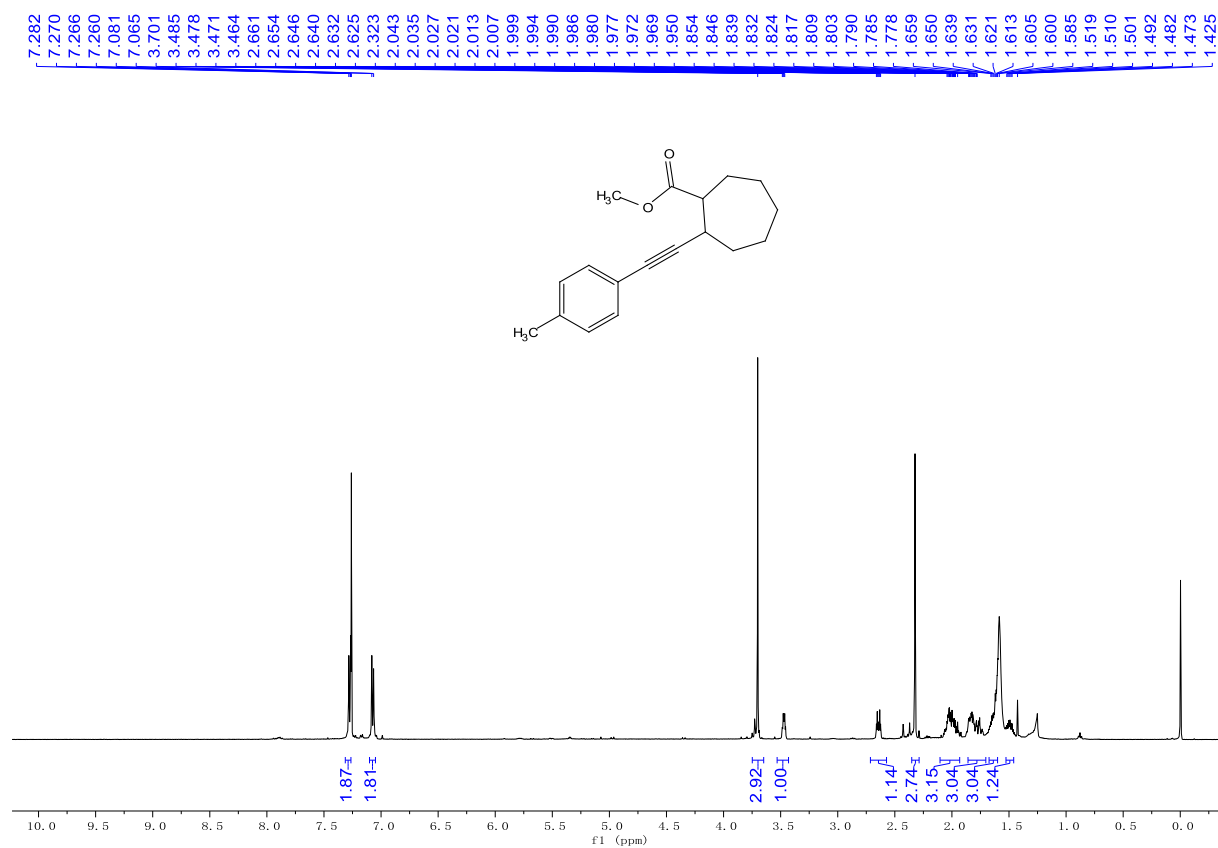


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 41

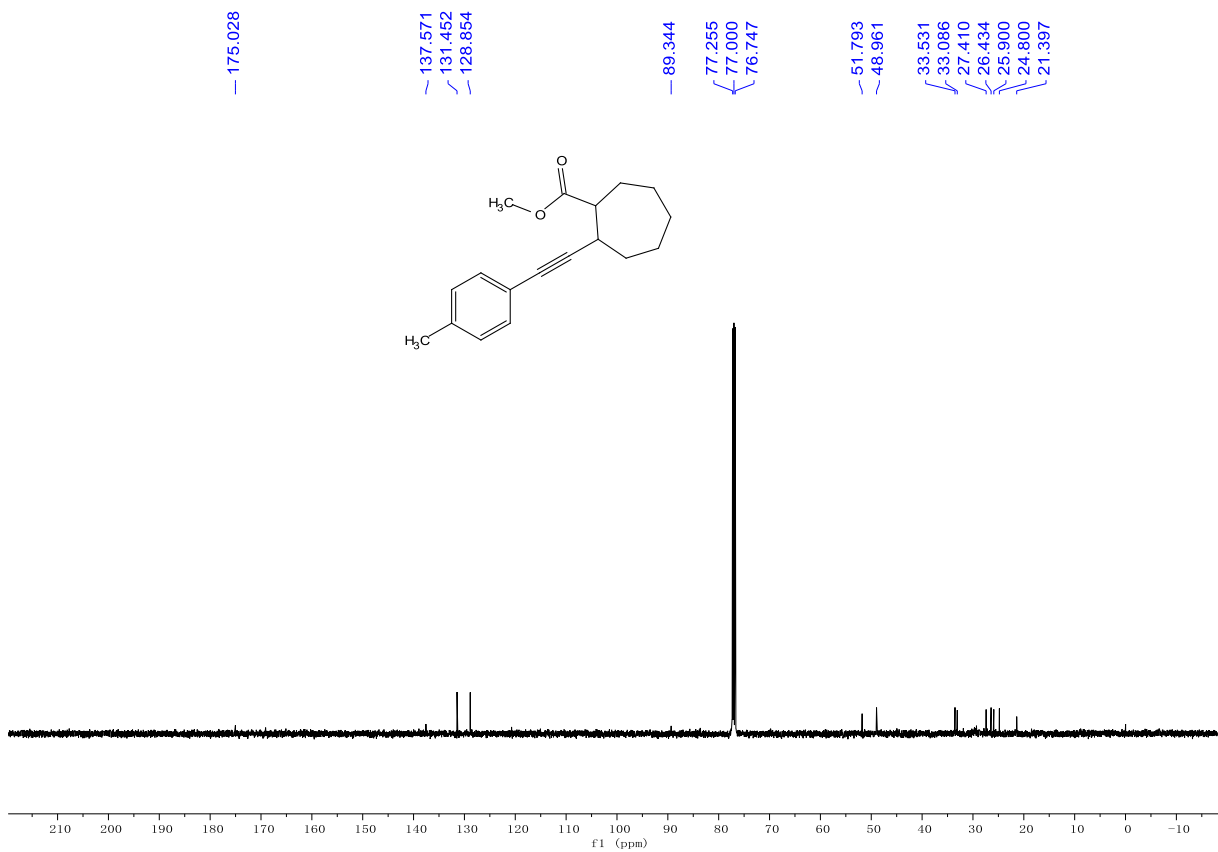


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4m

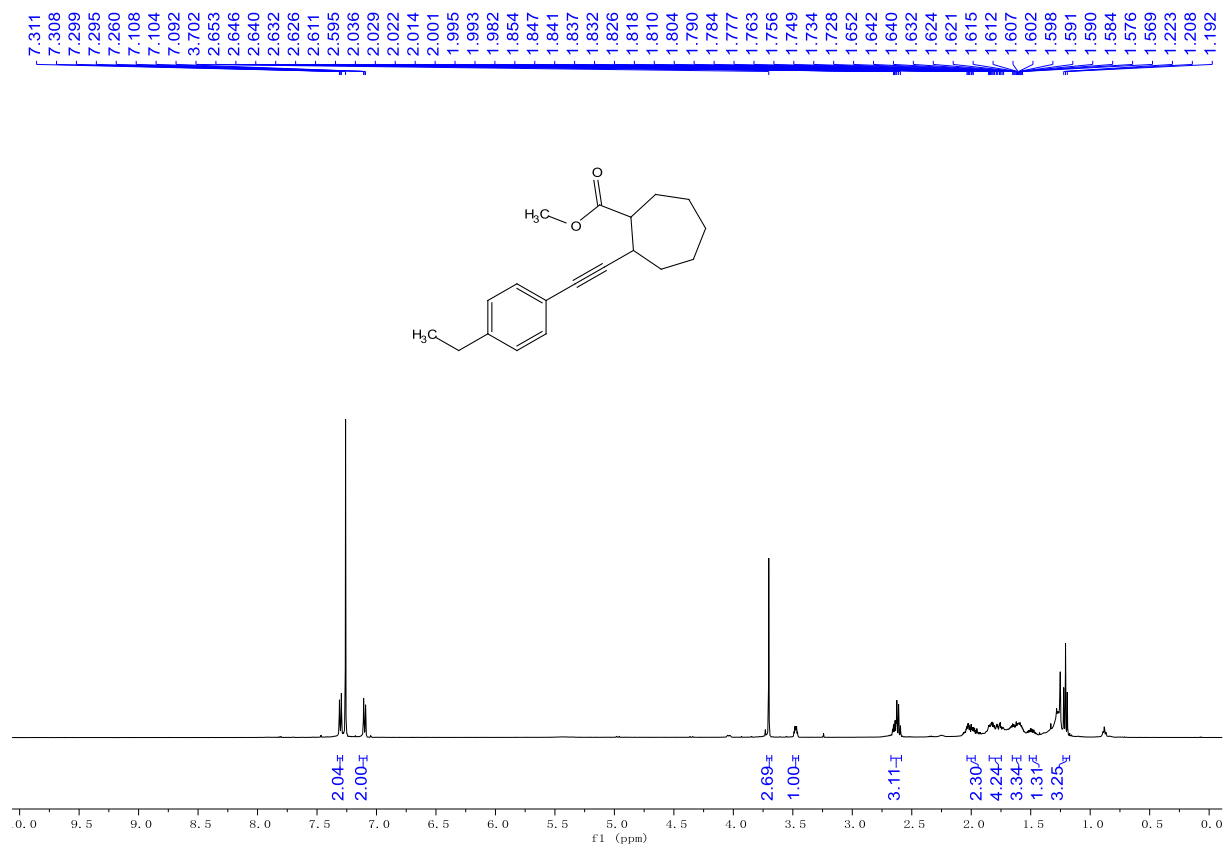


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4m

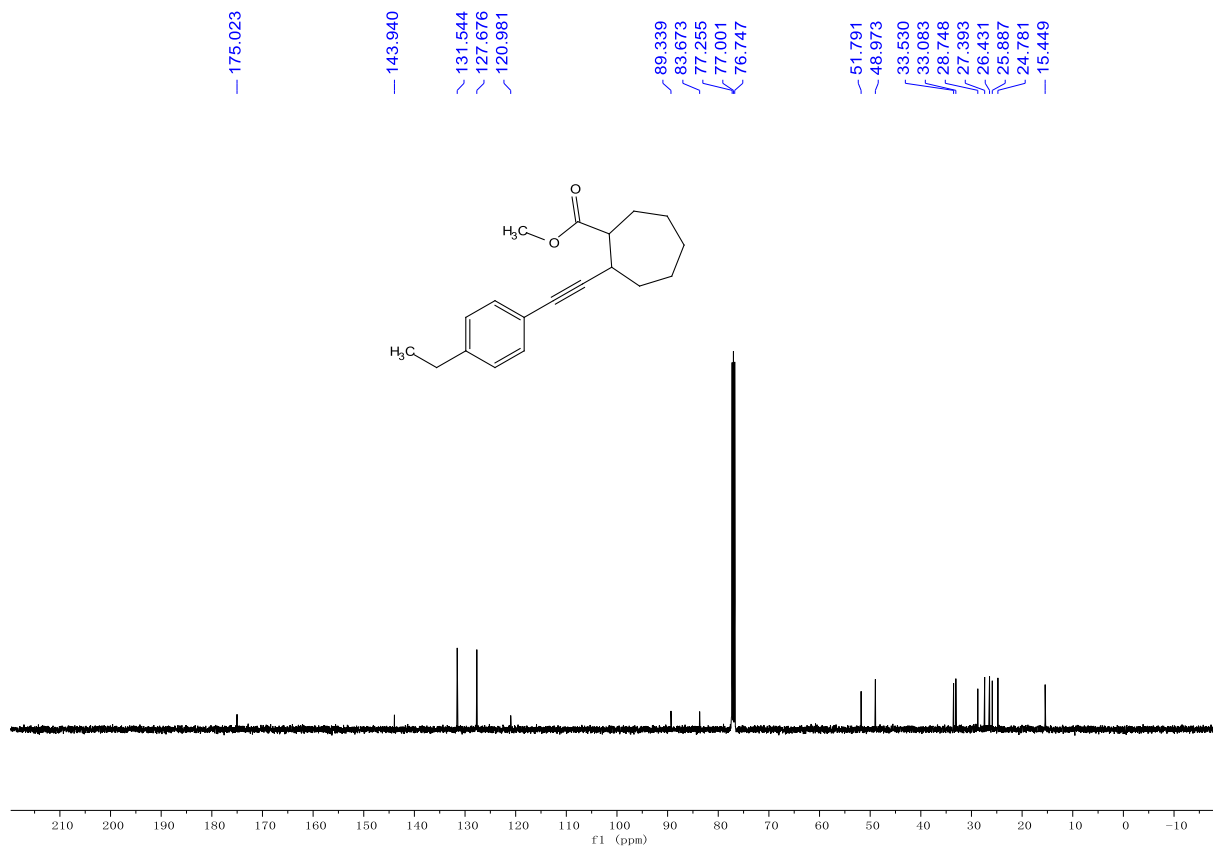


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4n

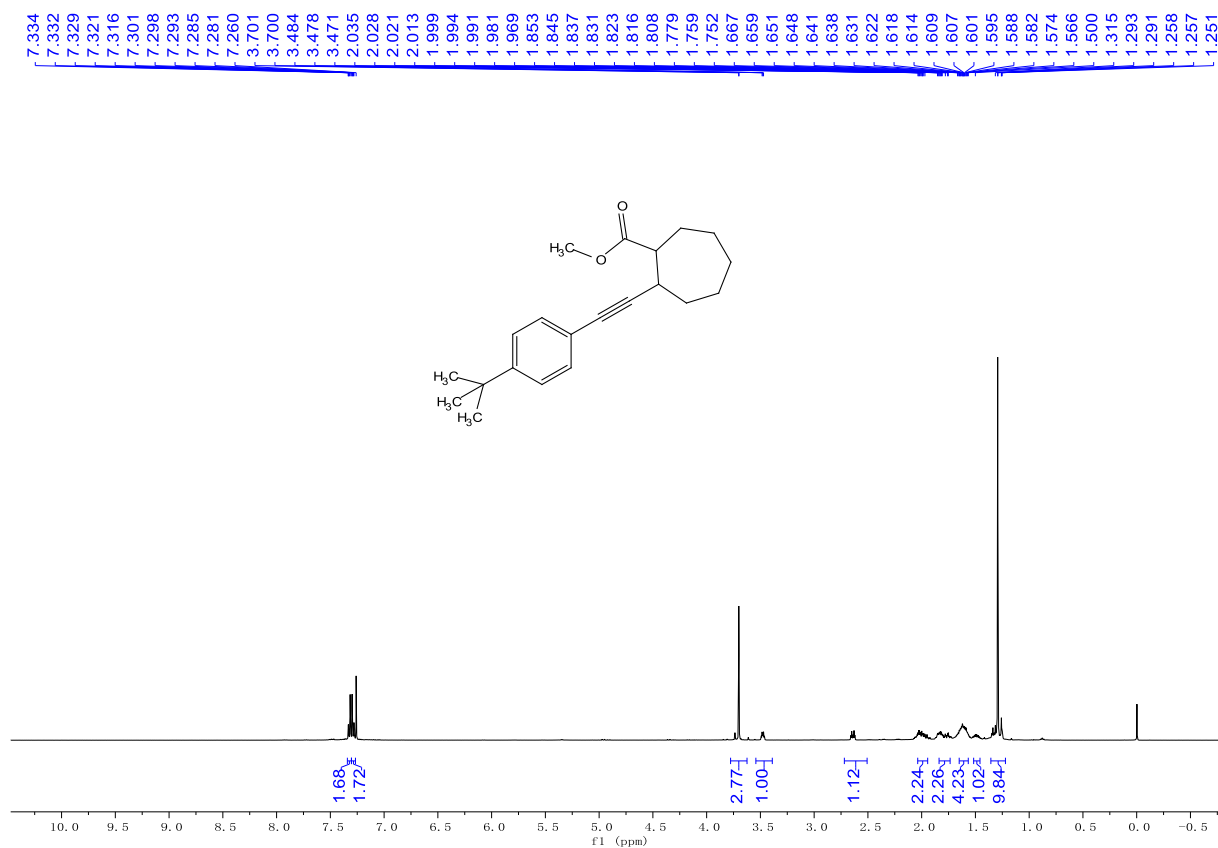


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4n

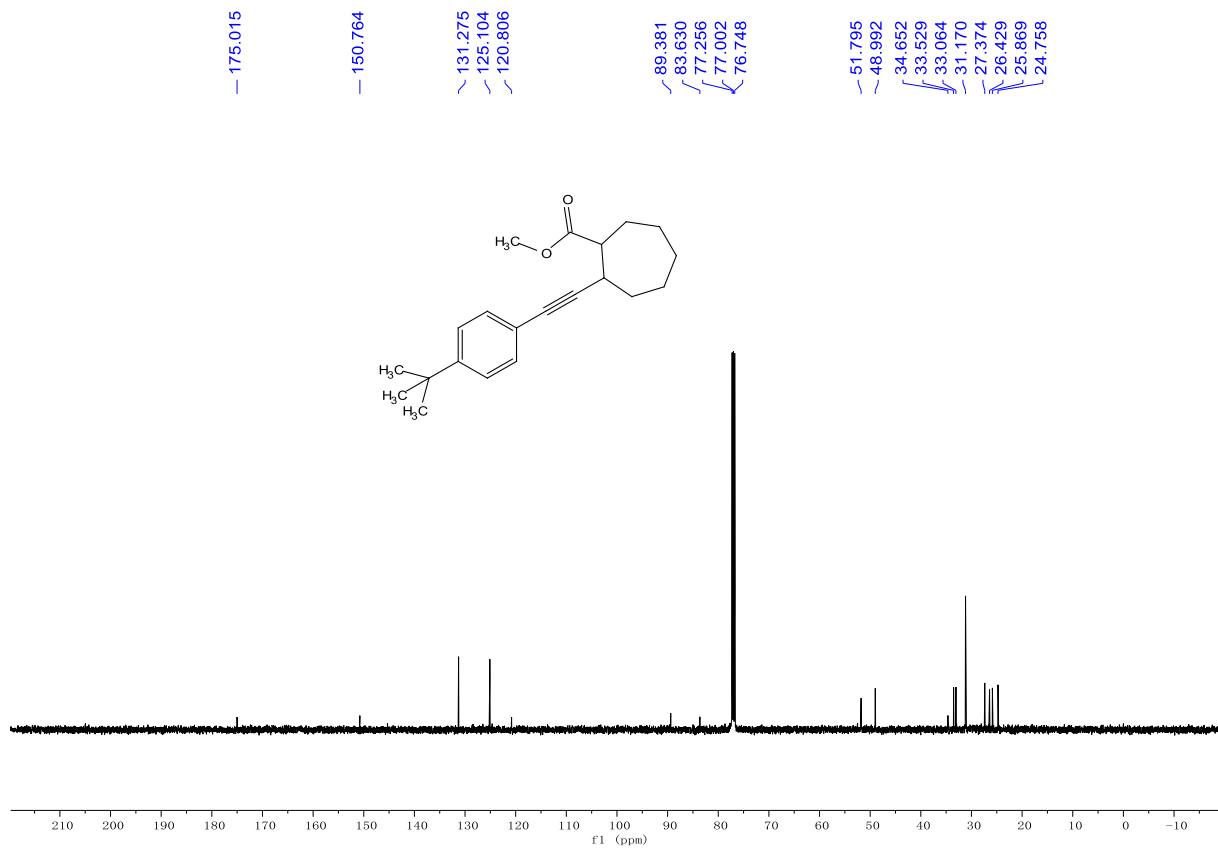


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4o

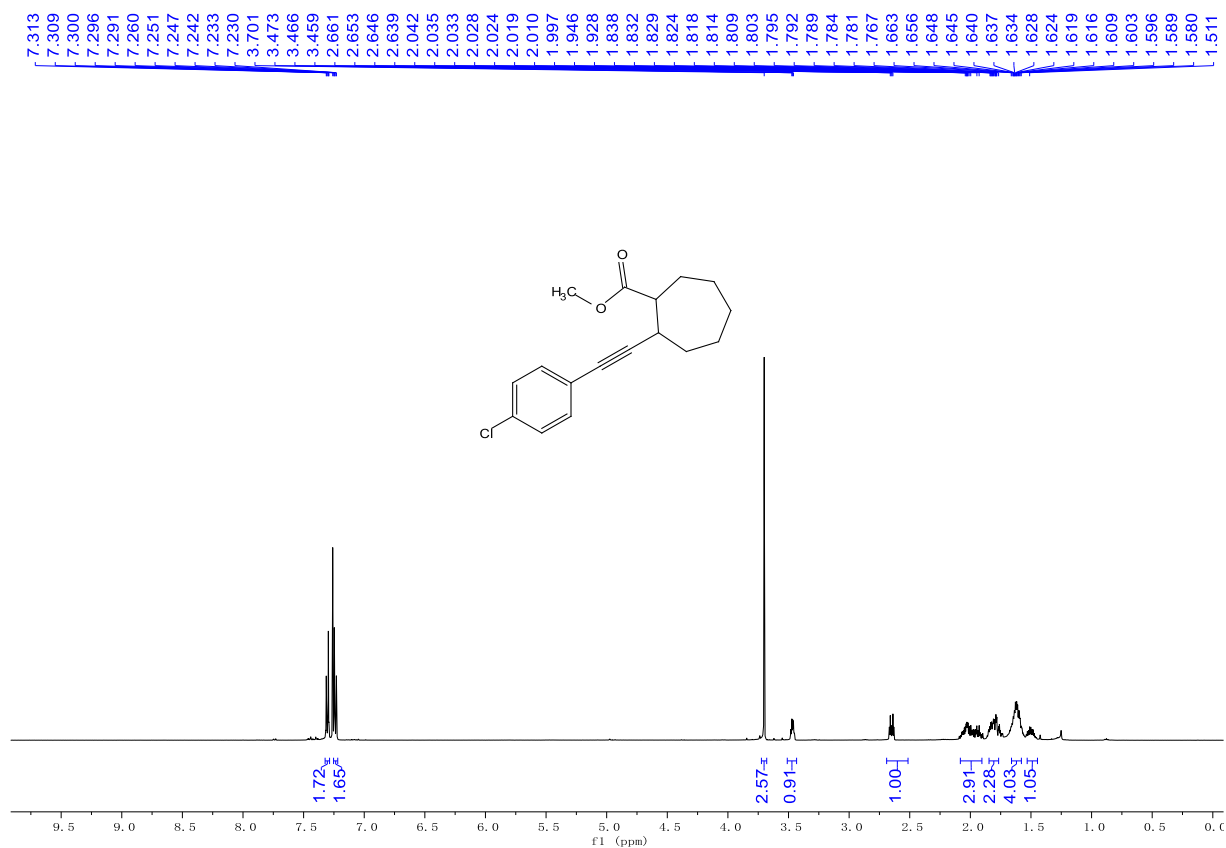


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4o

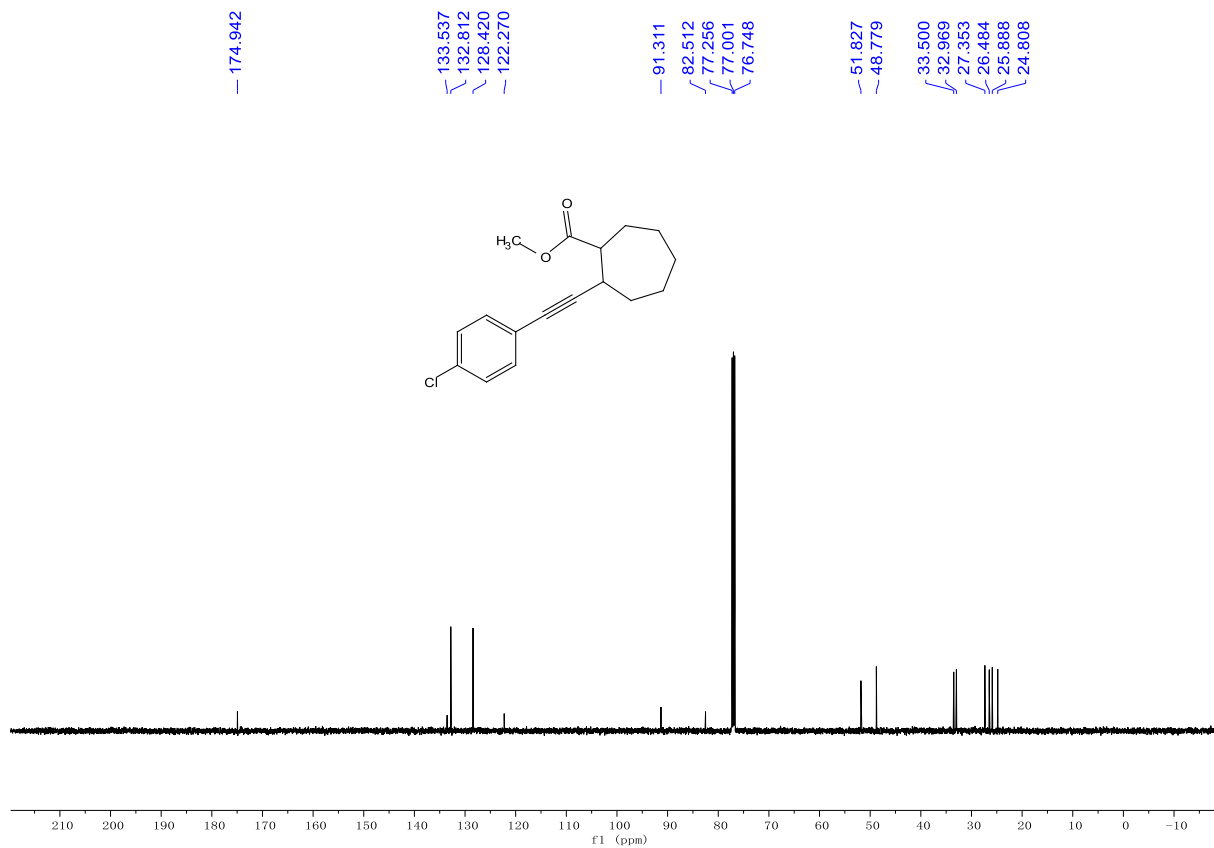


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4p

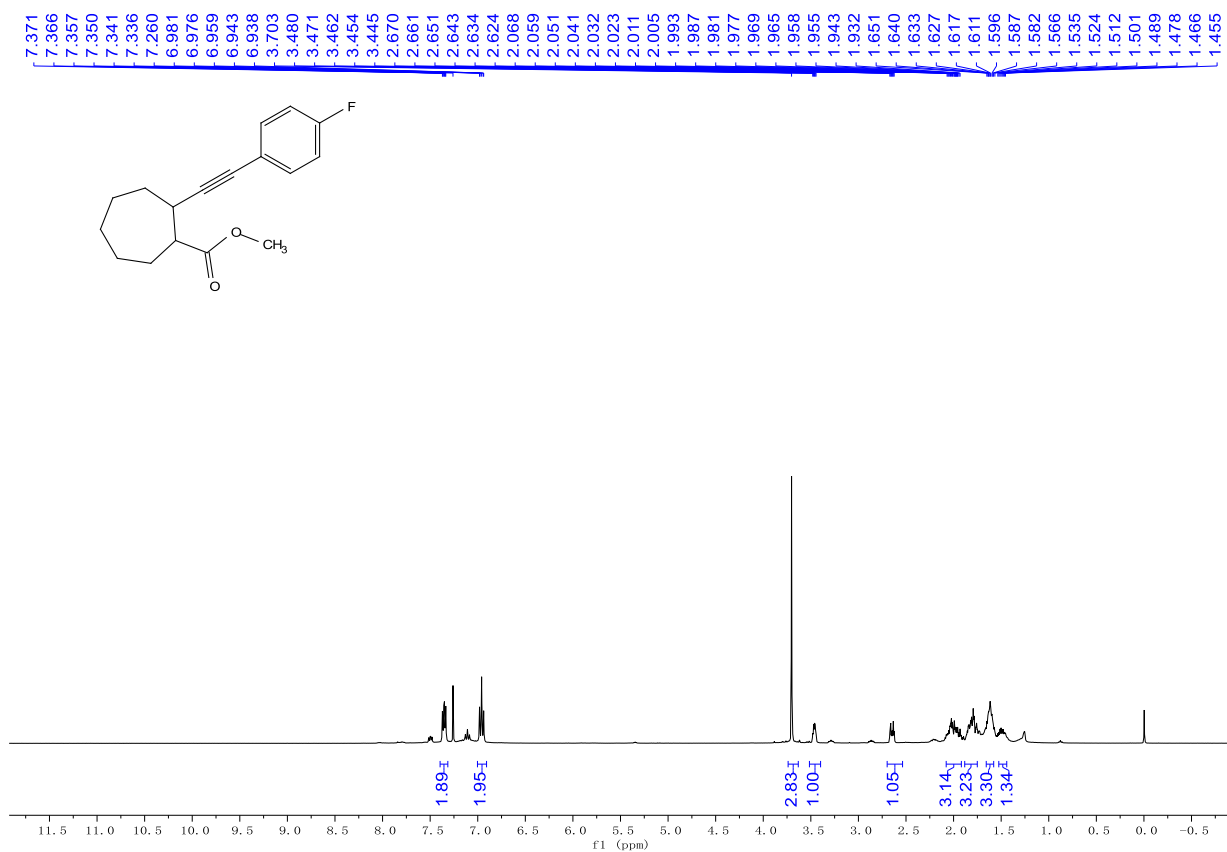


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4p

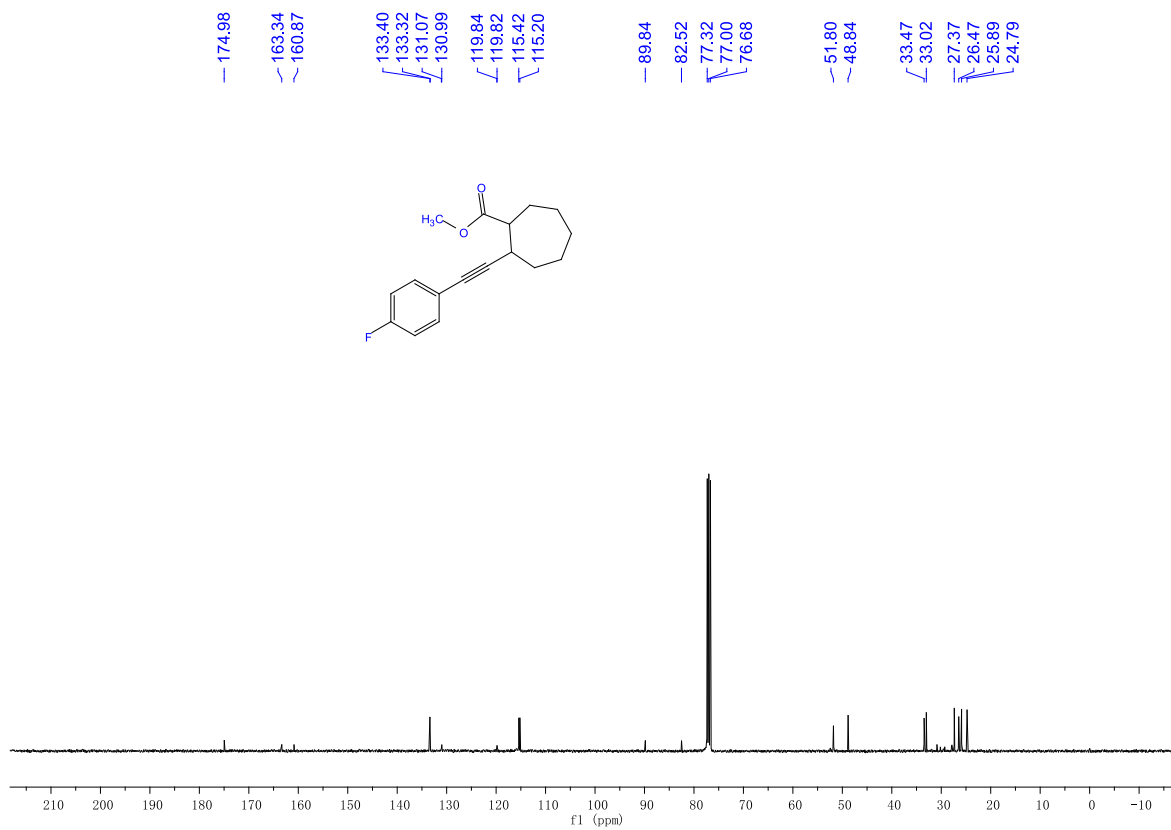


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4q

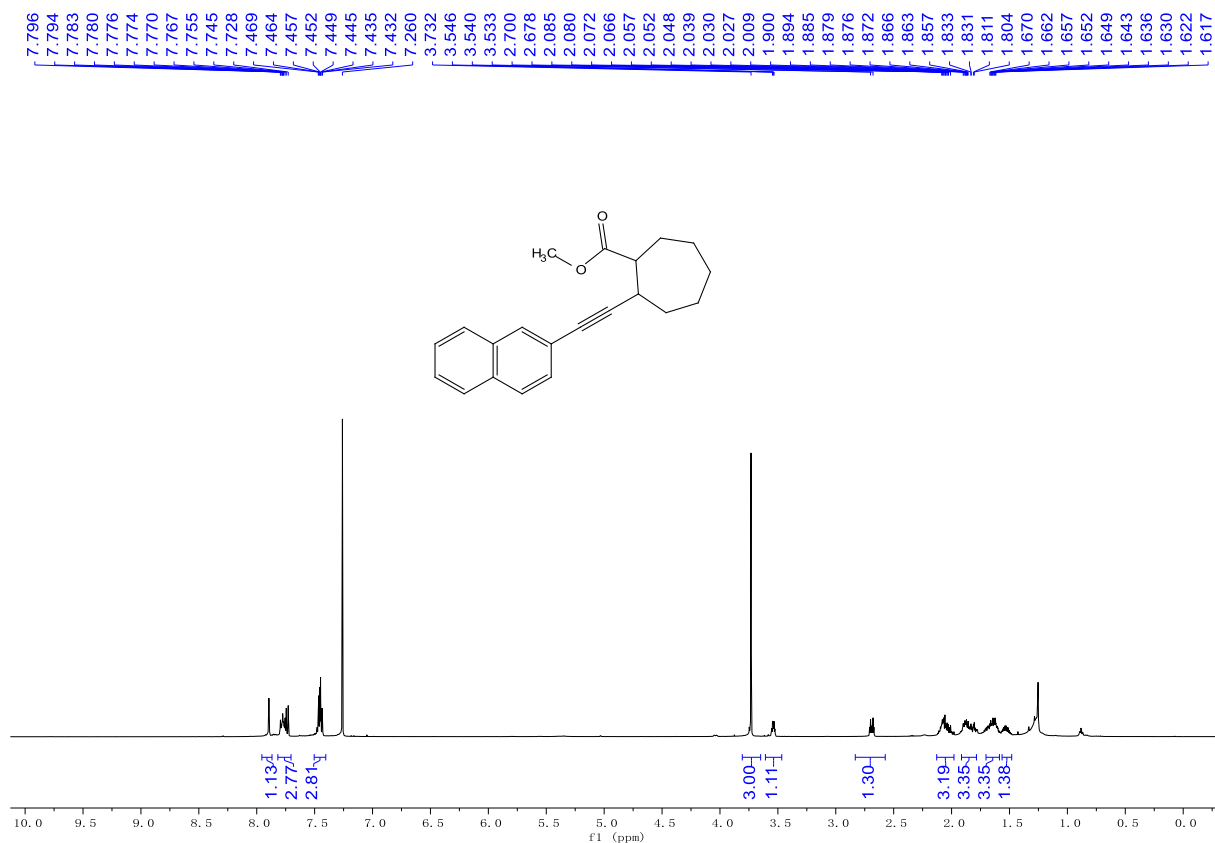


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4q

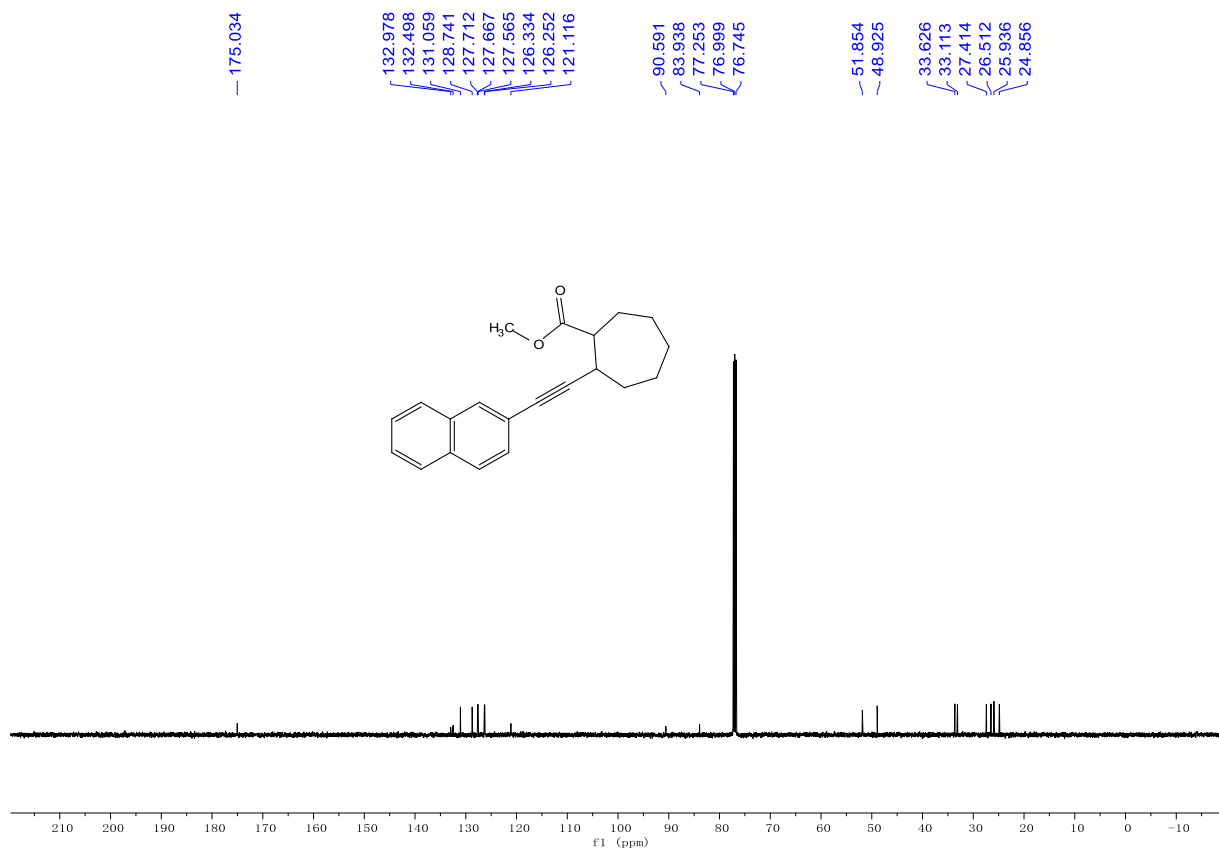


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4r

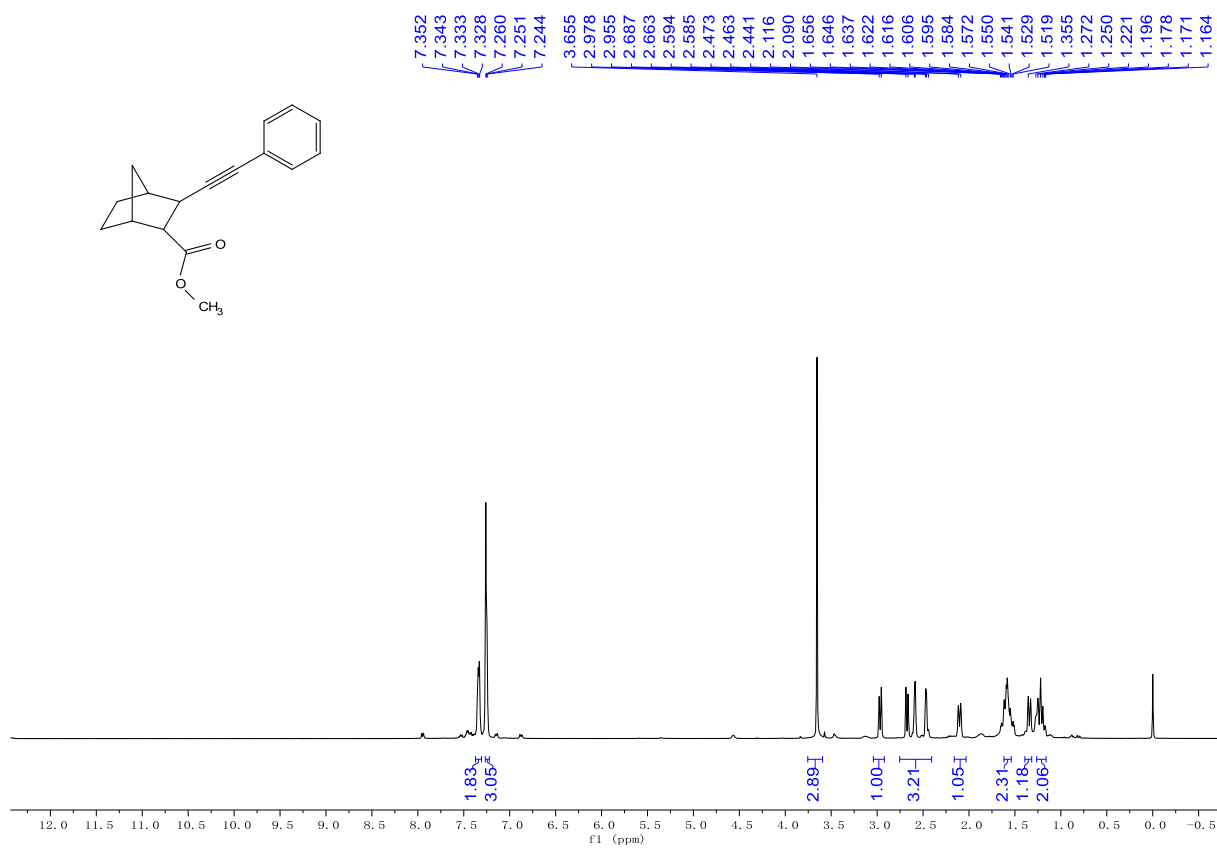


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4r

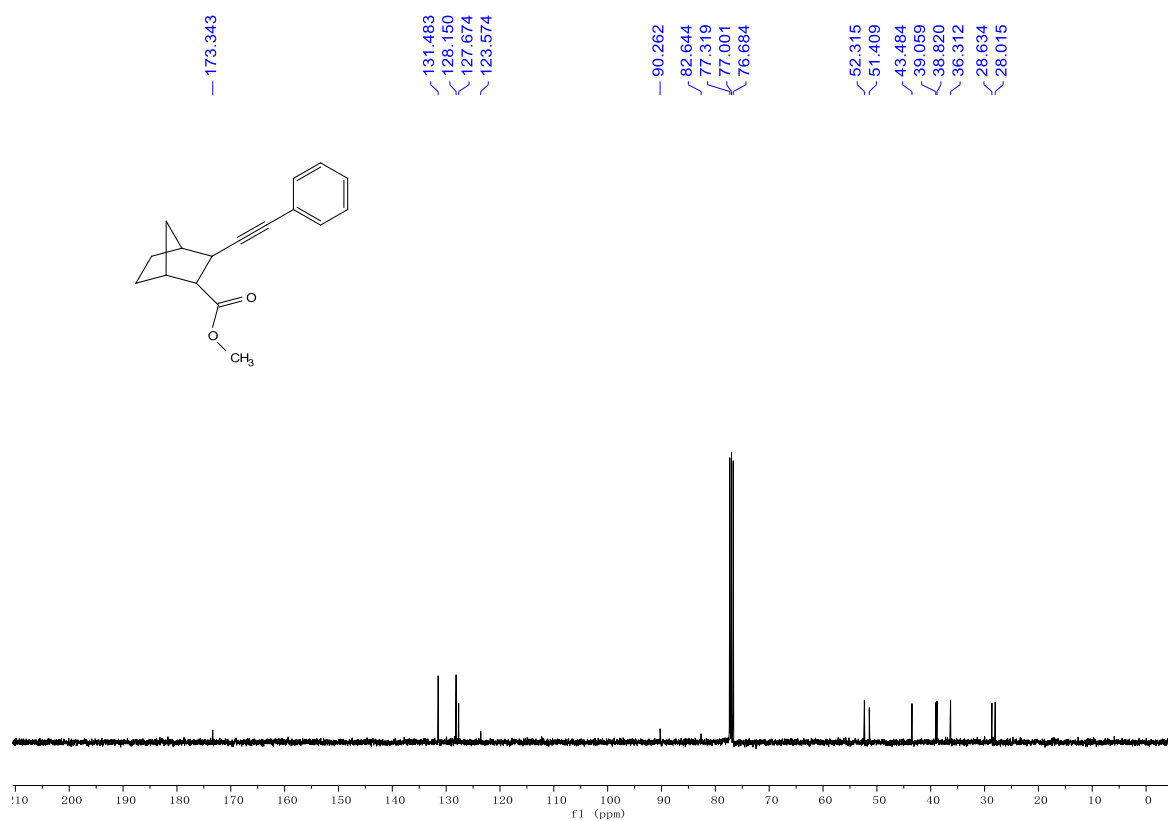


SUPPORTING INFORMATION

¹H NMR (400 MHz, CDCl₃) spectrum of compound 4s

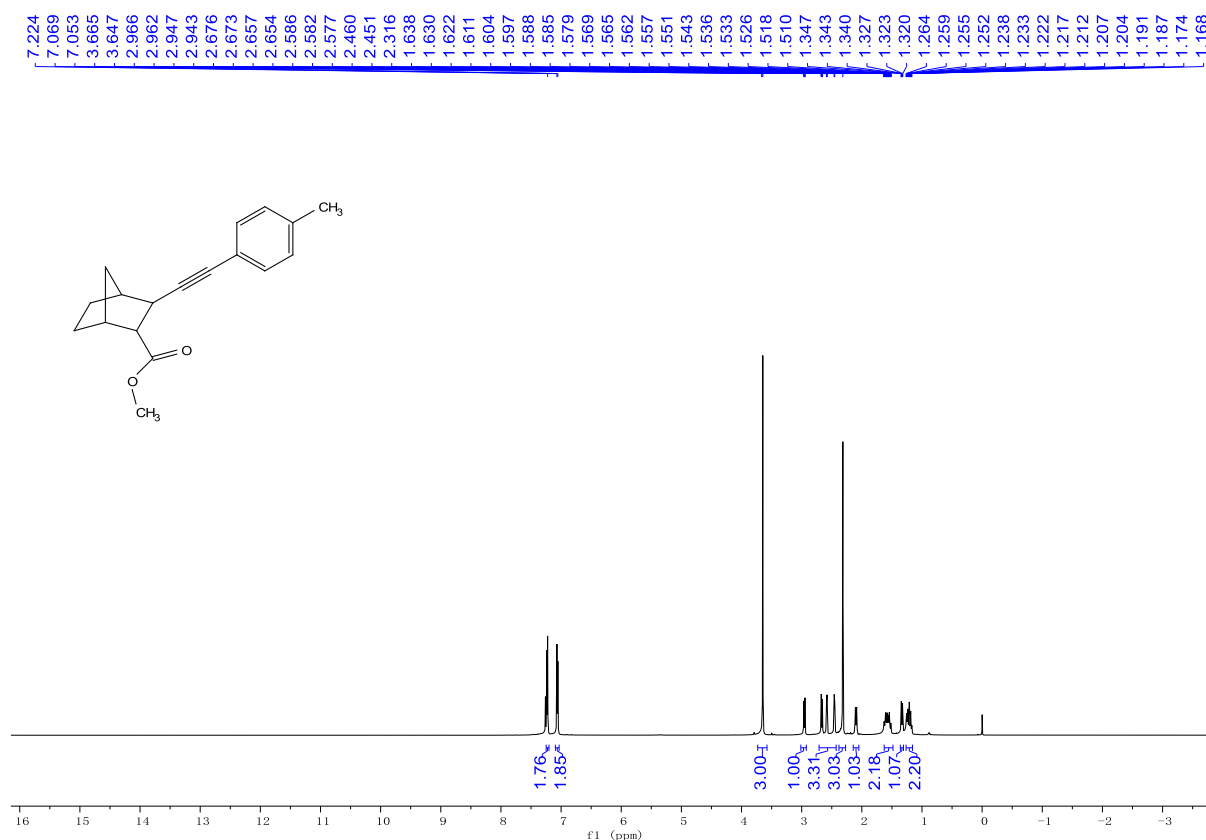


¹³C NMR (100 MHz, CDCl₃) spectrum of compound 4s

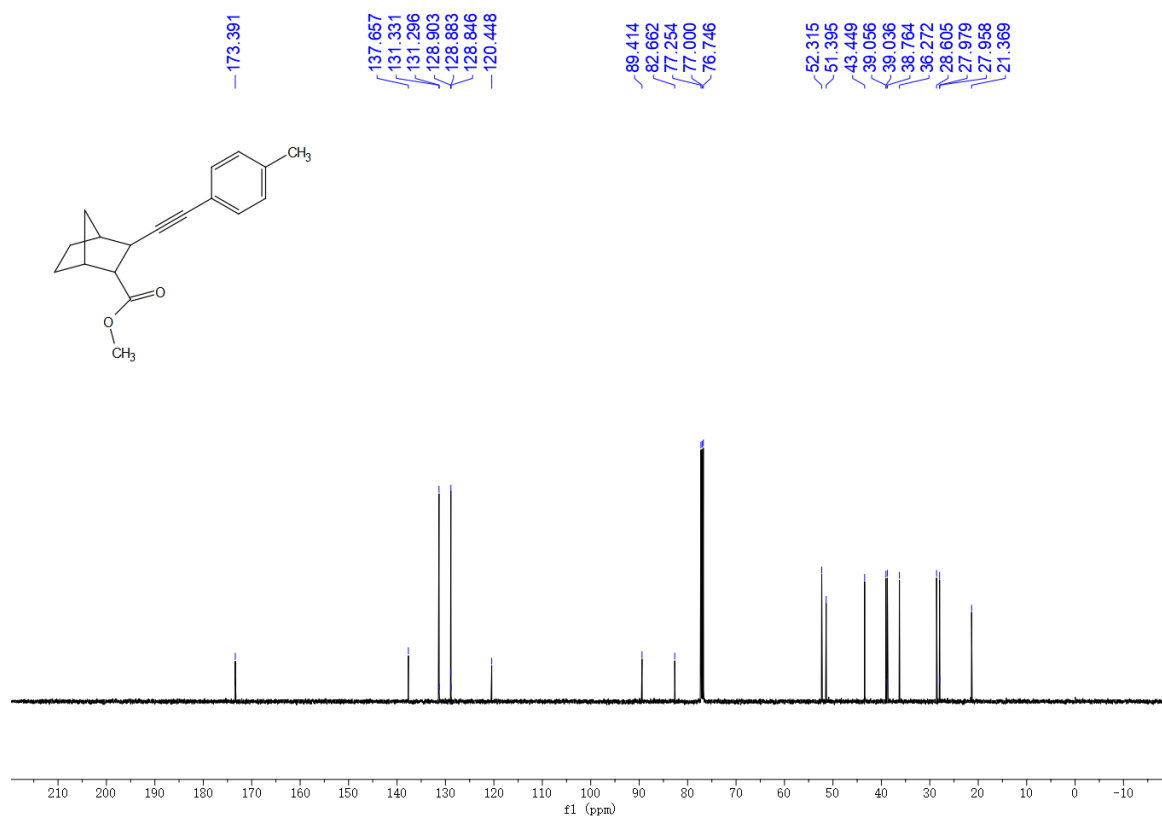


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4t

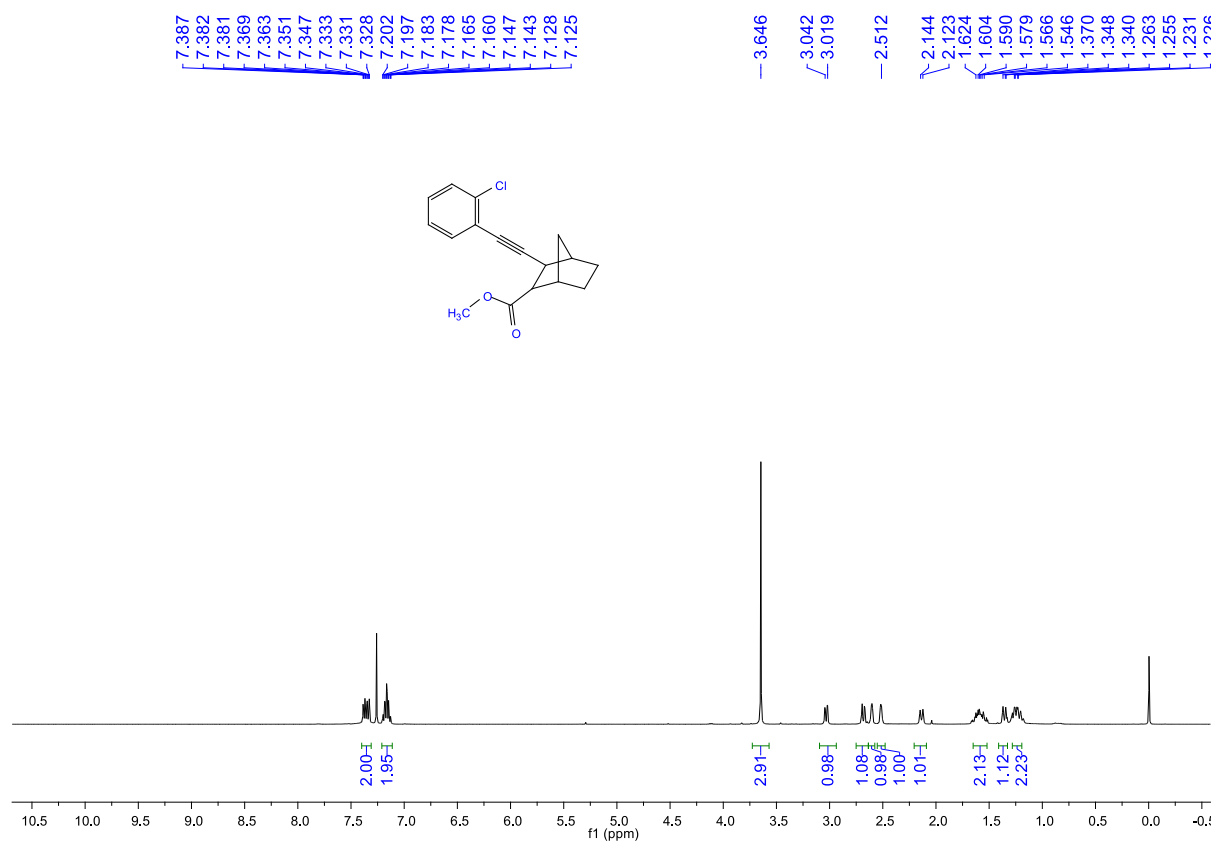


¹³C NMR (125 MHz, CD Cl₃) spectrum of compound 4t

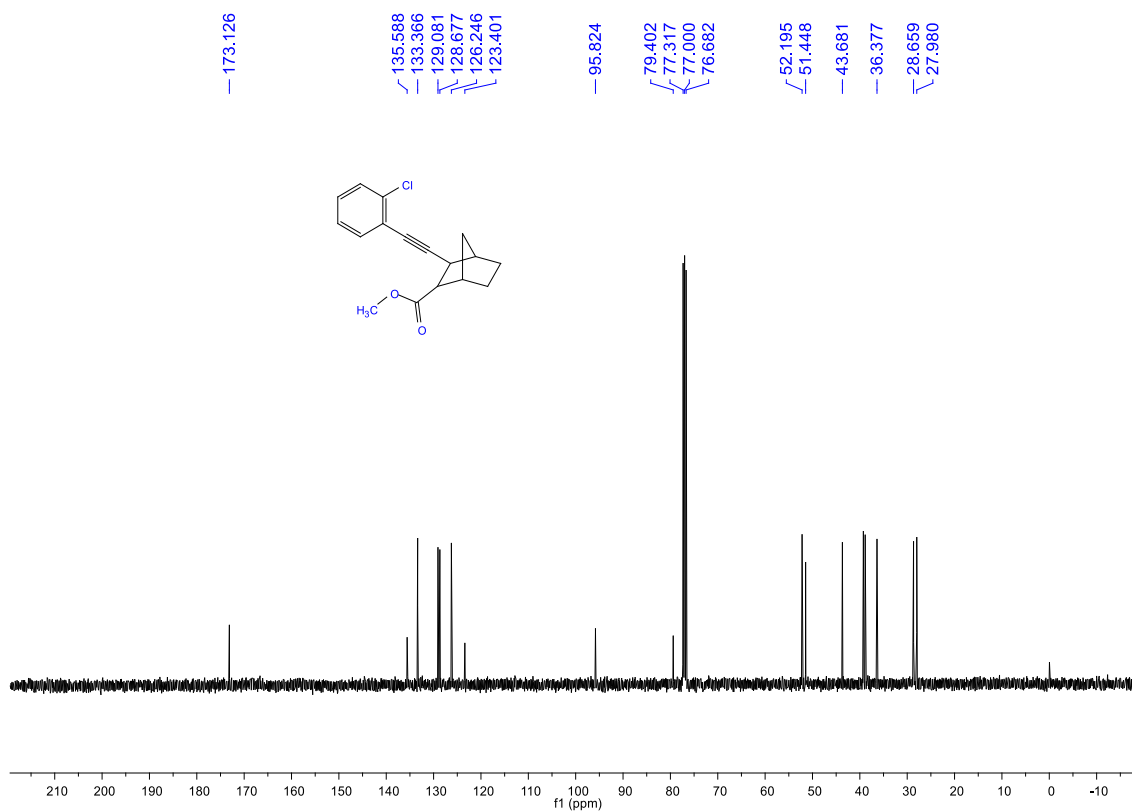


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4u

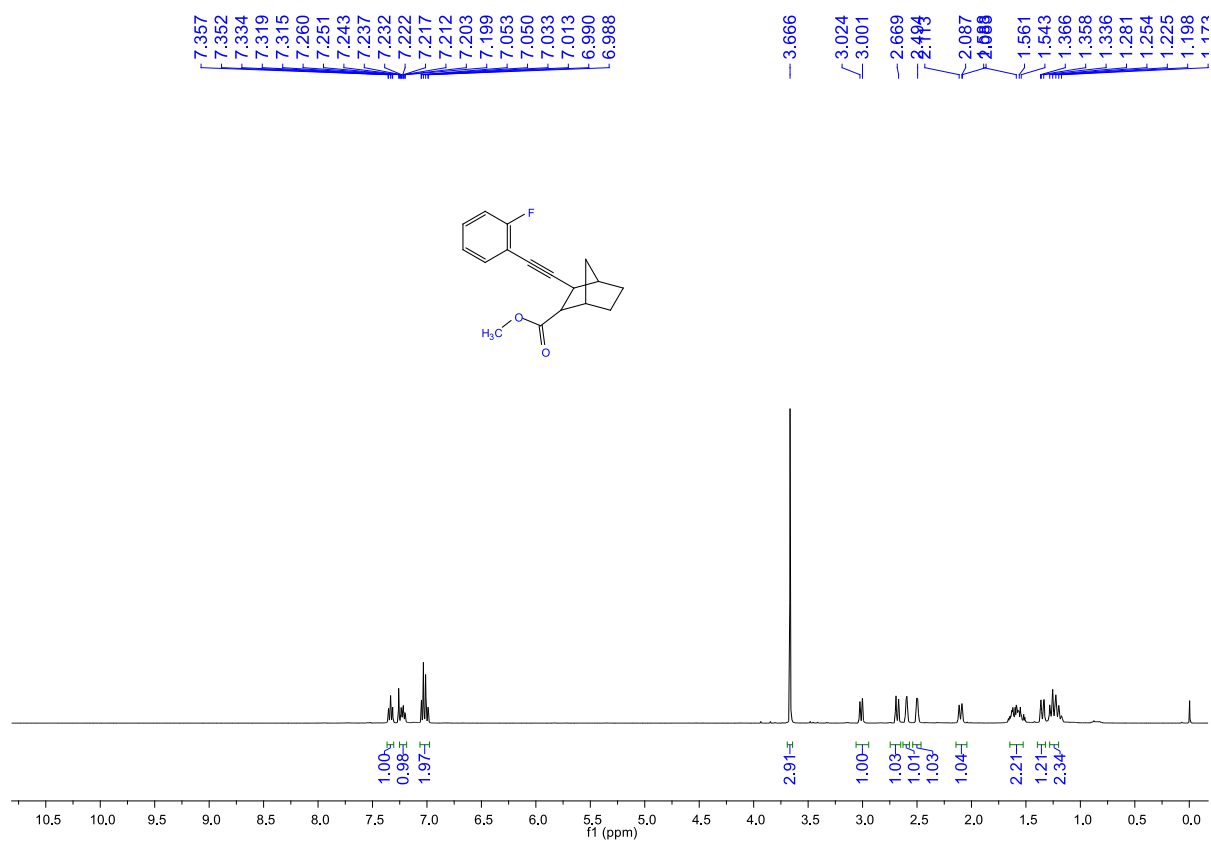


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4u

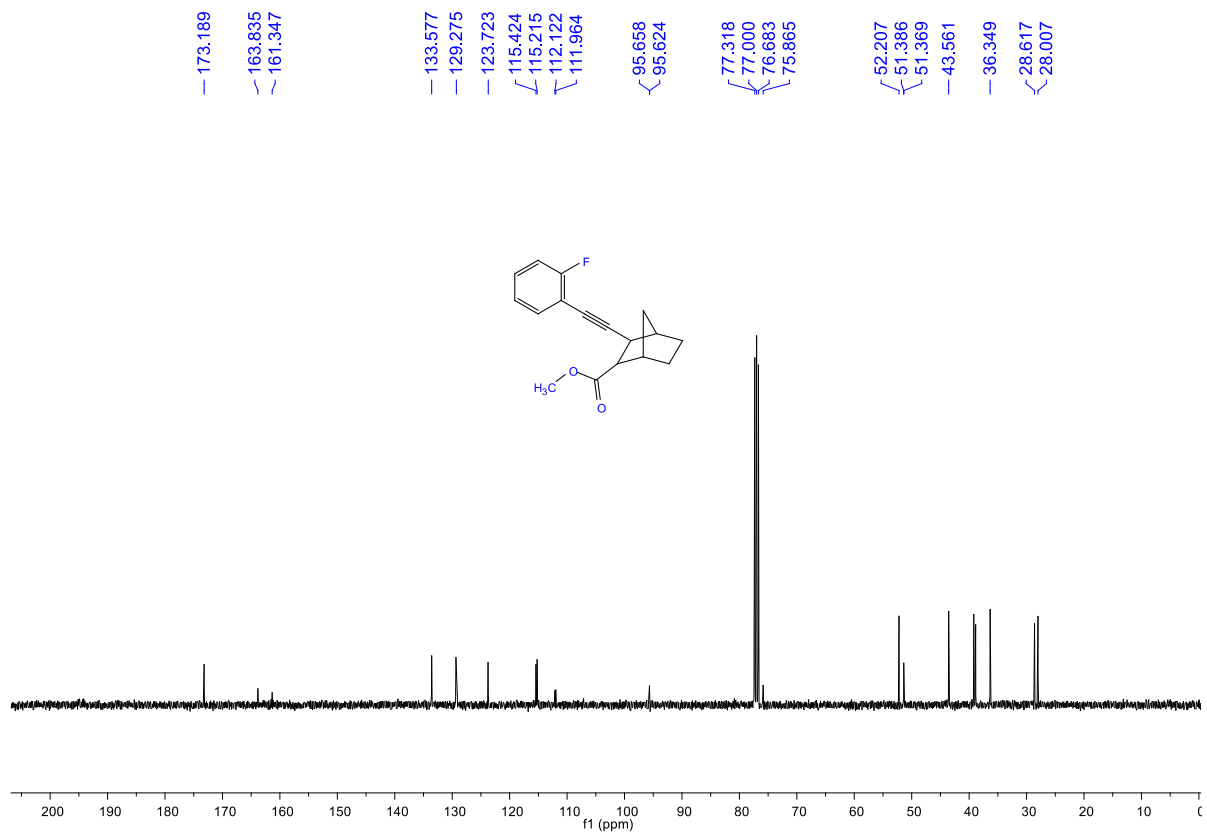


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4v

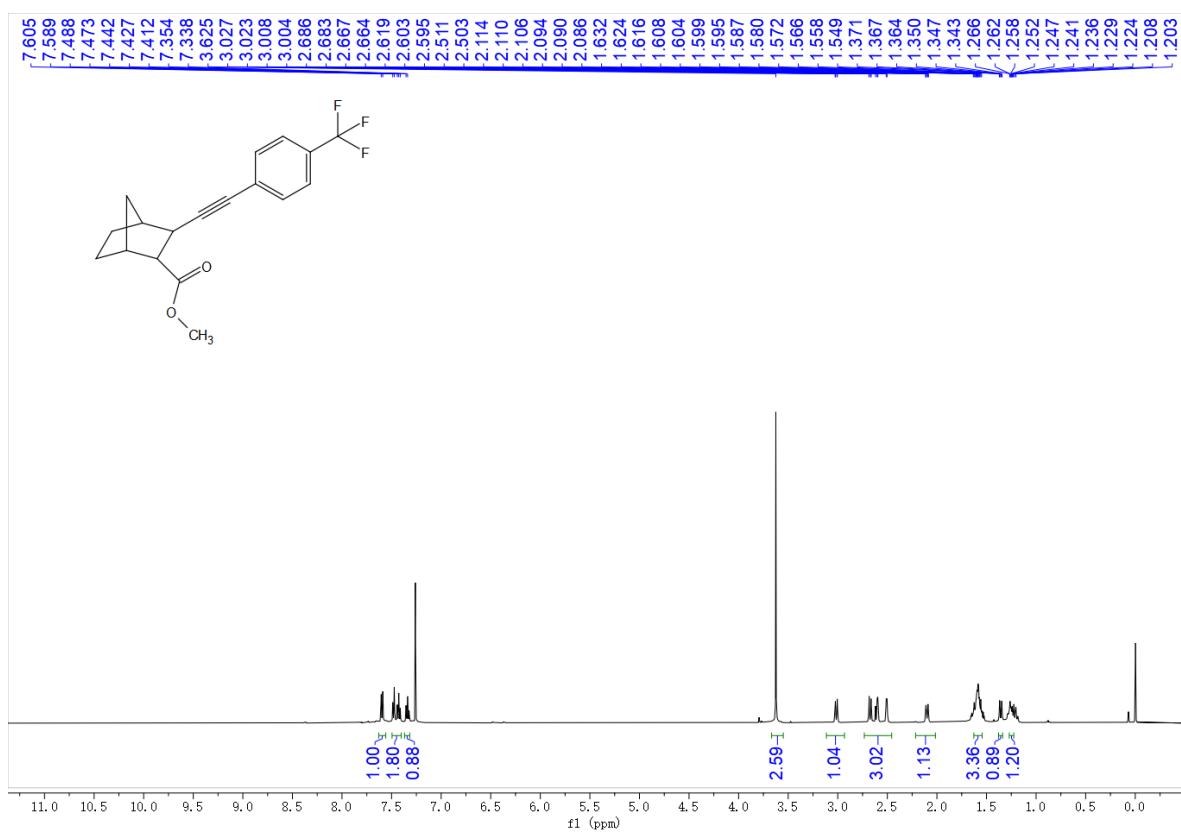


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4v

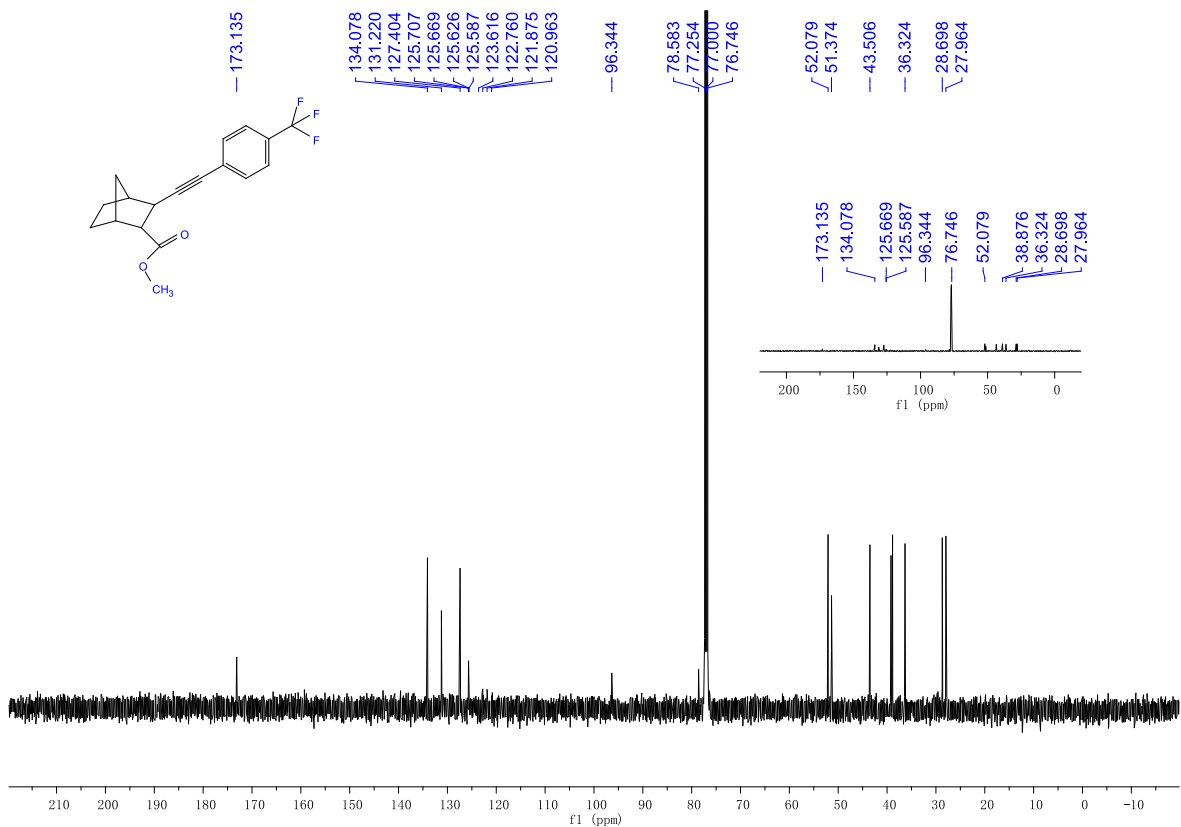


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4w

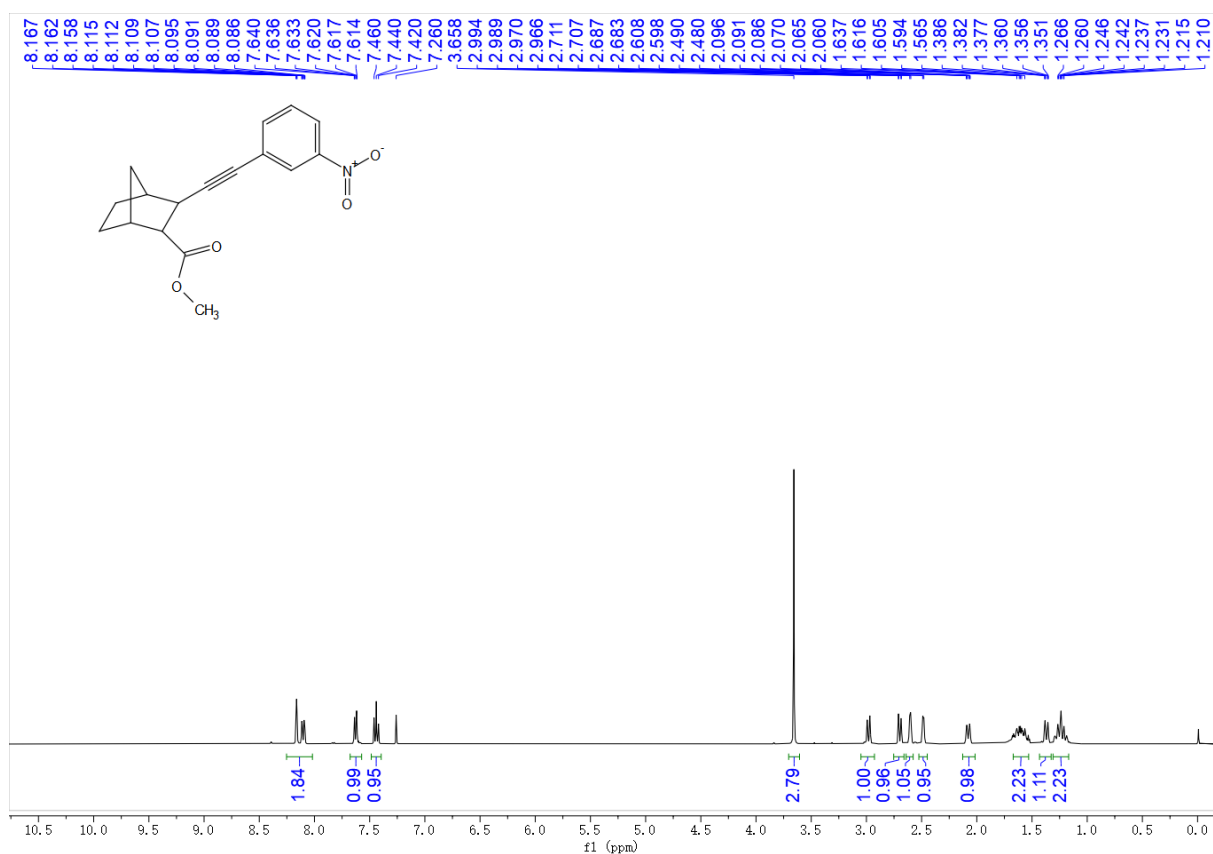


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4w

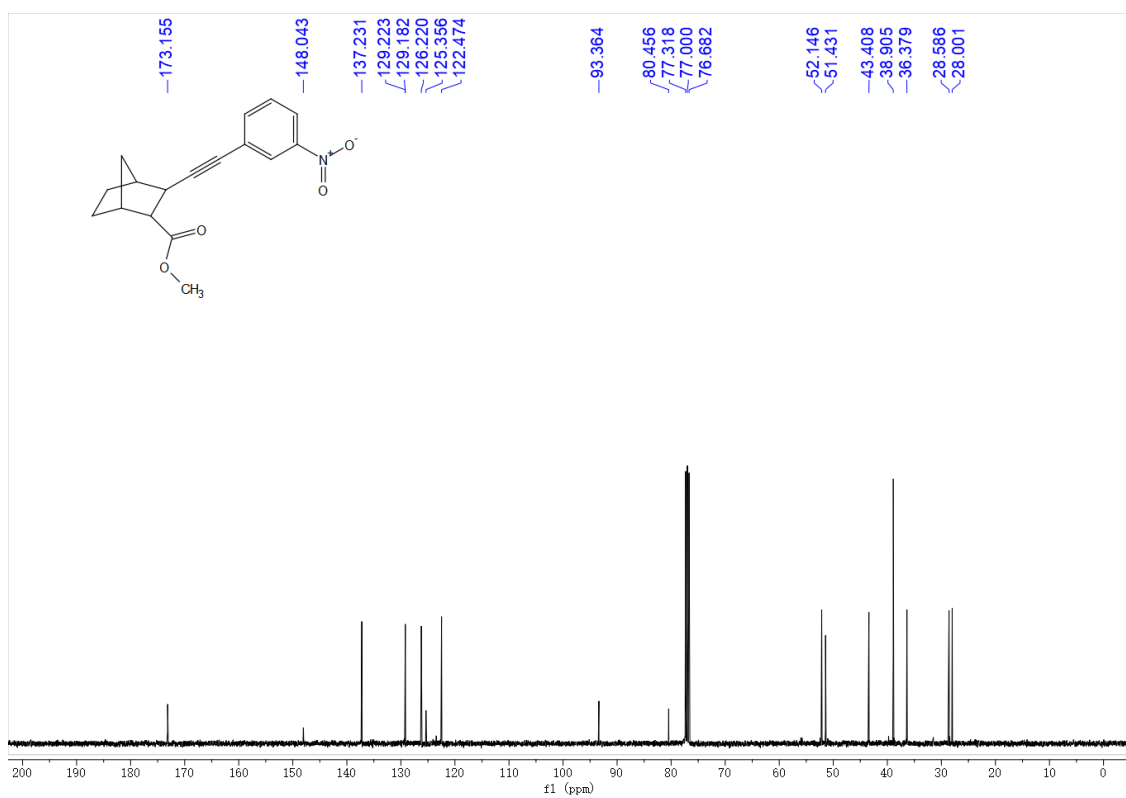


SUPPORTING INFORMATION

¹H NMR (400 MHz, CDCl₃) spectrum of compound 4x

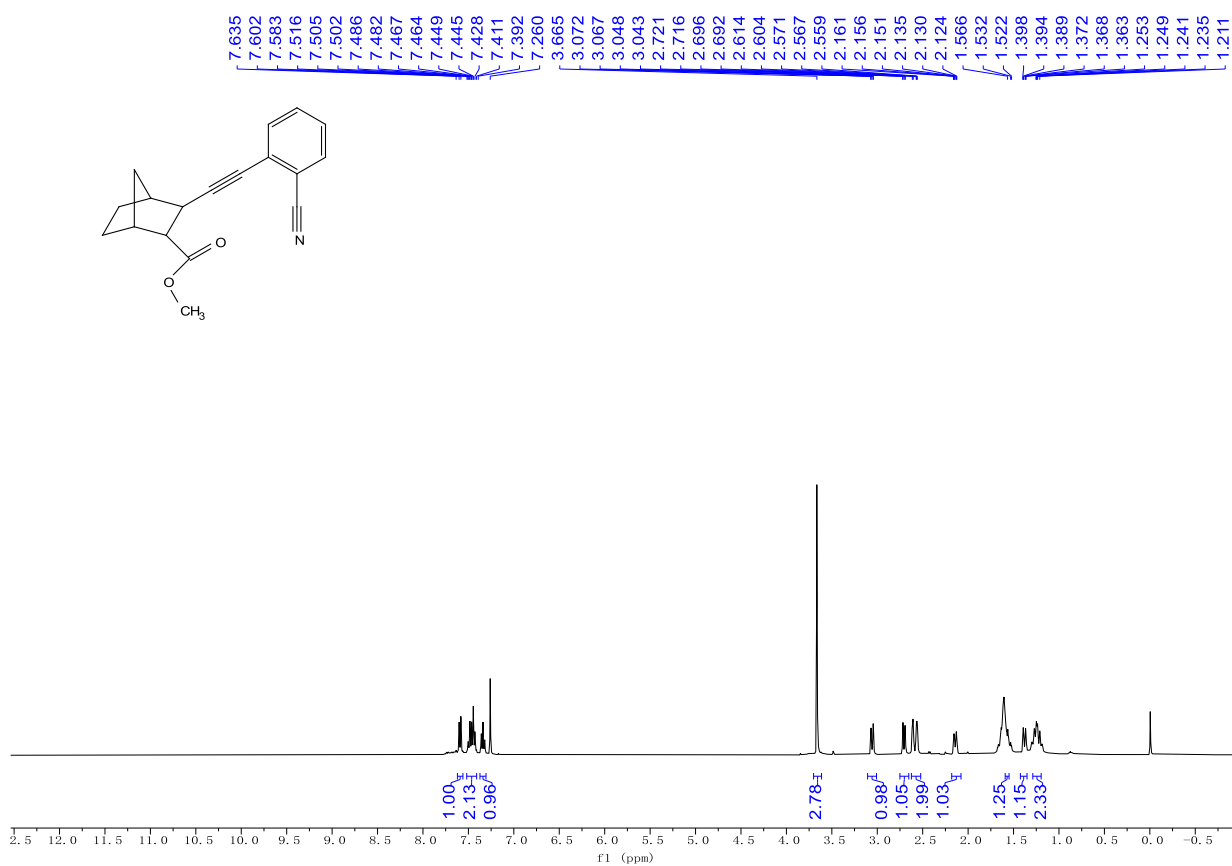


¹³C NMR (100 MHz, CDCl₃) spectrum of compound 4x

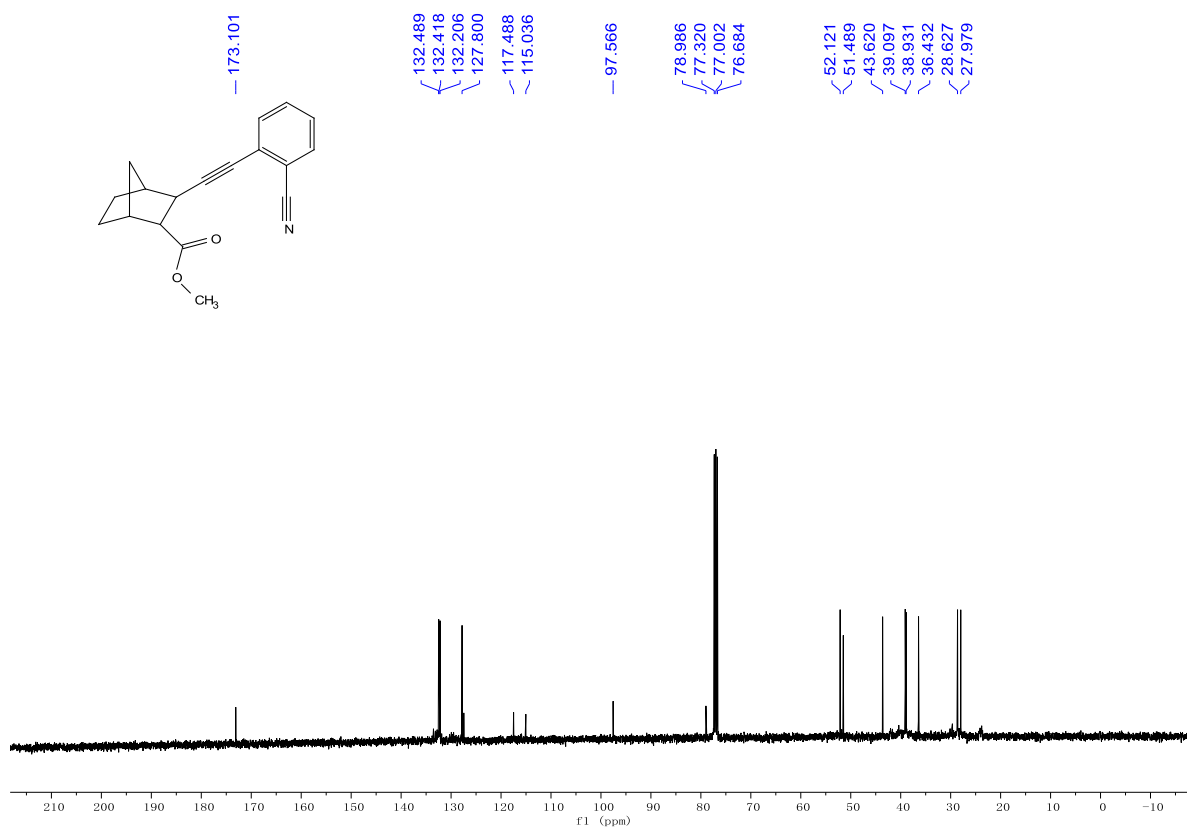


SUPPORTING INFORMATION

¹H NMR (400 MHz, CDCl₃) spectrum of compound 4y

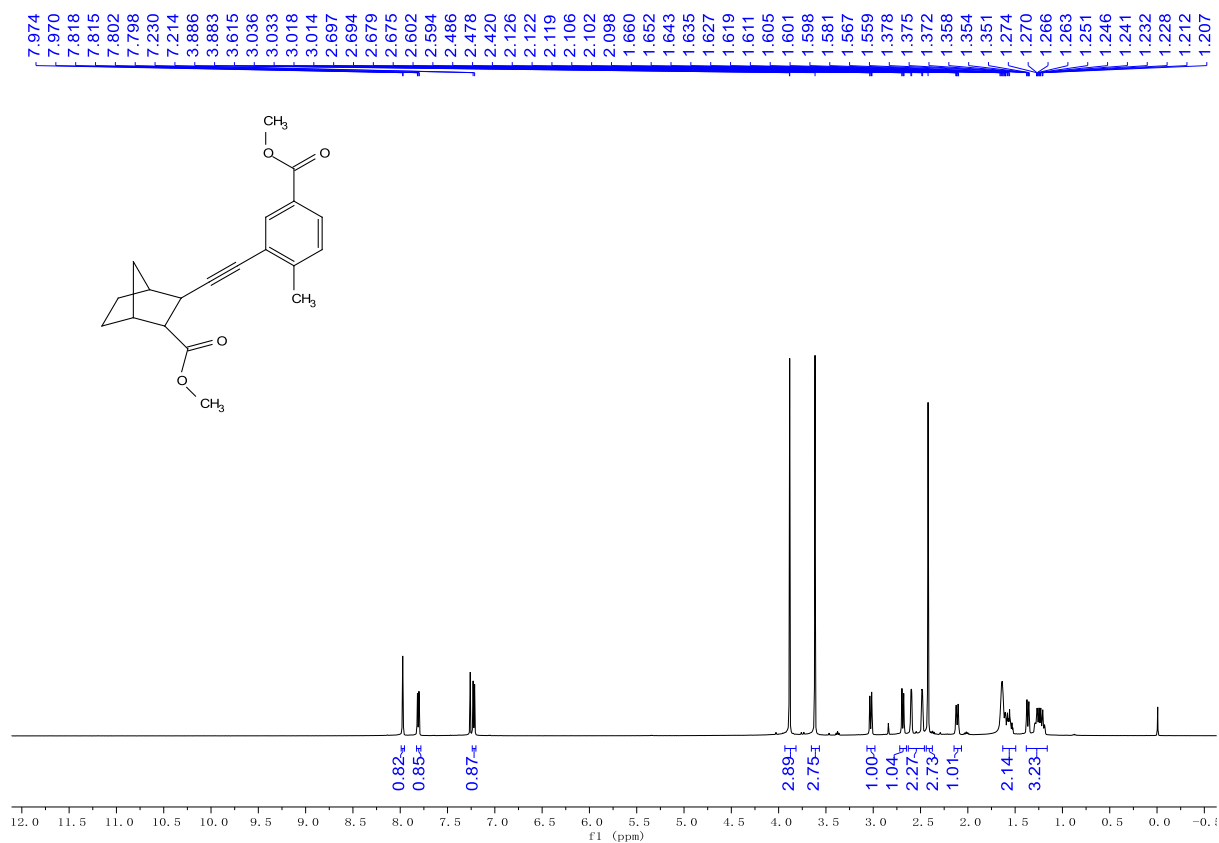


¹³C NMR (100 MHz, CDCl₃) spectrum of compound 4y

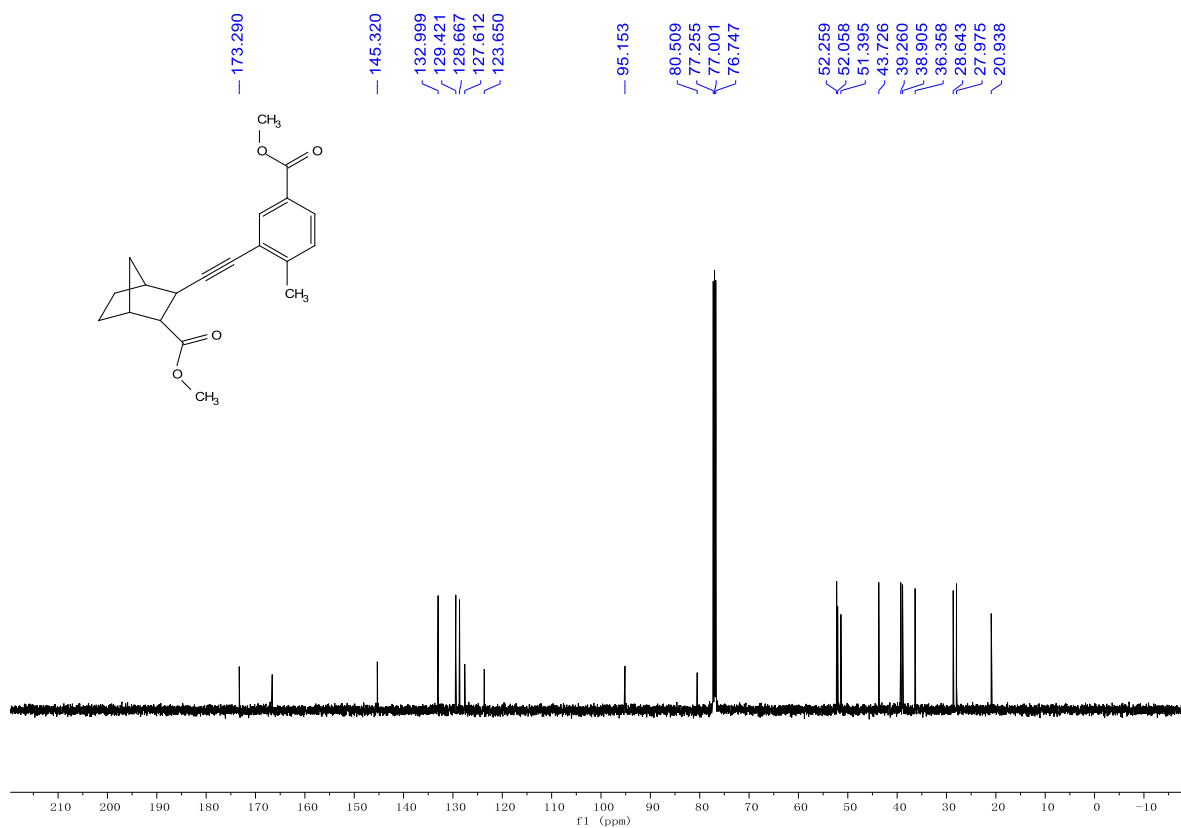


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4z

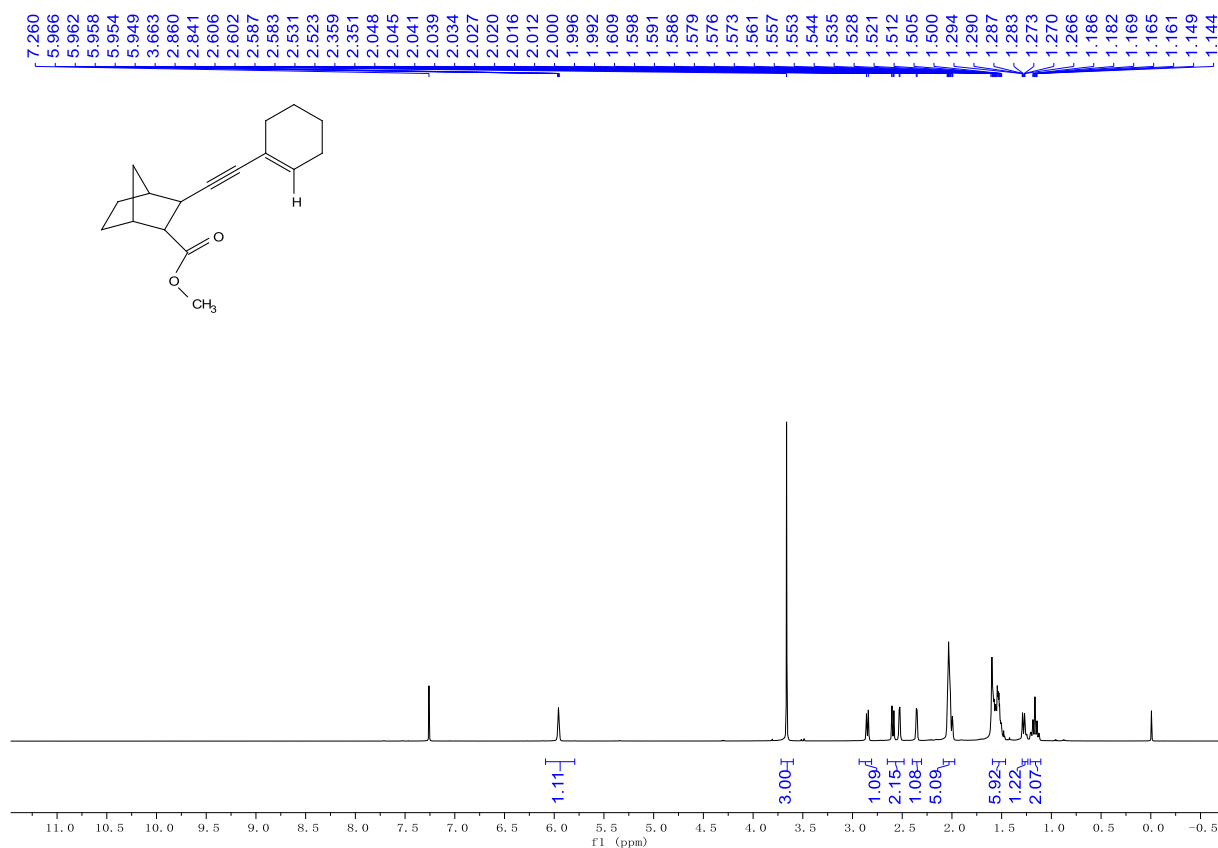


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4z

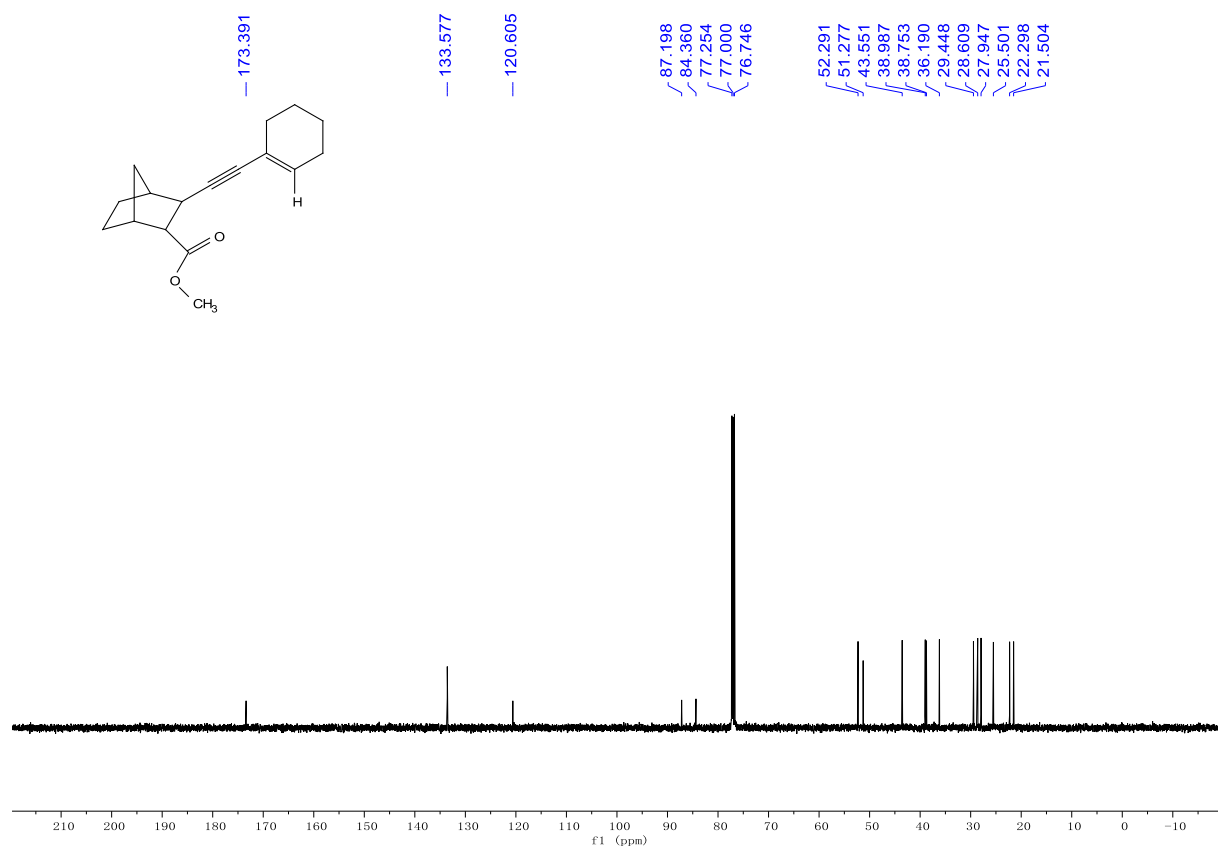


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4aa

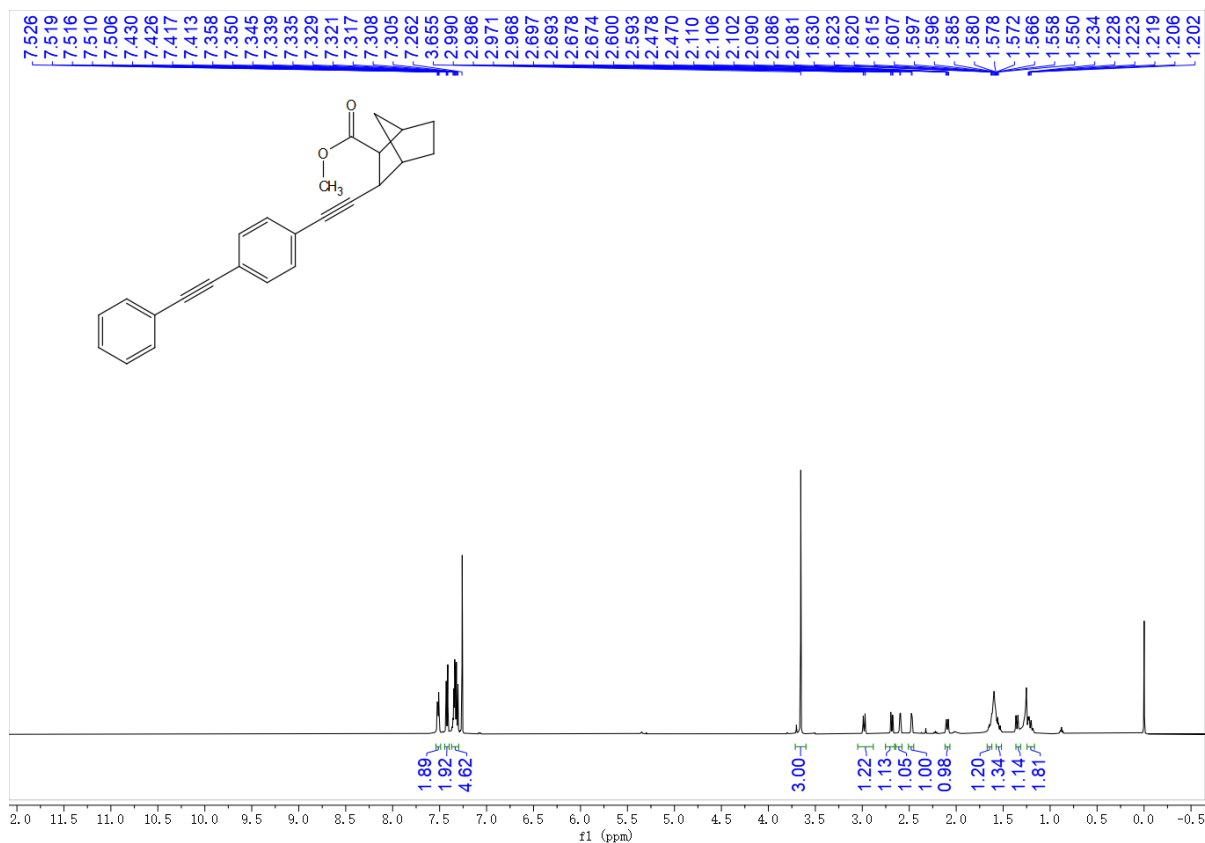


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4aa

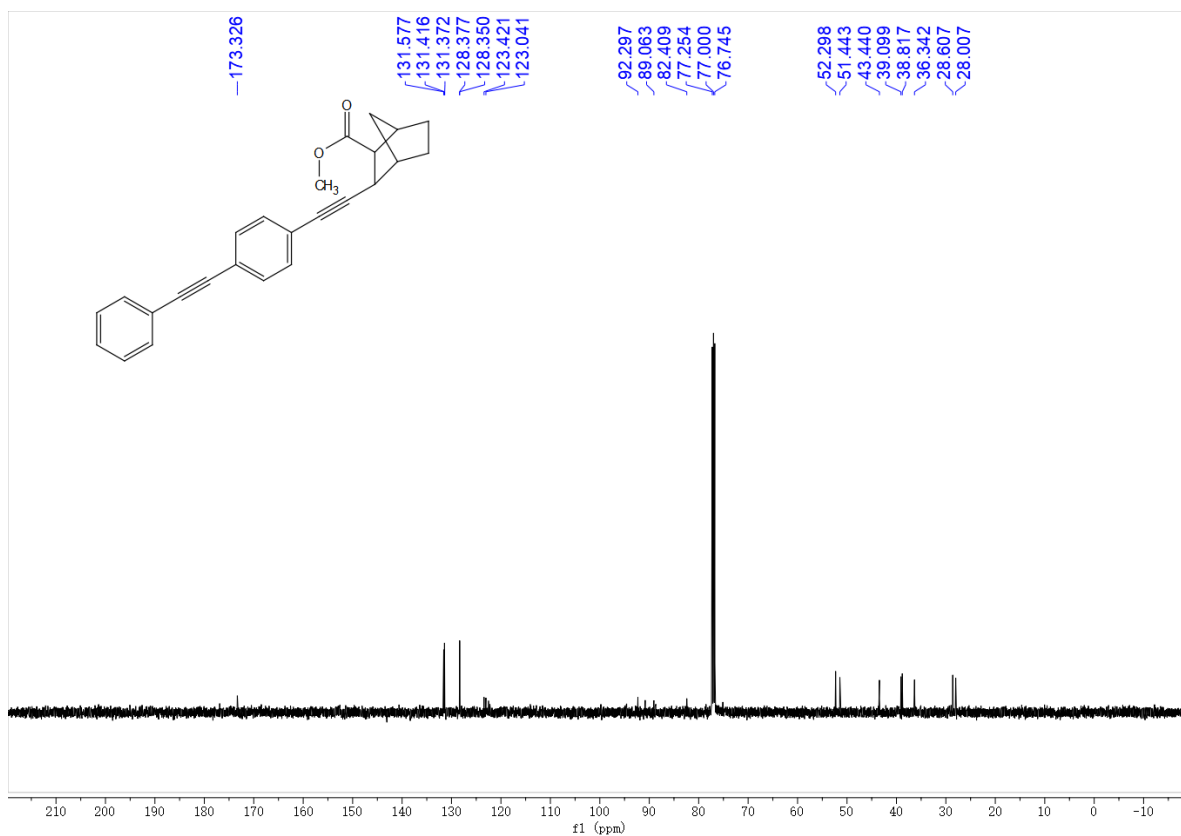


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4ab

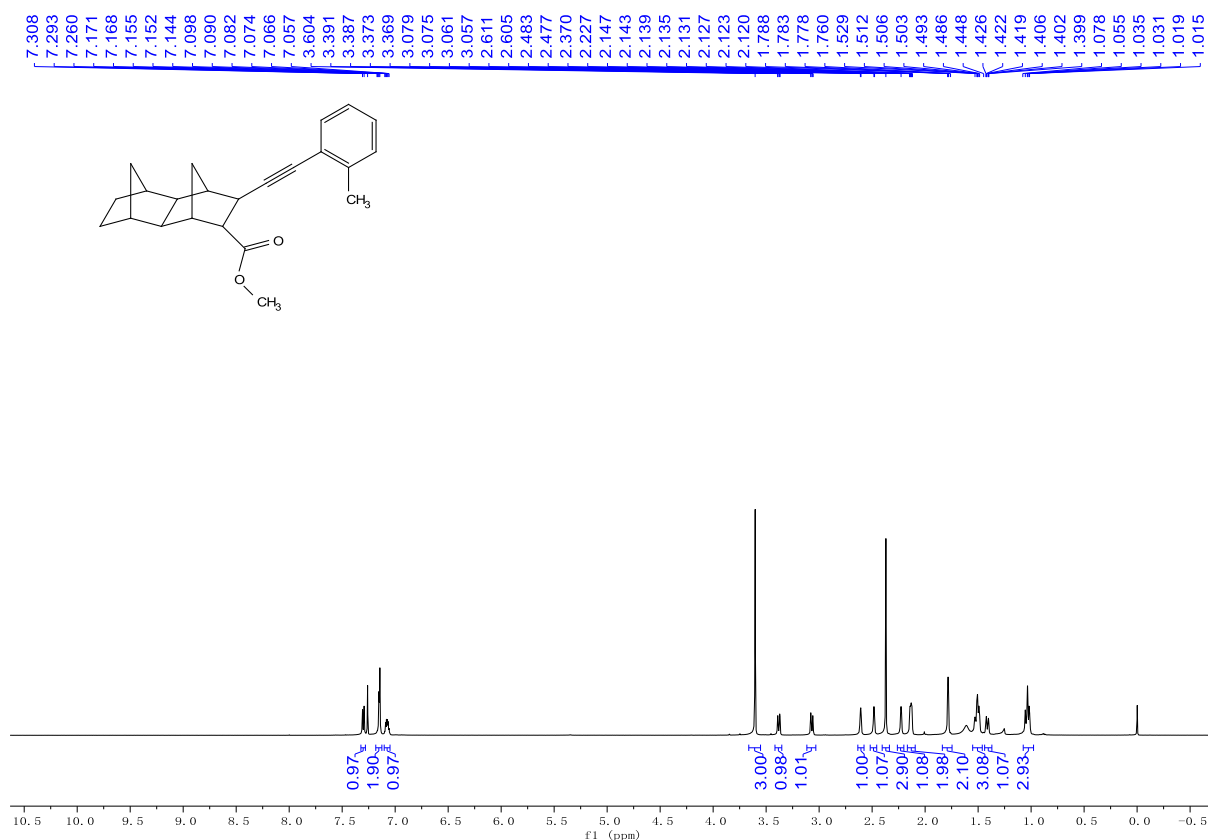


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4ab

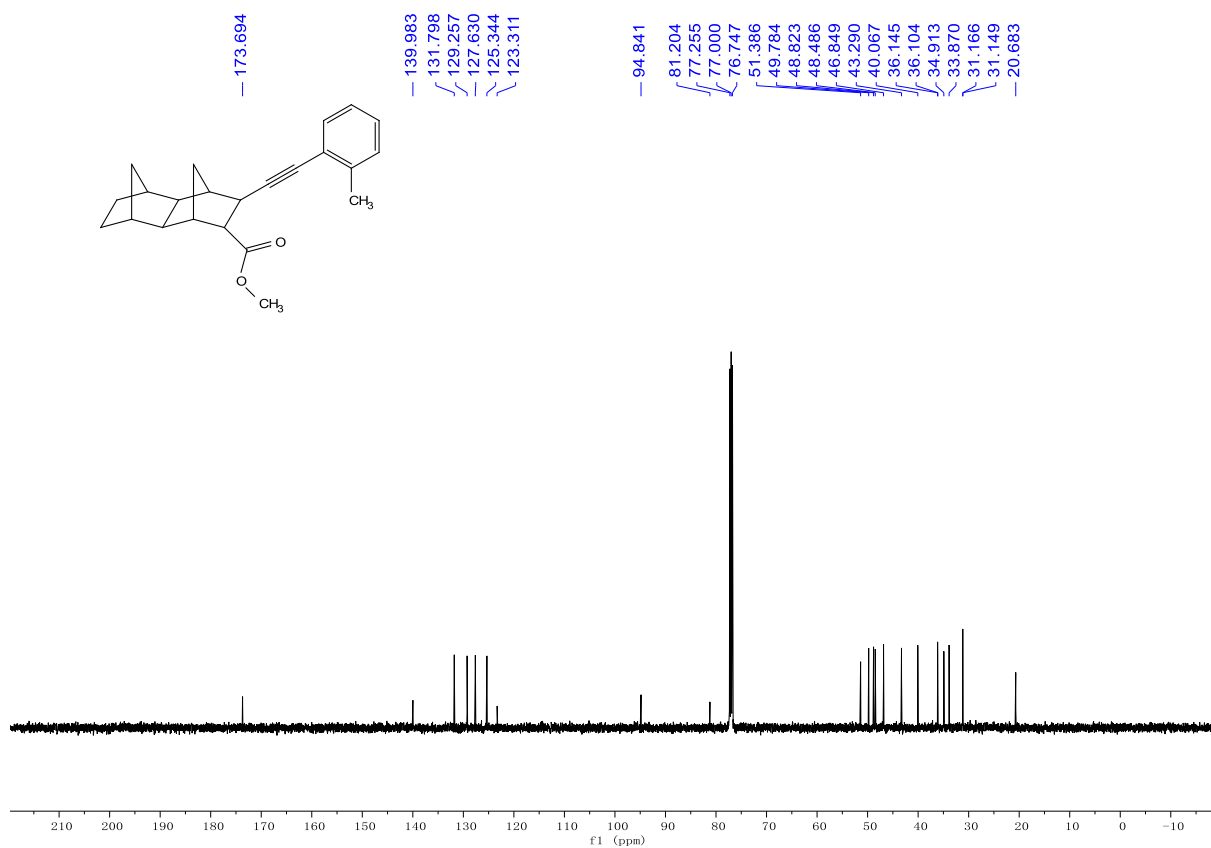


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4ac

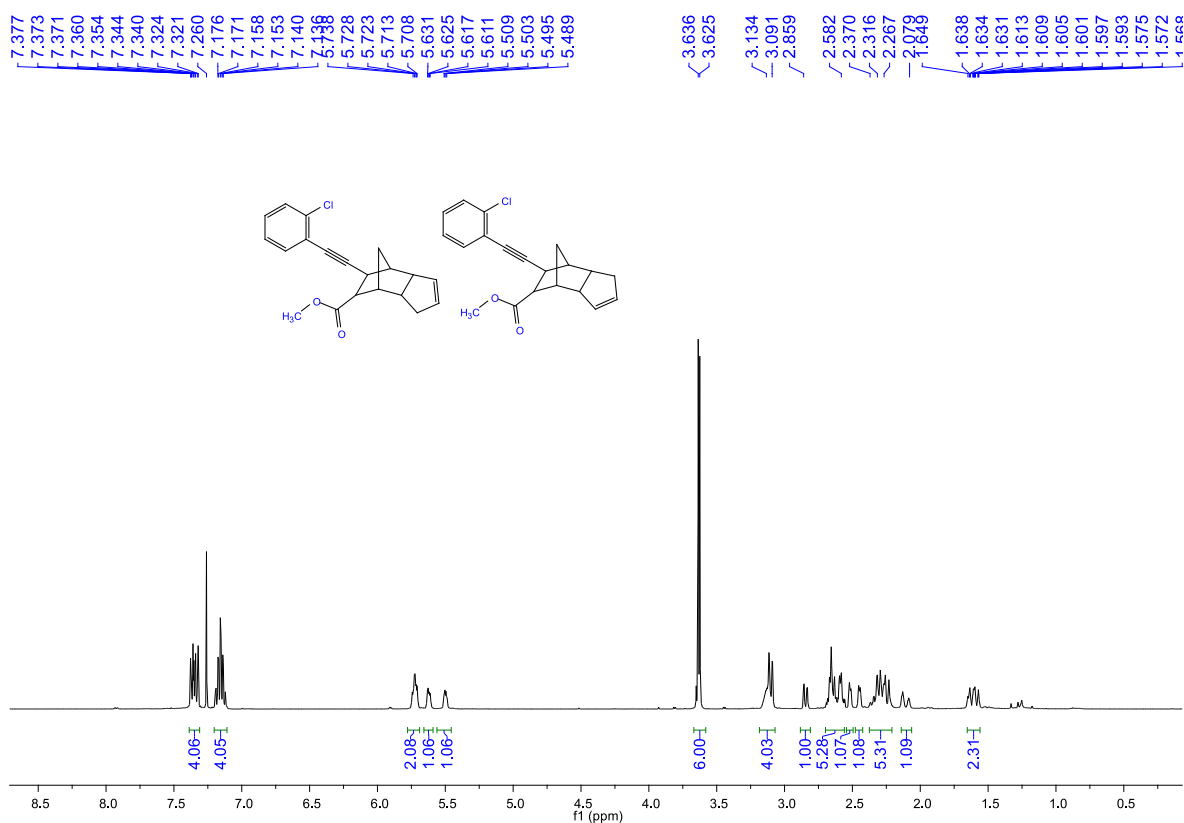


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4ac

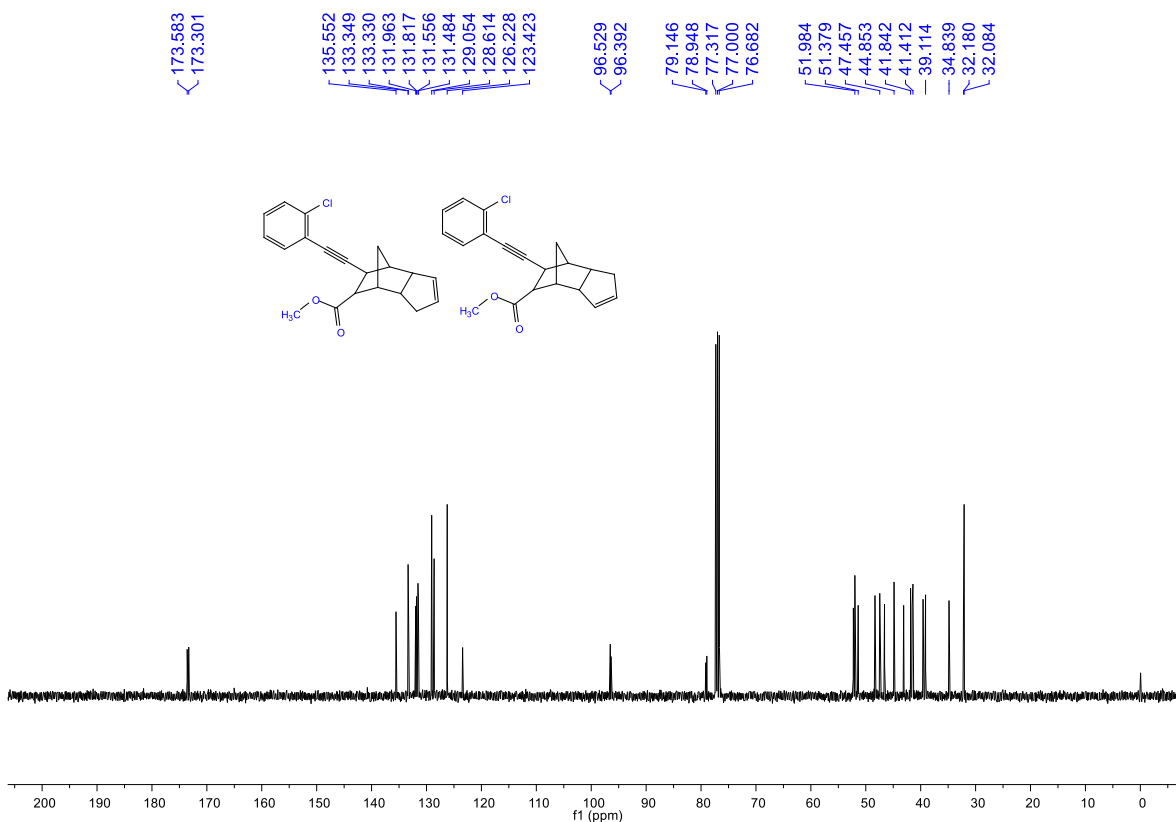


SUPPORTING INFORMATION

^1H NMR (400 MHz, CDCl_3) spectrum of compound 4ad-1+4ad-2

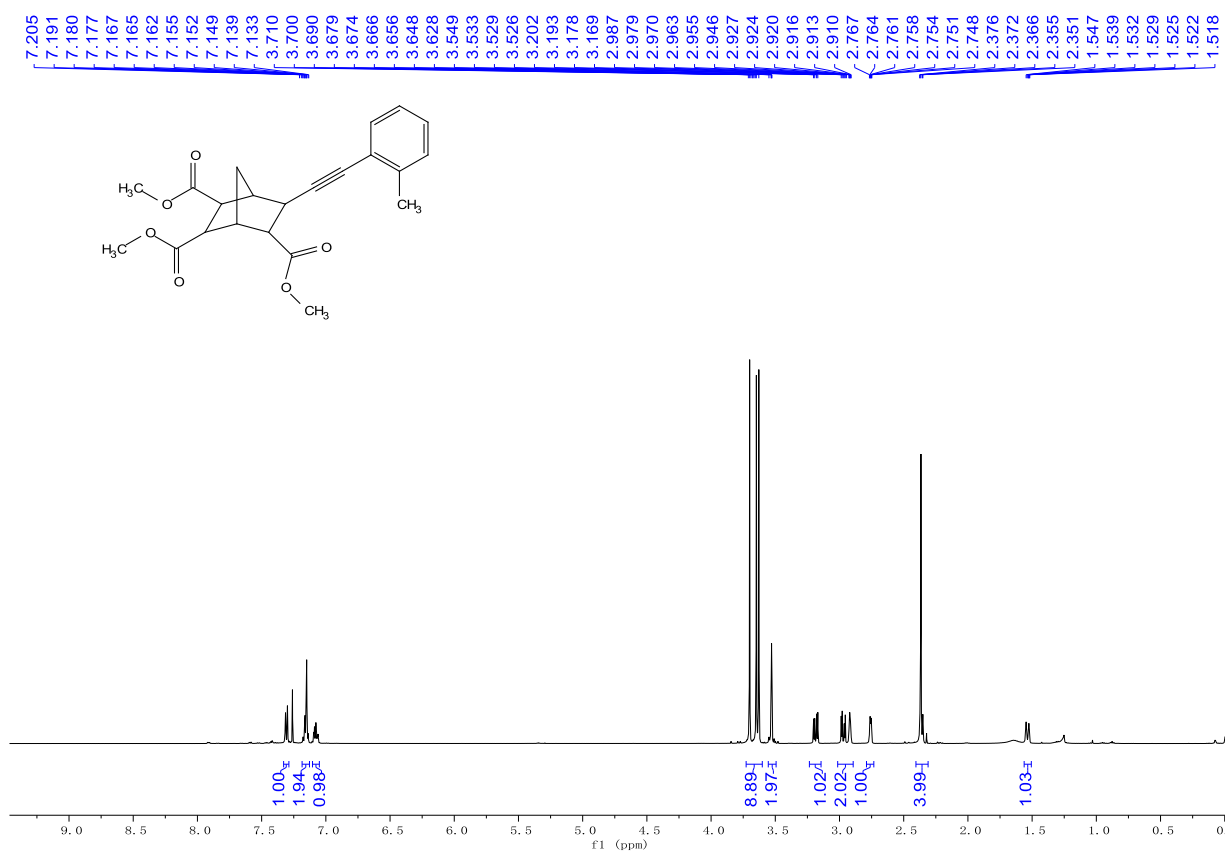


^{13}C NMR (100 MHz, CDCl_3) spectrum of compound 4ad-1+4ad-2

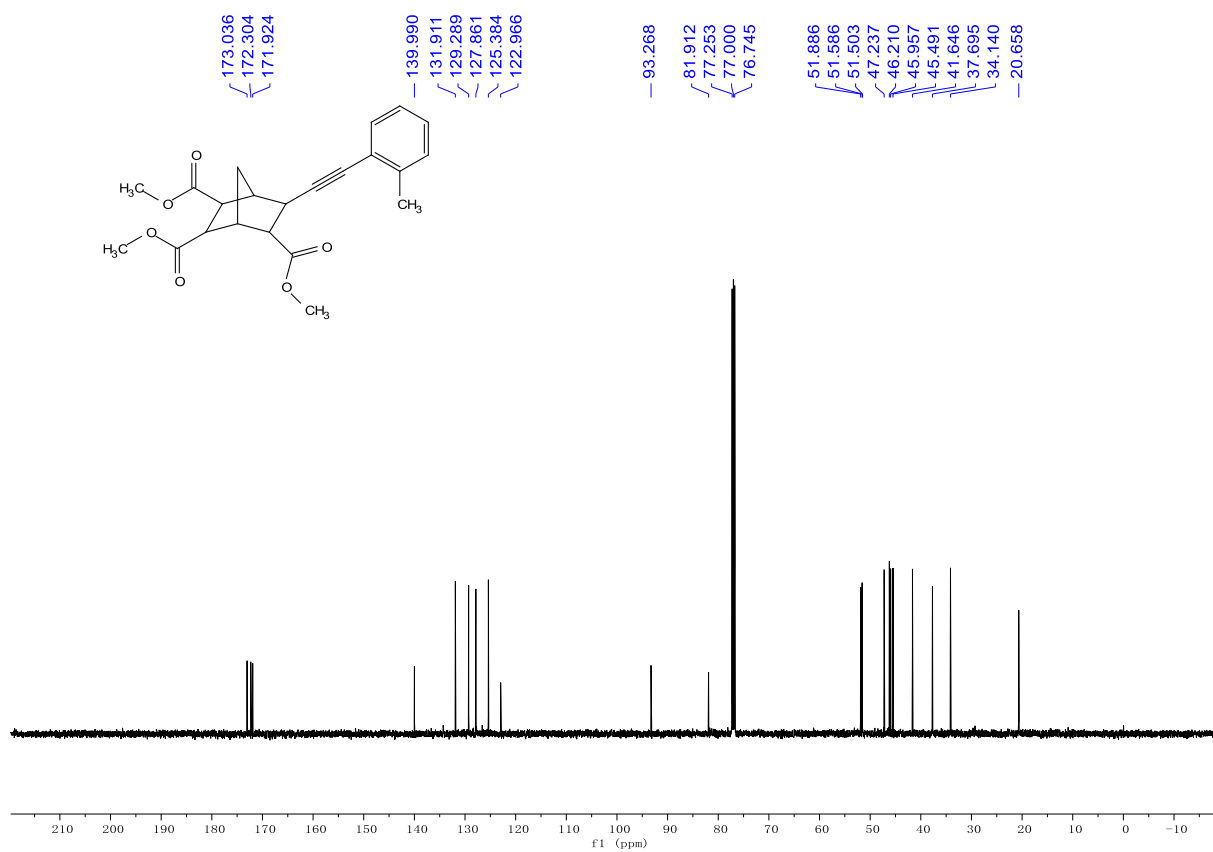


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4ae

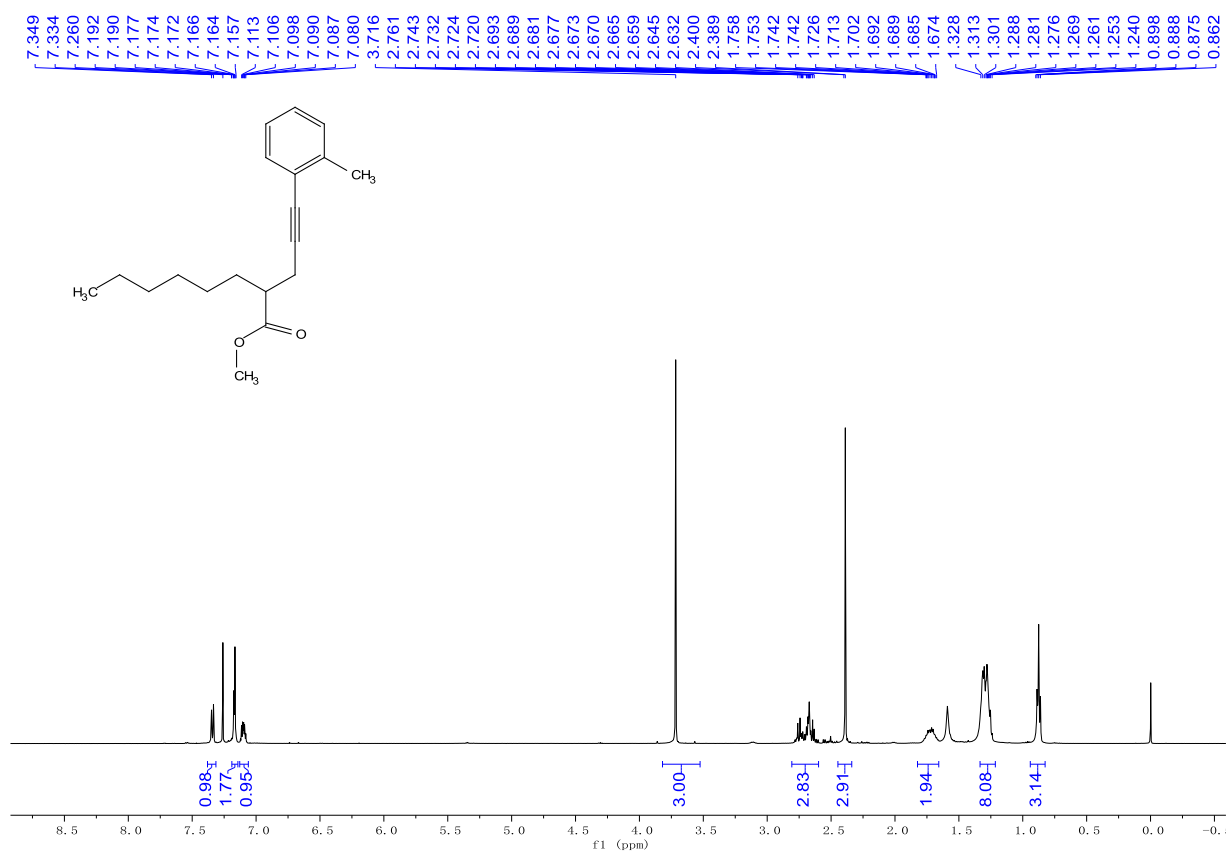


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4ae

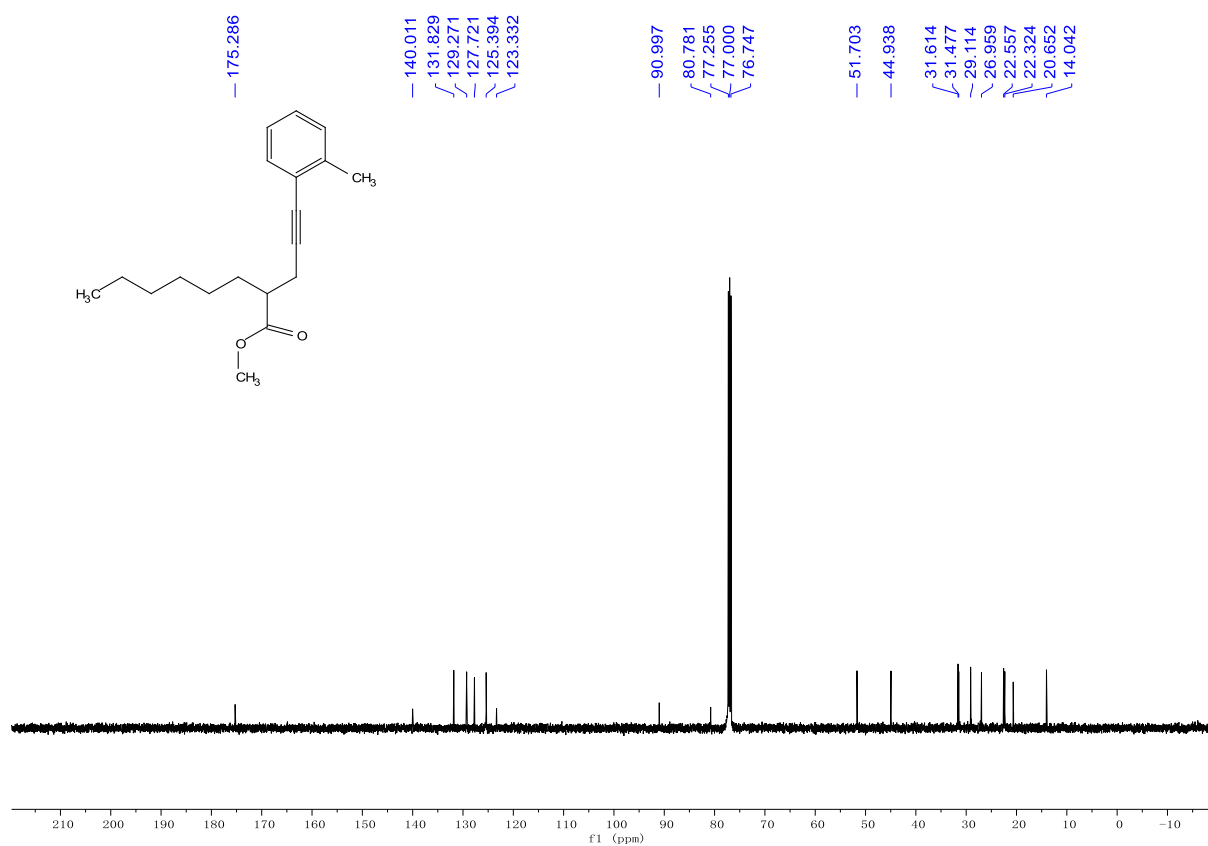


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4af

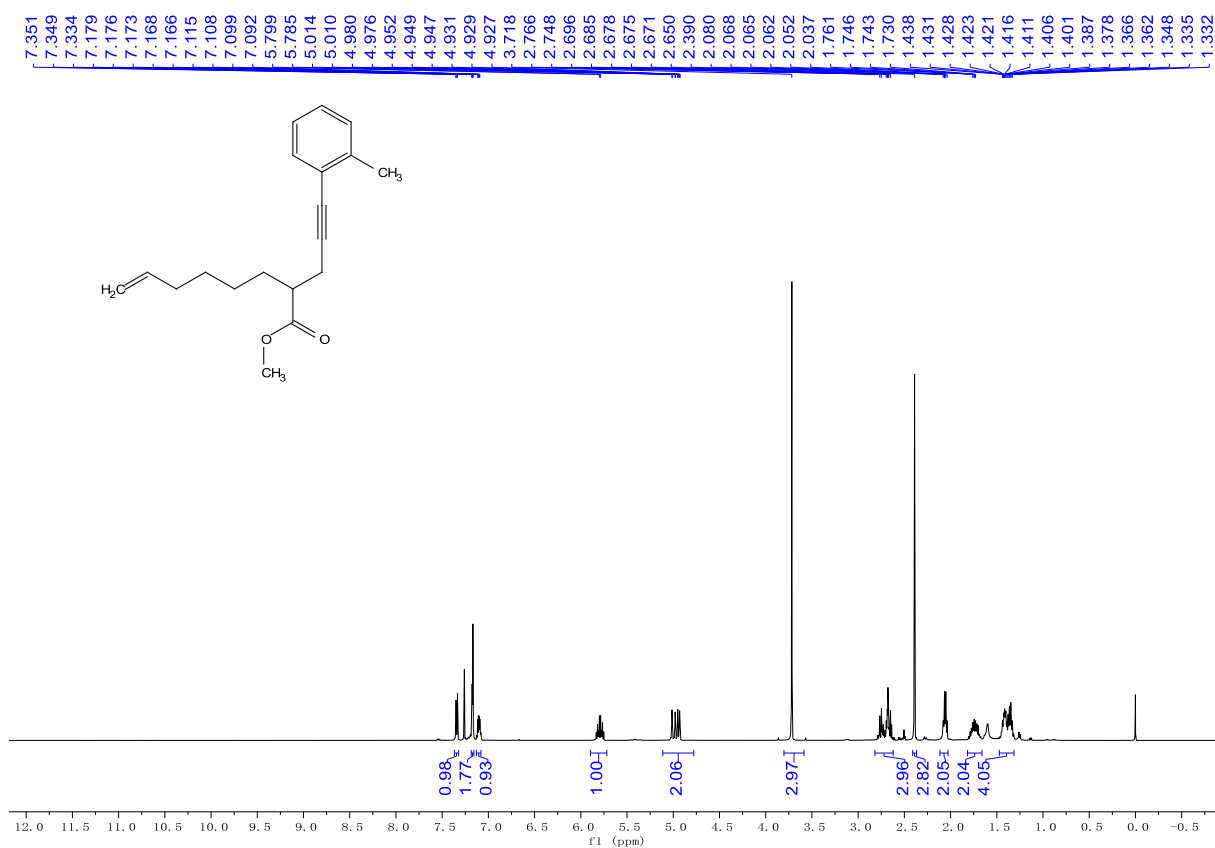


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4af

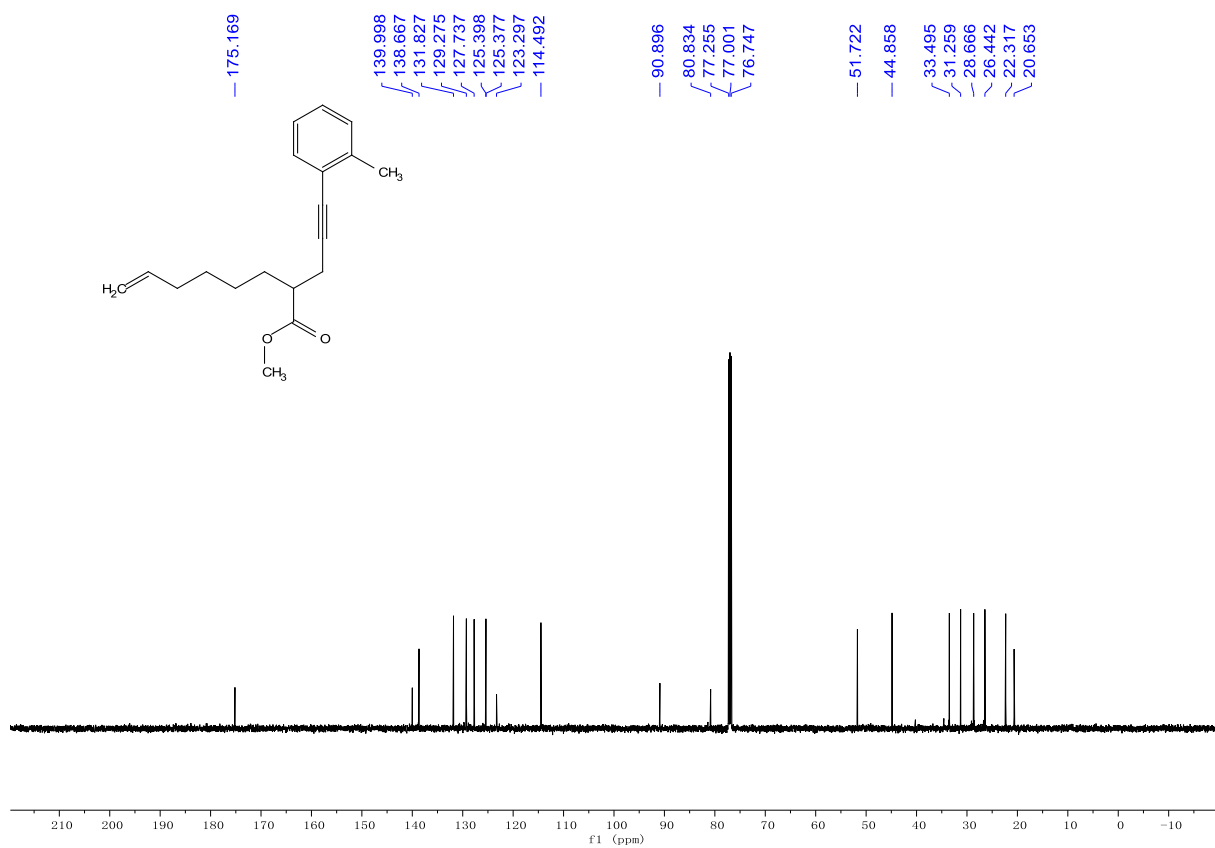


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4ag

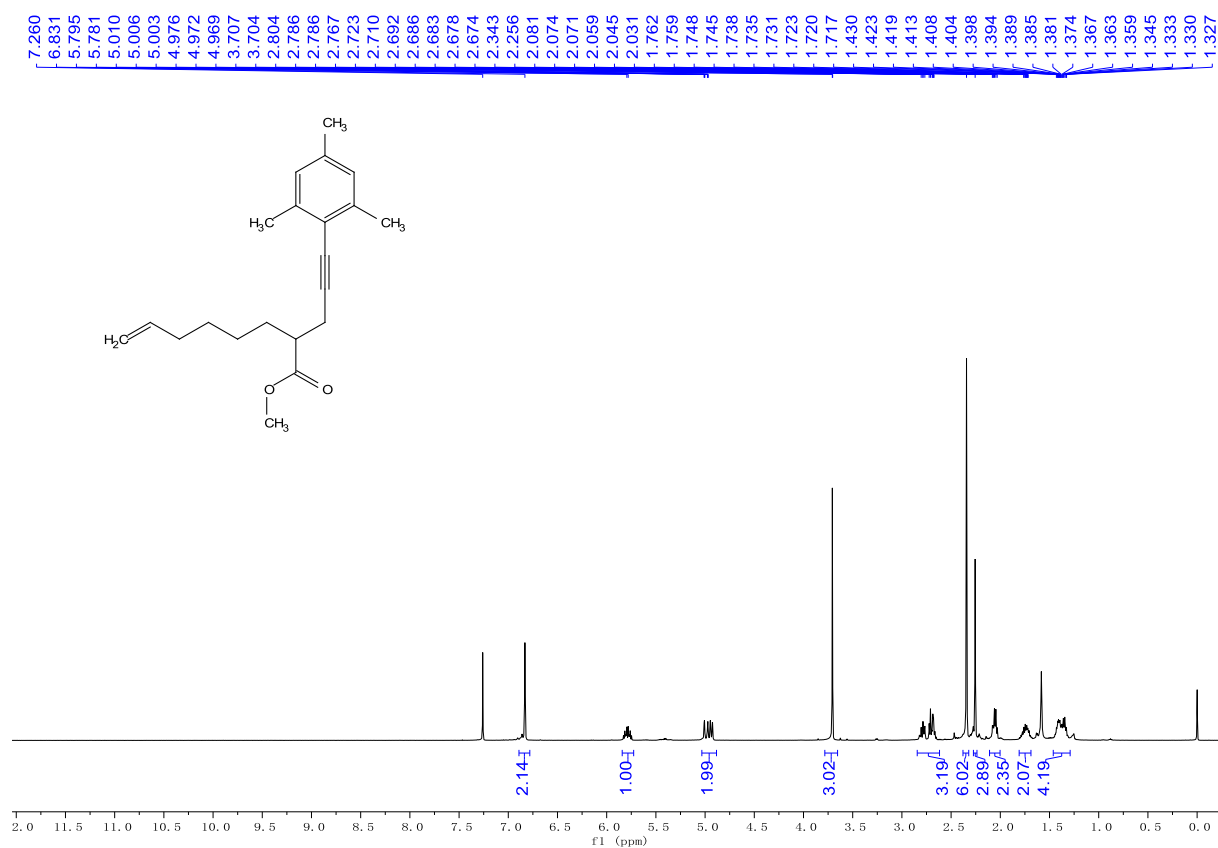


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4ag

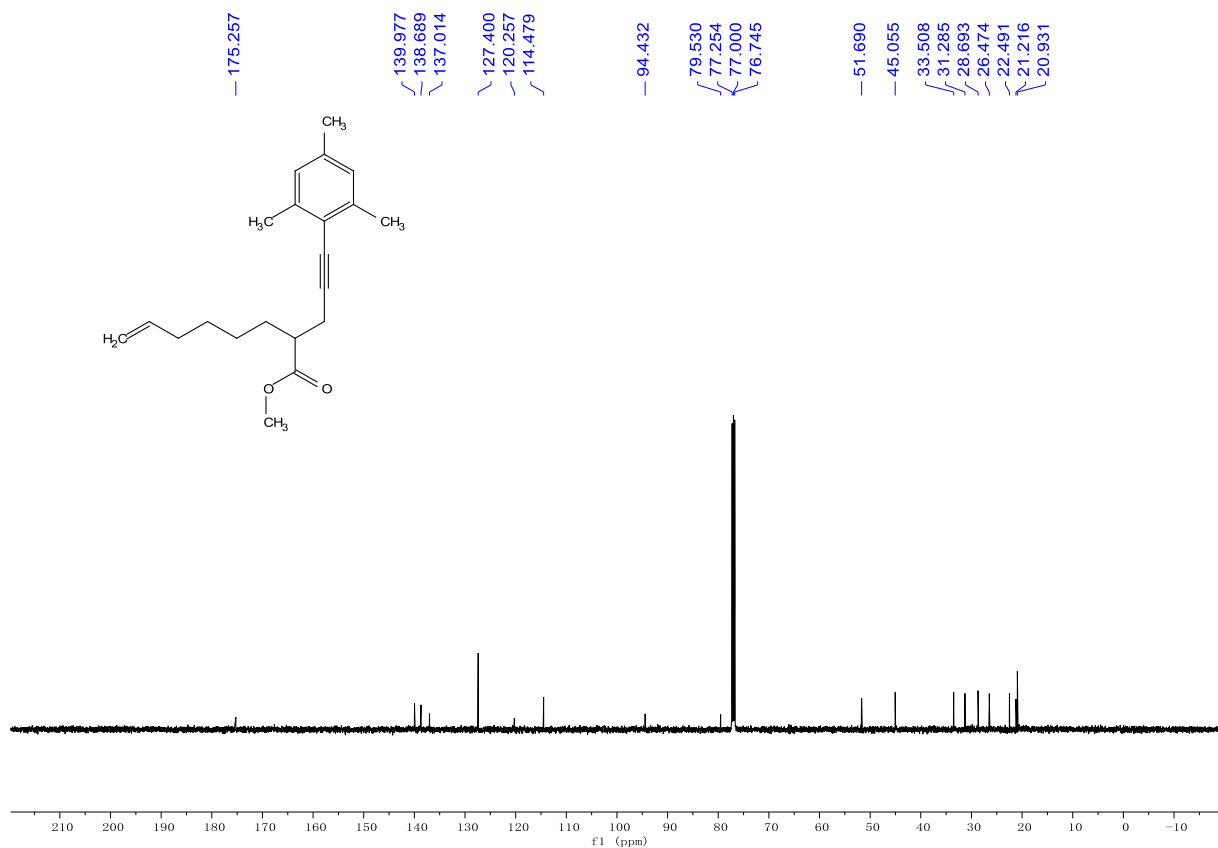


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4ah

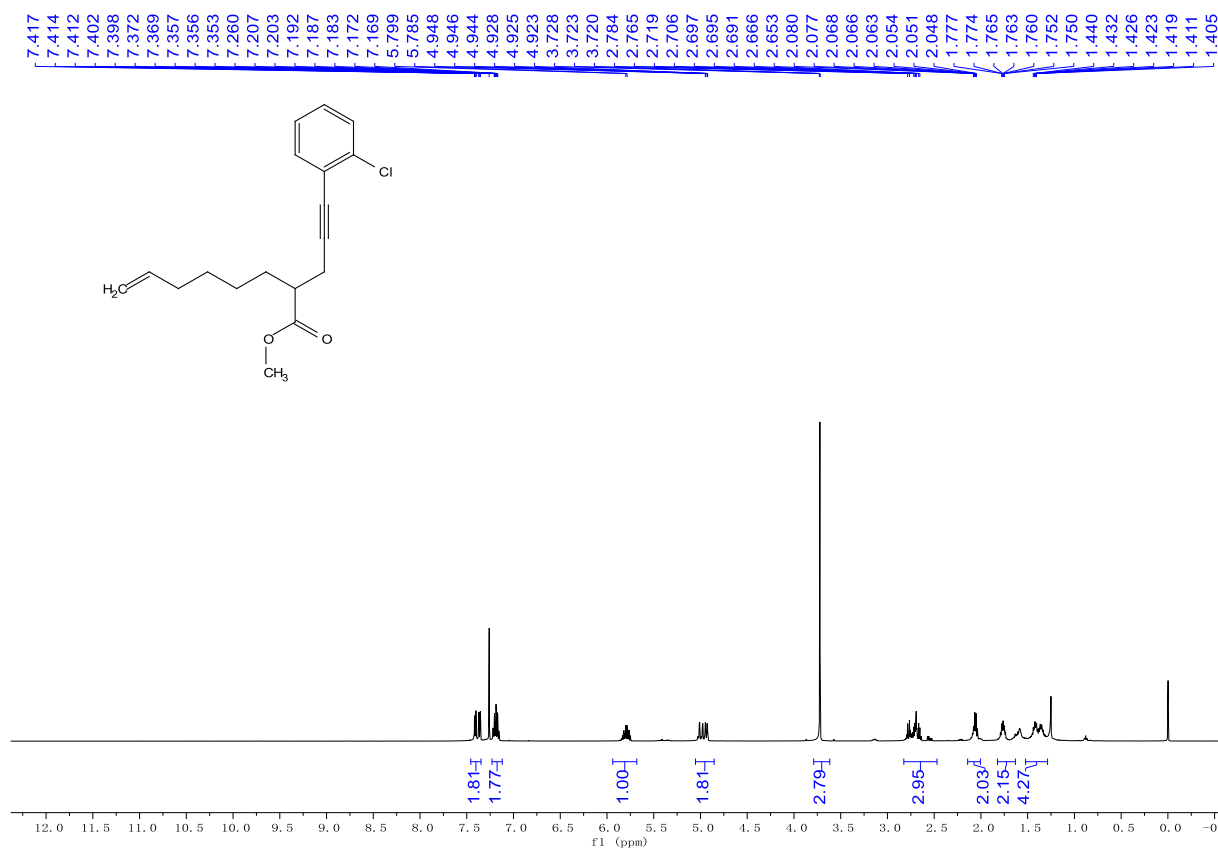


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4ah

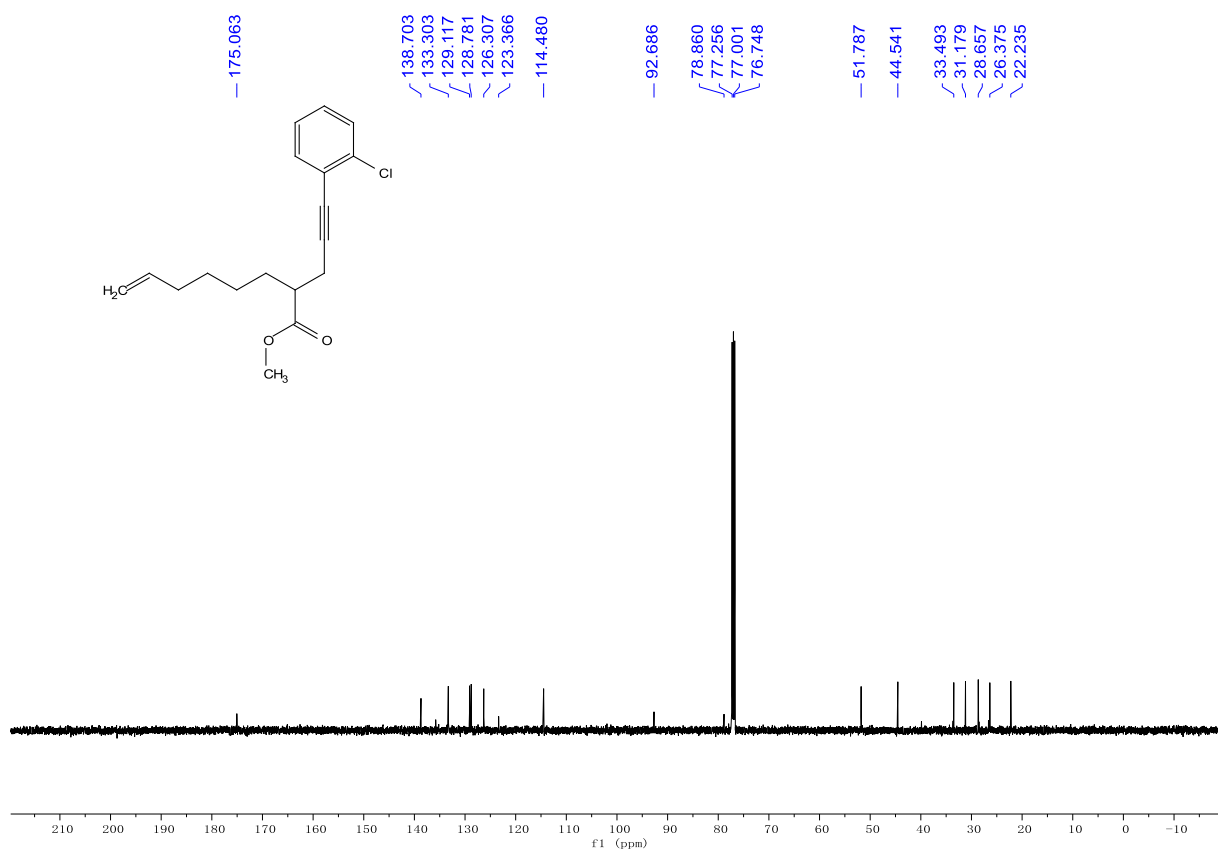


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4ai

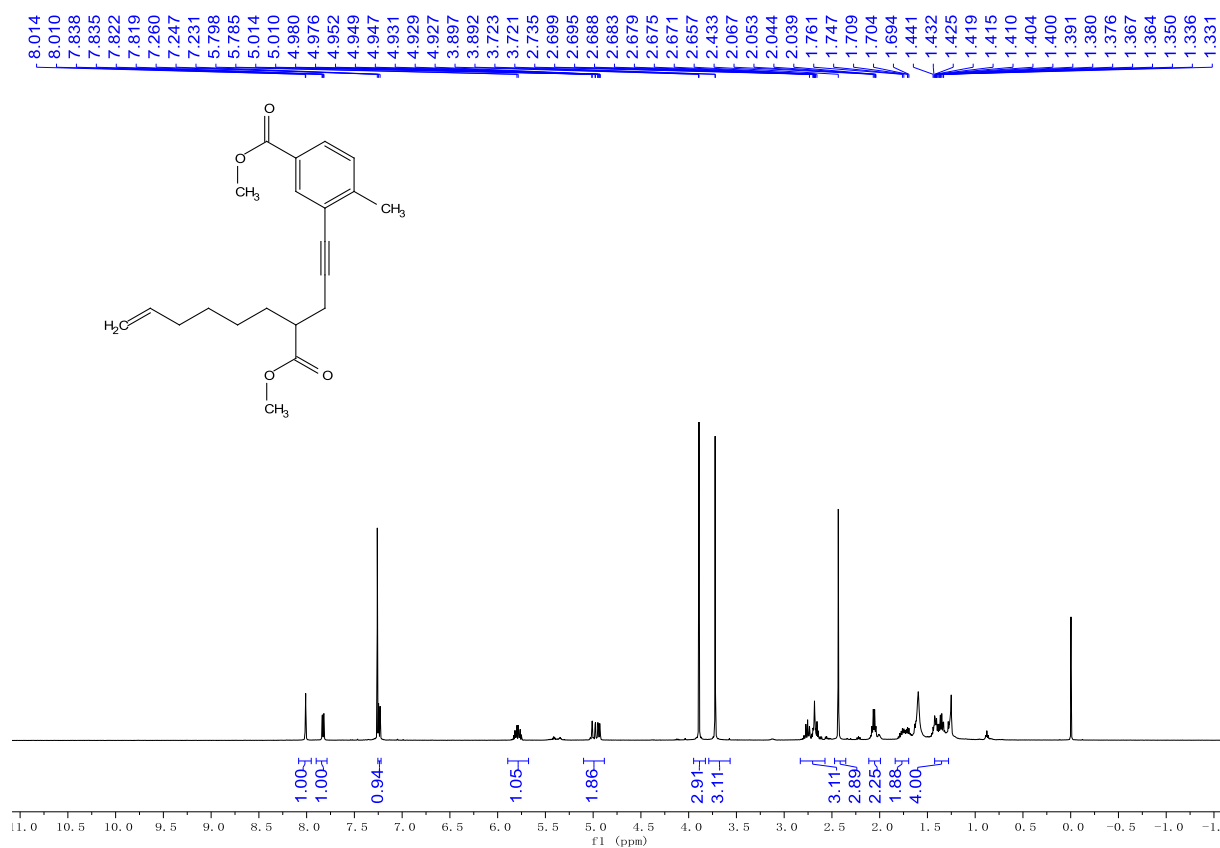


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4ai

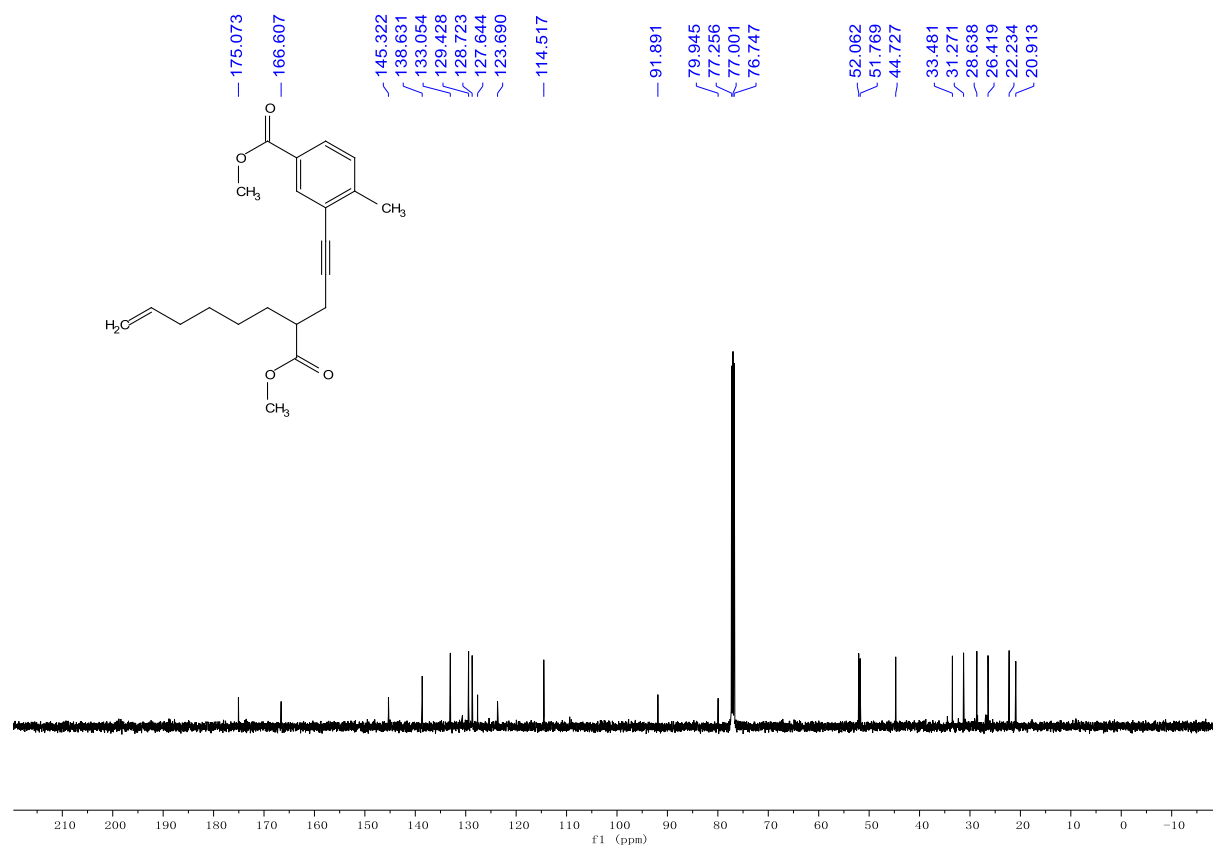


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4aj

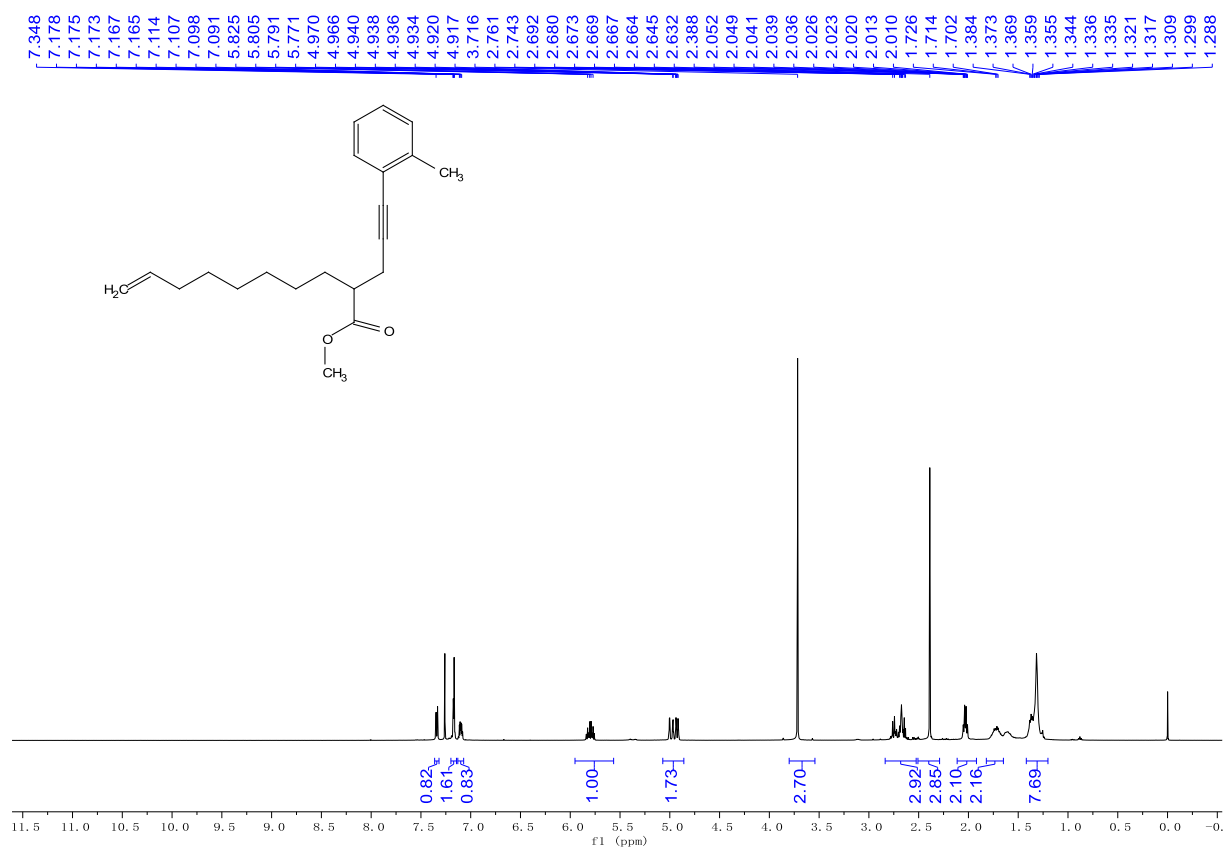


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4aj

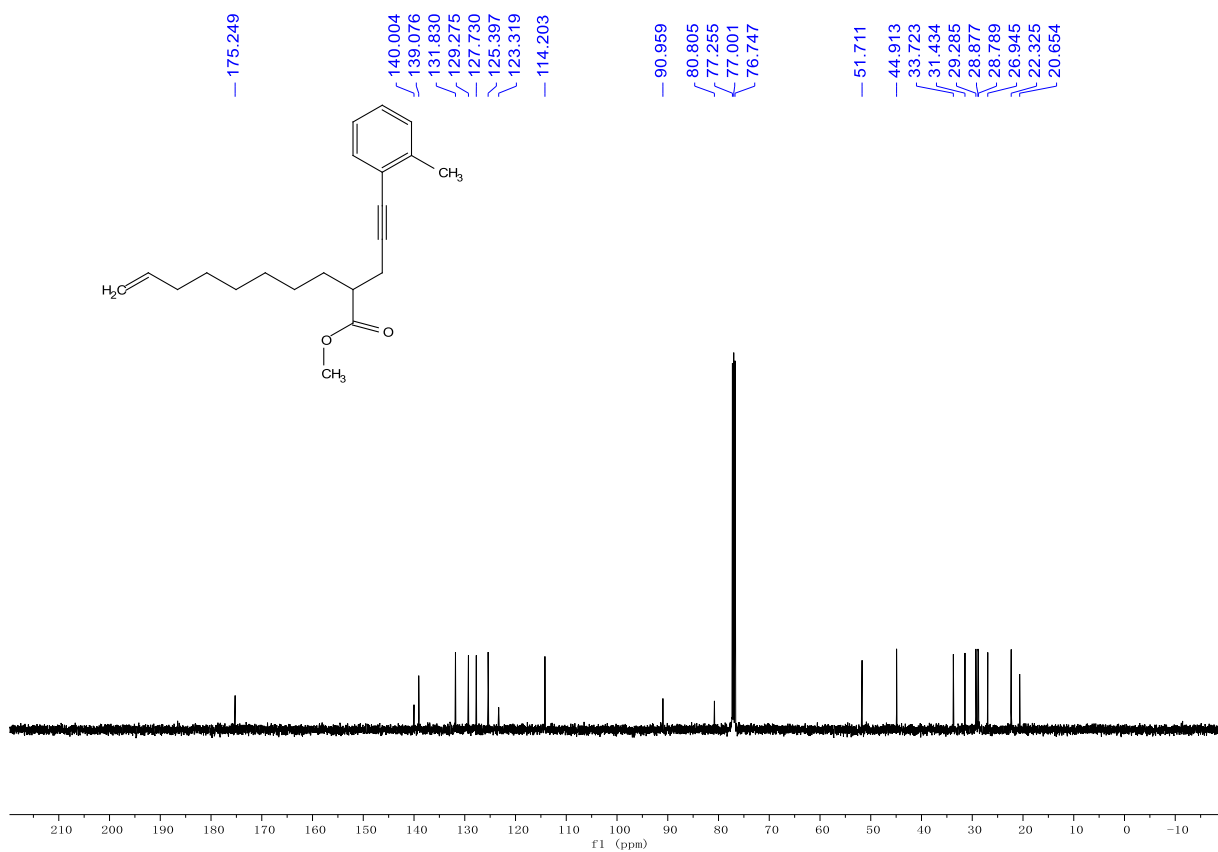


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4ak

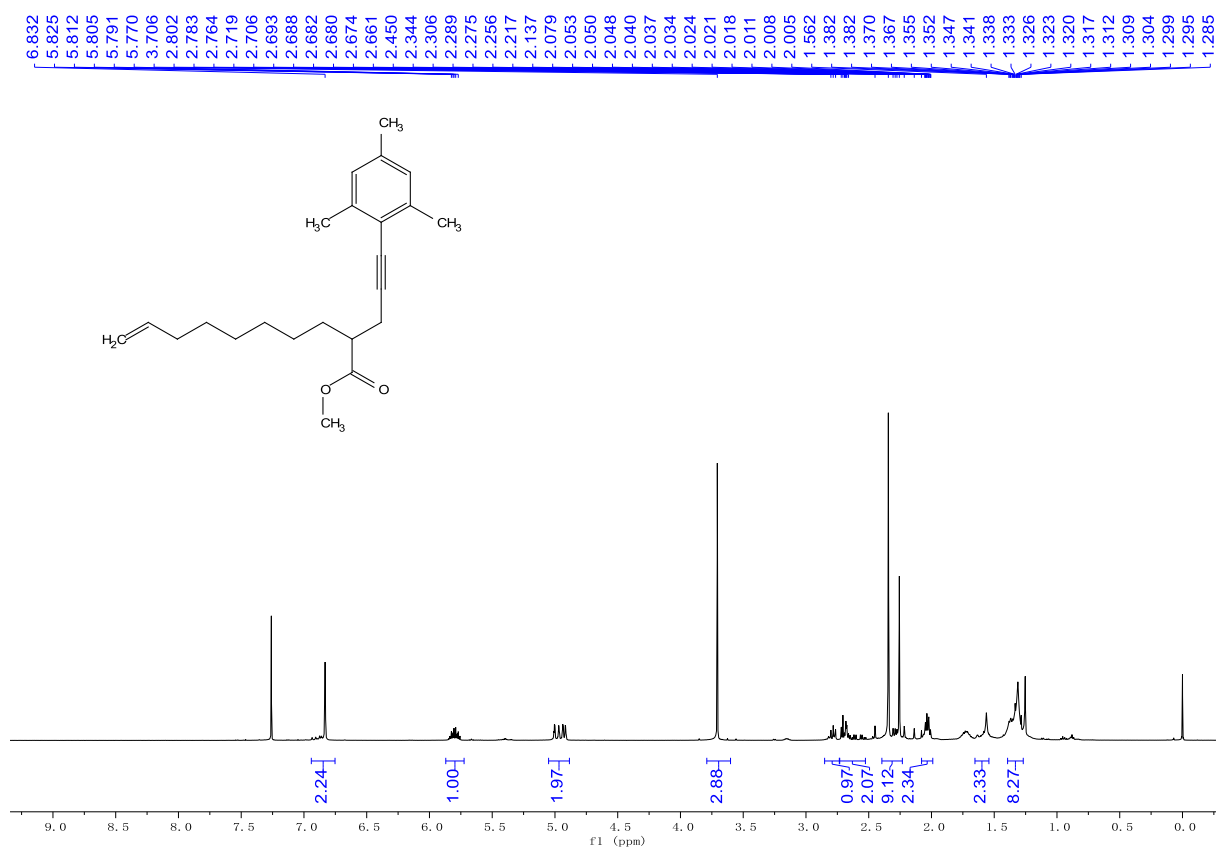


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4ak

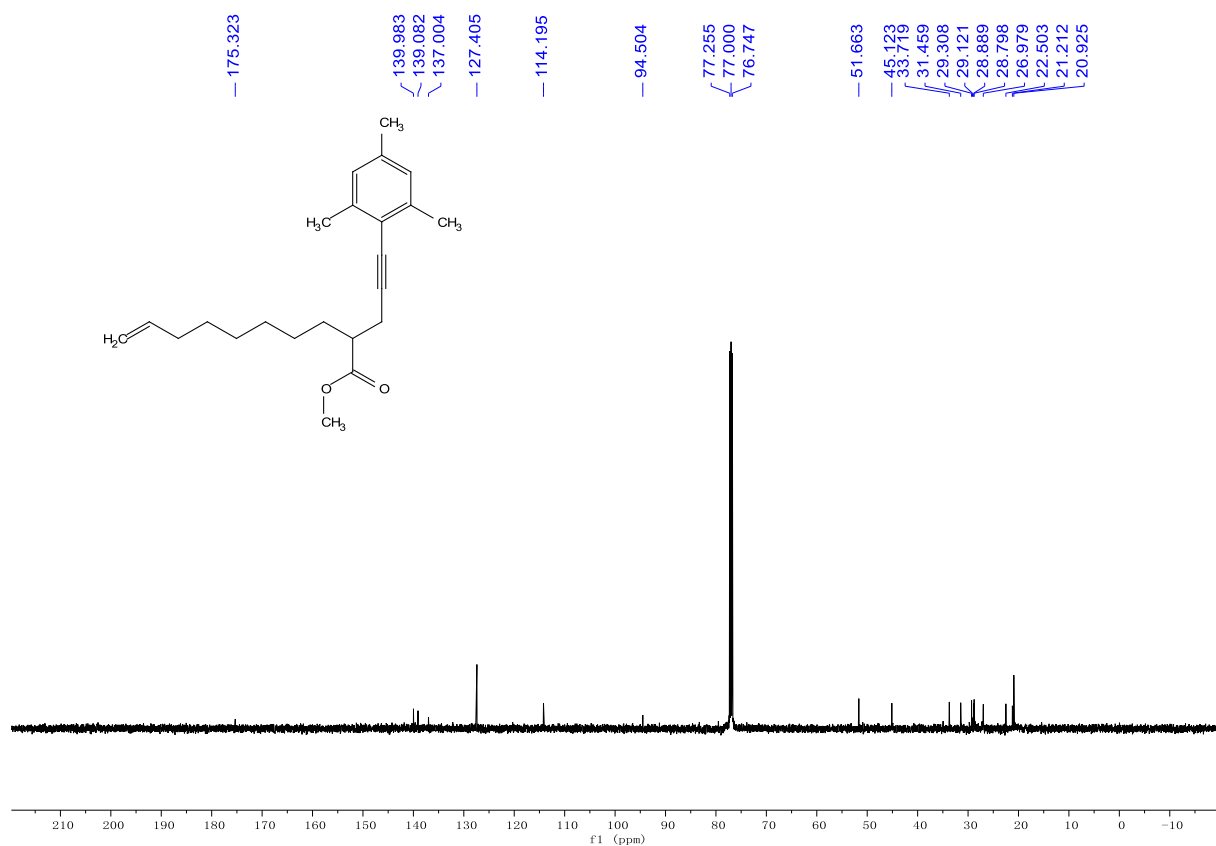


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4al

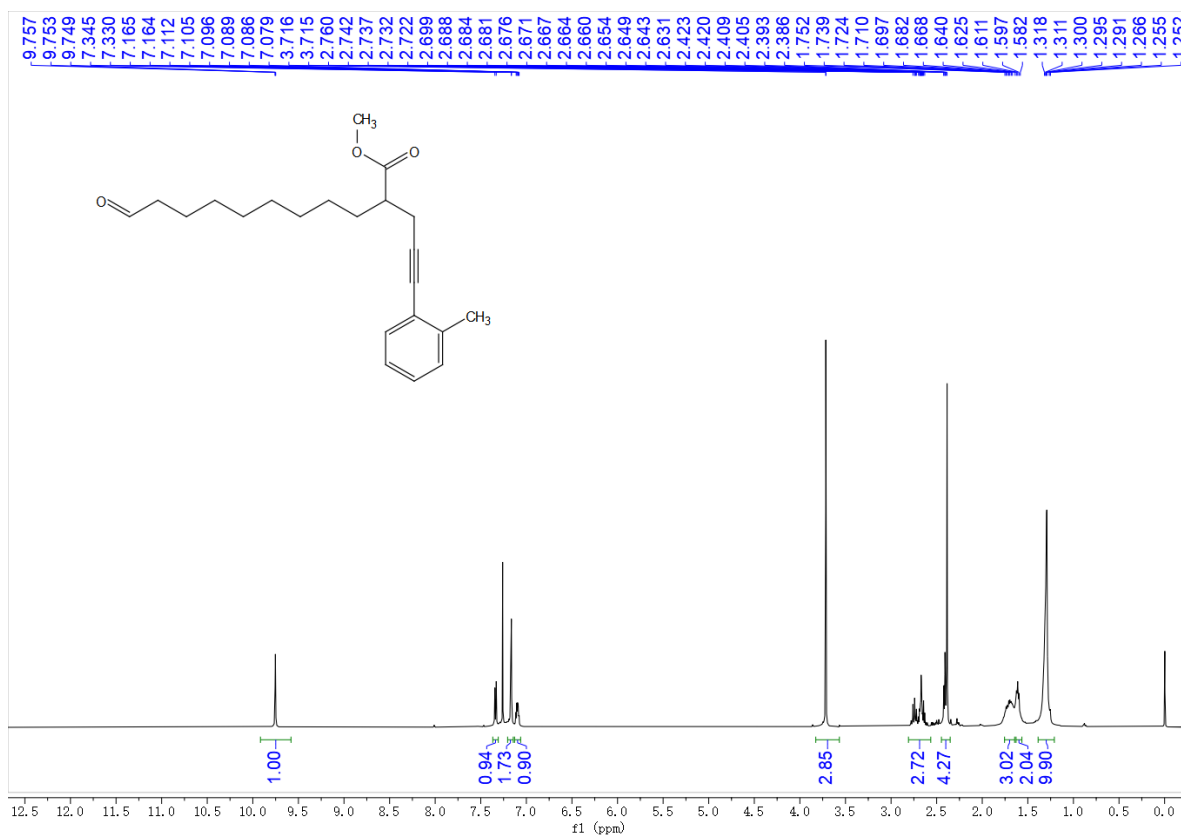


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4al

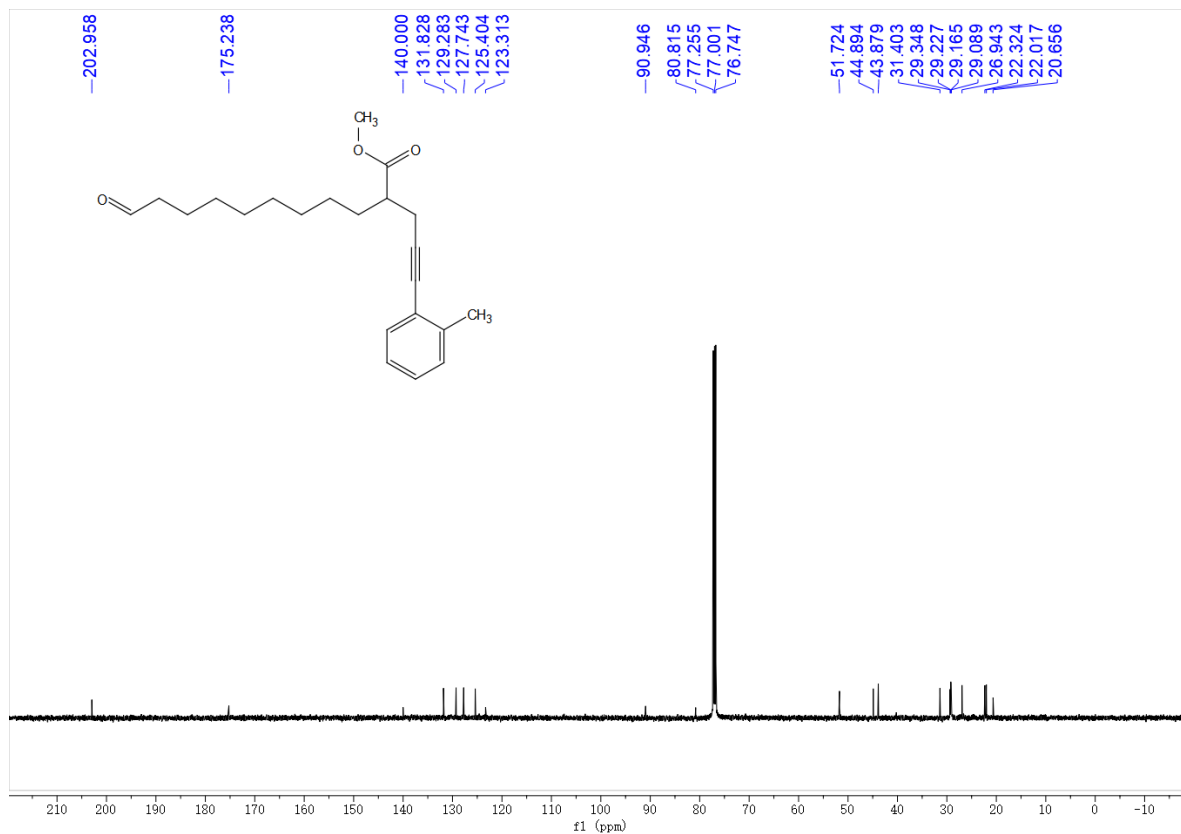


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4am

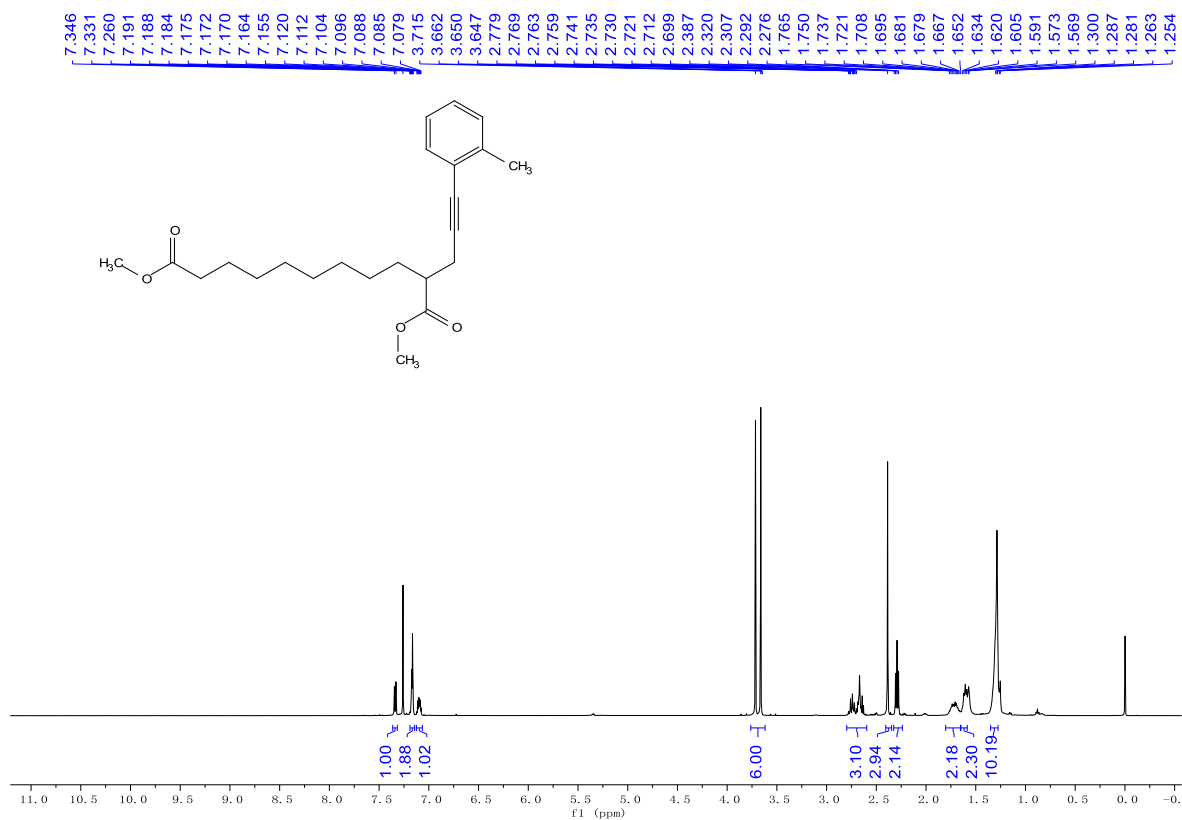


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4am

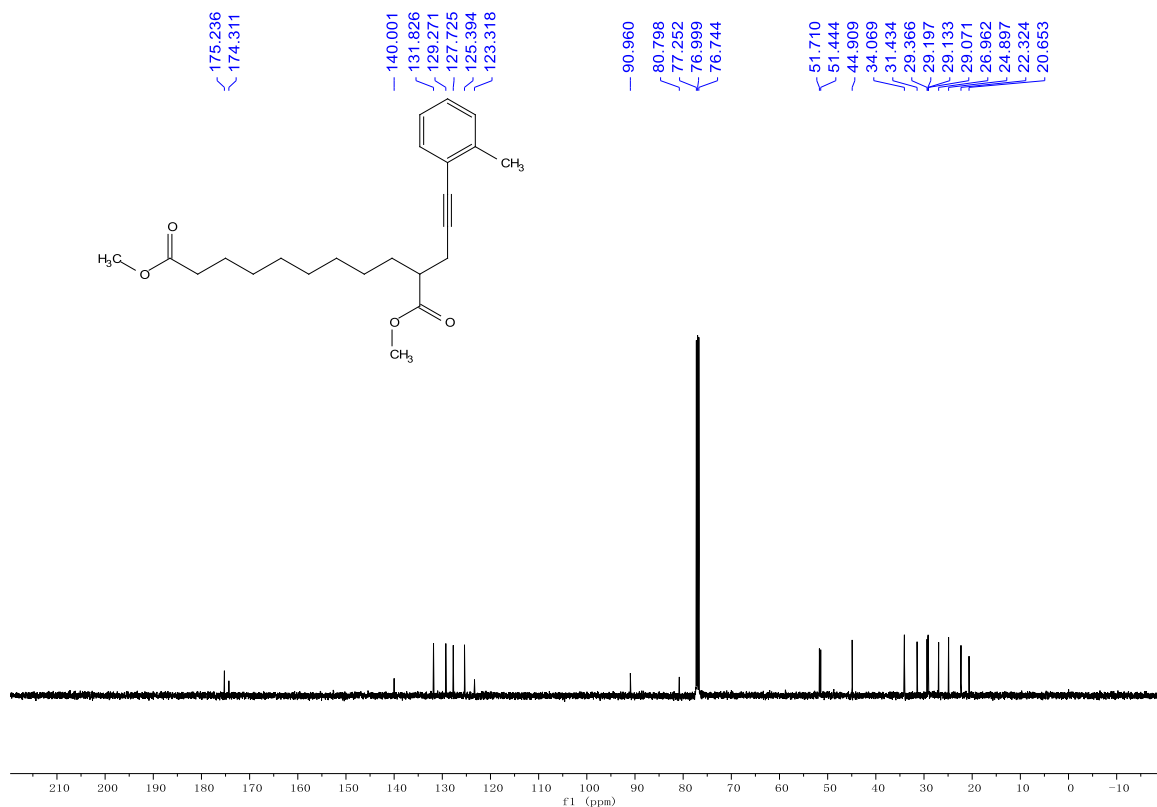


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4an

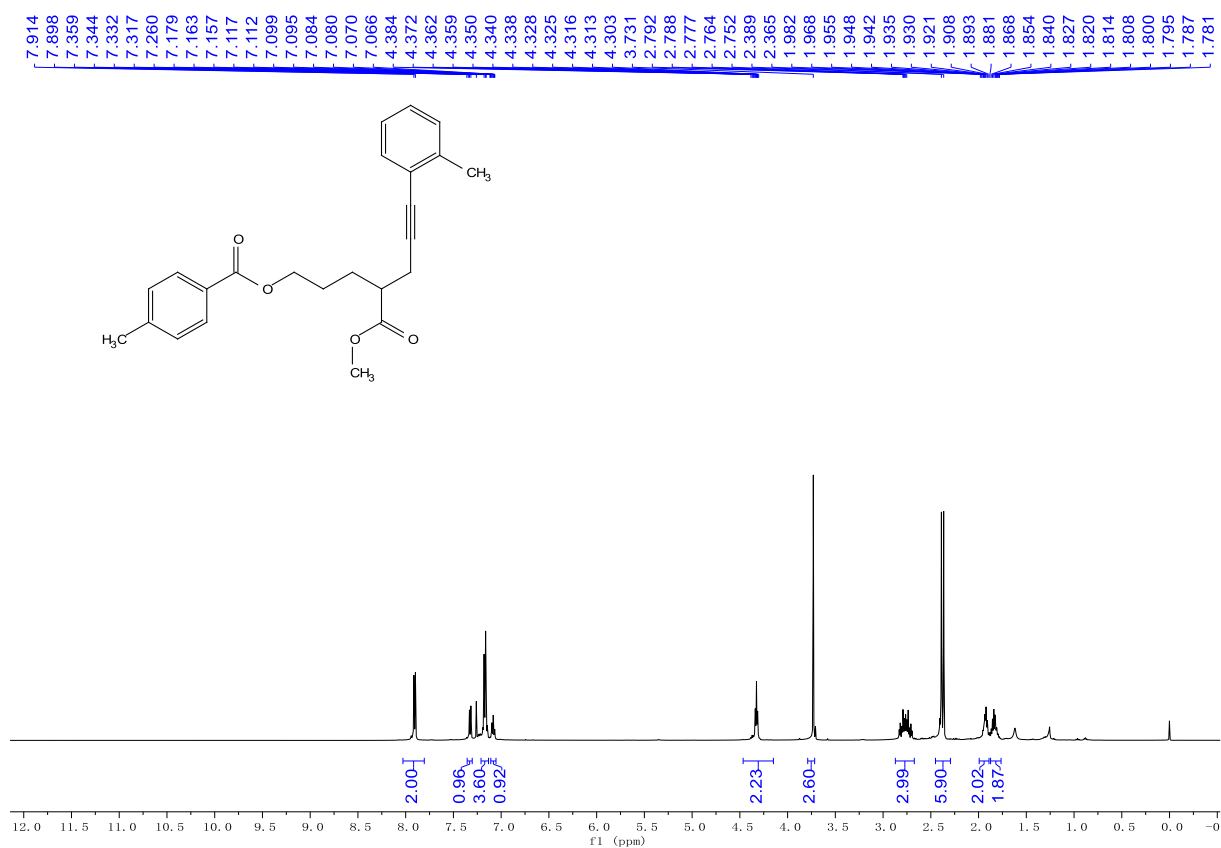


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4an

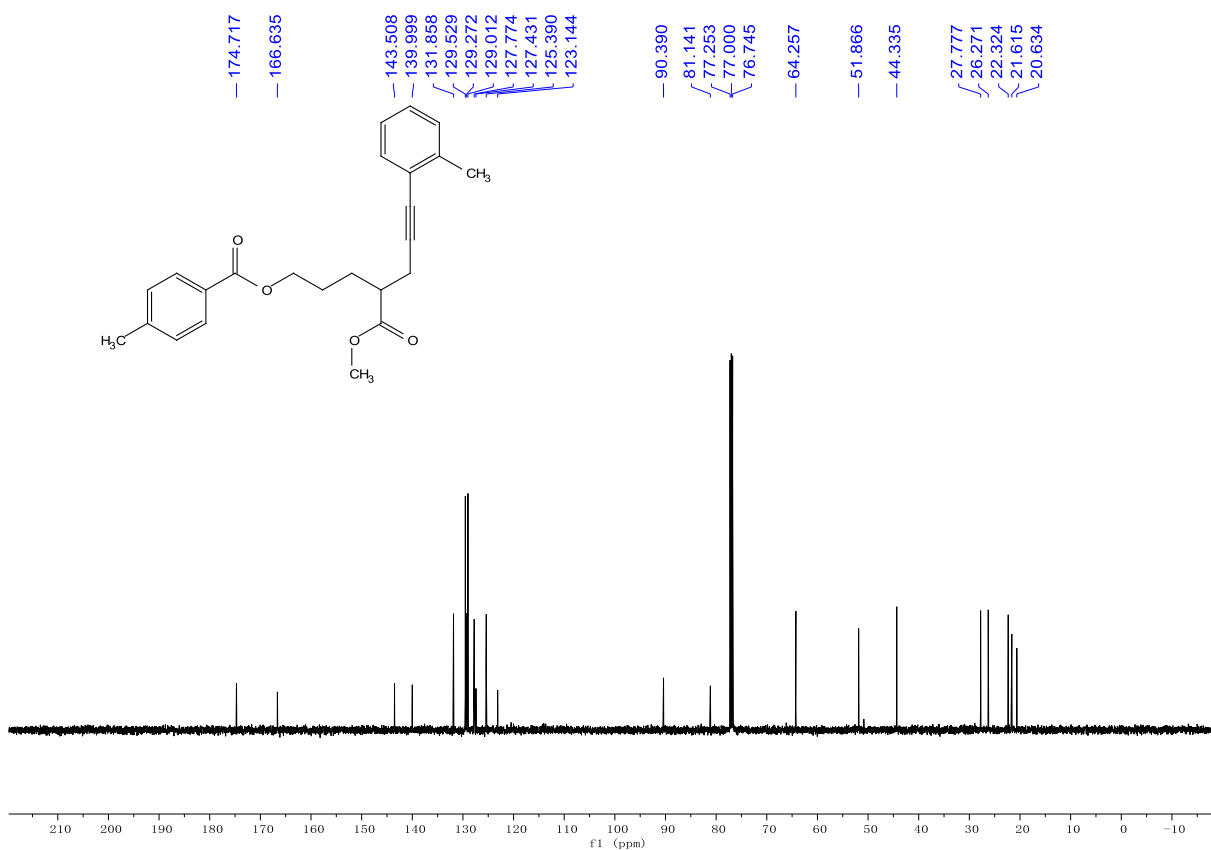


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4ao

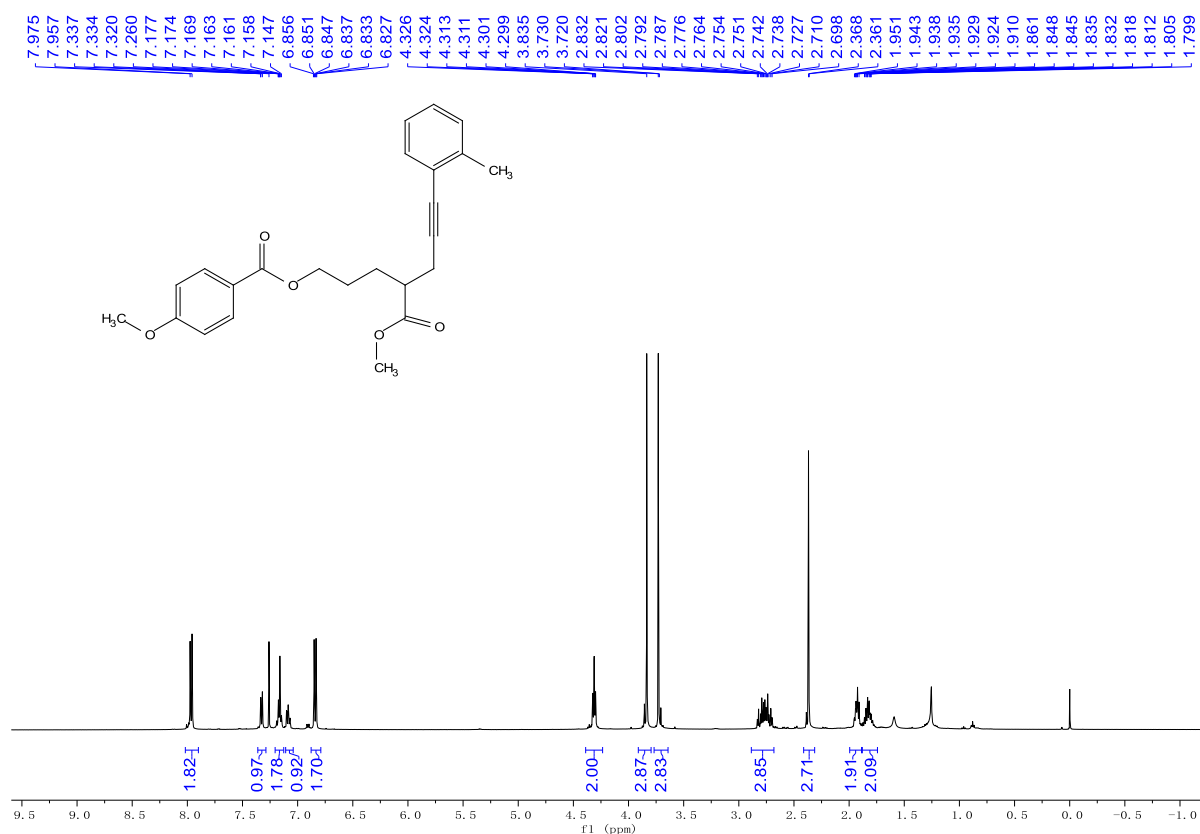


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4ao

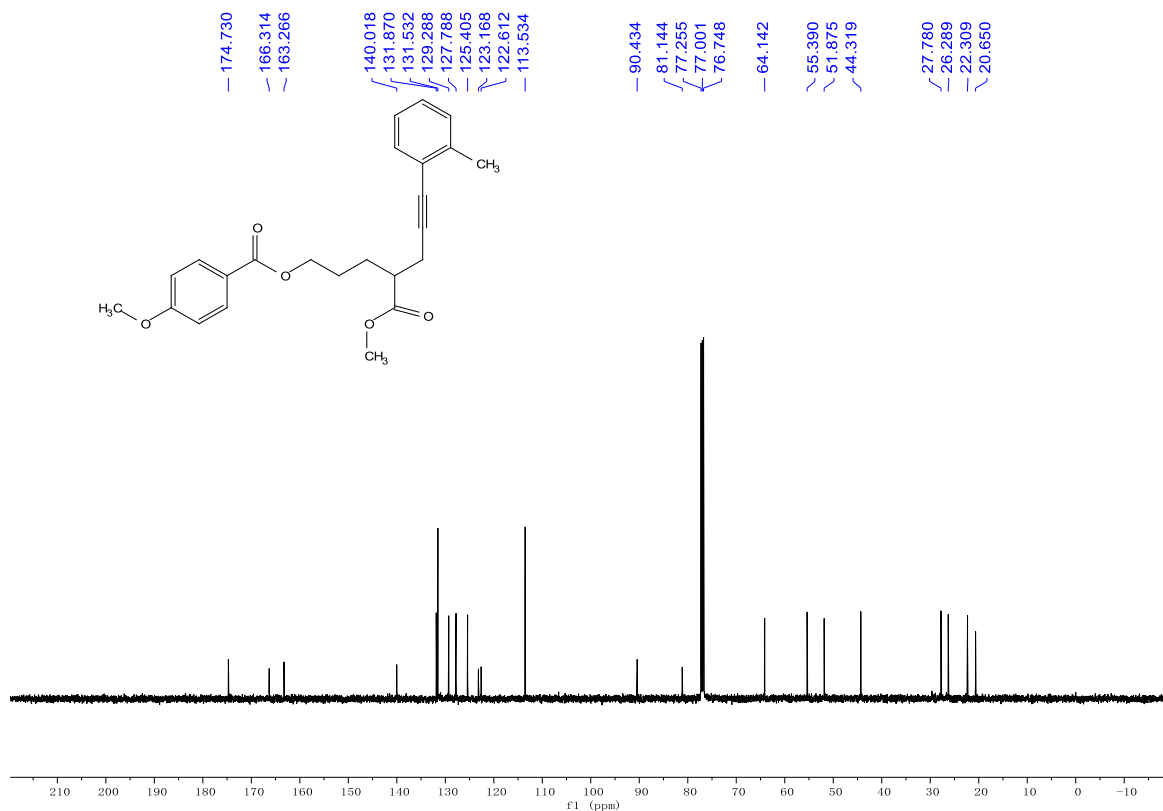


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¹H NMR (500 MHz, CDCl₃) spectrum of compound 4ap

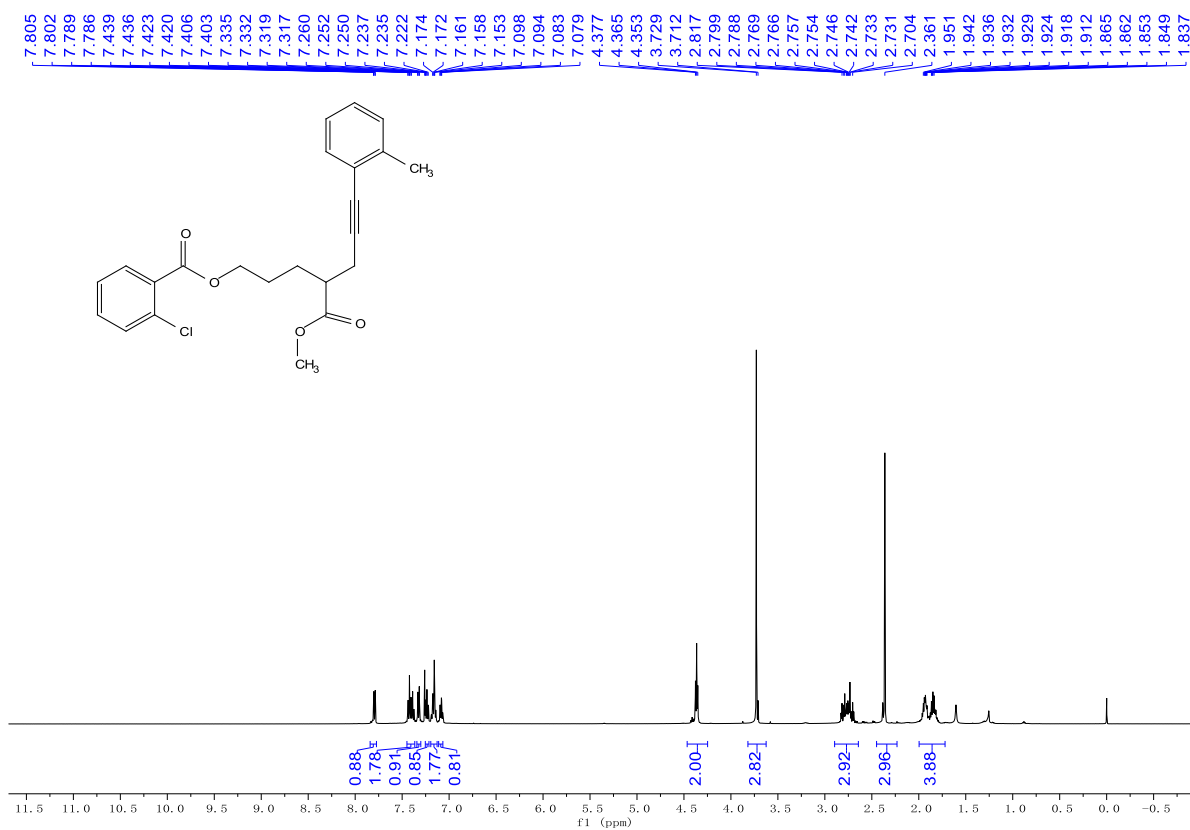


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4ap

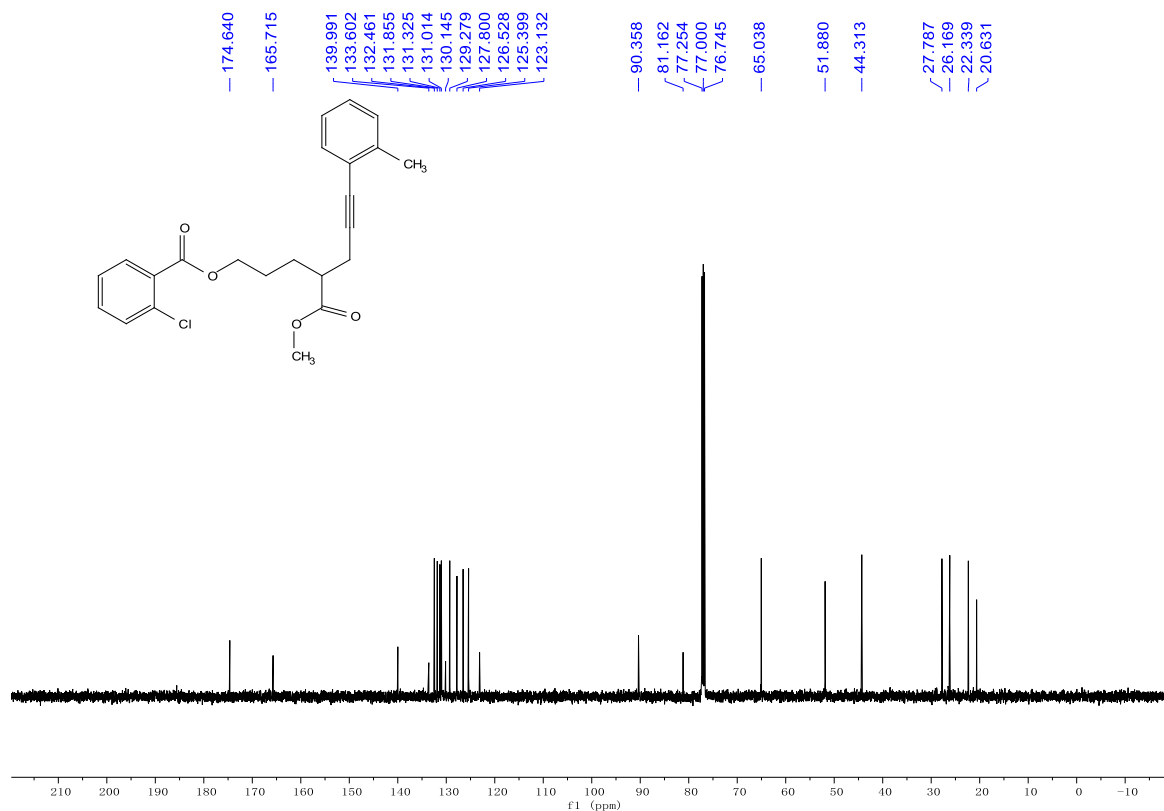


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4aq

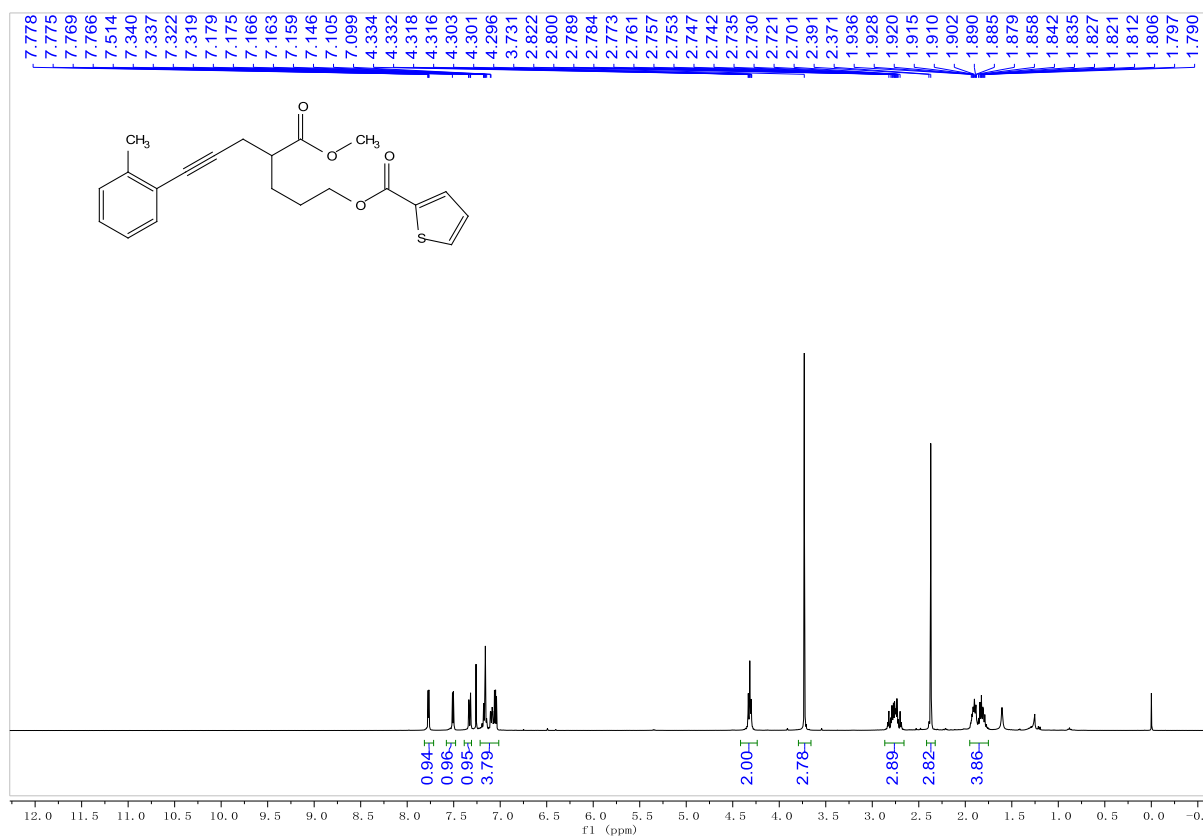


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4aq

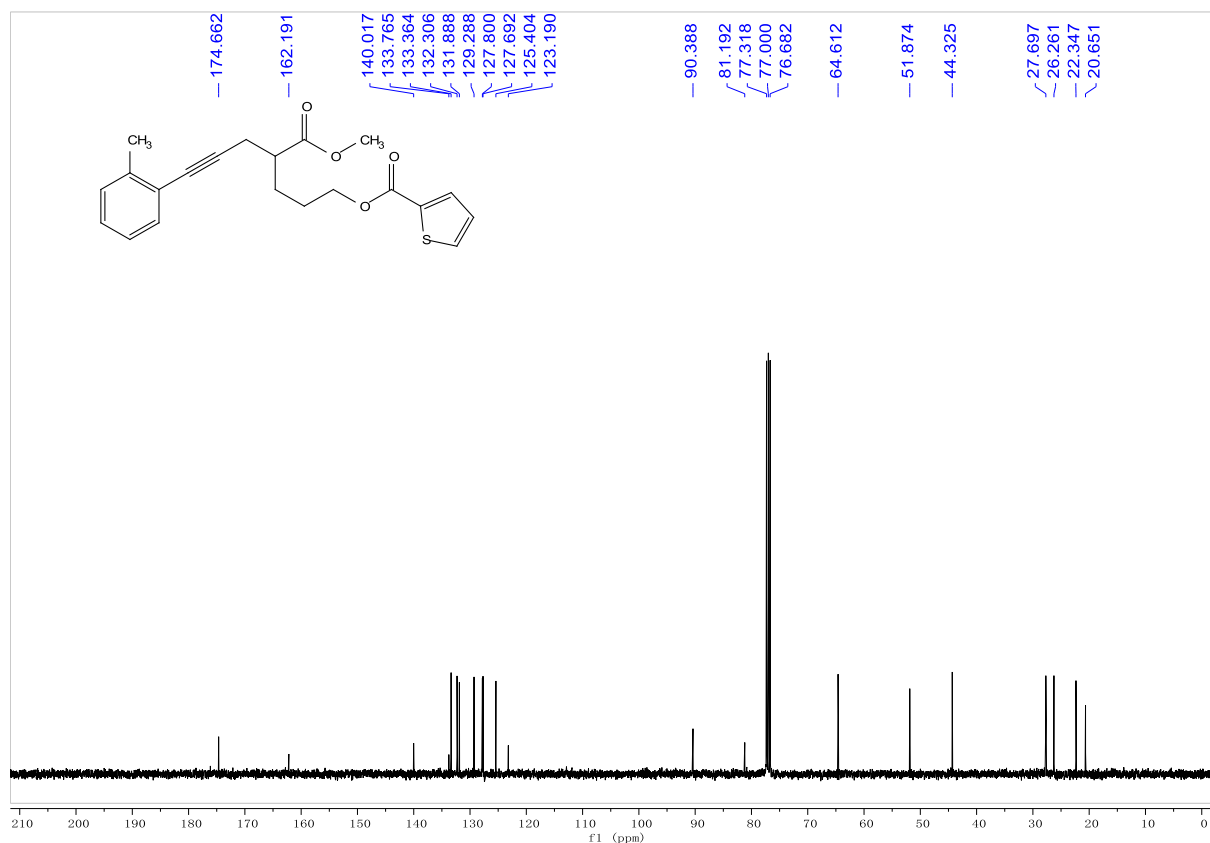


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¹H NMR (500 MHz, CDCl₃) spectrum of compound 4ar

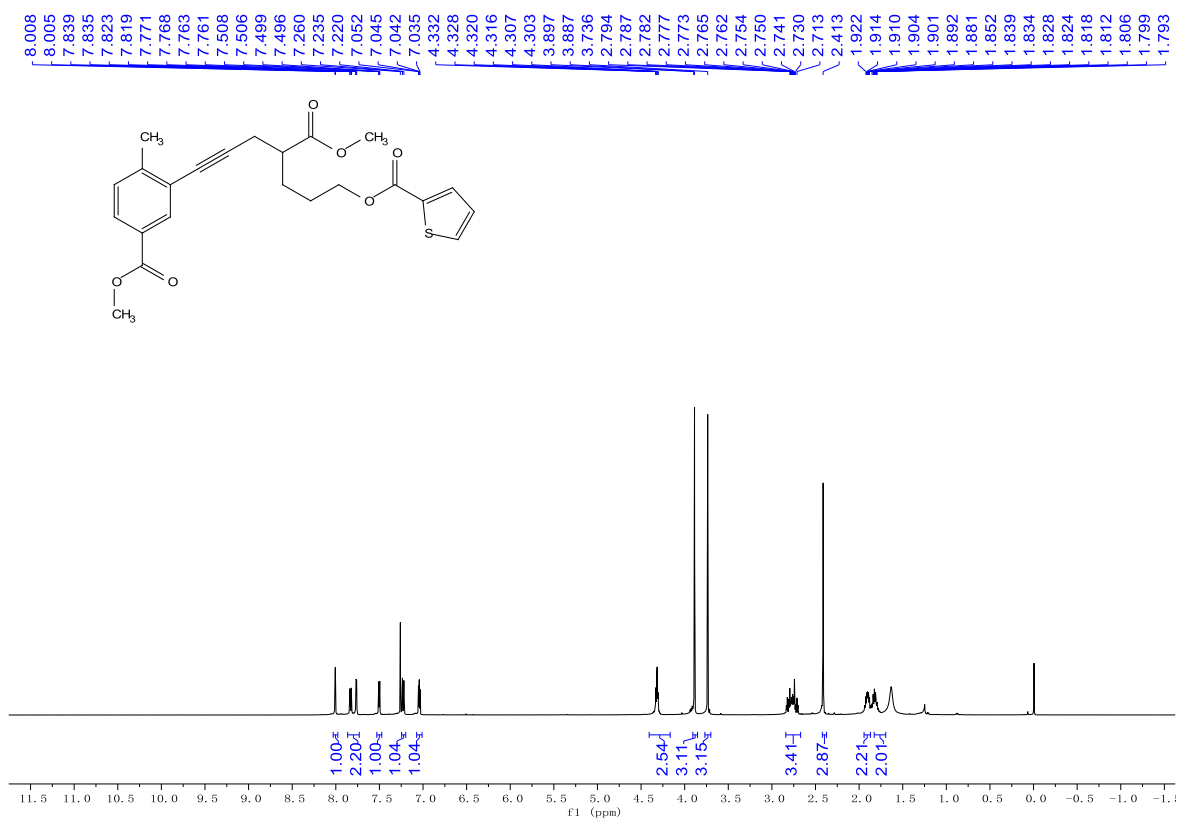


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4ar

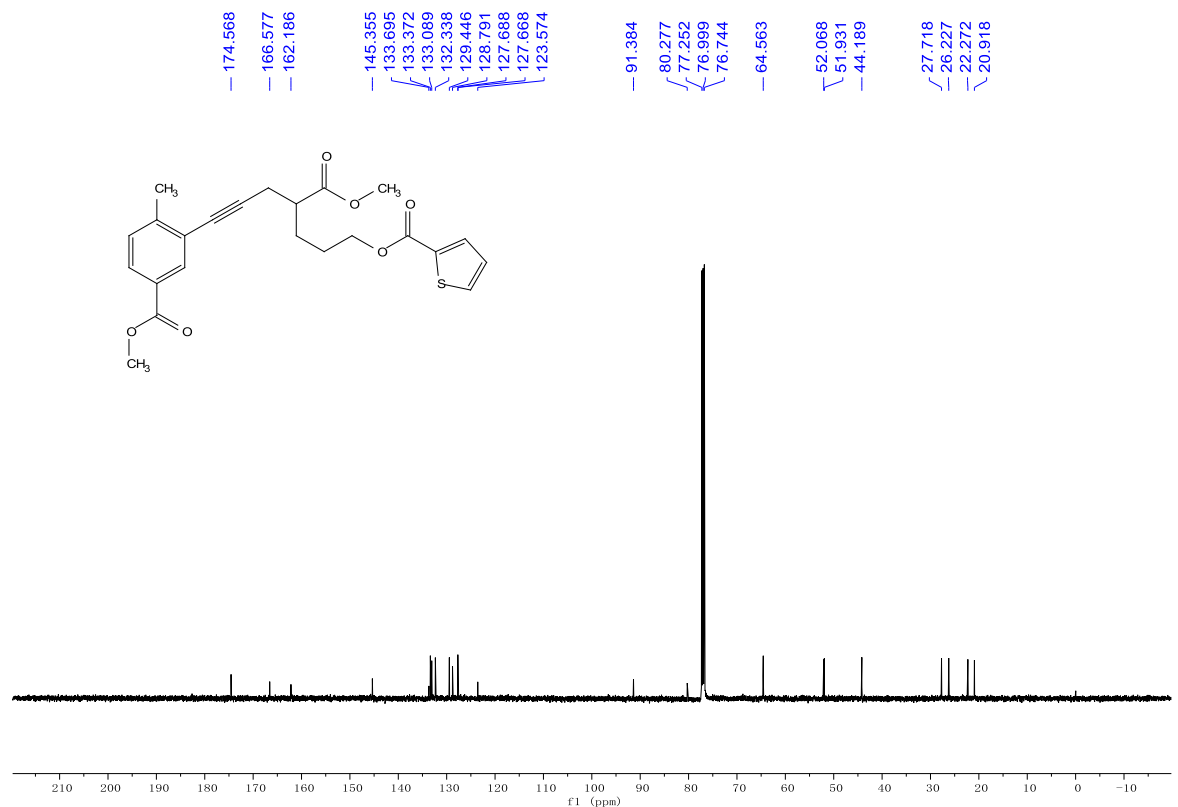


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4as

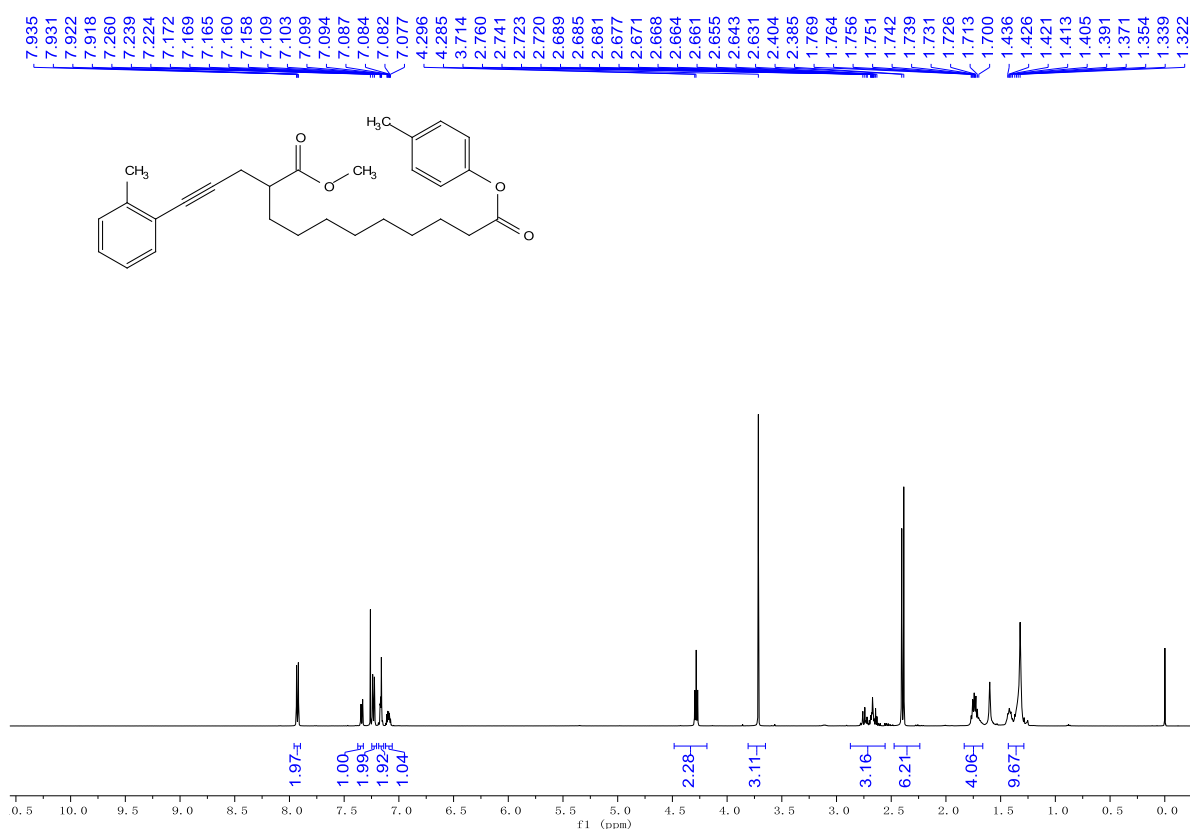


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4as

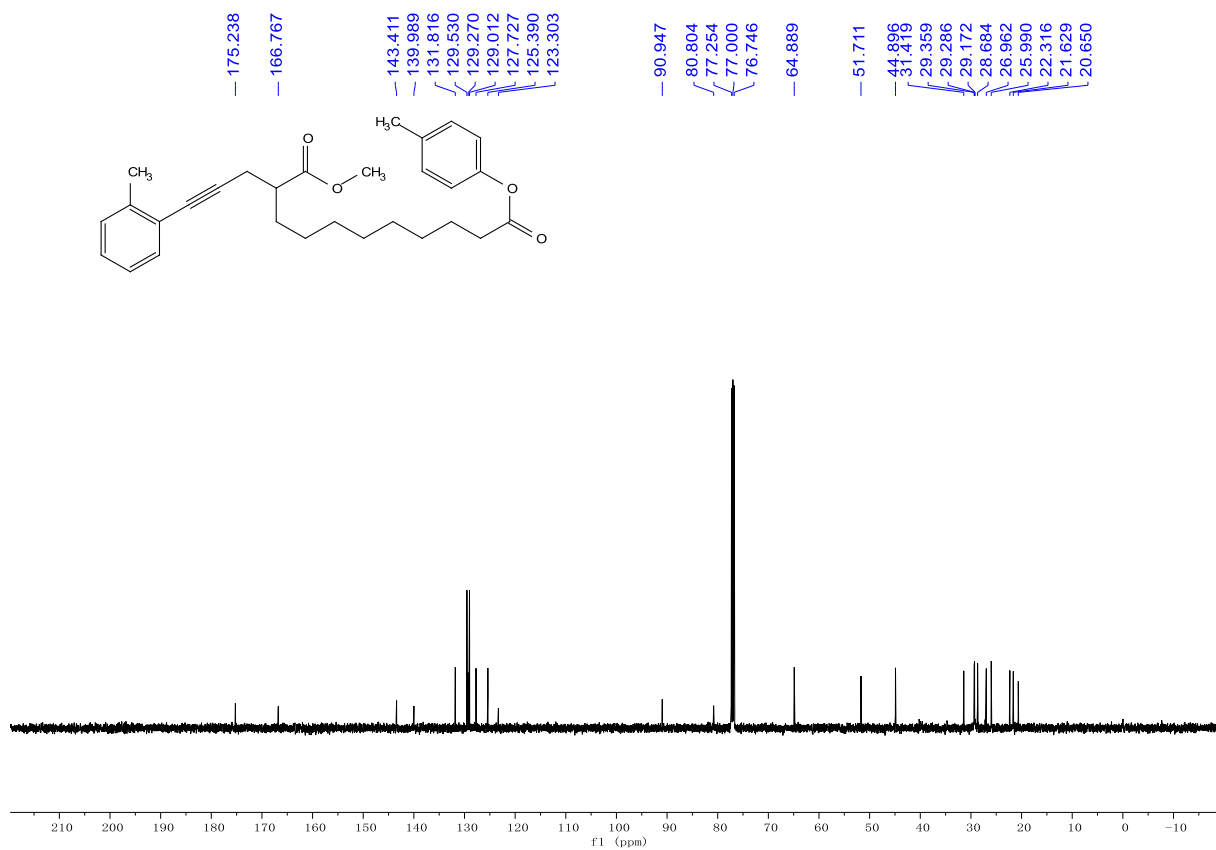


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4at

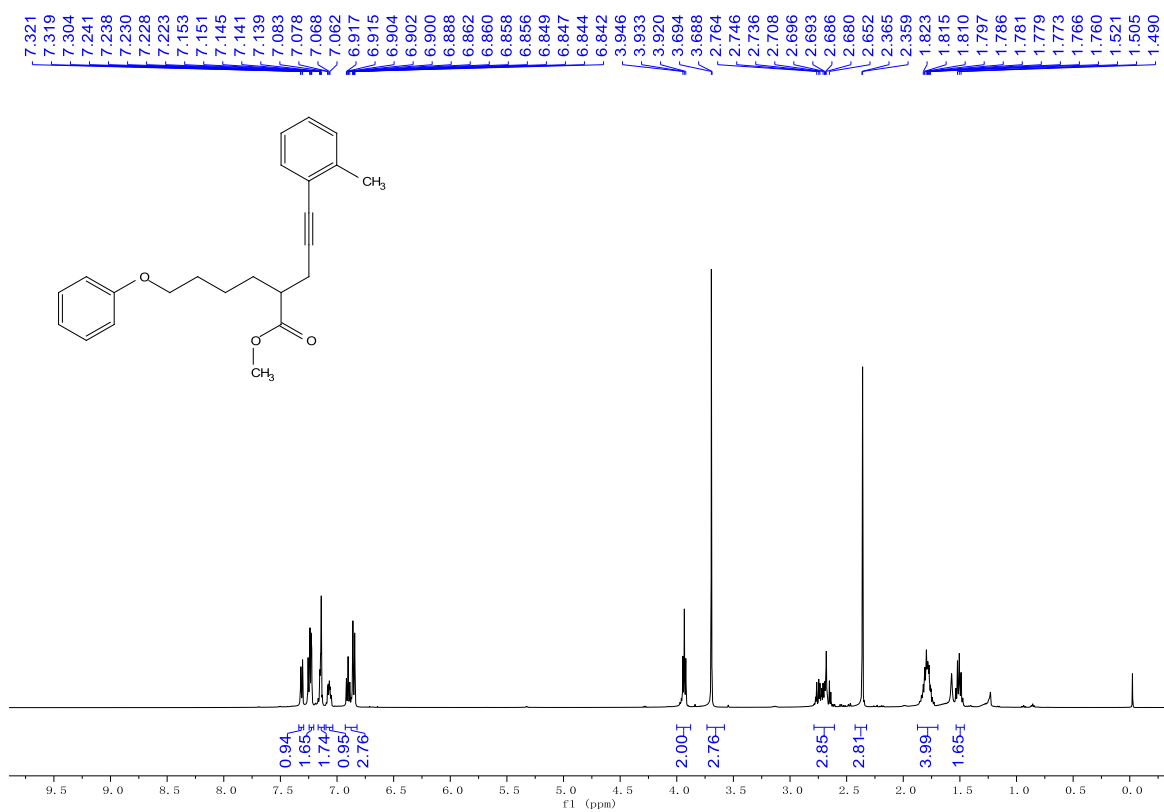


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4at

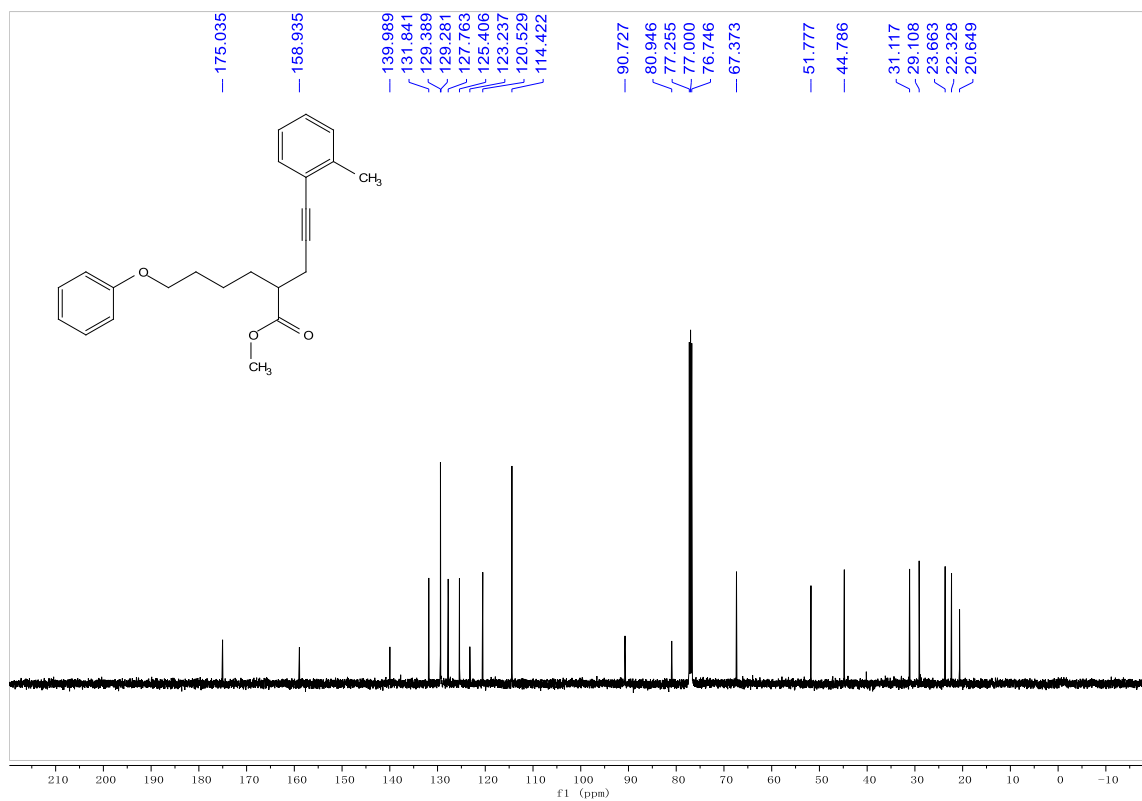


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4au

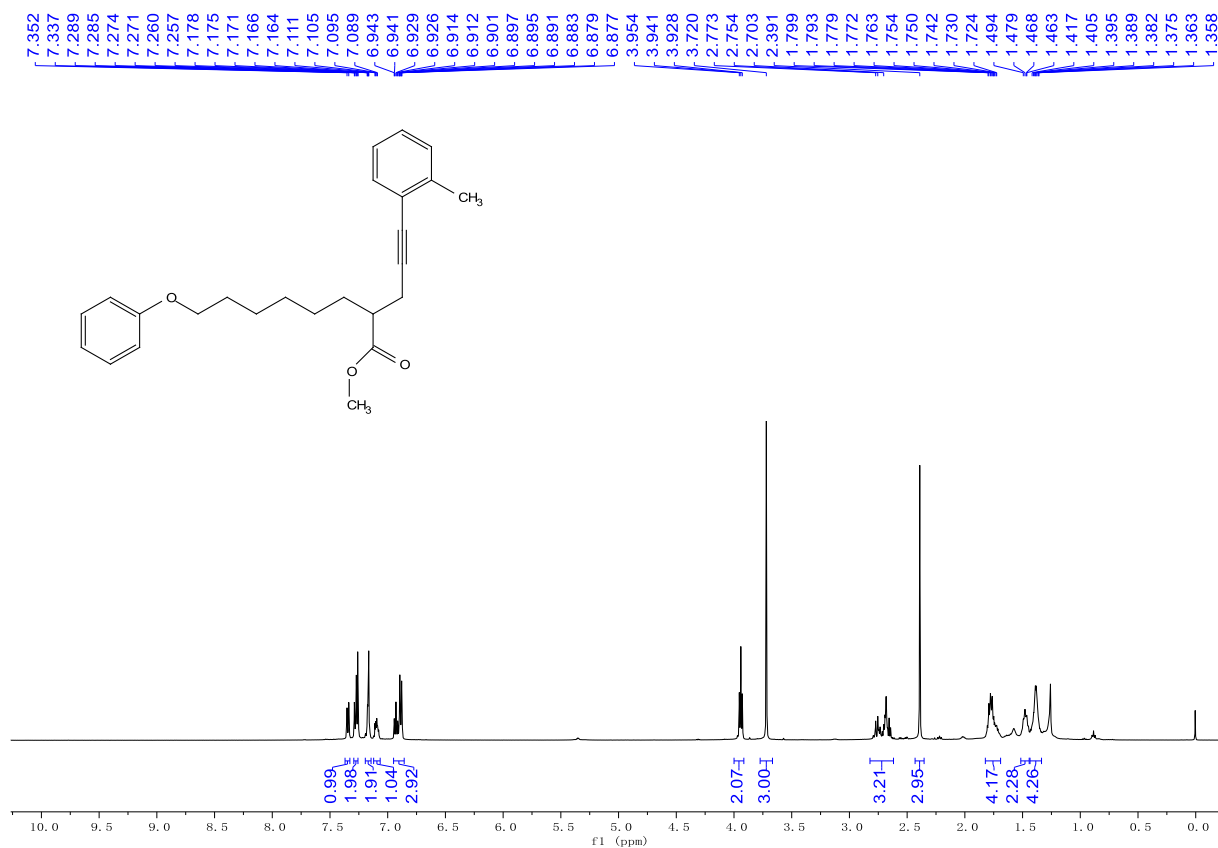


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4au

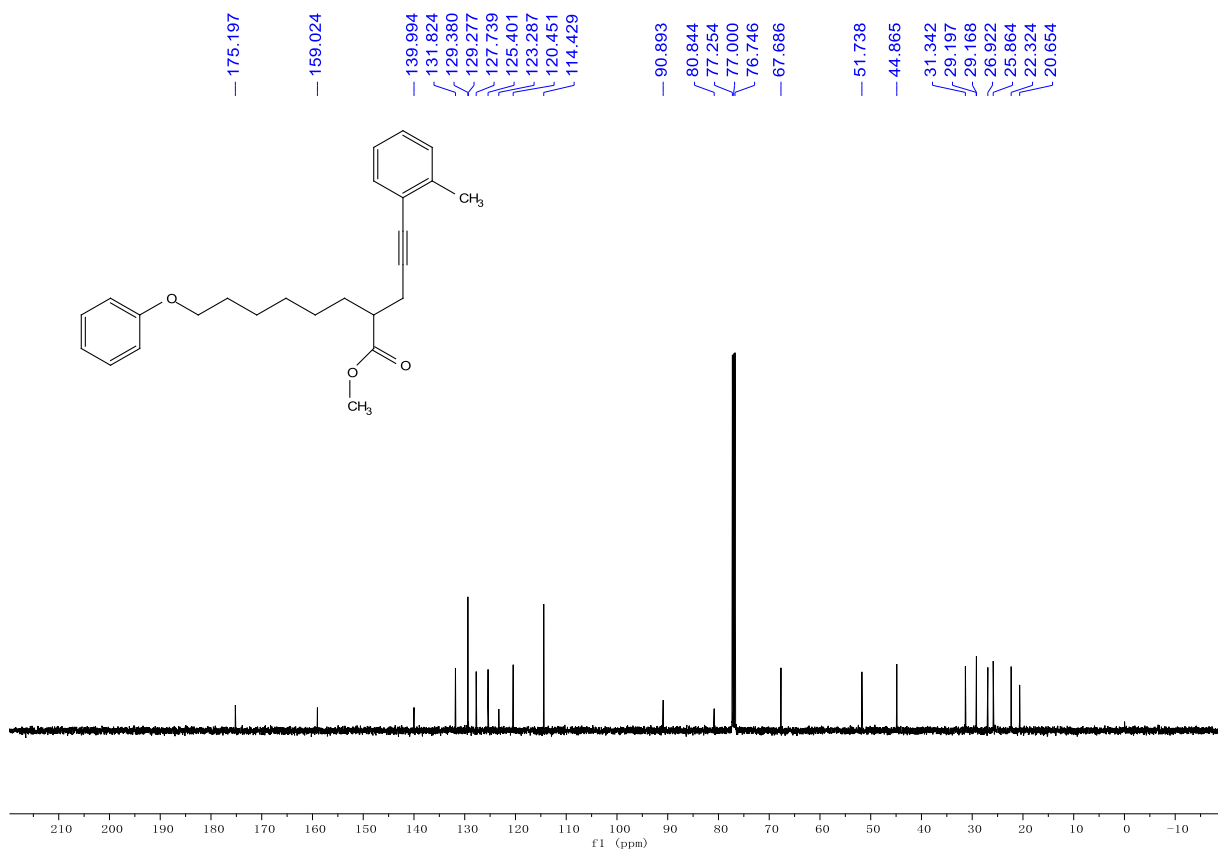


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4av

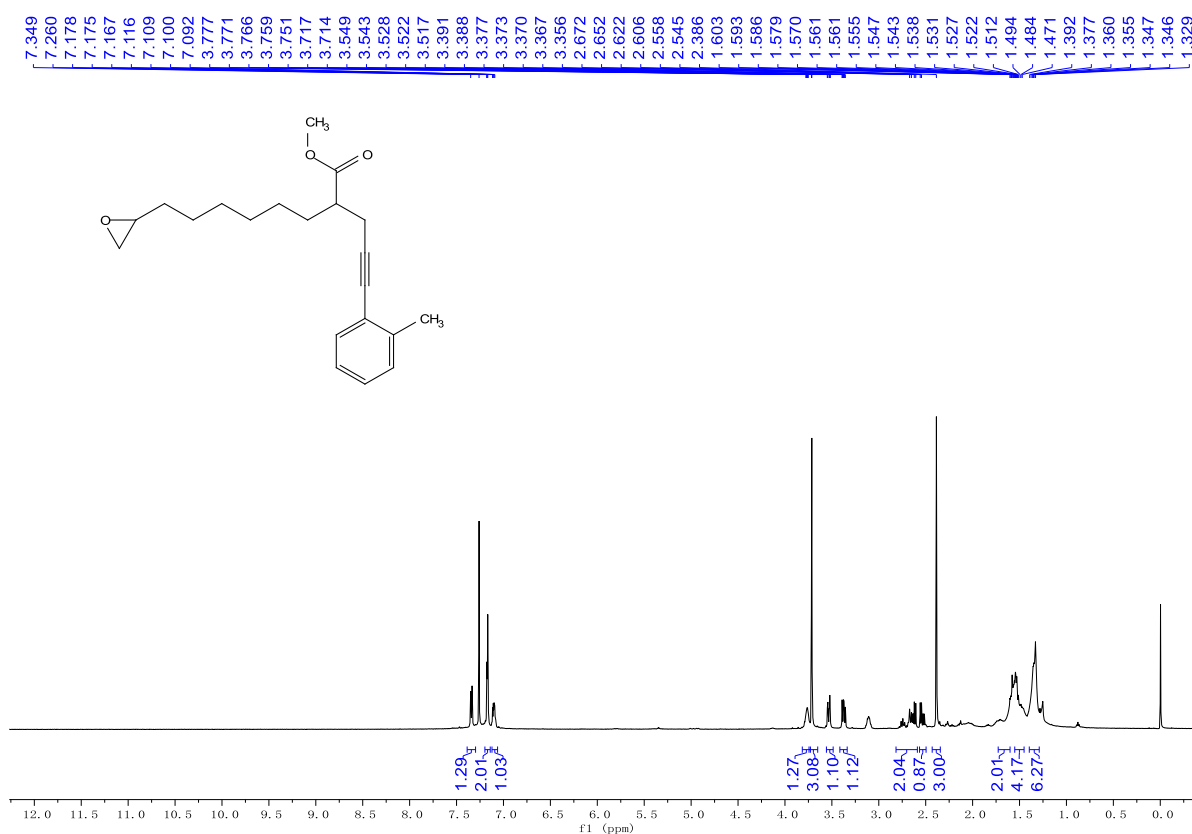


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4av

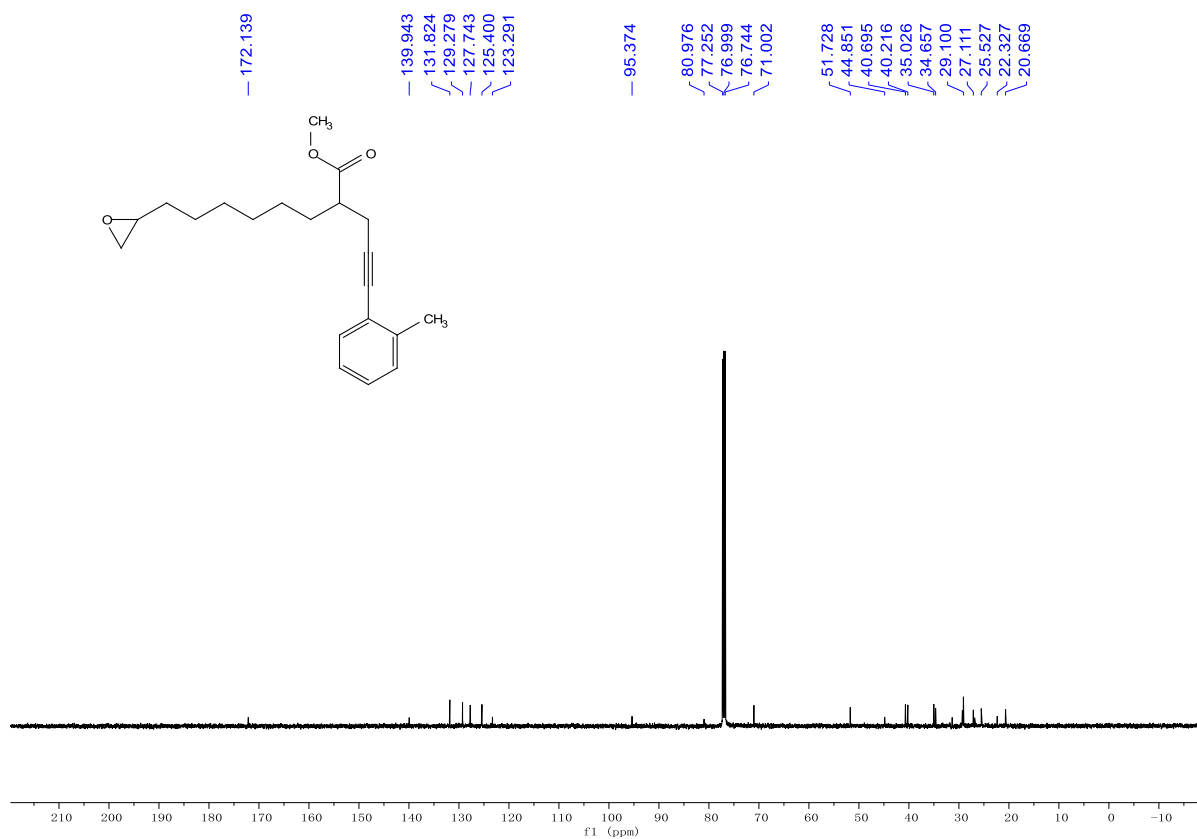


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4aw

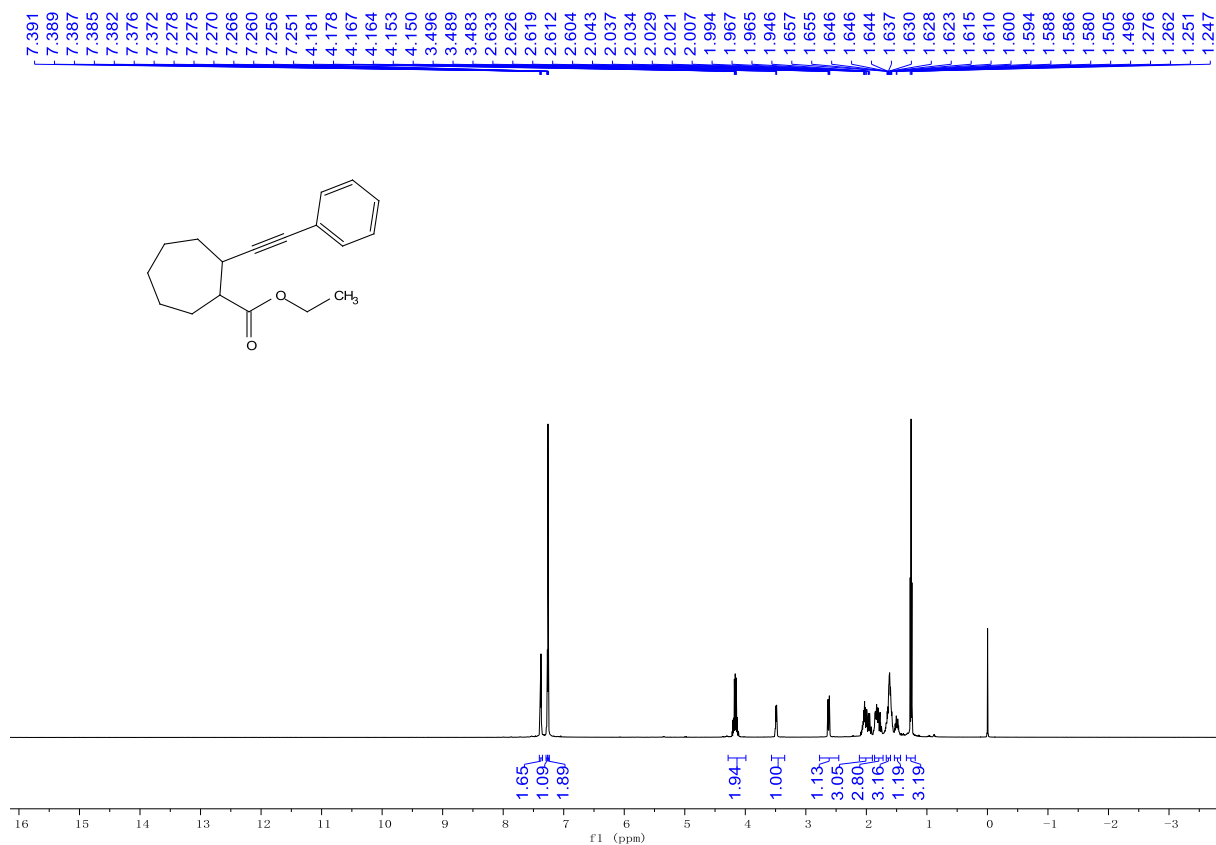


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4aw

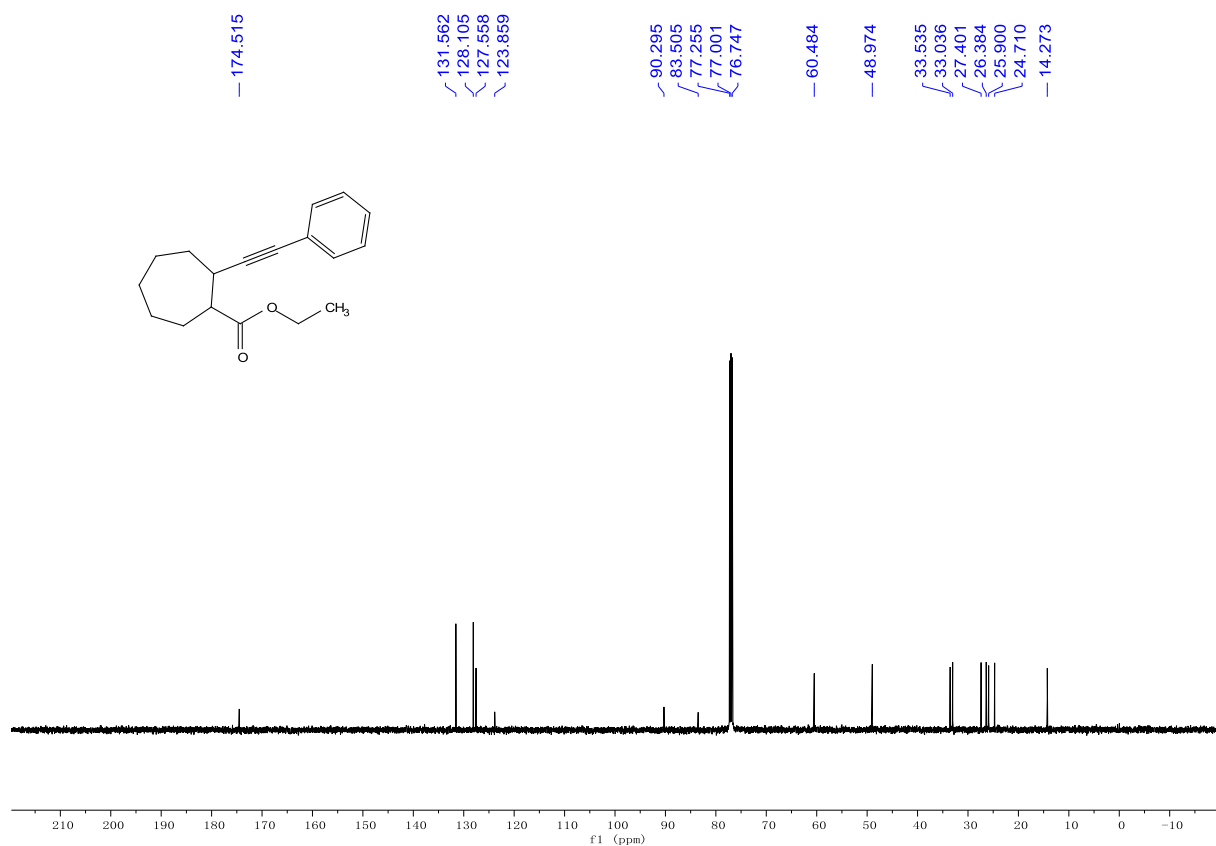


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 6a

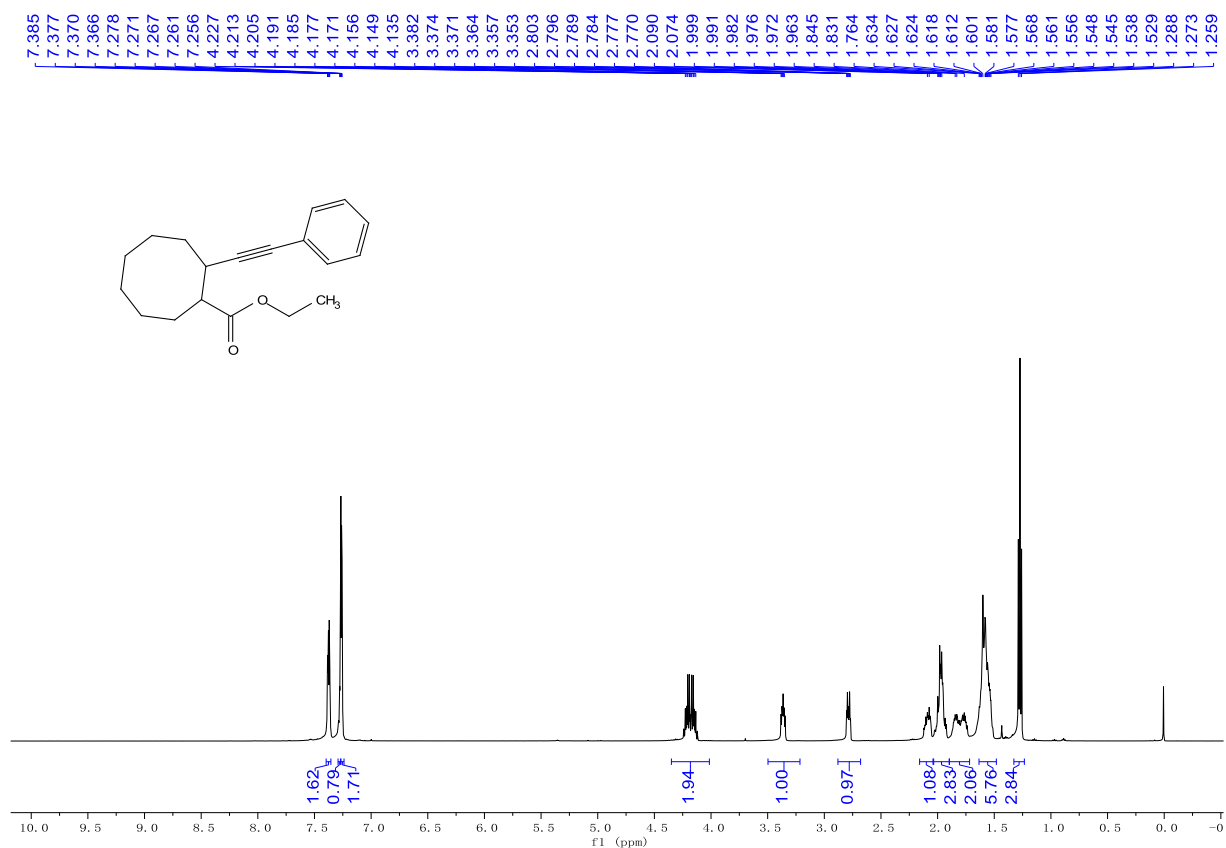


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 6a

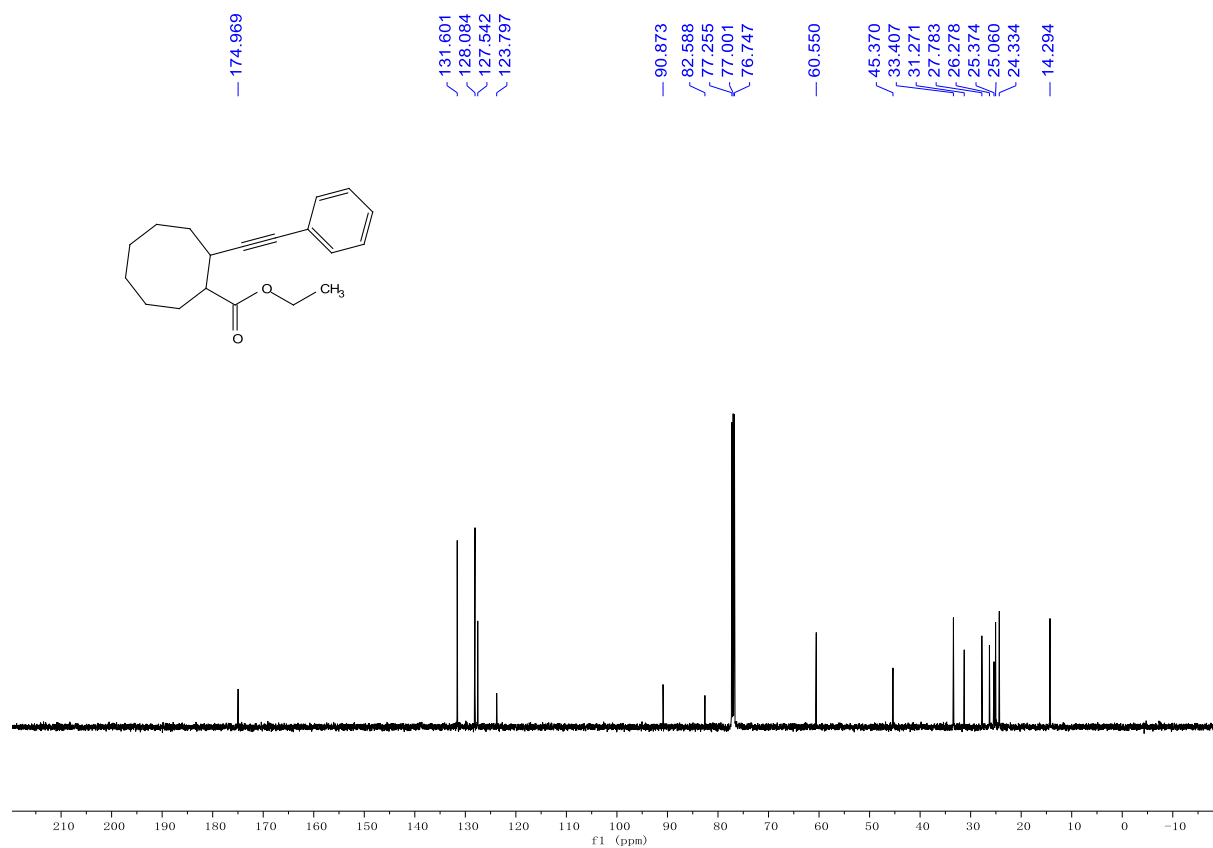


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 6b

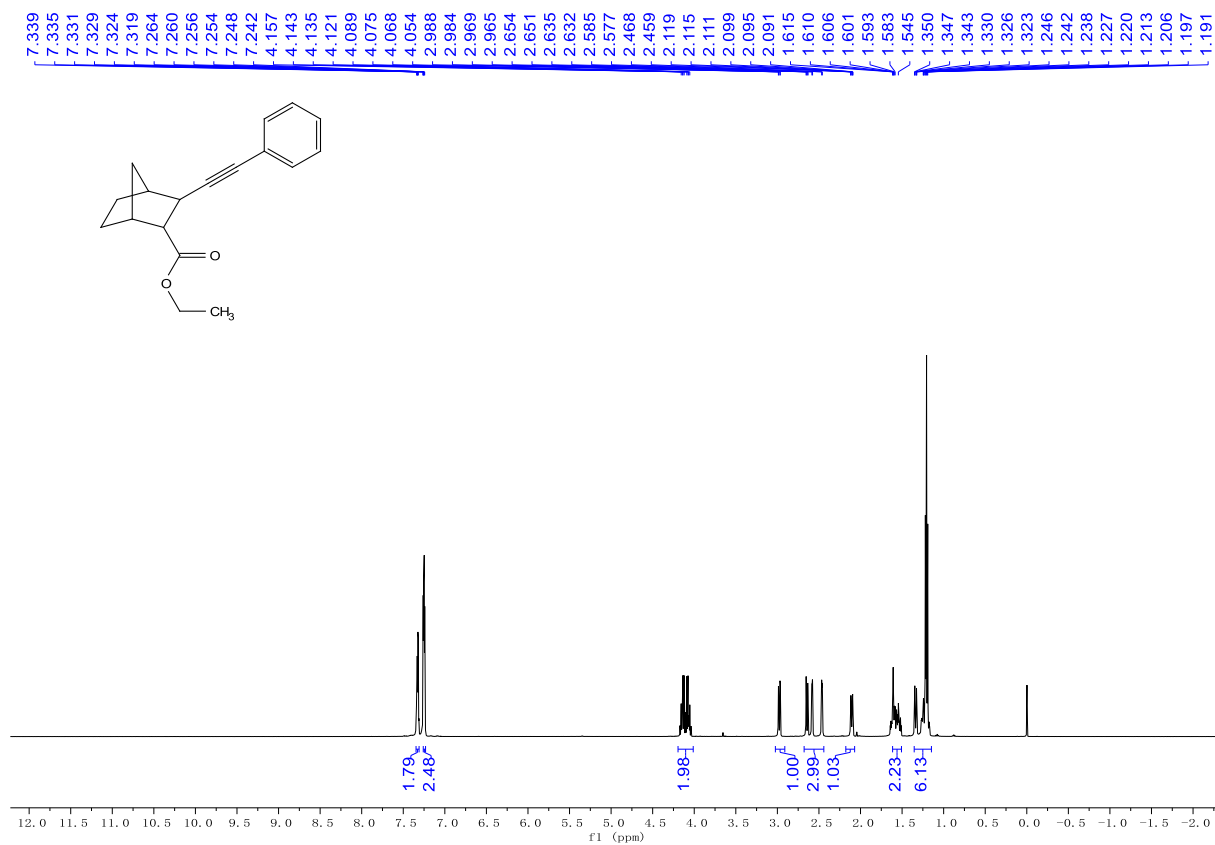


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 6b

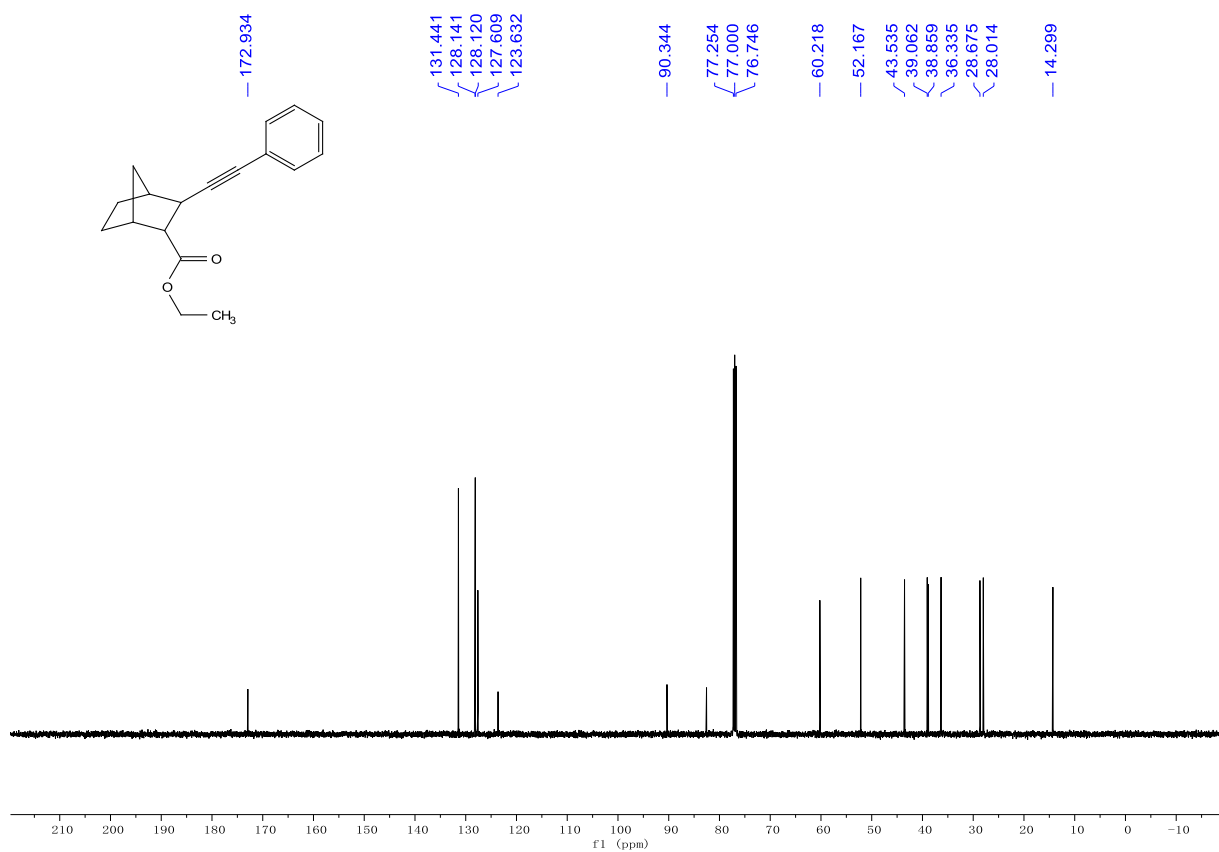


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 6c

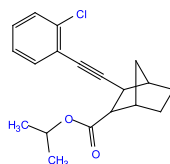
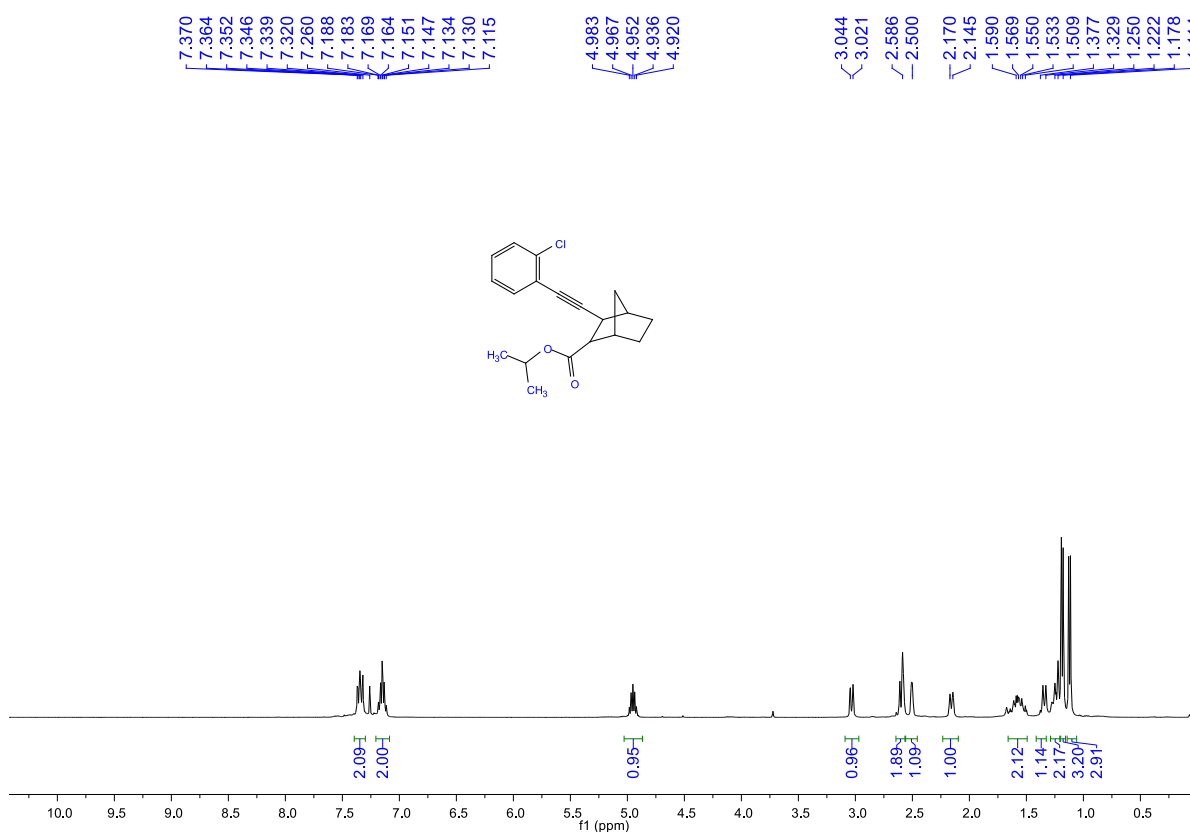


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 6c

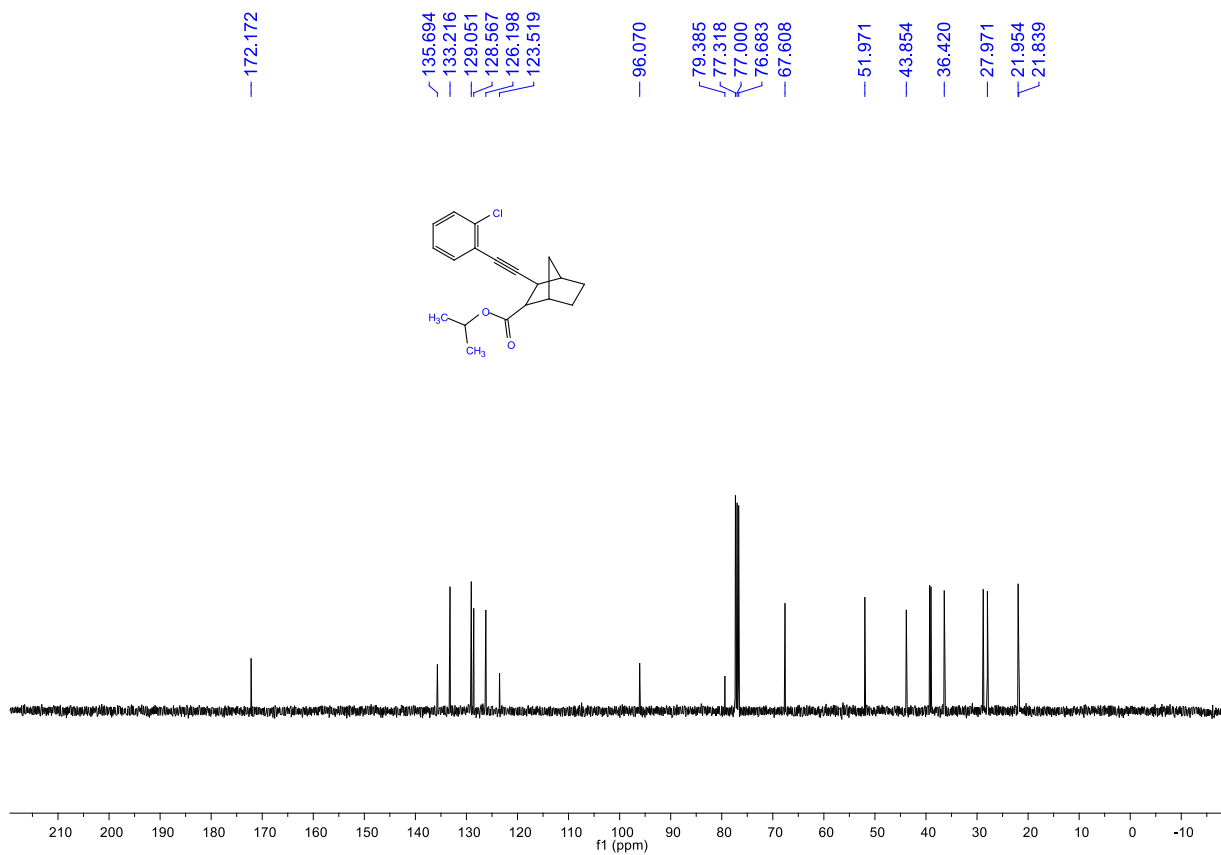


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 6d

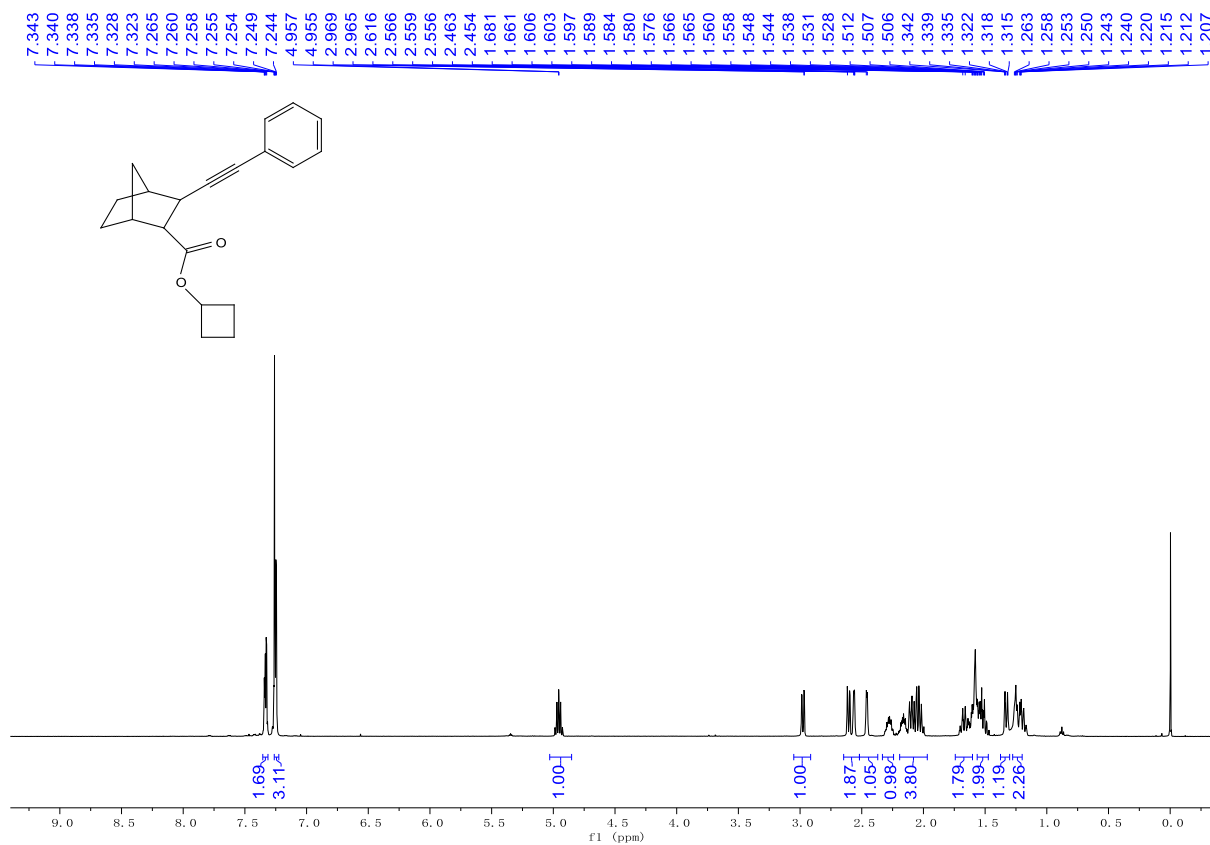


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 6d

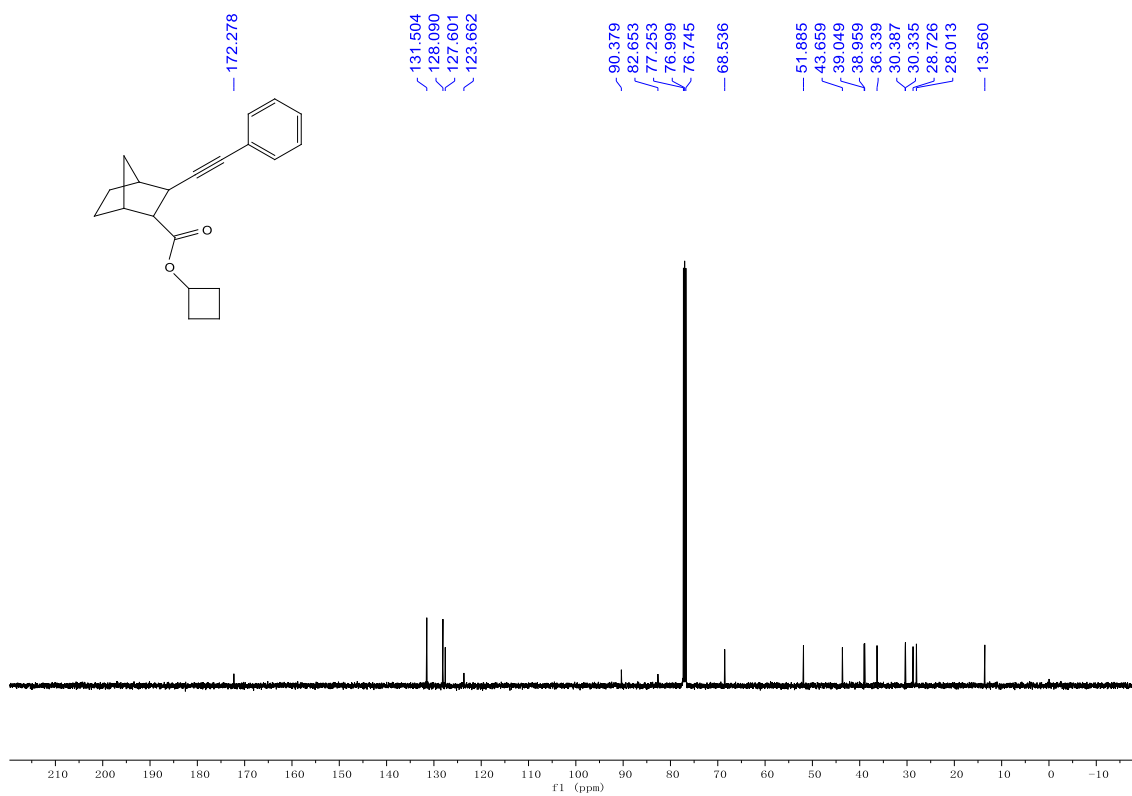


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 6e

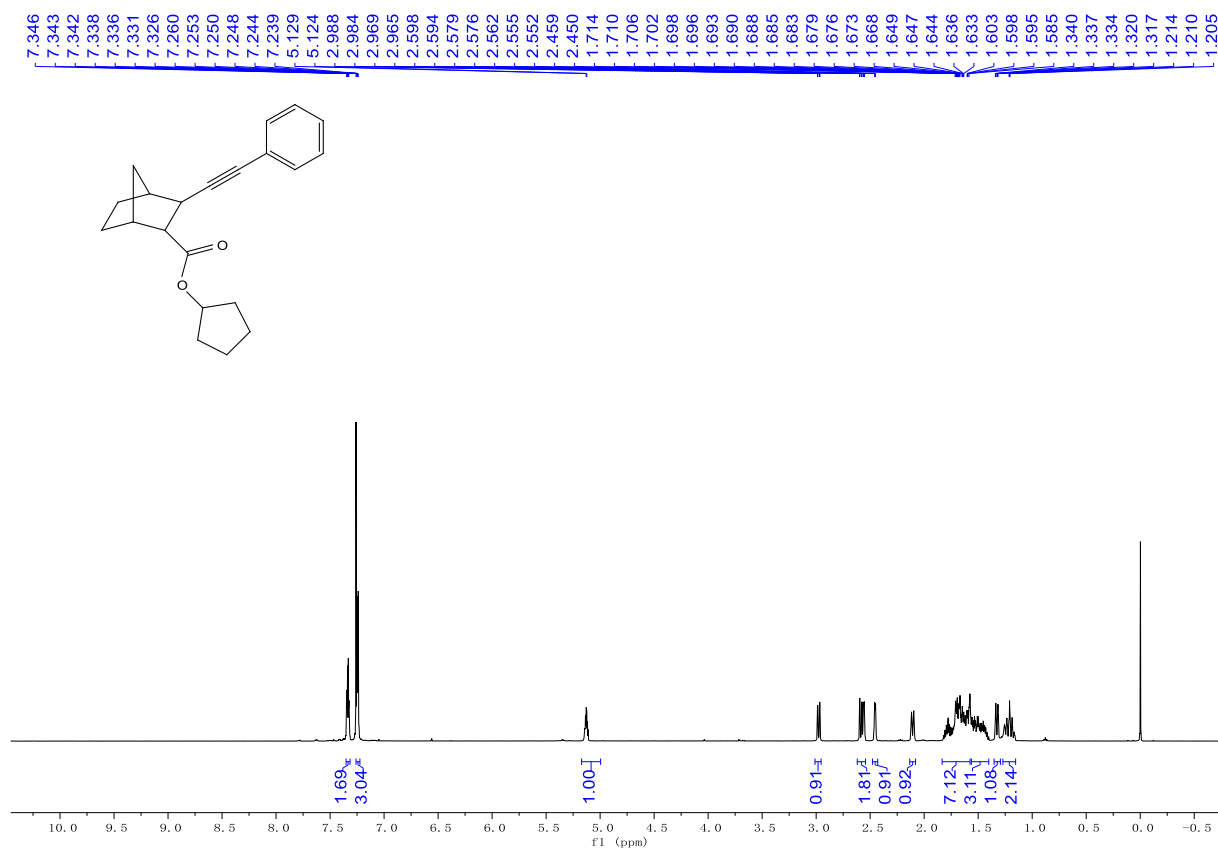


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 6e

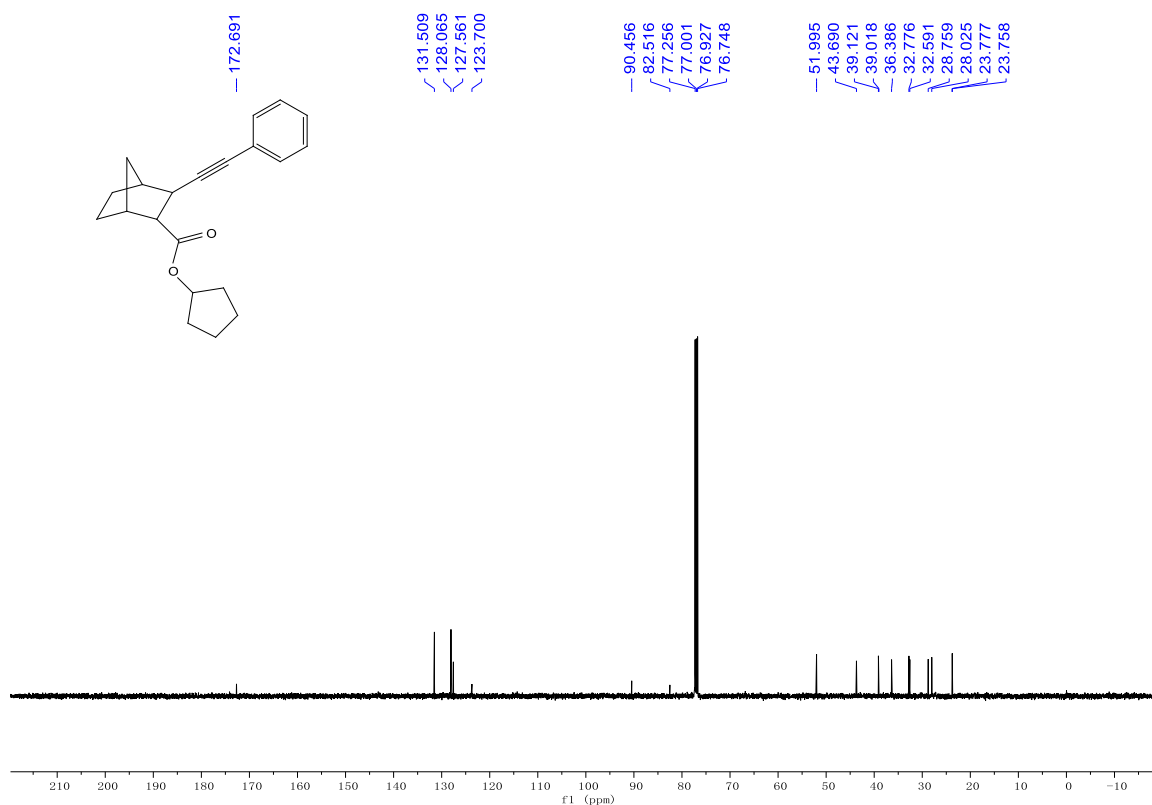


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 6f

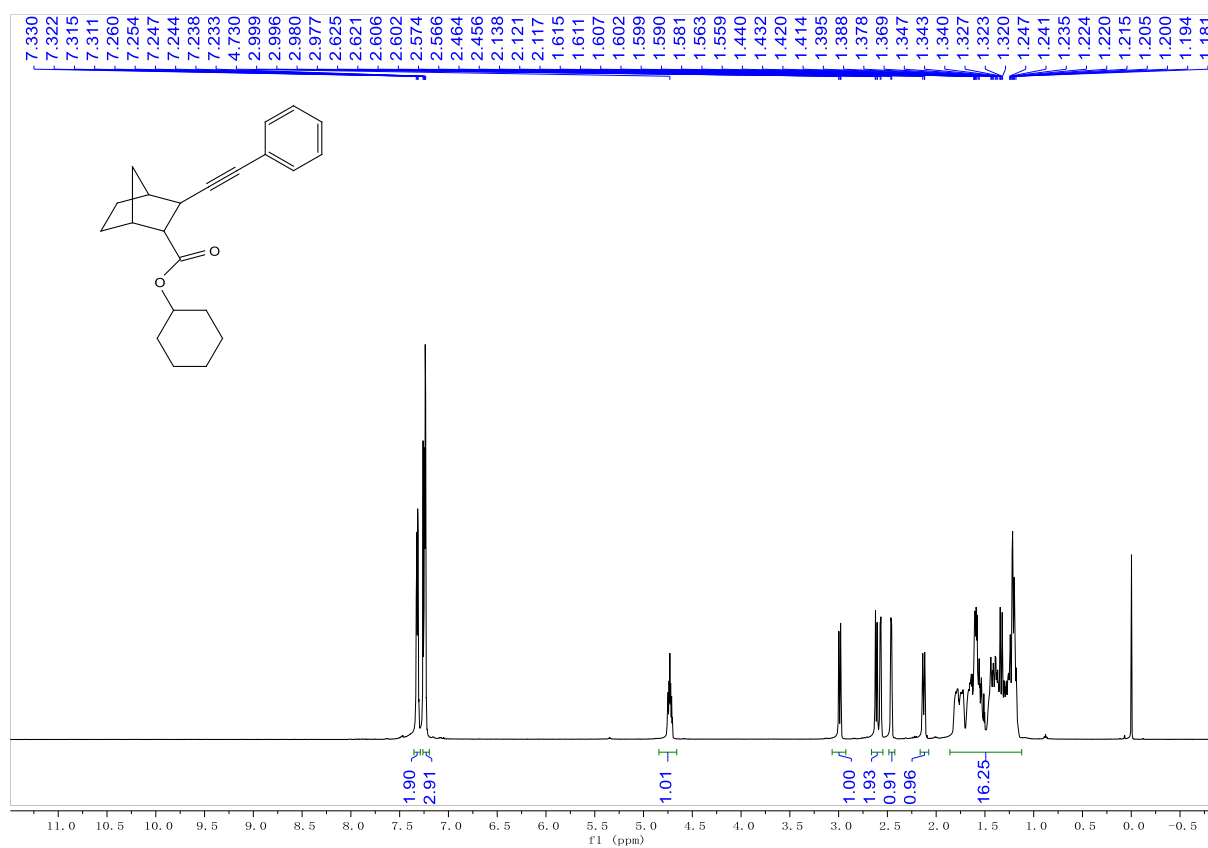


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 6f

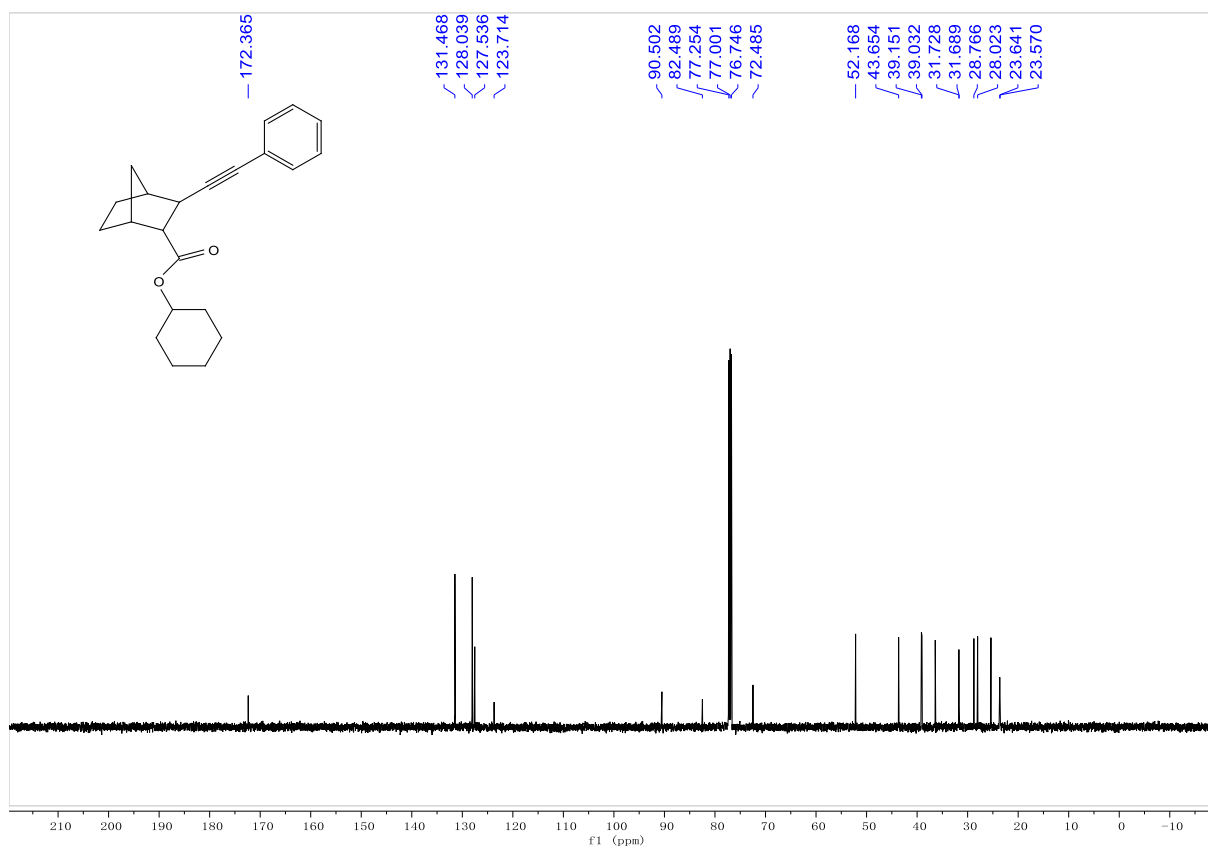


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 6g

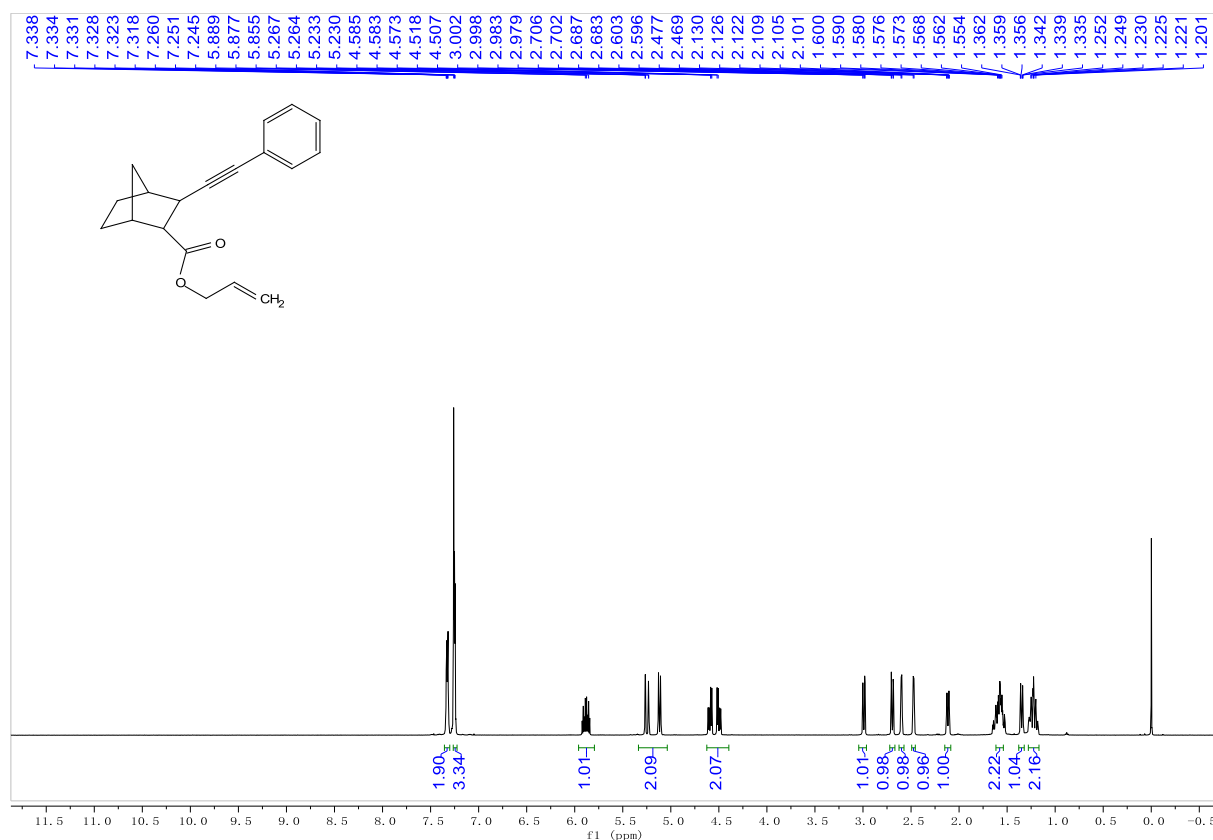


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 6g

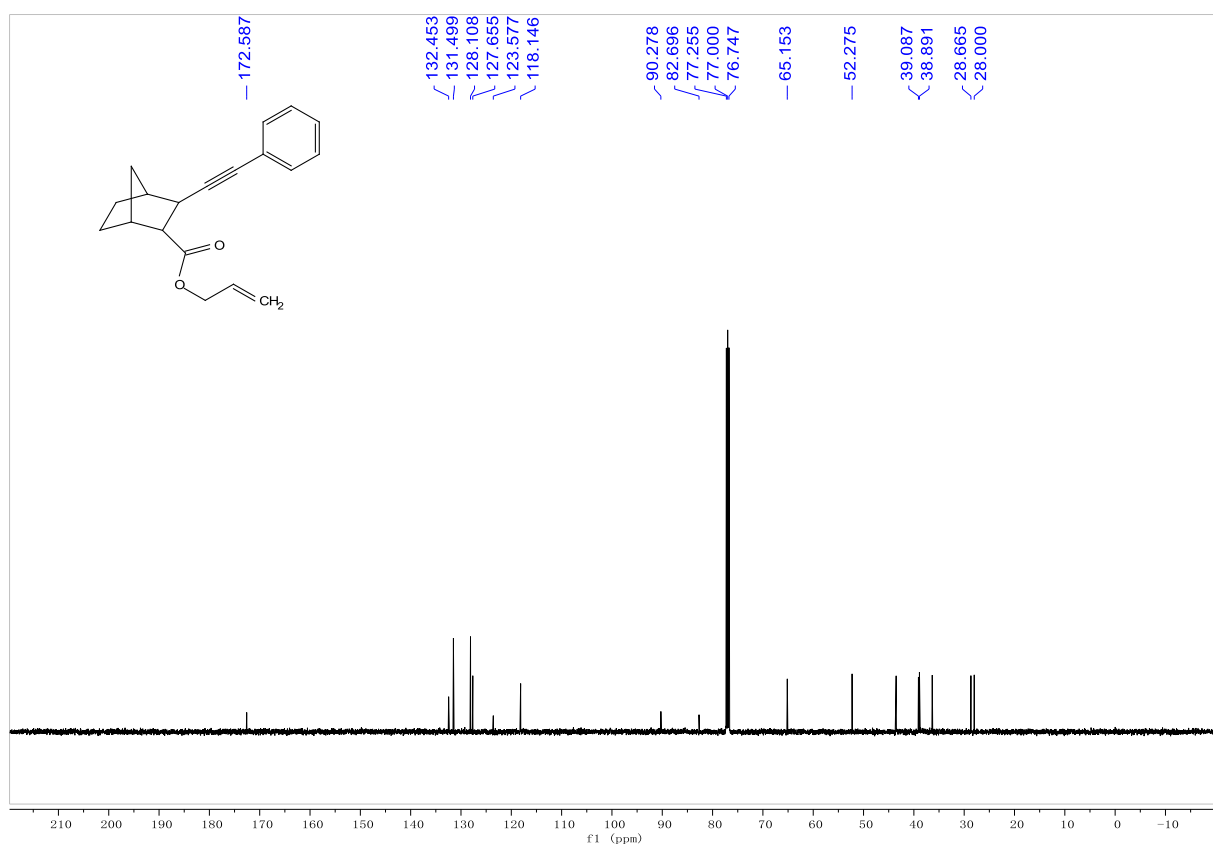


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 6h

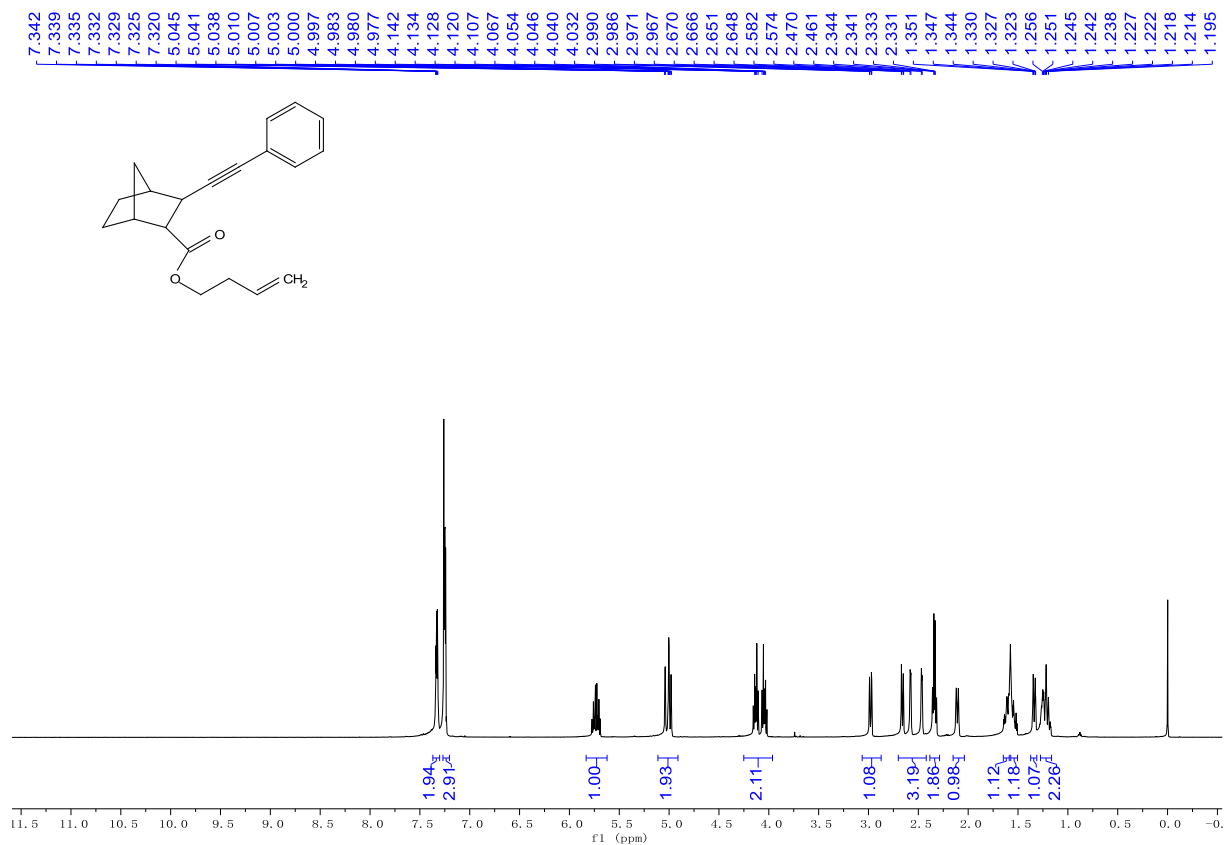


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 6h

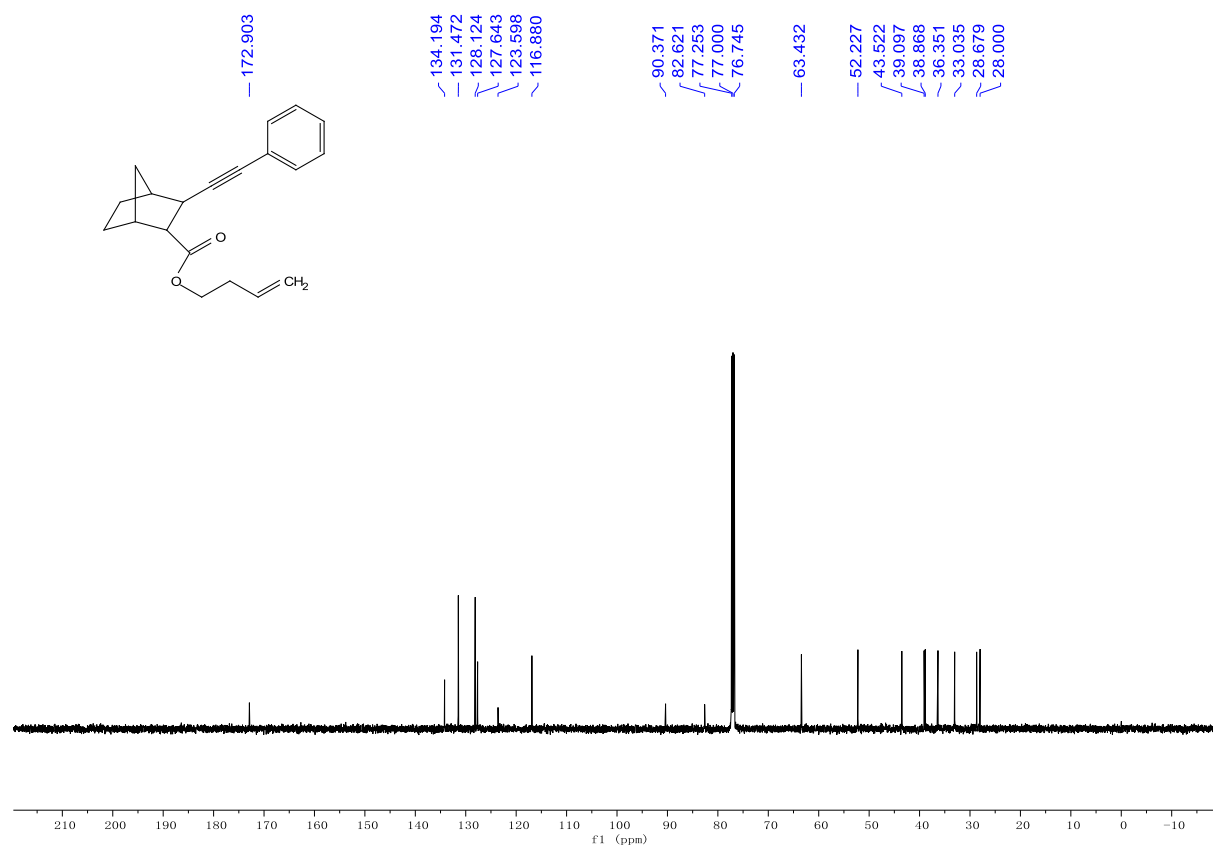


SUPPORTING INFORMATION

^1H NMR (500 MHz, CDCl_3) spectrum of compound 6i

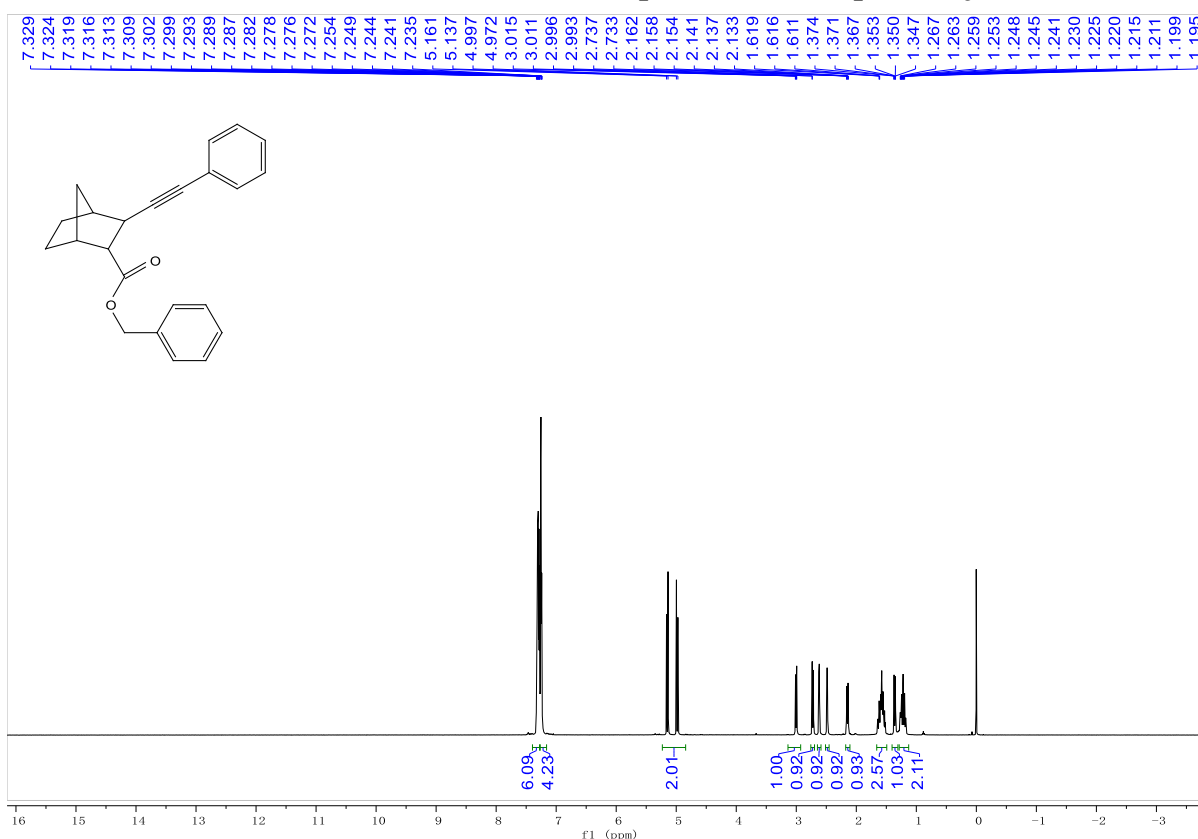


^{13}C NMR (125 MHz, CDCl_3) spectrum of compound 6i

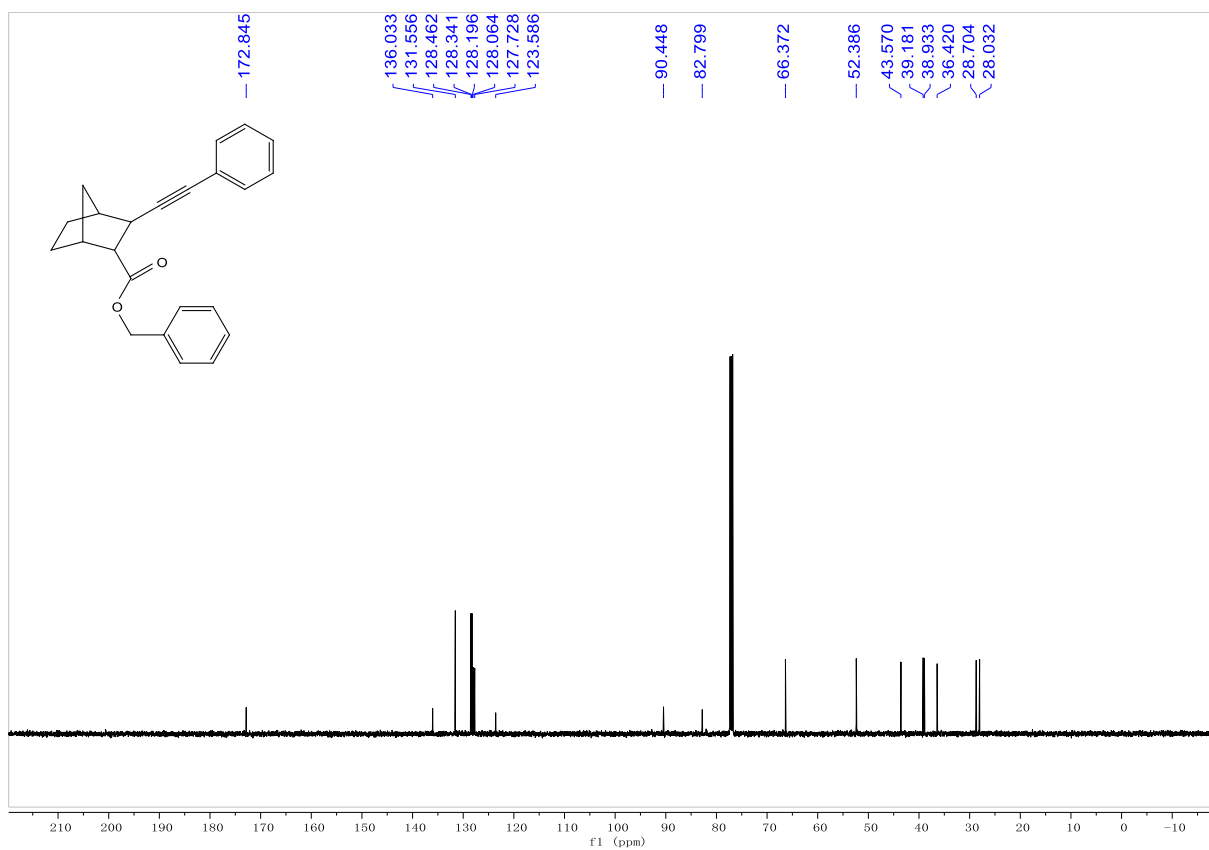


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 6j

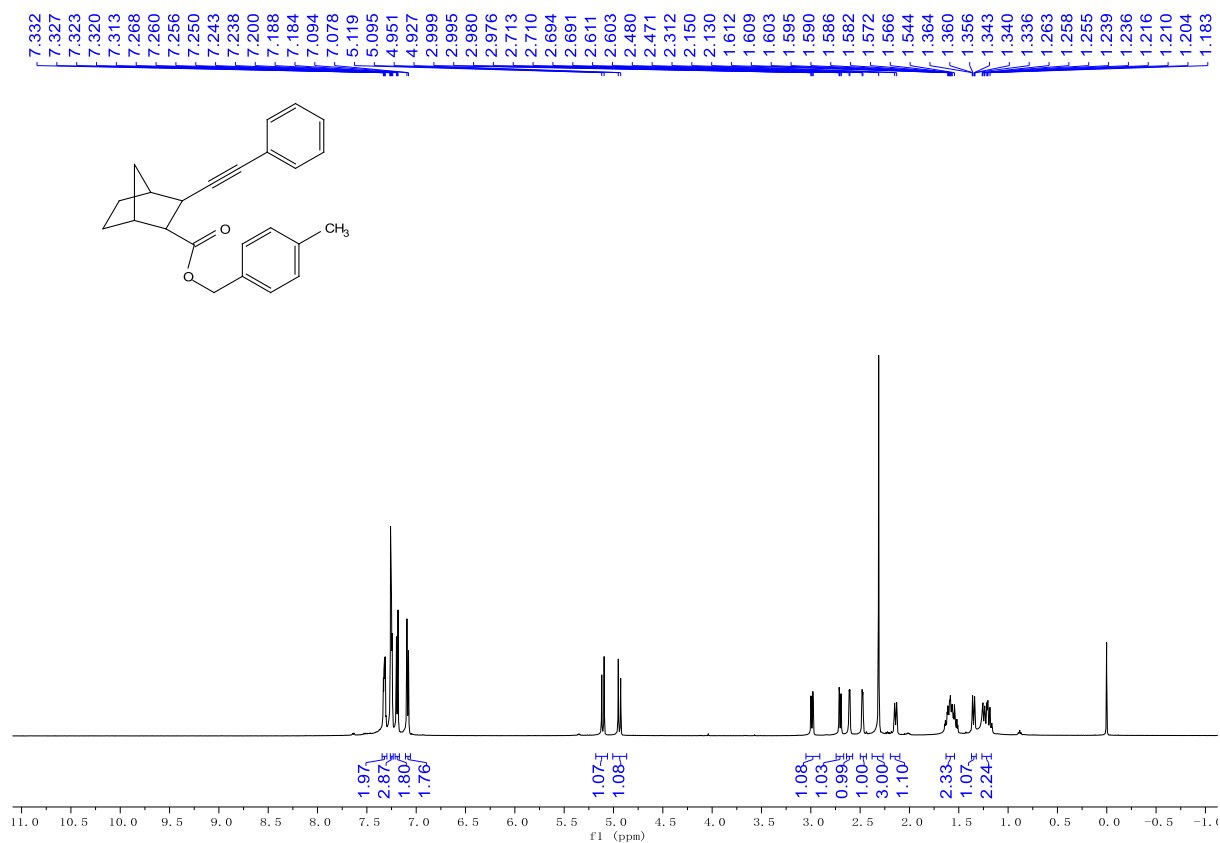


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 6j

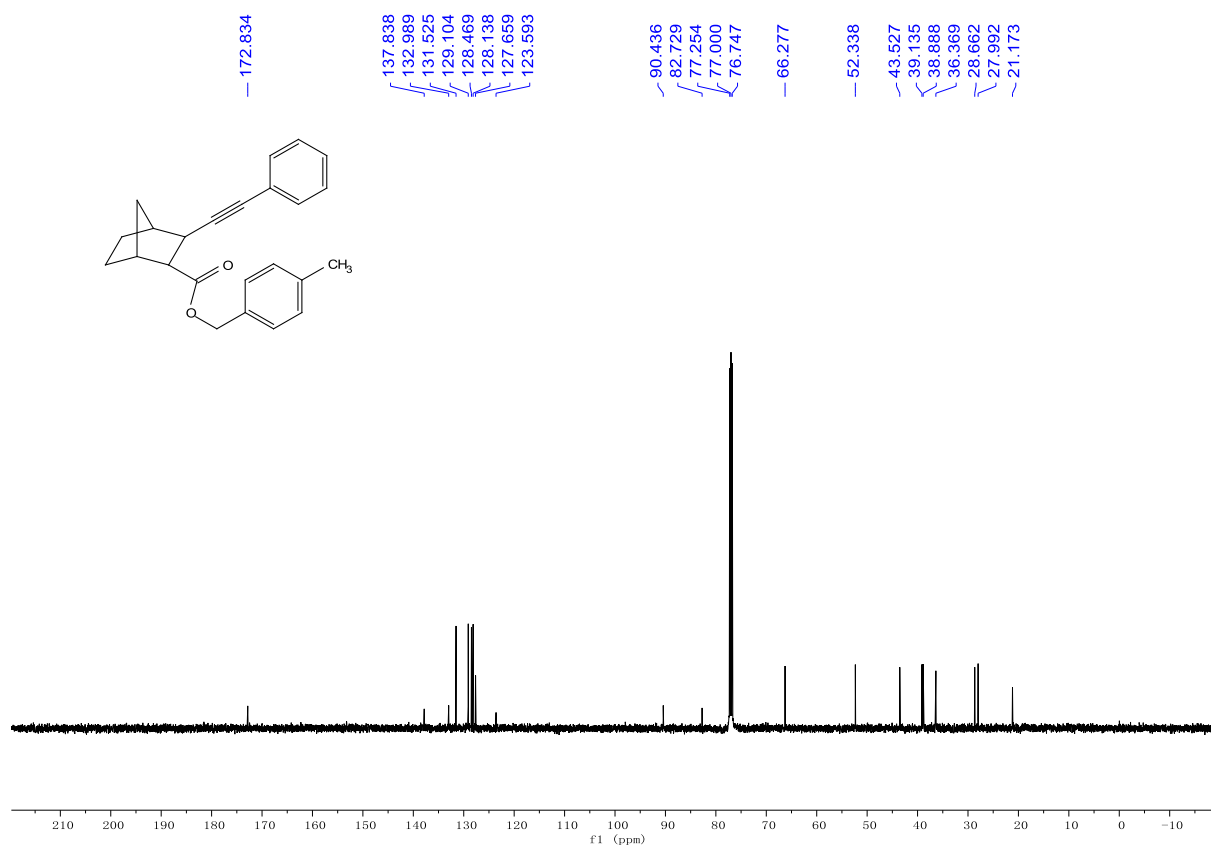


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 6k

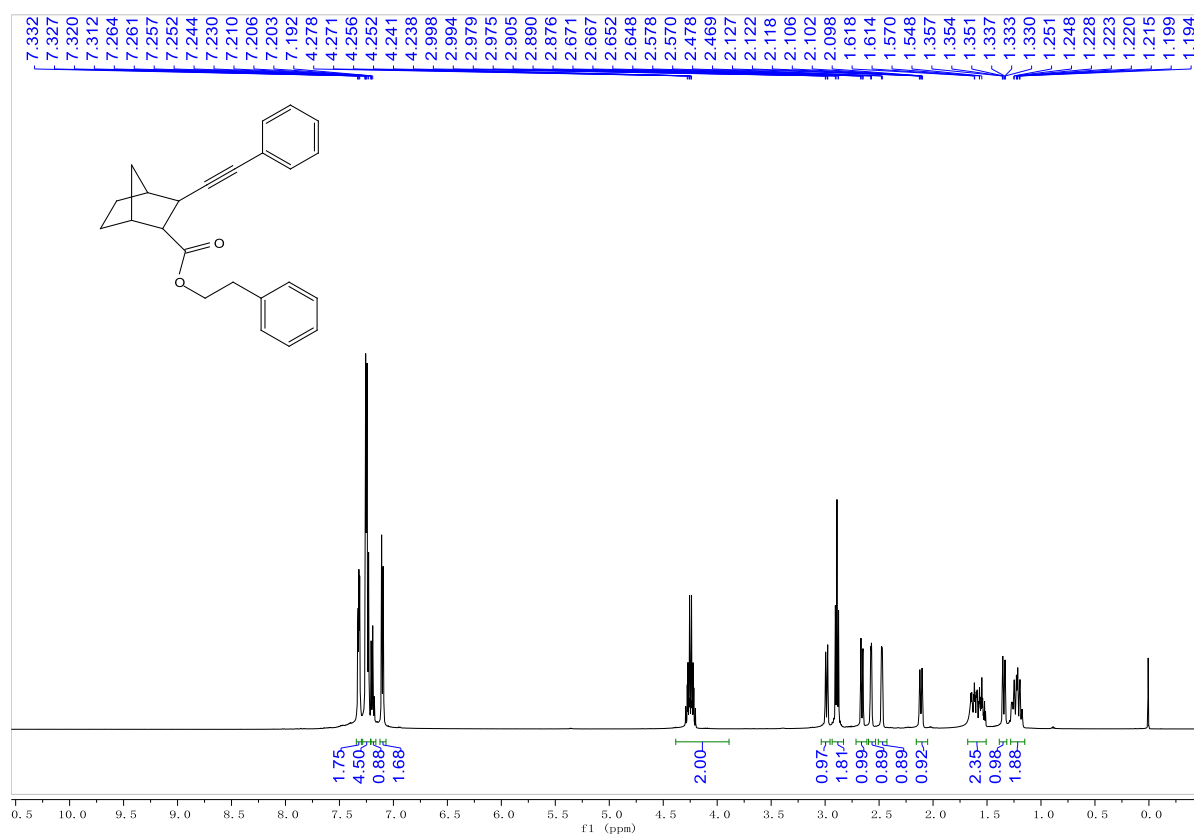


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 6k

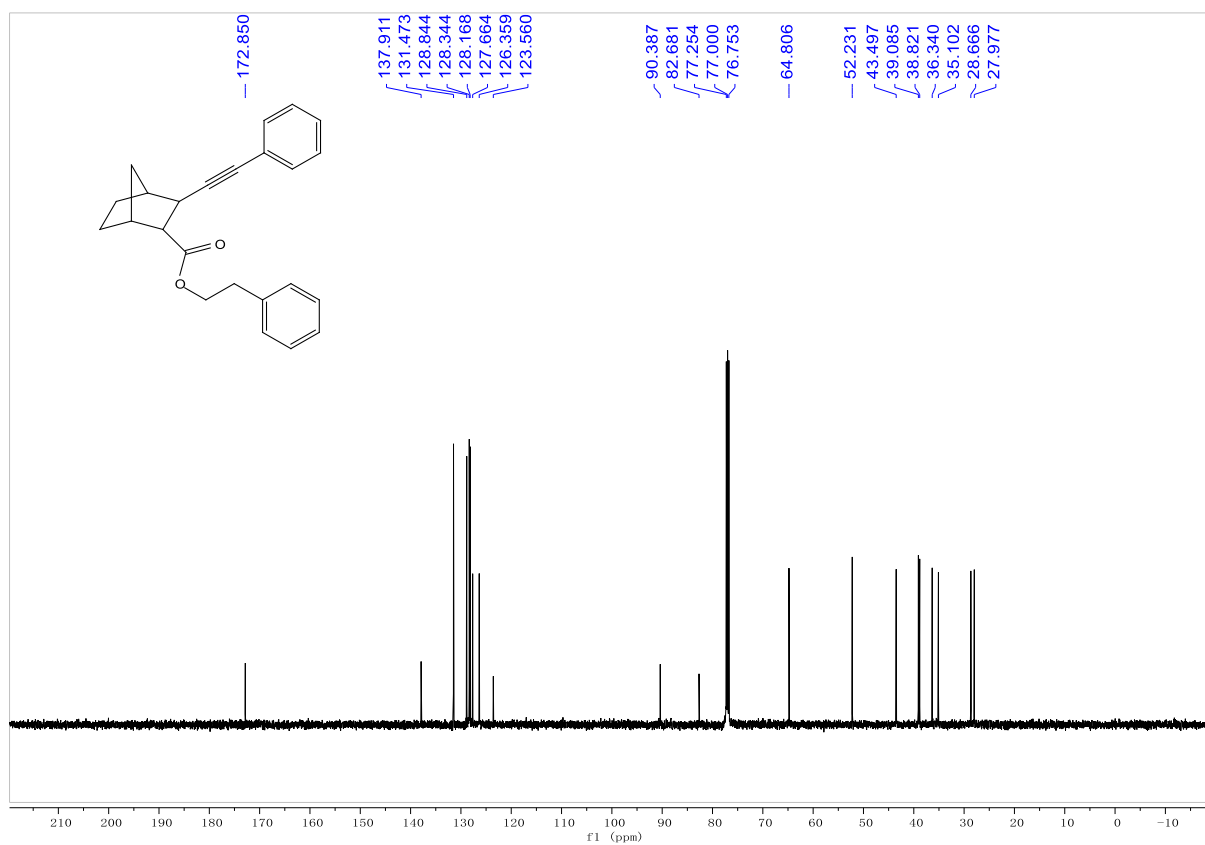


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 6l

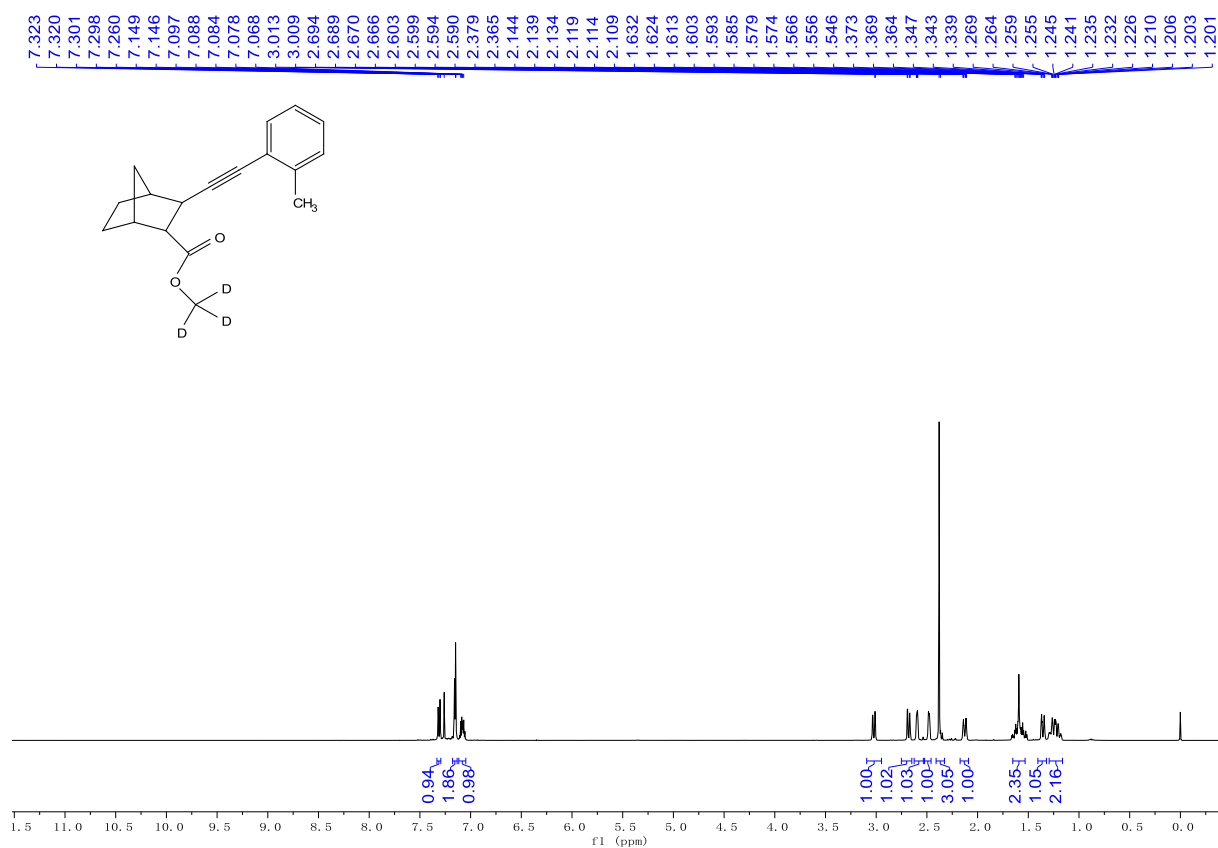


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 6l

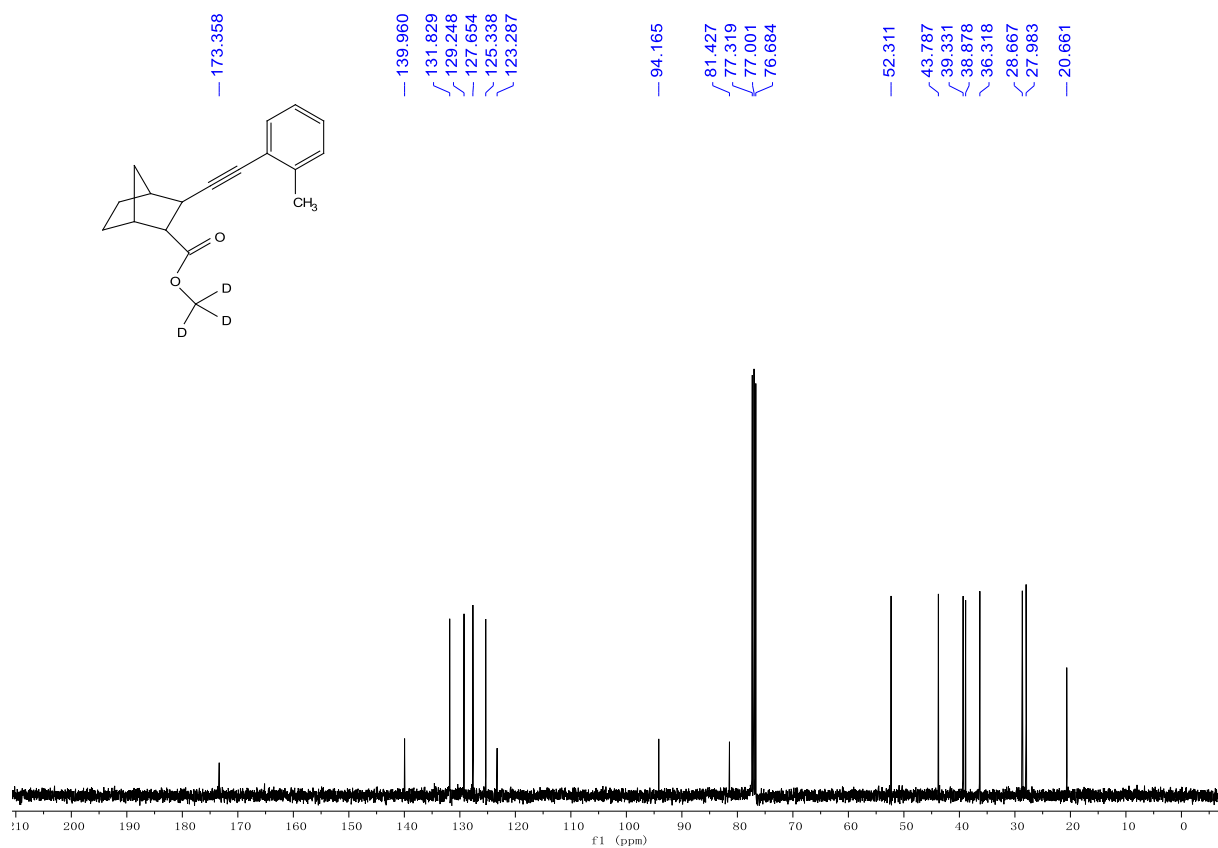


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 6m

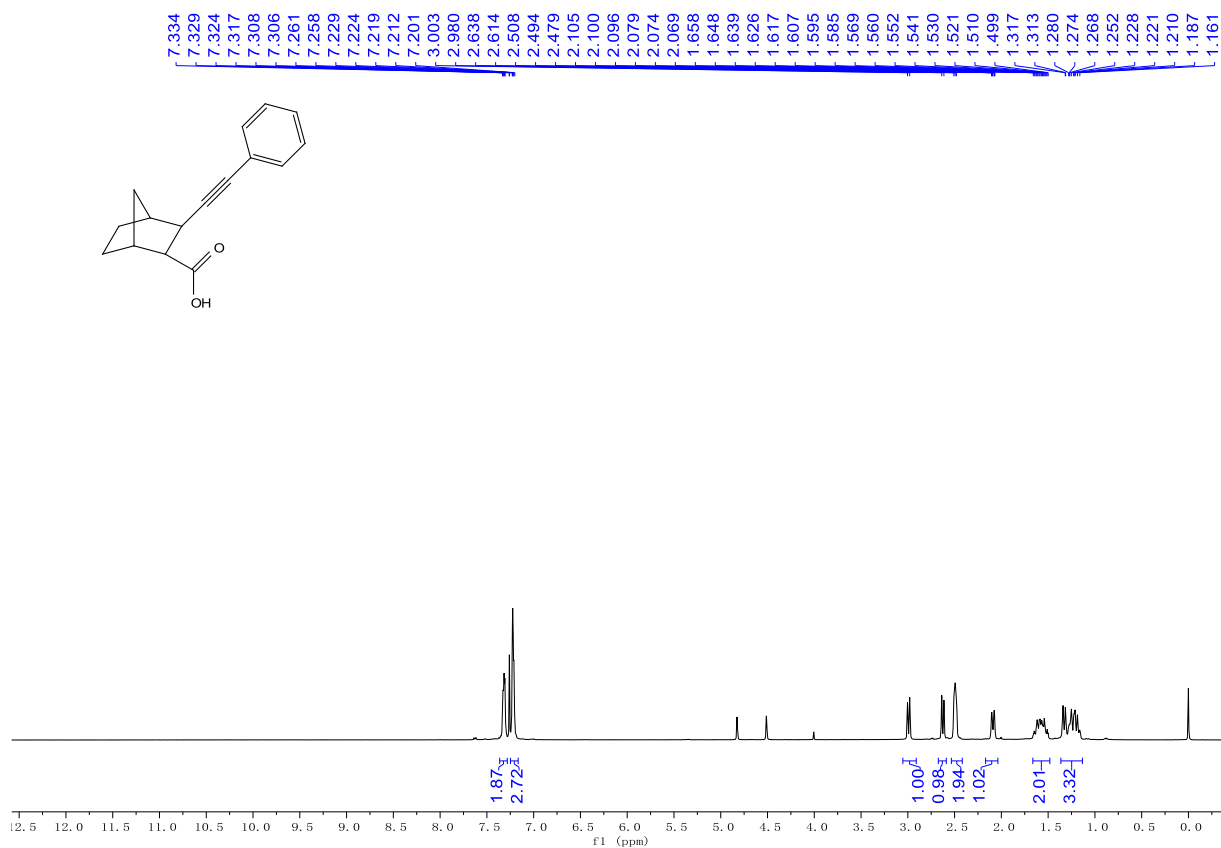


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 6m

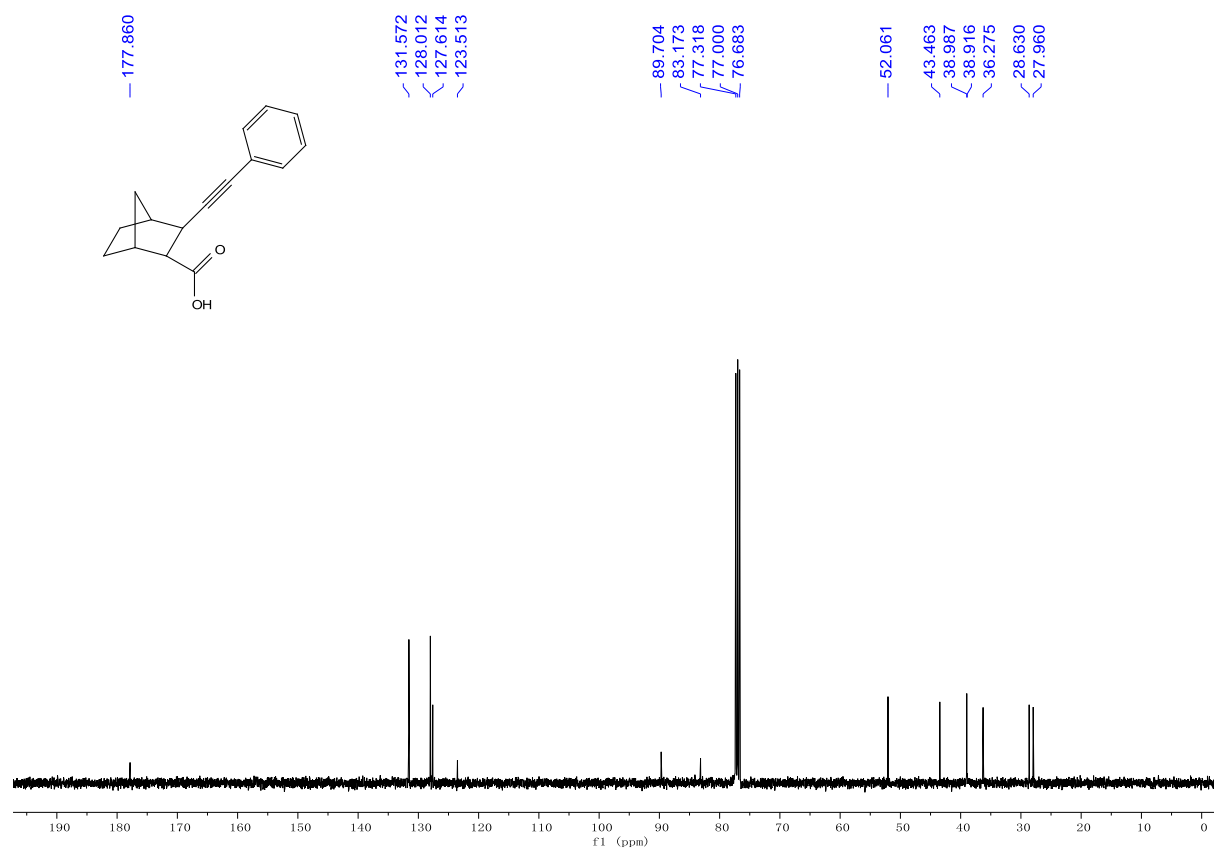


SUPPORTING INFORMATION

¹H NMR (400 MHz, CDCl₃) spectrum of compound 7a

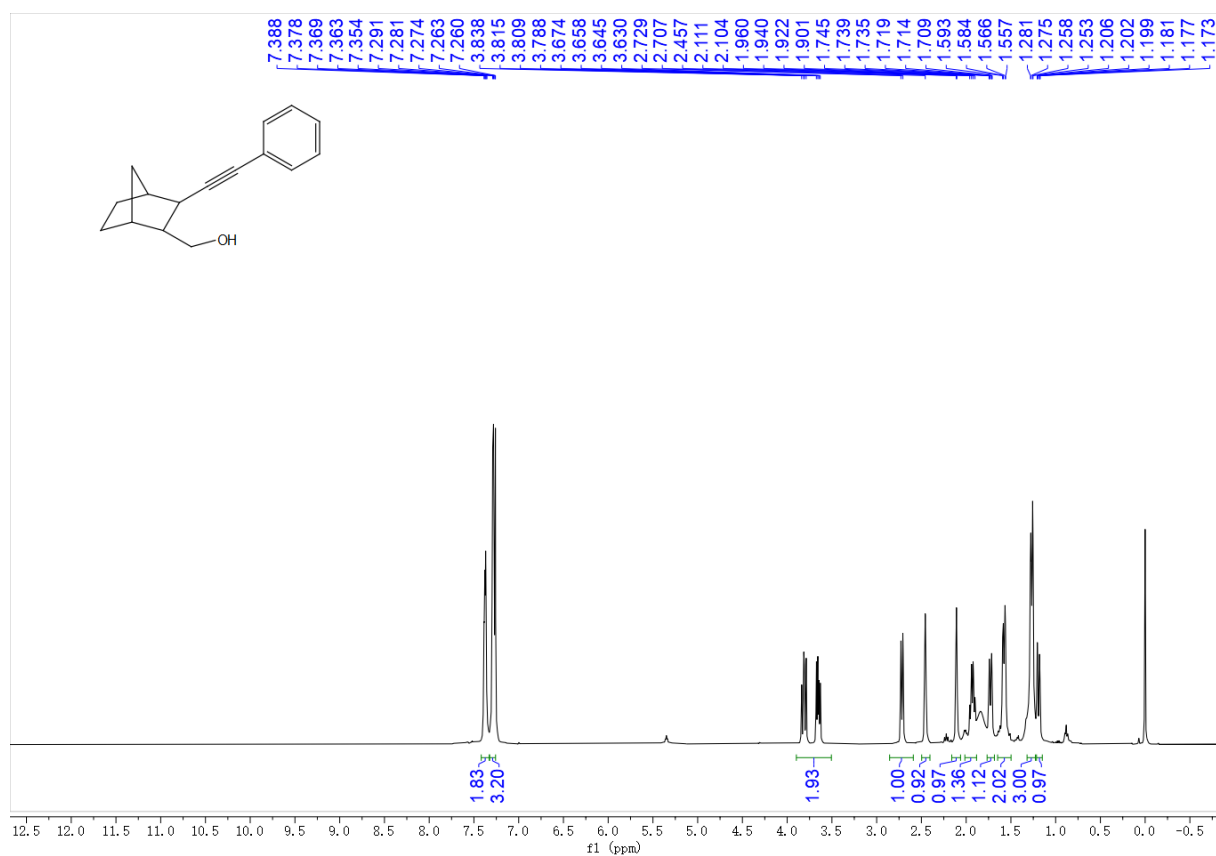


¹³C NMR (100 MHz, CDCl₃) spectrum of compound 7a

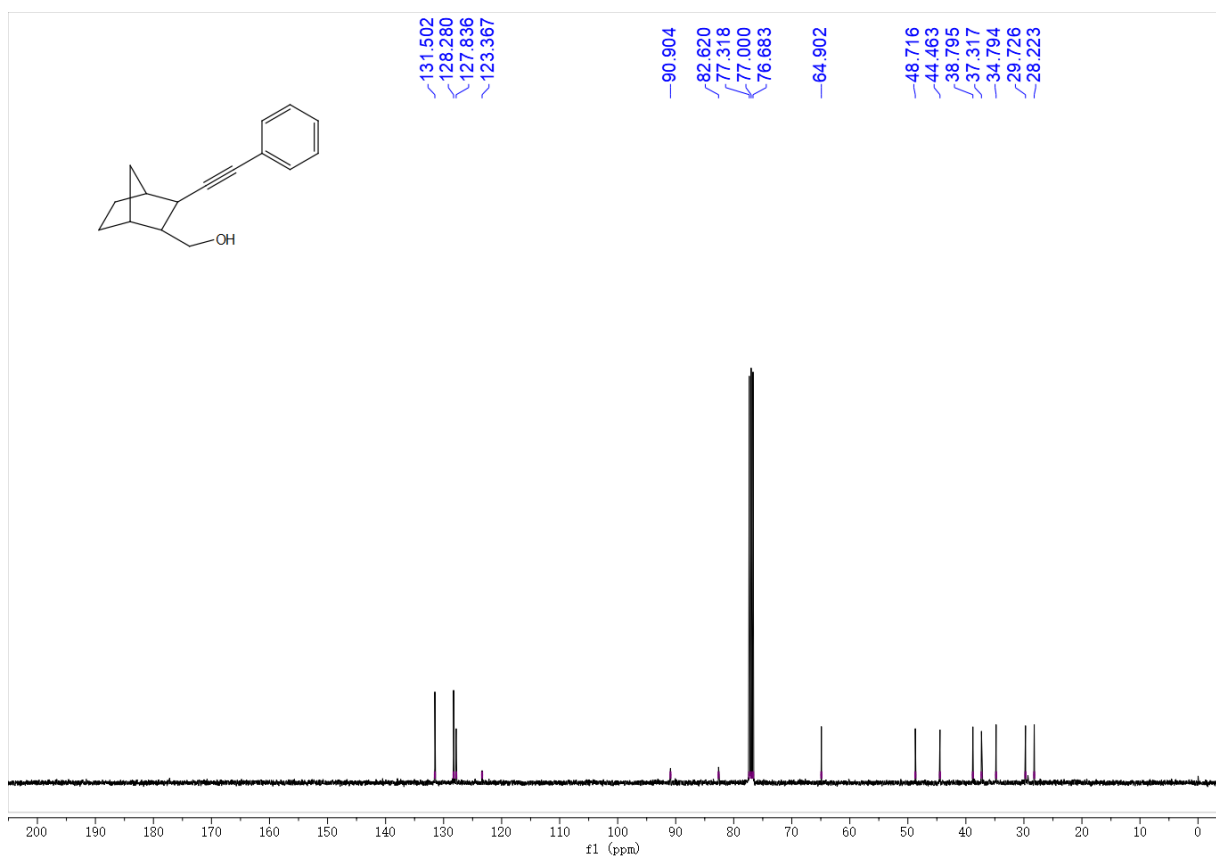


SUPPORTING INFORMATION

¹H NMR (400 MHz, CDCl₃) spectrum of compound 7b

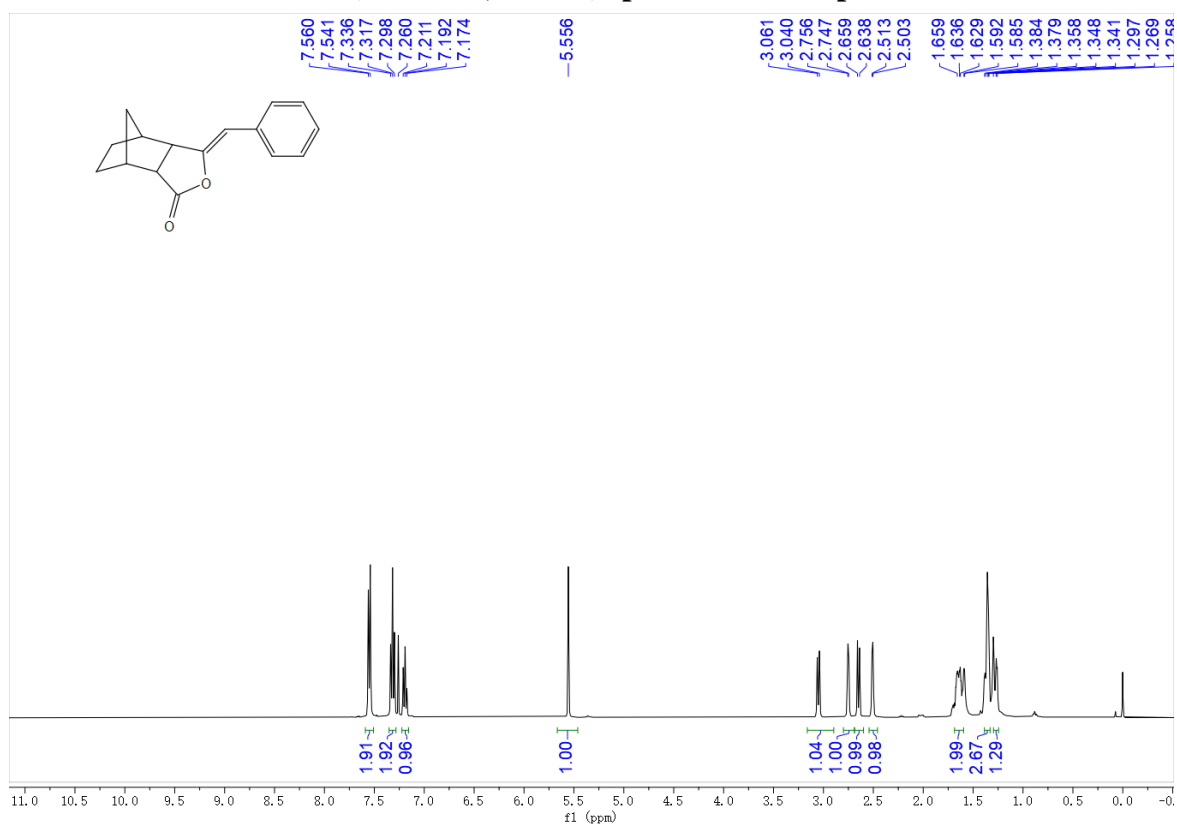


¹³C NMR (100 MHz, CDCl₃) spectrum of compound 7d

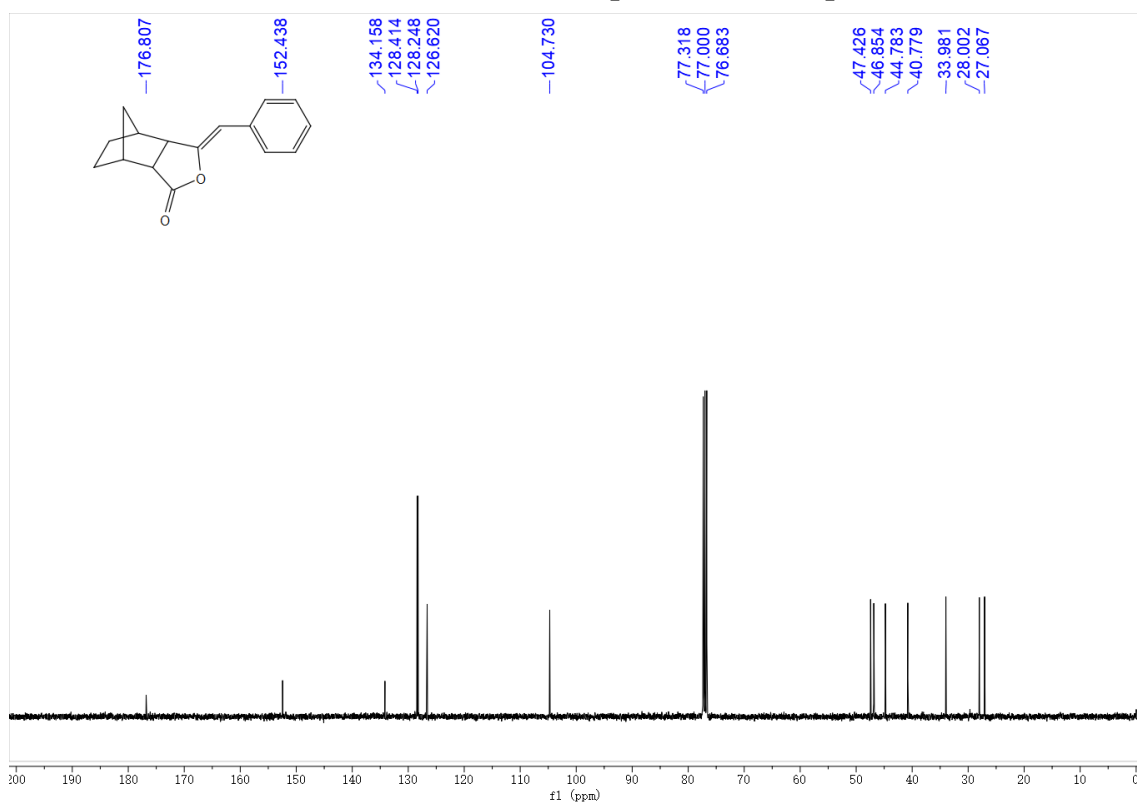


SUPPORTING INFORMATION

¹H NMR (400 MHz, CDCl₃) spectrum of compound 7c

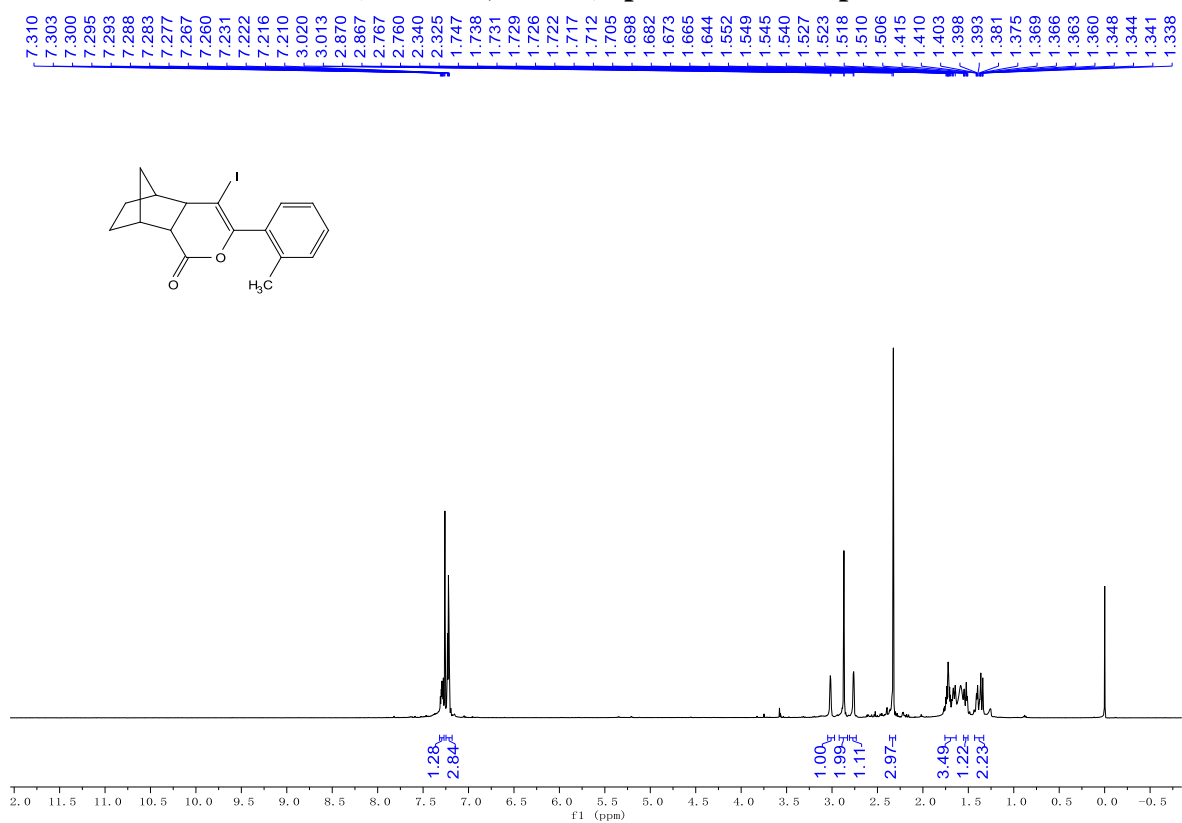


¹³C NMR (100 MHz, CDCl₃) spectrum of compound 7c

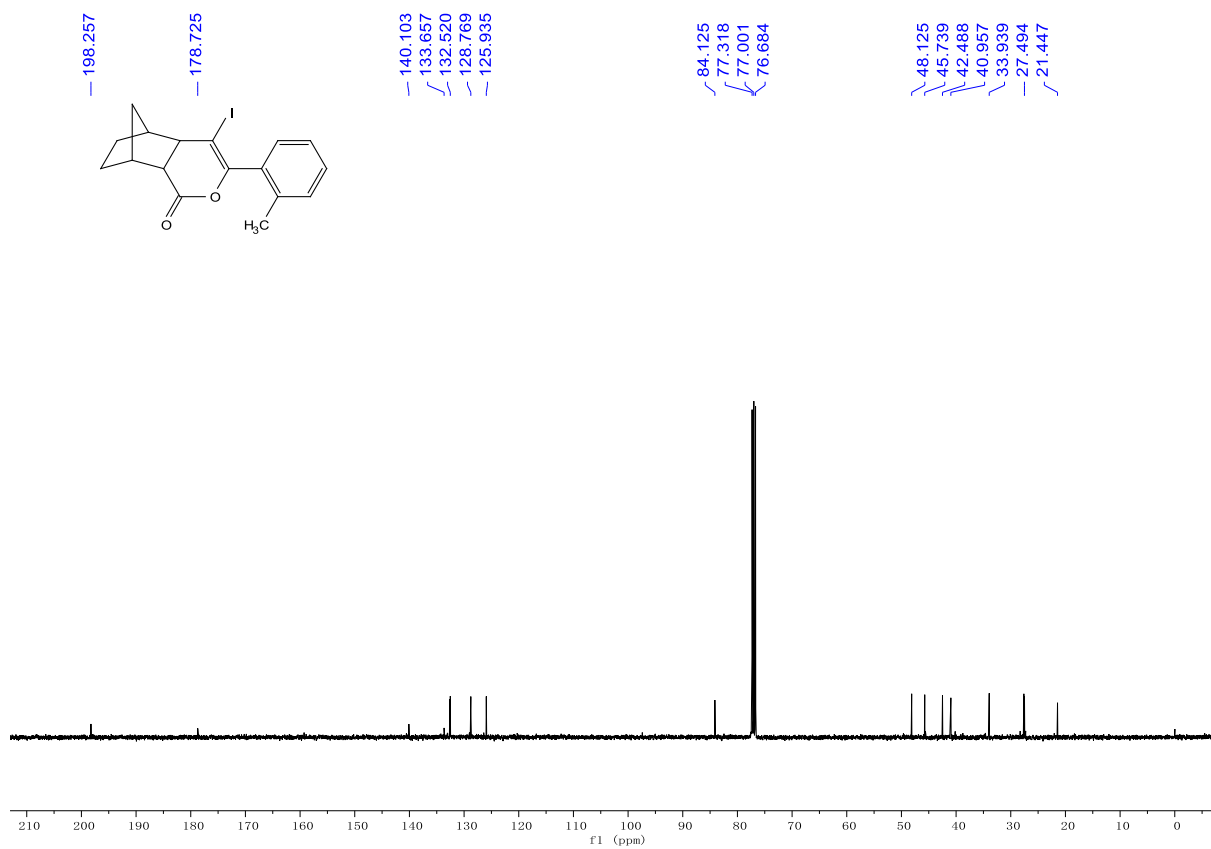


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¹H NMR (500 MHz, CDCl₃) spectrum of compound 7d

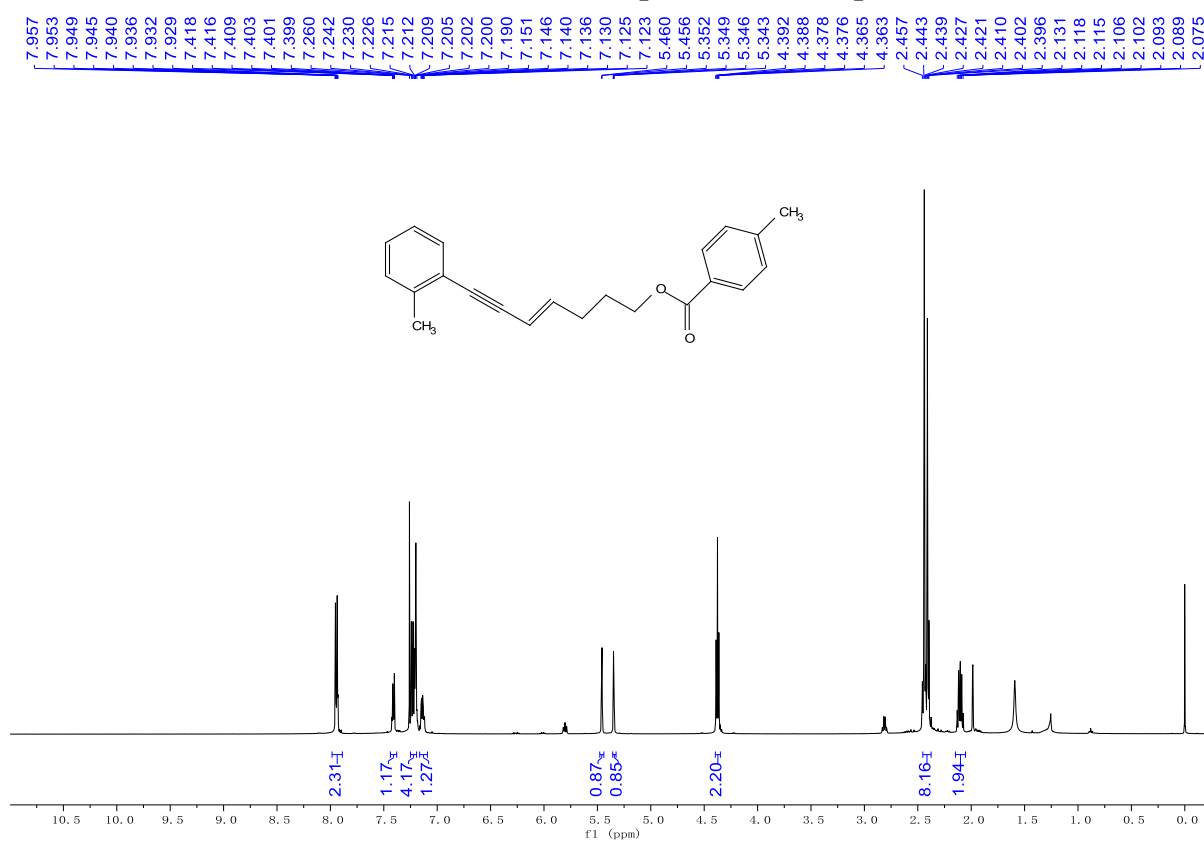


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 7d

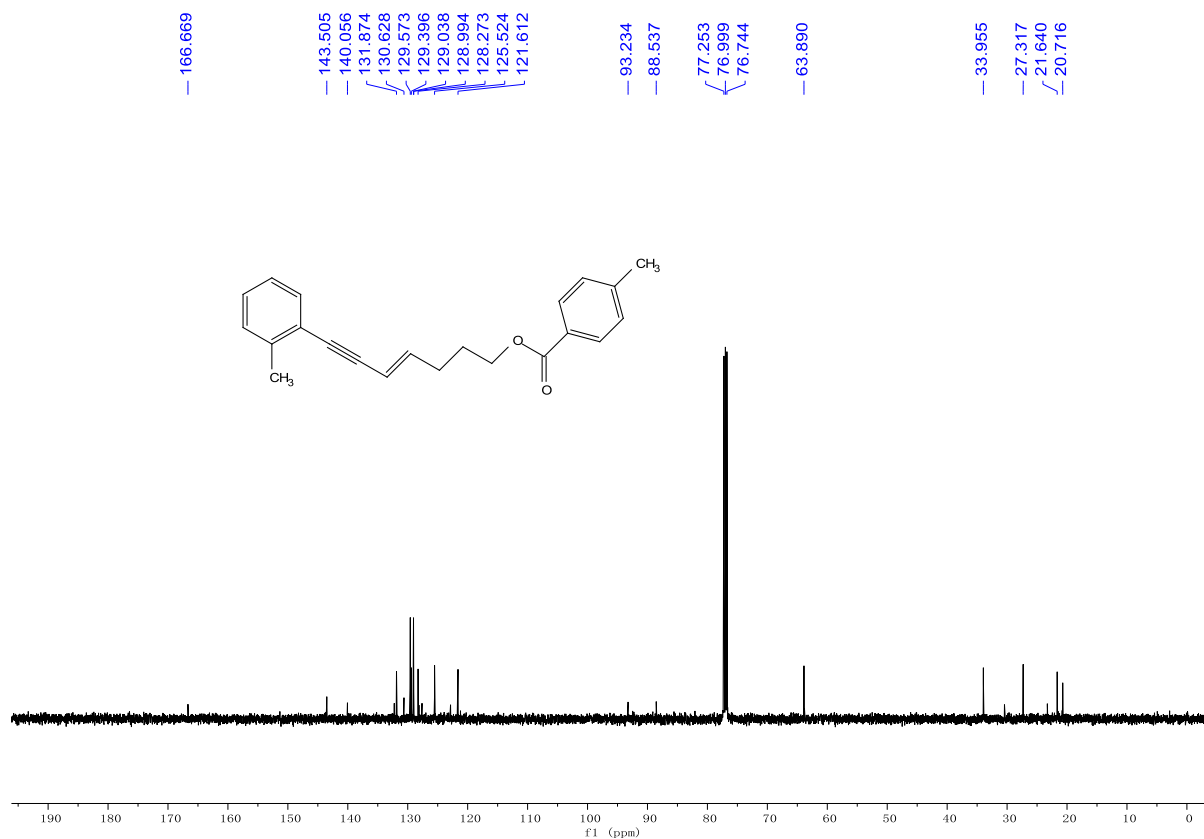


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 8a

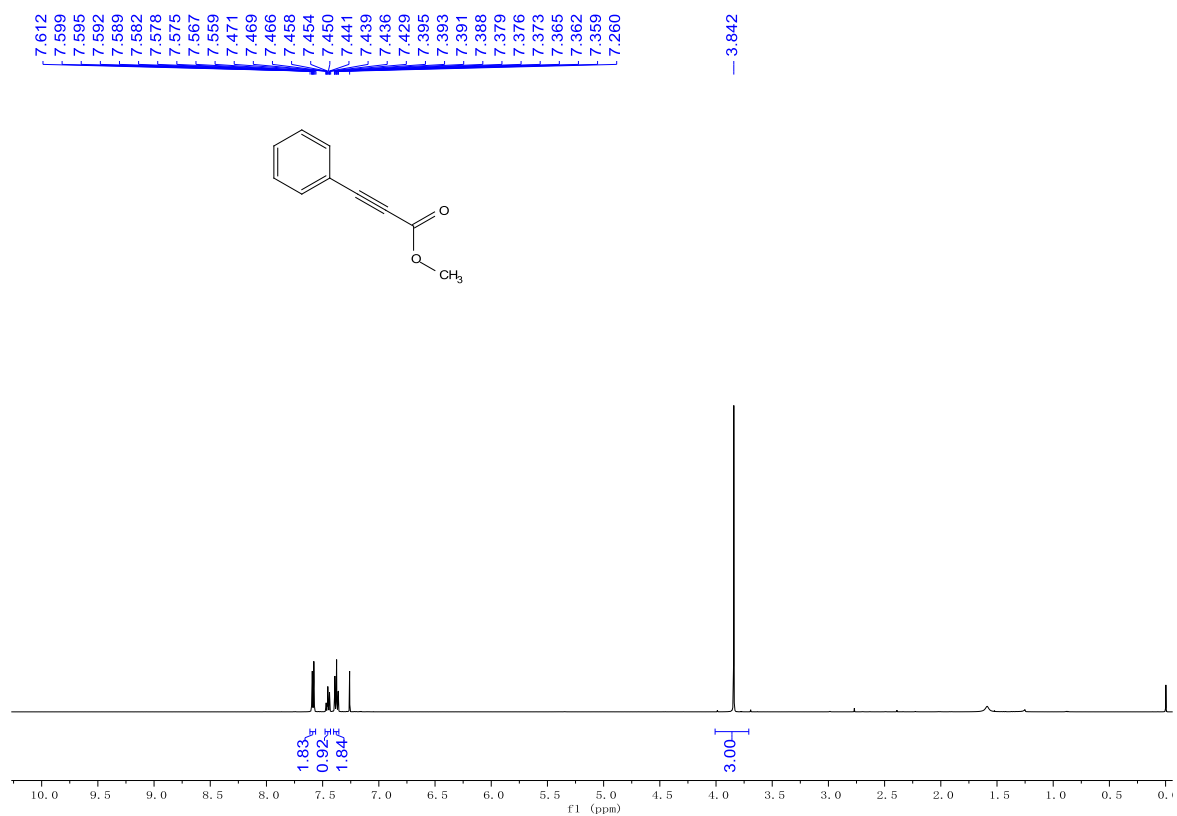


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 8a

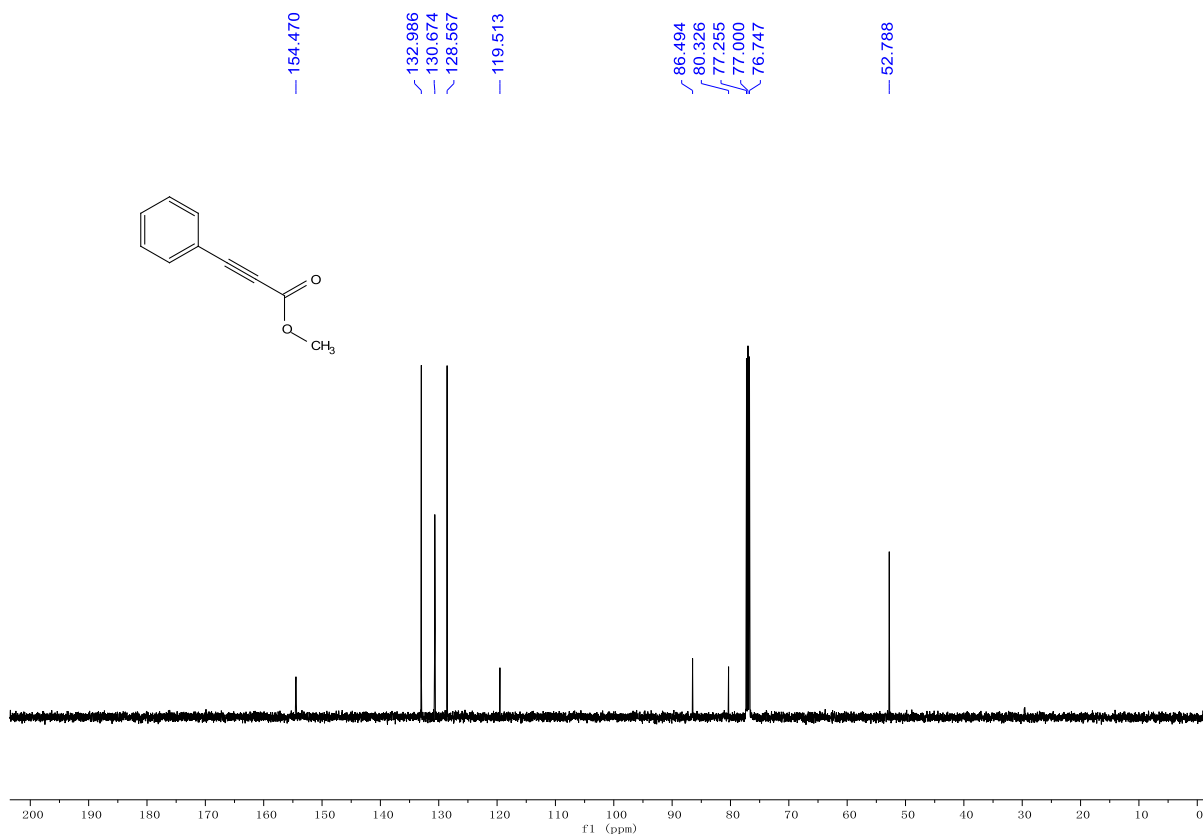


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 8b

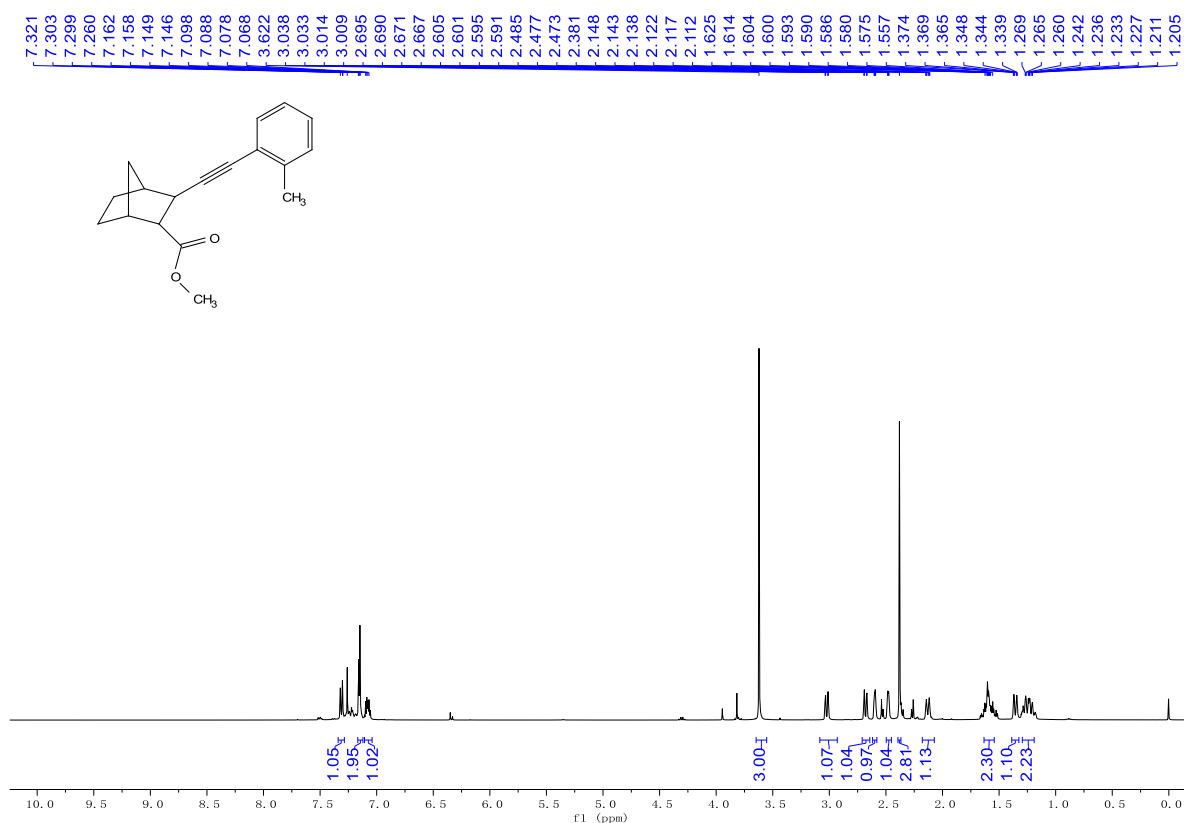


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 8b

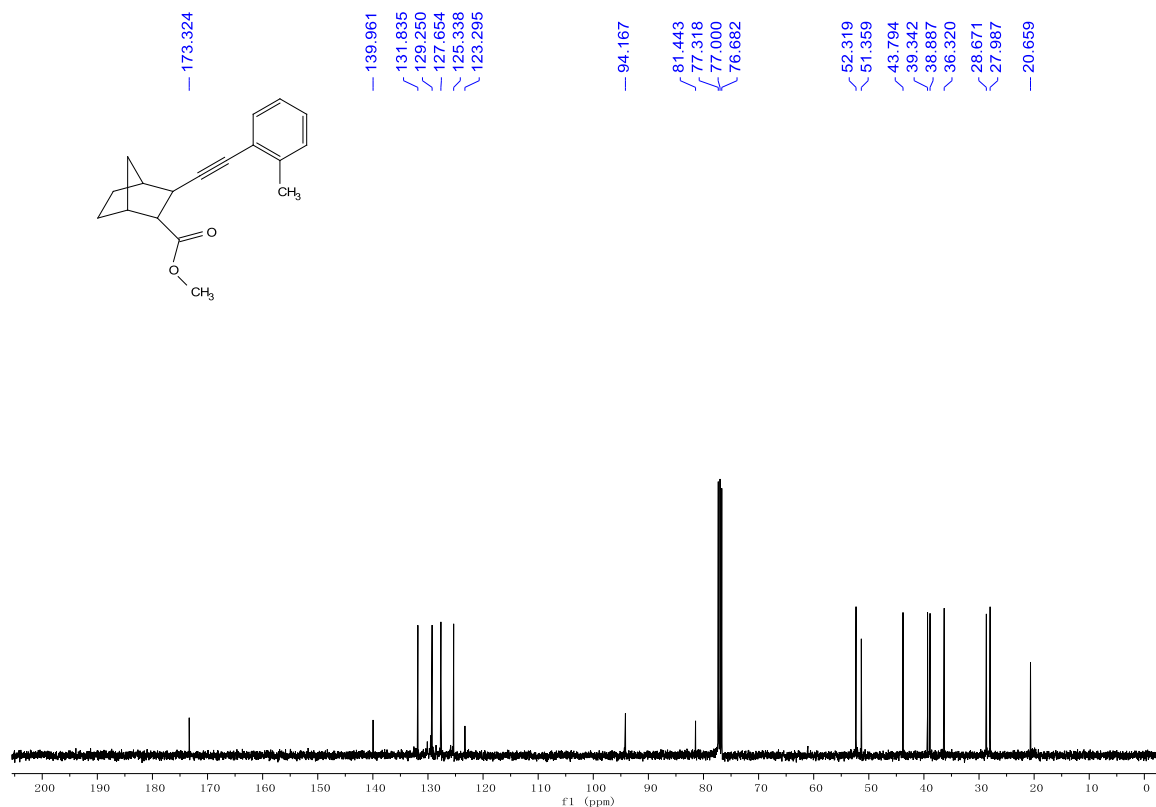


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4ax

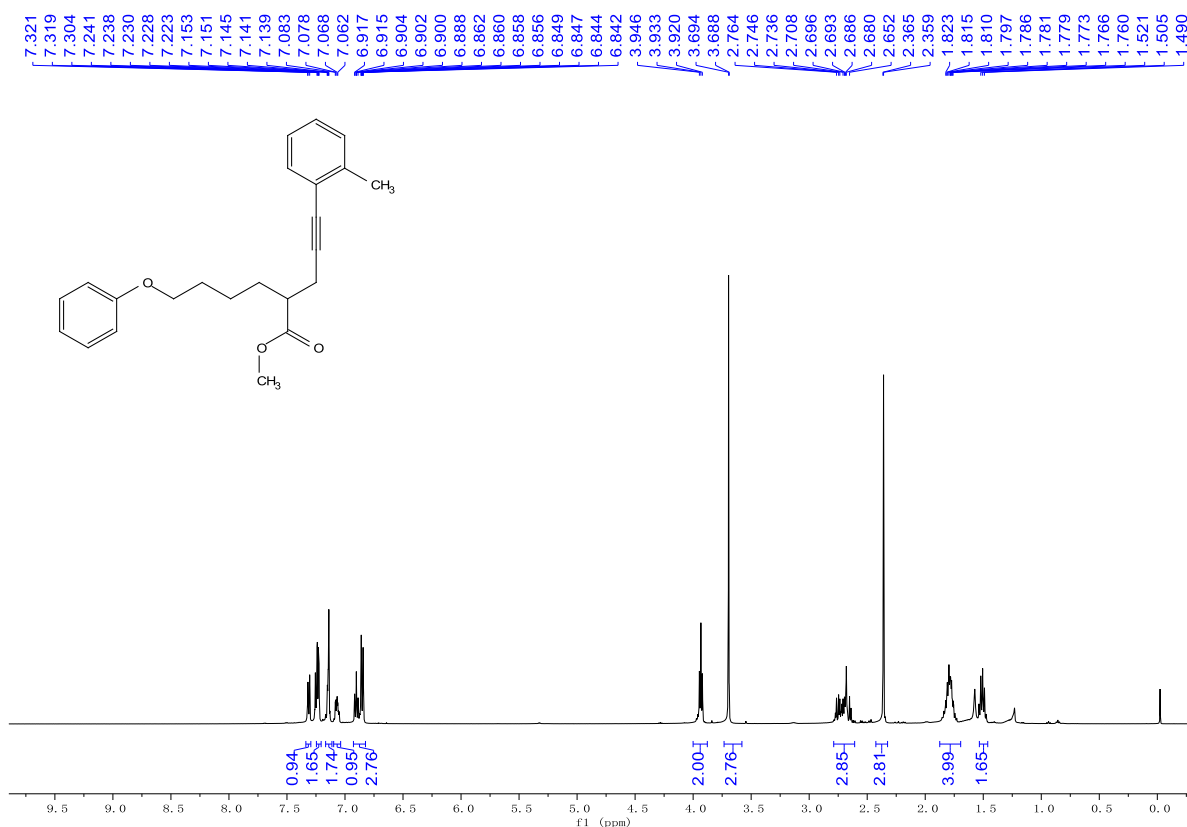


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4ax

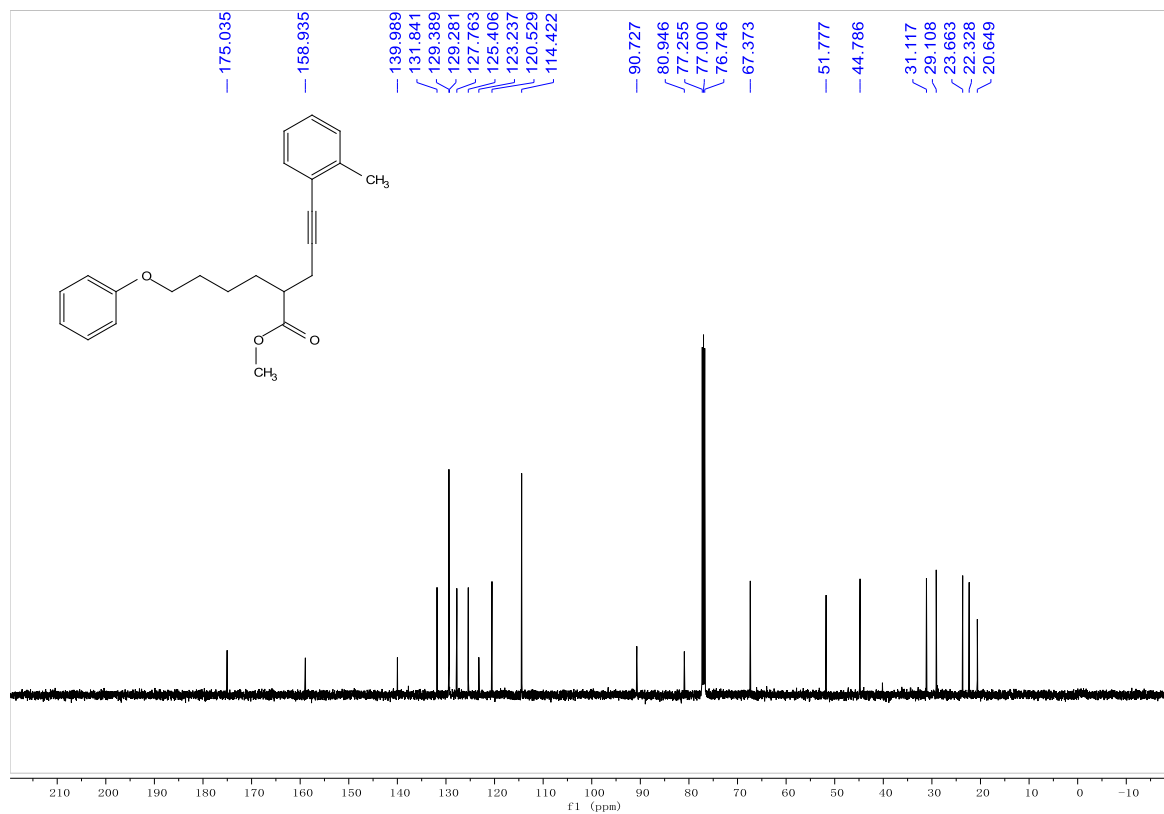


SUPPORTING INFORMATION

¹H NMR (500 MHz, CDCl₃) spectrum of compound 4au

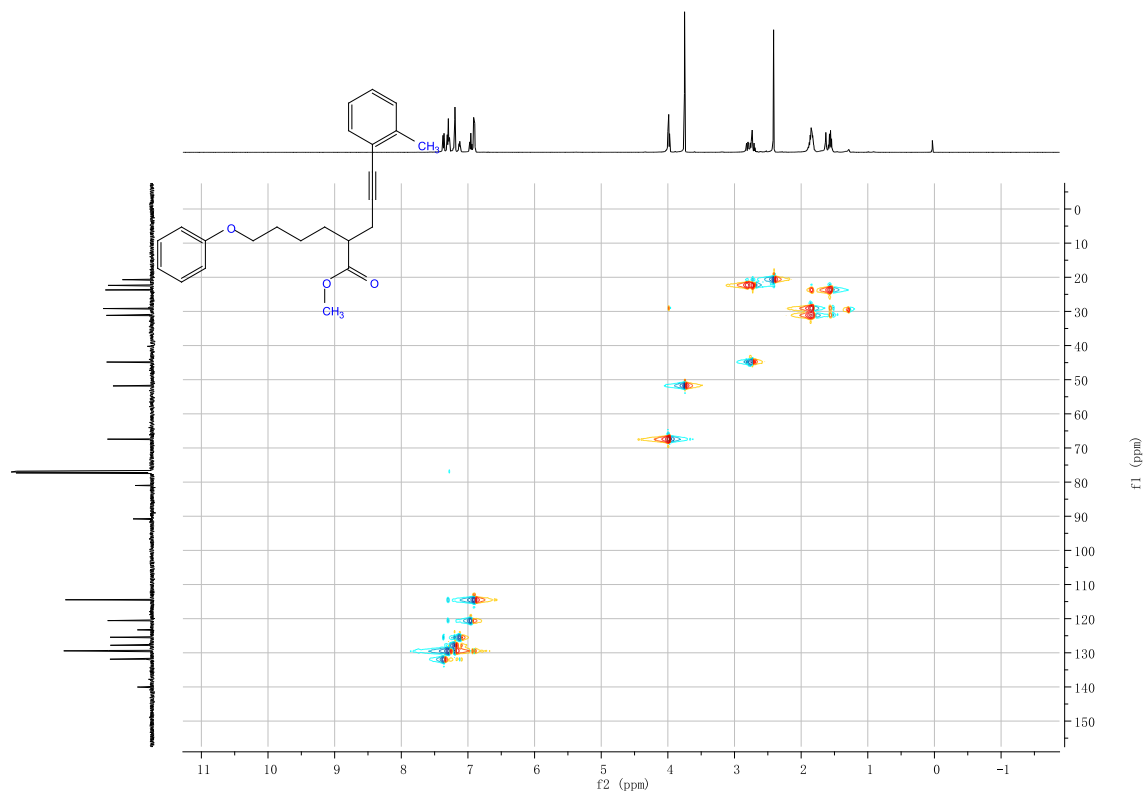


¹³C NMR (125 MHz, CDCl₃) spectrum of compound 4au

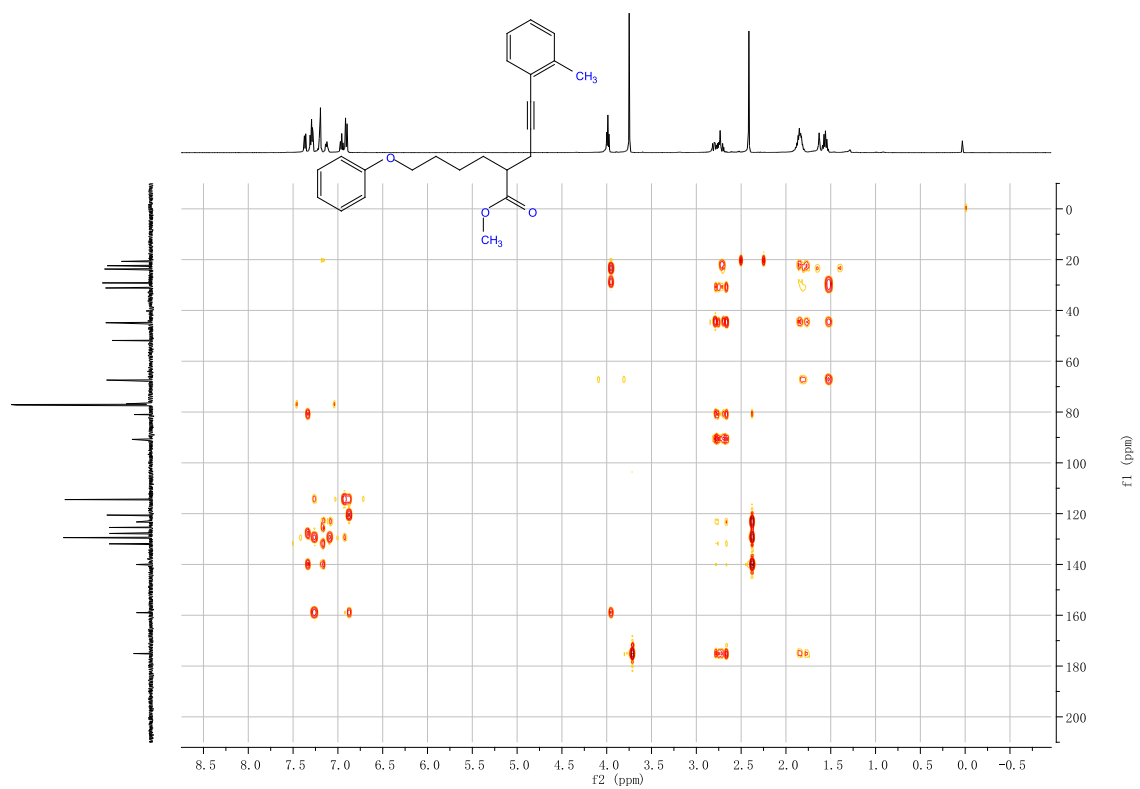


SUPPORTING INFORMATION

HSQC spectrum of compound 4au



HMBC spectrum of compound 4au

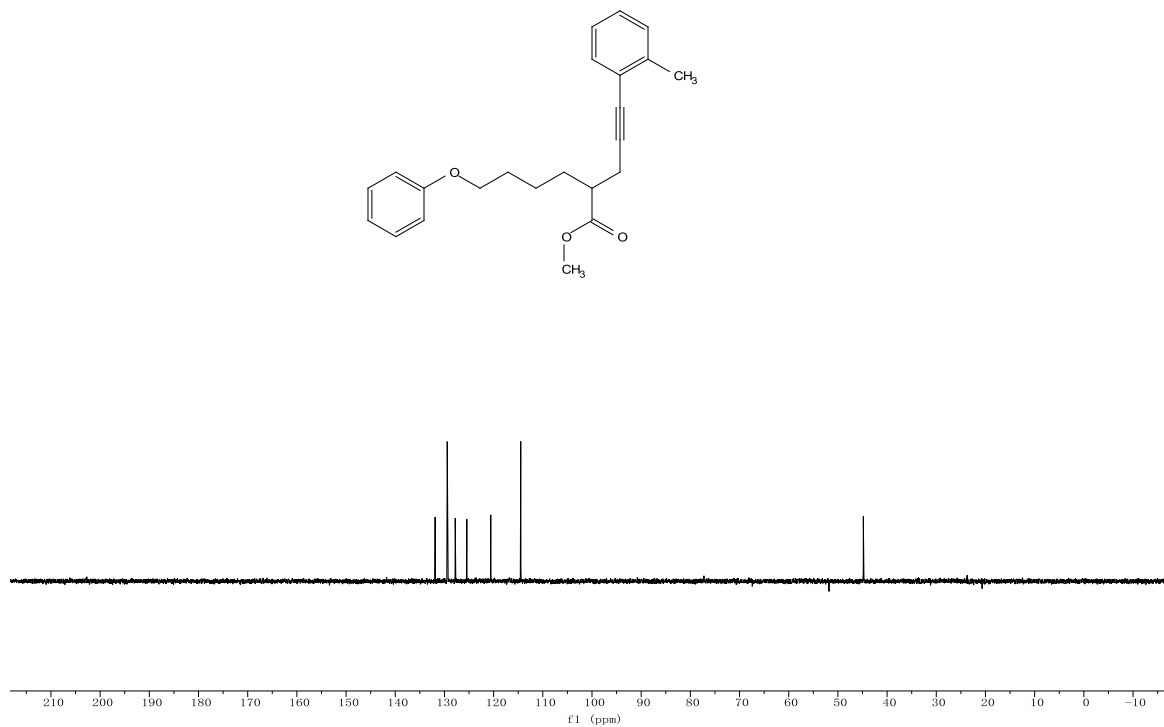


SUPPORTING INFORMATION

DEPT-135 spectrum of compound 4au



DEPT-90 spectrum of compound 4au



9. Density functional theory (DFT) calculations

Computational details

Considering acetonitrile as polar solvent, all structures were optimized and characterized in acetonitrile with the SMD^[8] solvent model (SCRF=SMD) at B3LYP^[9]-D3(BJ)^[10]/BSI level, BSI representing a basis set with SDD^[11] for Pd, Fe, Br and 6-31G(d,p) for other atoms. Harmonic frequency analysis calculations at the same level were performed to verify the optimized geometries to be minima (no imaginary frequency) or transition states (TSs, having unique one imaginary frequency). The energies were further improved by M06^[12]/BSII//B3LYP-D3(BJ)/BSI single-point calculations with solvent effects accounted by the SMD solvent model, using the experimental solvent (acetonitrile), BSII denotes a basis set with SDD for Pd and 6-311++G(d,p) for other atoms. All DFT calculations were carried out using Gaussian 09 program.^[13] Selected computed structures are illustrated using the CYLview.^[14]

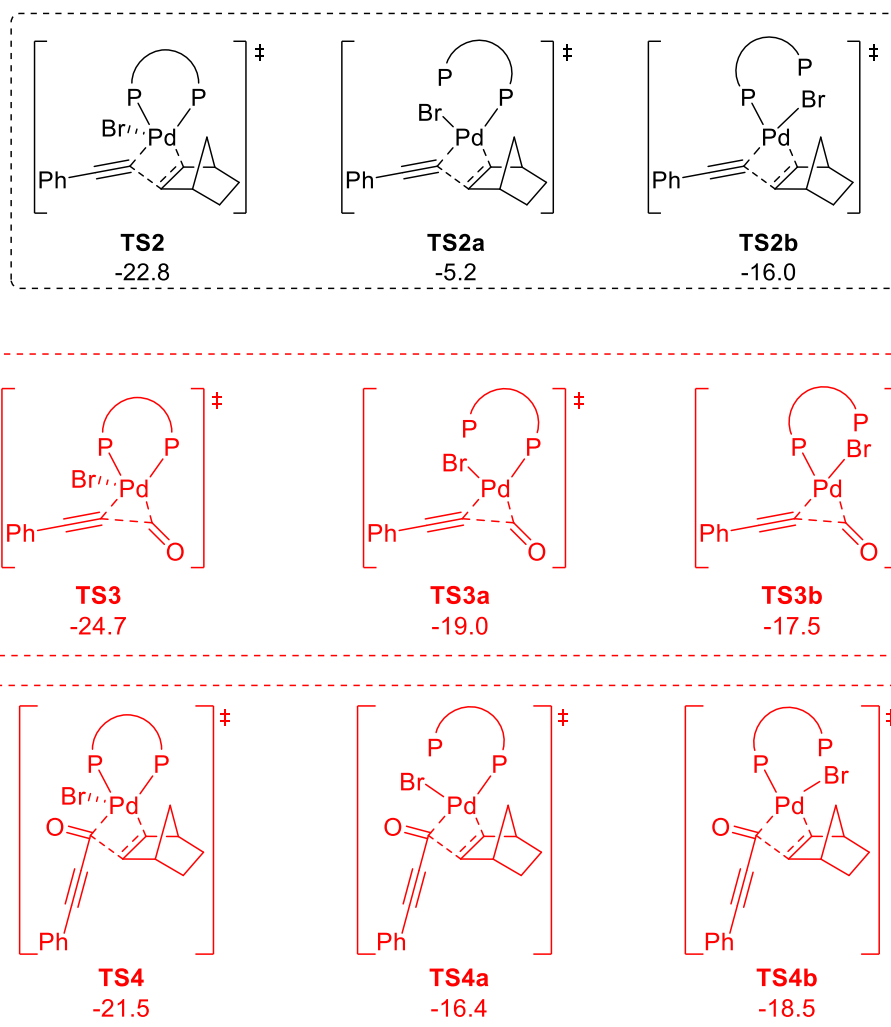


Figure S2. Conformational search of the key transition states.

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**Cartesian Coordinates in Å, SCF Energies and Free Energies (in a.u.) at 298.15 K and 1 atm
for the Optimized Structures [BSI=6-31G(d,p), BSII=6-311++G(d,p)]**

L₂Pd(0)

B3LYP-D3/BSI SCF energy in acetonitrile: -2247.248697 a.u.

M06/BSII SCF energy in acetonitrile: -2246.389538 a.u.

M06/BSII free energy in acetonitrile: -2245.93949 a.u.

Pd	0.00370100	-0.05603100	-1.58872100
P	-2.05772500	-0.01497600	-0.58245600
P	2.05528000	-0.02871100	-0.56906700
Fe	-0.01025100	0.16675500	2.20962500
C	2.06138900	0.17476800	2.38787800
C	0.73028100	-1.62821400	2.95323600
C	1.47792300	-0.53208600	3.48141900
C	-0.86753600	1.81528100	1.30059000
C	-1.50934300	1.02209500	3.36942000
C	-0.76557300	2.04277500	2.70282000
H	2.66677500	1.06748200	2.45870900
H	0.13966200	-2.33205300	3.52508700
H	1.55387900	-0.25692100	4.52557300
H	-0.38404000	2.39318700	0.52571000
H	-1.59150500	0.89027200	4.44073700
H	-0.18506000	2.82256600	3.17838300
C	0.84254300	-1.59265100	1.53361900
C	1.67678600	-0.47986200	1.17051800
C	-2.07892900	0.16848000	2.37804900
C	-1.68855400	0.65436800	1.08555900
H	0.35843300	-2.26510100	0.83967200
H	-2.67431100	-0.71386500	2.56628500
C	-3.51141500	1.00333900	-1.09938100
C	-3.85086400	1.00699300	-2.46236100
C	-4.27824300	1.76651700	-0.20449300
C	-4.94538500	1.74316000	-2.91939600
H	-3.25248000	0.43324600	-3.16704400
C	-5.36711200	2.51145200	-0.66489900
H	-4.02980600	1.77720500	0.85245300
C	-5.70473100	2.49884900	-2.02080600
H	-5.19933100	1.73486100	-3.97576100
H	-5.95247400	3.09909800	0.03712700
H	-6.55141200	3.07932400	-2.37641600
C	3.45179000	-1.16407800	-0.98562600
C	4.20961700	-1.84945600	-0.02296700
C	3.75444600	-1.34286900	-2.34555600
C	5.25279800	-2.69238400	-0.41568400
H	3.98938500	-1.72392500	1.03289700
C	4.80409900	-2.17594500	-2.73607500
H	3.16198600	-0.82858500	-3.09933300

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C	5.55367900	-2.85505200	-1.77069200
H	5.83161000	-3.21957000	0.33783200
H	5.02998100	-2.30259600	-3.79130500
H	6.36483700	-3.51127100	-2.07341900
C	2.90314800	1.60190200	-0.36042300
C	4.19067600	1.71921600	0.18863000
C	2.21639000	2.76632600	-0.73838300
C	4.77056700	2.97660800	0.36810100
H	4.74286700	0.82995800	0.47796400
C	2.79441700	4.02487600	-0.55221300
H	1.22661600	2.68189400	-1.17991700
C	4.07205600	4.13182400	0.00286300
H	5.76744200	3.05414000	0.79325900
H	2.24962100	4.91775300	-0.84625700
H	4.52548800	5.10907300	0.14329300
C	-2.83011900	-1.64888600	-0.18614100
C	-4.09264200	-1.75912000	0.41932400
C	-2.11259300	-2.81910800	-0.48002900
C	-4.61668500	-3.01335000	0.73828200
H	-4.66871000	-0.86644400	0.64383700
C	-2.63583800	-4.07408600	-0.15731300
H	-1.14158100	-2.74189800	-0.96328600
C	-3.88787900	-4.17277300	0.45465800
H	-5.59386700	-3.08534600	1.20782800
H	-2.06822800	-4.97115100	-0.38877800
H	-4.29775600	-5.14766400	0.70345600

CO

B3LYP-D3/BSI SCF energy in acetonitrile: -113.3020108 a.u.

M06/BSII SCF energy in acetonitrile: -113.280864 a.u.

M06/BSII free energy in acetonitrile: -113.29497 a.u.

C	0.00000000	0.00000000	-0.64995200
O	0.00000000	0.00000000	0.48746400

L₂Pd(0)(CO)₂

B3LYP-D3/BSI SCF energy in acetonitrile: -2473.946021 a.u.

M06/BSII SCF energy in acetonitrile: -2473.022382 a.u.

M06/BSII free energy in acetonitrile: -2472.563839 a.u.

Pd	0.01634900	0.18941600	-1.69493700
P	1.94116400	0.04982100	-0.19842300
P	-1.93470400	0.01764600	-0.22594800
Fe	-0.01082600	-0.43175300	2.55718700
C	-2.07456300	-0.42091700	2.68973500
C	-0.73647600	1.30382200	3.44976500
C	-1.51755500	0.17972000	3.85708000
C	0.79466600	-1.98071700	1.46661600
C	1.48047700	-1.43920300	3.60270000
C	0.70979800	-2.36547900	2.83530600

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H	-2.69342600	-1.30670100	2.66305500
H	-0.15538500	1.94585200	4.09875800
H	-1.63264300	-0.18151600	4.87081400
H	0.29861900	-2.45568500	0.63243300
H	1.58029400	-1.43361700	4.68041900
H	0.12355000	-3.18610000	3.22771000
C	-0.80126800	1.39434400	2.02976400
C	-1.63162300	0.32619200	1.54525200
C	2.04937500	-0.48476500	2.70847800
C	1.62522200	-0.81196800	1.37539900
H	-0.29398300	2.12261800	1.41418600
H	2.65854300	0.36404600	2.98542800
C	3.34413500	-0.90839700	-0.91844300
C	3.70953300	-0.63469600	-2.24757100
C	4.04322600	-1.89593400	-0.20879500
C	4.76034100	-1.32633900	-2.85043000
H	3.16323200	0.11715900	-2.81190200
C	5.08825800	-2.59639700	-0.81898500
H	3.77573900	-2.12045800	0.81912900
C	5.45027600	-2.31245000	-2.13765000
H	5.03406400	-1.10289600	-3.87790100
H	5.61992500	-3.36193900	-0.26045800
H	6.26247900	-2.85803900	-2.60969900
C	-3.25897100	1.23865500	-0.63020600
C	-3.94938400	1.97165000	0.34679900
C	-3.57654900	1.43850100	-1.98436000
C	-4.93866200	2.88670800	-0.02529800
H	-3.71925700	1.83059000	1.39825000
C	-4.57261800	2.34334300	-2.35289300
H	-3.03514500	0.88876400	-2.75038500
C	-5.25413800	3.07251500	-1.37323800
H	-5.46403300	3.45069400	0.74056700
H	-4.80995000	2.48584700	-3.40356200
H	-6.02375900	3.78356100	-1.66002400
C	-2.86645800	-1.57825200	-0.18400900
C	-4.17979600	-1.65193200	0.31100900
C	-2.24405000	-2.75133300	-0.63312900
C	-4.84771800	-2.87631600	0.36384600
H	-4.68350400	-0.75355400	0.65513400
C	-2.91080000	-3.97819400	-0.57475500
H	-1.23685600	-2.70643900	-1.03358400
C	-4.21359800	-4.04283200	-0.07579400
H	-5.86341200	-2.91900900	0.74712300
H	-2.41360600	-4.87838200	-0.92517000
H	-4.73556200	-4.99468600	-0.03513000
C	2.76728100	1.60661700	0.35275900
C	4.05166200	1.59811300	0.92301600
C	2.09277100	2.82760100	0.21345300
C	4.63798800	2.78753900	1.35843100
H	4.59507500	0.66351300	1.02575400

SUPPORTING INFORMATION

C	2.67877700	4.01801000	0.65229100
H	1.10766000	2.84750100	-0.24126200
C	3.95160400	3.99929400	1.22690900
H	5.63154200	2.76895900	1.79752500
H	2.14299300	4.95627500	0.53876600
H	4.41098700	4.92394300	1.56471200
C	-0.18701700	1.97879700	-2.46720100
O	-0.36358800	3.03894900	-2.89300800
C	0.27303700	-1.40176400	-2.80696800
O	0.52674400	-2.34783300	-3.42176400

1a

B3LYP-D3/BSI SCF energy in acetonitrile: -321.1744861 a.u.

M06/BSII SCF energy in acetonitrile: -320.9685184 a.u.

M06/BSII free energy in acetonitrile: -320.9025884 a.u.

C	-1.37453000	0.00013400	0.00000000
C	-2.08499600	1.21699800	0.00000000
C	-2.08472900	-1.21688500	0.00000000
C	-3.47853100	1.21054500	0.00000000
H	-1.53885900	2.15518200	0.00000000
C	-3.47828400	-1.21072200	0.00000000
H	-1.53840000	-2.15495200	0.00000000
C	-4.17817800	-0.00016800	0.00000000
H	-4.01931700	2.15241300	0.00000000
H	-4.01886500	-2.15270600	0.00000000
H	-5.26436900	-0.00031800	0.00000000
Br	3.10066700	-0.00003000	0.00000000
C	0.05513700	0.00021100	0.00000000
C	1.26685600	0.00012400	0.00000000

INT1

B3LYP-D3/BSI SCF energy in acetonitrile: -2568.496482 a.u.

M06/BSII SCF energy in acetonitrile: -2567.412503 a.u.

M06/BSII free energy in acetonitrile: -2566.871266 a.u.

Pd	0.48327600	-0.69814600	-0.07189900
P	-1.86654000	-0.55516100	-0.07359300
P	1.05552300	1.58119100	-0.06096800
Fe	-1.89451000	2.55902200	1.32630400
C	-0.29752700	3.86699200	1.25096100
C	-1.02303600	2.84767400	3.19611500
C	-1.01929400	4.07323000	2.46272800
C	-2.70602000	2.19681000	-0.52898800
C	-3.97445000	2.66314700	1.34389000
C	-3.46496100	3.20849800	0.12703500
H	-0.15581900	4.59691800	0.46687000
H	-1.52610600	2.67125500	4.13774900
H	-1.52072700	4.98816400	2.75063700

SUPPORTING INFORMATION

H	-2.17025800	2.30864800	-1.45967100
H	-4.55557000	3.19406100	2.08661700
H	-3.59005900	4.22677100	-0.21730600
C	-0.30650500	1.87799800	2.43809700
C	0.15027000	2.50180700	1.22340300
C	-3.54030500	1.30850500	1.43838800
C	-2.74826400	1.00749900	0.27874600
H	-0.16322100	0.83697300	2.69597200
H	-3.73940200	0.63138500	2.25710300
C	-2.62305800	-1.10717700	-1.66036000
C	-1.91816400	-2.03715200	-2.44263800
C	-3.86505900	-0.63469000	-2.11407600
C	-2.44928000	-2.49266400	-3.65041300
H	-0.95217800	-2.39938200	-2.10366600
C	-4.39149800	-1.08855700	-3.32569700
H	-4.42145100	0.08830800	-1.52616500
C	-3.68629100	-2.01757400	-4.09525700
H	-1.89350900	-3.21170700	-4.24586100
H	-5.35268800	-0.71497600	-3.66758400
H	-4.09665300	-2.36659300	-5.03863300
C	2.81709400	2.00548400	0.27141700
C	3.25537300	2.33033200	1.56380200
C	3.76089600	1.89325200	-0.76288400
C	4.61412400	2.53976800	1.81559700
H	2.54116600	2.41766500	2.37699700
C	5.11564800	2.10826200	-0.50923100
H	3.43881400	1.63735900	-1.76856800
C	5.54698700	2.43008900	0.78137600
H	4.94059600	2.79327300	2.82035900
H	5.83521200	2.01832200	-1.31809400
H	6.60244800	2.59395600	0.97884000
C	0.71785700	2.46686900	-1.63804200
C	1.11657600	3.79867900	-1.84060100
C	0.04997500	1.78850600	-2.66931600
C	0.82213000	4.44729500	-3.04066200
H	1.66408600	4.32649700	-1.06558700
C	-0.24077100	2.43843200	-3.87181200
H	-0.25120100	0.75467000	-2.52712700
C	0.13962600	3.76954900	-4.05659000
H	1.12995700	5.47902800	-3.18509400
H	-0.76184600	1.90339600	-4.66072000
H	-0.08589200	4.27613300	-4.99073000
C	-2.59033700	-1.66705900	1.20758900
C	-3.88560600	-2.19518900	1.09558100
C	-1.82881900	-1.95463300	2.35017300
C	-4.40716600	-2.99984600	2.11048300
H	-4.48937500	-1.98334400	0.21834200
C	-2.35666300	-2.74988900	3.36986300
H	-0.81802300	-1.56544100	2.43400300
C	-3.64552400	-3.27619300	3.25028000

SUPPORTING INFORMATION

H	-5.40868800	-3.40917100	2.01167500
H	-1.75783900	-2.96512800	4.25051100
H	-4.05392300	-3.90191400	4.03888100
C	4.22544400	-3.25075700	-0.57842100
C	5.61119800	-3.39036800	-0.51984600
C	6.38706500	-2.44876000	0.16581700
C	5.76469200	-1.36320900	0.78923600
C	4.37943600	-1.21320100	0.72594200
C	3.58650800	-2.15797000	0.04713000
H	3.62429400	-3.98090700	-1.11269400
H	6.08752300	-4.23593700	-1.00889200
H	7.46692800	-2.55925600	0.20955600
H	6.35845000	-0.62251600	1.31738000
H	3.90090300	-0.36262200	1.19891900
C	2.14562800	-2.03144000	-0.01024900
C	1.00778800	-2.63195800	-0.08060200
Br	0.33976000	-4.46961400	-0.02742600

TS1

B3LYP-D3/BSI SCF energy in acetonitrile: -2568.454992 a.u.

M06/BSII SCF energy in acetonitrile: -2567.375635 a.u.

M06/BSII free energy in acetonitrile: -2566.836703 a.u.

Pd	-0.22607000	-0.11647200	-1.12727500
P	-2.32279300	-0.09045100	-0.03460400
P	1.66271700	1.13556600	-0.45692900
Fe	-0.37785700	1.62349500	2.26727200
C	1.59006300	2.27470600	2.27801000
C	0.84299700	0.44383500	3.47561800
C	1.22507000	1.81591700	3.57804200
C	-1.65905600	2.54514100	0.92932600
C	-2.04706500	2.43480500	3.20119500
C	-1.61411000	3.29012900	2.14227400
H	1.89725800	3.27910400	2.02304100
H	0.48029400	-0.17961400	4.28238000
H	1.19943100	2.41845700	4.47693100
H	-1.36166500	2.89980500	-0.04715900
H	-2.08296000	2.69068300	4.25227400
H	-1.26513400	4.30906900	2.24719300
C	0.96446900	0.05385100	2.11249800
C	1.43428200	1.18502700	1.35632400
C	-2.37114200	1.16358200	2.64088900
C	-2.13959800	1.22363100	1.22628300
H	0.72157600	-0.91641400	1.70296800
H	-2.70543500	0.29278200	3.18722600
C	-3.88371300	0.35744500	-0.90199200
C	-4.13154800	-0.26351500	-2.13763200
C	-4.81462900	1.27926500	-0.39917400
C	-5.29757600	0.01921000	-2.85016500
H	-3.40549500	-0.96623900	-2.54028200

SUPPORTING INFORMATION

C	-5.97641200	1.56890500	-1.11997400
H	-4.63553400	1.76957700	0.55303300
C	-6.22135900	0.93842600	-2.34285800
H	-5.48044200	-0.46989300	-3.80301600
H	-6.69095600	2.28511000	-0.72363700
H	-7.12533000	1.16568700	-2.90091600
C	3.39352200	0.54808000	-0.66731400
C	4.32208200	0.49143200	0.38229300
C	3.78669700	0.14564800	-1.95431400
C	5.62572200	0.04800600	0.14463500
H	4.03040800	0.79229100	1.38382700
C	5.09274200	-0.28499100	-2.19218300
H	3.06621500	0.16657000	-2.76889800
C	6.01438500	-0.33658800	-1.14114600
H	6.33720000	0.00403500	0.96455500
H	5.38717600	-0.59176400	-3.19190500
H	7.02845400	-0.68111800	-1.32292300
C	1.77775500	2.91442500	-0.92749200
C	2.84611700	3.73091600	-0.52142300
C	0.75788200	3.46481800	-1.71840100
C	2.87807400	5.07910200	-0.88156600
H	3.65264800	3.31322500	0.07439400
C	0.79003200	4.81520400	-2.07699000
H	-0.06110700	2.83161800	-2.05214800
C	1.84841100	5.62408100	-1.65619100
H	3.70741700	5.70338500	-0.56081600
H	-0.00639400	5.23074600	-2.68799800
H	1.87685500	6.67318200	-1.93681500
C	-2.80567000	-1.54280800	0.99350400
C	-4.07647600	-1.66106600	1.58004400
C	-1.84991000	-2.54316900	1.22244700
C	-4.37727700	-2.75799200	2.38961000
H	-4.83112100	-0.89941200	1.40698600
C	-2.15162300	-3.63851900	2.03563500
H	-0.87566100	-2.46551600	0.75395200
C	-3.41507200	-3.74668900	2.62171500
H	-5.36281600	-2.84119700	2.83924500
H	-1.40171100	-4.40692600	2.20303200
H	-3.65329200	-4.59978700	3.25077800
C	3.67965000	-3.06772900	-0.21884800
C	4.63556100	-3.47525700	0.70614300
C	4.25158900	-3.92689300	1.97437000
C	2.89316400	-3.96904600	2.30938400
C	1.92552400	-3.56417000	1.39408300
C	2.30169000	-3.09813500	0.10837100
H	3.98348000	-2.70296900	-1.19396300
H	5.68766900	-3.43287400	0.43874600
H	5.00202700	-4.24191800	2.69352100
H	2.58596200	-4.31799000	3.29161800
H	0.87509300	-3.59631400	1.66295300

SUPPORTING INFORMATION

C	1.32764000	-2.66308900	-0.81911600
C	0.46307400	-2.04975600	-1.47911500
Br	-0.67043500	-2.57835200	-3.04172500

INT2

B3LYP-D3/BSI SCF energy in acetonitrile: -2568.538136 a.u.

M06/BSII SCF energy in acetonitrile: -2567.449943 a.u.

M06/BSII free energy in acetonitrile: -2566.903438 a.u.

Pd	0.30335500	-0.91807800	0.11746300
P	-2.09133100	-0.69058800	-0.04859400
P	0.92331600	1.31722100	-0.03538200
Fe	-2.16350200	2.61761500	0.60189000
C	-0.49023800	3.81192800	0.62838400
C	-1.61908100	3.16977400	2.54224400
C	-1.38667000	4.25418500	1.64354000
C	-2.58958100	1.91918500	-1.27443900
C	-4.18603200	2.82767600	0.12360100
C	-3.38170200	3.07598500	-1.02757100
H	-0.15604200	4.39518900	-0.21681300
H	-2.28776500	3.17895900	3.39273100
H	-1.84917500	5.23128200	1.69179900
H	-1.84581700	1.82222100	-2.05003400
H	-4.86548400	3.52828700	0.59071900
H	-3.33893900	3.99918800	-1.59019900
C	-0.86918600	2.04878500	2.08843600
C	-0.16791500	2.43355700	0.89141300
C	-3.90045700	1.51287200	0.59049800
C	-2.90214600	0.93363500	-0.27180700
H	-0.85566900	1.06314700	2.53192200
H	-4.32388500	1.04891300	1.46867200
C	-2.71926900	-1.67845800	-1.47318800
C	-3.18803300	-2.99093100	-1.30615400
C	-2.64397100	-1.14187900	-2.76957100
C	-3.59022900	-3.74230400	-2.41227400
H	-3.23691200	-3.43047100	-0.31763600
C	-3.04111400	-1.89912600	-3.87329100
H	-2.27364900	-0.13661300	-2.93103100
C	-3.51684600	-3.20101800	-3.69797900
H	-3.95862400	-4.75380700	-2.26584000
H	-2.98032200	-1.46750700	-4.86837700
H	-3.82809000	-3.78884100	-4.55682200
C	2.57978200	1.78174900	0.61414800
C	2.73184000	2.04377100	1.98435400
C	3.70138300	1.83916900	-0.22672400
C	3.98716600	2.37103800	2.50180400
H	1.87665900	1.99700900	2.65140400
C	4.95257100	2.17079800	0.29466200
H	3.60549900	1.62270200	-1.28528200
C	5.09869200	2.43952000	1.65828400

SUPPORTING INFORMATION

H	4.09227500	2.57693400	3.56310800
H	5.81380200	2.21185300	-0.36557400
H	6.07420300	2.69564100	2.06134600
C	0.92048300	1.86701900	-1.78154300
C	1.34885500	3.15496200	-2.14575300
C	0.46562500	0.98598500	-2.77476900
C	1.28694800	3.56135700	-3.47915800
H	1.74283700	3.83482300	-1.39738200
C	0.40800500	1.39604000	-4.10841900
H	0.14681700	-0.01584700	-2.50325200
C	0.81171600	2.68583400	-4.46082100
H	1.61583400	4.55991500	-3.75147200
H	0.04710300	0.70725700	-4.86664900
H	0.76608900	3.00612800	-5.49764600
C	-2.94476800	-1.33048700	1.44280400
C	-4.32047700	-1.61484600	1.43097300
C	-2.22388600	-1.47554600	2.63647400
C	-4.96067500	-2.03922500	2.59601100
H	-4.89287000	-1.50334100	0.51534900
C	-2.86881200	-1.89078800	3.80355900
H	-1.15745800	-1.27634200	2.65067300
C	-4.23650400	-2.17536400	3.78429300
H	-6.02383700	-2.26051700	2.57547100
H	-2.30086800	-1.99827300	4.72323100
H	-4.73688000	-2.50402600	4.69075300
C	5.45933100	-2.64690500	-0.83272600
C	6.83592900	-2.86788800	-0.82625800
C	7.64596900	-2.25890000	0.13760700
C	7.06710000	-1.42243300	1.09747700
C	5.69221200	-1.19281700	1.09604000
C	4.86376000	-1.80315700	0.12917600
H	4.83263800	-3.12306000	-1.58135700
H	7.27771800	-3.51935800	-1.57539600
H	8.71797100	-2.43454000	0.14039700
H	7.68905400	-0.94340600	1.84886200
H	5.24661000	-0.53468800	1.83479600
C	3.45579400	-1.55730100	0.12335200
C	2.25330900	-1.31138700	0.13519700
Br	-0.10654600	-3.46511700	0.38586900

2a

B3LYP-D3/BSI SCF energy in acetonitrile: -272.7556147 a.u.

M06/BSII SCF energy in acetonitrile: -272.5833188 a.u.

M06/BSII free energy in acetonitrile: -272.4589688 a.u.

C	-1.28016500	-0.67102100	-0.50439500
C	-0.08760200	-1.12890500	0.32485100
C	-0.08782200	1.12891100	0.32481600
C	-1.28028000	0.67082400	-0.50442900

SUPPORTING INFORMATION

H	-1.91802100	-1.33013900	-1.08546000
H	-1.91830400	1.32983100	-1.08544600
C	-0.03400600	0.00002600	1.38172100
H	0.88957900	0.00009300	1.97244800
H	-0.89840900	-0.00009000	2.05359800
C	1.18780400	-0.78061600	-0.52076900
H	2.08531100	-1.17638200	-0.03365700
H	1.13821200	-1.20810000	-1.52632400
C	1.18769100	0.78075500	-0.52077300
H	2.08505100	1.17665000	-0.03344300
H	1.13817600	1.20823000	-1.52630000
H	-0.11748700	-2.15786800	0.68933500
H	-0.11783200	2.15793200	0.68912000

INT3

B3LYP-D3/BSI SCF energy in acetonitrile: -2841.304316 a.u.

M06/BSII SCF energy in acetonitrile: -2840.03374 a.u.

M06/BSII free energy in acetonitrile: -2839.342408 a.u.

Pd	-0.06358000	0.82342500	0.06649400
P	-1.02817900	-1.32494700	0.20958100
P	2.25040500	0.14842900	0.15280100
Fe	1.70129700	-2.99158100	-1.02840200
C	3.60995800	-2.23780900	-0.93722500
C	2.44492200	-2.50560900	-2.91656800
C	3.48740100	-3.04620400	-2.10414600
C	0.96328500	-3.36424700	0.84871200
C	0.73407700	-4.83736800	-0.91743000
C	1.44589700	-4.58297300	0.29357200
H	4.28673200	-2.42037300	-0.11594000
H	2.08605900	-2.91884700	-3.84997800
H	4.05509500	-3.94438000	-2.30941100
H	1.31798900	-2.89074500	1.75221300
H	0.89830500	-5.66847100	-1.59048800
H	2.24945100	-5.18410300	0.69834100
C	1.91371700	-1.36219100	-2.25731100
C	2.62475200	-1.19128200	-1.01752200
C	-0.19747600	-3.77930500	-1.11679900
C	-0.05956100	-2.85157700	-0.02449500
H	1.11269400	-0.72364200	-2.60496200
H	-0.87005000	-3.67010500	-1.95512500
C	-1.77164000	-1.62772900	1.86717000
C	-1.96841000	-0.57929600	2.77886100
C	-2.09819500	-2.93938500	2.25564800
C	-2.48626500	-0.83517300	4.04968000
H	-1.71188900	0.43512800	2.49964500
C	-2.62676000	-3.18948400	3.52273600
H	-1.93724700	-3.76853000	1.57462700
C	-2.81923200	-2.13910400	4.42365300
H	-2.62418100	-0.01362800	4.74672300

SUPPORTING INFORMATION

H	-2.87989100	-4.20692800	3.80618400
H	-3.22110100	-2.33703700	5.41320800
C	3.56608500	1.36736200	-0.26604500
C	3.78339200	1.67649200	-1.61955000
C	4.30187900	2.04145100	0.71977700
C	4.73006800	2.63797700	-1.97574000
H	3.19352900	1.19415700	-2.39215600
C	5.24598500	3.00504400	0.35689000
H	4.14732100	1.81874100	1.76977700
C	5.46283000	3.30505500	-0.98971600
H	4.89071000	2.86840900	-3.02523900
H	5.81110100	3.51837300	1.12962400
H	6.19778000	4.05427800	-1.26985300
C	2.68464300	-0.45273000	1.82925300
C	3.97398300	-0.91406500	2.14701100
C	1.69198500	-0.46507100	2.82119000
C	4.24673900	-1.41414800	3.42059400
H	4.76852300	-0.86980200	1.40951800
C	1.96718700	-0.96557800	4.09540600
H	0.69870400	-0.09325400	2.59582500
C	3.24253700	-1.44902000	4.39418700
H	5.24514400	-1.77235600	3.65403000
H	1.18278300	-0.97804900	4.84684200
H	3.45893400	-1.84183300	5.38347800
C	-2.32756500	-1.55606100	-1.07162500
C	-3.46653600	-2.33804800	-0.84031800
C	-2.11249800	-0.99593600	-2.34070200
C	-4.37944300	-2.56527100	-1.87356400
H	-3.65411500	-2.76711800	0.13793400
C	-3.02268100	-1.23759400	-3.37103700
H	-1.25966300	-0.34609800	-2.52187600
C	-4.15614200	-2.02387100	-3.14148600
H	-5.26555300	-3.16378100	-1.68274500
H	-2.85041400	-0.80019300	-4.35055000
H	-4.86634500	-2.20388800	-3.94345000
C	-5.36849500	2.22037400	1.07149200
C	-6.76132900	2.27410600	1.03130100
C	-7.46315500	1.65906400	-0.01037500
C	-6.76082400	0.98602100	-1.01579000
C	-5.36906900	0.92529900	-0.98351000
C	-4.65092600	1.54411400	0.06312800
H	-4.82506100	2.69775300	1.88180600
H	-7.30075400	2.79783800	1.81574600
H	-8.54822100	1.70314200	-0.03790300
H	-7.29896800	0.50326000	-1.82704200
H	-4.82350400	0.39942500	-1.76045800
C	-3.22551800	1.45505300	0.09658400
C	-2.01121100	1.28861900	0.08384000
Br	0.37283000	1.88840000	-3.38141300
C	0.90883600	3.00492600	0.16484000

SUPPORTING INFORMATION

C	1.24079000	3.50173900	1.56748700
C	-0.93021500	4.01942000	1.17480300
C	-0.40918500	3.33264300	-0.06730000
H	1.63085100	2.90980600	-0.63493100
H	-0.85117600	3.39993400	-1.05407500
C	-0.11423000	3.32493600	2.28656800
H	-0.16185800	3.85548800	3.24247000
H	-0.39301800	2.27753300	2.43287200
C	1.28179000	5.05934800	1.41608300
H	1.63268100	5.51515000	2.34705200
H	1.95557500	5.37353100	0.61385800
C	-0.21157800	5.41784500	1.13530100
H	-0.62599000	6.05491200	1.92227800
H	-0.35796800	5.92965500	0.17991000
H	2.12112300	3.06598500	2.03739800
H	-2.01321200	4.06345000	1.28318300

TS2

B3LYP-D3/BSI SCF energy in acetonitrile: -2841.299613 a.u.

M06/BSII SCF energy in acetonitrile: -2840.028011 a.u.

M06/BSII free energy in acetonitrile: -2839.337373 a.u.

Pd	0.02221500	0.79693000	0.12047100
P	-1.01748600	-1.34846400	0.09761000
P	2.28364400	0.10566500	0.25239400
Fe	1.73522400	-2.91635400	-1.21032300
C	3.65277700	-2.20512700	-0.98318800
C	2.55868100	-2.28112000	-3.01902600
C	3.56001600	-2.90994300	-2.21827600
C	0.92023900	-3.46675900	0.59304100
C	0.75666300	-4.75302900	-1.31971700
C	1.42498300	-4.62507700	-0.06430800
H	4.29216200	-2.47109900	-0.15481700
H	2.22820600	-2.60750400	-3.99637100
H	4.11826800	-3.80000400	-2.47796600
H	1.23966600	-3.08677400	1.55246200
H	0.94632300	-5.51052300	-2.06881900
H	2.21447600	-5.26597300	0.30567500
C	2.02280900	-1.18676300	-2.28404900
C	2.69395300	-1.13288900	-1.01165400
C	-0.17102700	-3.67828100	-1.44073600
C	-0.07486600	-2.86931700	-0.25682200
H	1.24477000	-0.50577900	-2.60505100
H	-0.81343100	-3.48033100	-2.28694200
C	-1.80088100	-1.75375000	1.71439900
C	-2.04549500	-0.74064300	2.65509900
C	-2.12601300	-3.08144900	2.04215000
C	-2.60630600	-1.04797800	3.89611000
H	-1.79534900	0.28664800	2.41884600
C	-2.69150100	-3.38442900	3.28188900

SUPPORTING INFORMATION

H	-1.93529300	-3.88155000	1.33422800
C	-2.93067300	-2.36951600	4.21222500
H	-2.78357000	-0.25364100	4.61559000
H	-2.93955300	-4.41449400	3.52119200
H	-3.36390800	-2.60855300	5.17927500
C	3.55952600	1.40151700	-0.02277600
C	3.72849500	1.89384200	-1.32840900
C	4.29064500	1.97389300	1.02831000
C	4.62704400	2.93224000	-1.57509800
H	3.13248500	1.49611700	-2.14492300
C	5.18728800	3.01550700	0.77490200
H	4.16644900	1.61389700	2.04395100
C	5.35891000	3.49548400	-0.52516500
H	4.74915300	3.30586300	-2.58799800
H	5.74950200	3.44986700	1.59667000
H	6.05604200	4.30556600	-0.71959200
C	2.67711000	-0.63312400	1.88158200
C	3.95666000	-1.12334200	2.19483100
C	1.65628800	-0.72523300	2.84049100
C	4.19239500	-1.73039100	3.42899500
H	4.77193600	-1.01945900	1.48635400
C	1.89455300	-1.33330600	4.07476500
H	0.67033100	-0.33247000	2.61736600
C	3.16075900	-1.84448900	4.36711400
H	5.18334400	-2.11053100	3.65968600
H	1.08944500	-1.40658600	4.80040500
H	3.34836200	-2.32183000	5.32464800
C	-2.33563500	-1.43928500	-1.18308600
C	-3.51519600	-2.17360800	-0.99878100
C	-2.10791900	-0.78819000	-2.40615100
C	-4.45366600	-2.26264600	-2.03014500
H	-3.71273900	-2.67288800	-0.05599600
C	-3.04411000	-0.89109500	-3.43676900
H	-1.22217300	-0.17374800	-2.55052900
C	-4.21797900	-1.62805100	-3.25200800
H	-5.36947100	-2.82570700	-1.87430600
H	-2.86054700	-0.38250500	-4.37922900
H	-4.94958500	-1.69822900	-4.05203400
C	-5.21170900	1.83013000	1.39988400
C	-6.60199400	1.74815500	1.44542600
C	-7.32604500	1.38602500	0.30444100
C	-6.65005300	1.10300300	-0.88739100
C	-5.26060600	1.18260400	-0.94458700
C	-4.52077900	1.54840200	0.20139500
H	-4.64702100	2.10598700	2.28558700
H	-7.12296700	1.96577000	2.37367200
H	-8.40969200	1.32252400	0.34457800
H	-7.20748900	0.81583100	-1.77464500
H	-4.73253600	0.95042500	-1.86386500
C	-3.09911000	1.59268200	0.15356800

SUPPORTING INFORMATION

C	-1.87155400	1.54569800	0.11156200
Br	0.38873900	2.07052700	-3.38248100
C	0.71134600	2.86270600	0.22732500
C	1.08421300	3.39088600	1.61351500
C	-1.06219200	4.02719600	1.24715300
C	-0.63873300	3.25840800	0.01550000
H	1.40489700	2.91455200	-0.60559800
H	-1.00492800	3.47555100	-0.98153800
C	-0.26658000	3.31347800	2.36028700
H	-0.26485900	3.87306700	3.30061200
H	-0.60959600	2.29188100	2.54656500
C	1.21922800	4.93194200	1.41892900
H	1.59392500	5.39713900	2.33647800
H	1.91061700	5.18194000	0.60890000
C	-0.25021200	5.36612000	1.12277100
H	-0.62098900	6.07255100	1.87100900
H	-0.37081000	5.83050800	0.13959600
H	1.94383200	2.91452700	2.08406400
H	-2.13614100	4.15341900	1.37921200

TS2[†]

B3LYP-D3/BSI SCF energy in acetonitrile: -2827.731429 a.u.

M06/BSII SCF energy in acetonitrile: -2826.494492 a.u.

M06/BSII free energy in acetonitrile: -2825.798484 a.u.

Pd	0.01660700	0.90777000	-0.31960200
P	-0.94018000	-1.22961900	0.17113700
P	2.30511500	0.31622700	-0.14464000
Fe	1.79394200	-2.94256900	-0.93745600
C	3.68954200	-2.14029500	-1.03147800
C	2.43392400	-2.65980000	-2.90360000
C	3.53013700	-3.07937400	-2.09081300
C	1.12190300	-3.11527400	0.99713200
C	0.92029500	-4.79980900	-0.57053400
C	1.65282300	-4.36698000	0.57563900
H	4.41095000	-2.21096900	-0.23093800
H	2.03793000	-3.18754800	-3.76103000
H	4.11020900	-3.98322300	-2.22319600
H	1.47746300	-2.52004400	1.82461400
H	1.10909200	-5.69581200	-1.14704600
H	2.49865000	-4.87390900	1.02093600
C	1.90640700	-1.46024100	-2.34929400
C	2.67629900	-1.12988200	-1.17748000
C	-0.07294500	-3.82026500	-0.85950000
C	0.04700800	-2.76255800	0.10790300
H	1.04850300	-0.90883300	-2.70776000
H	-0.77202300	-3.84493600	-1.68303100
C	-1.64741800	-1.28171100	1.86847800
C	-1.92380600	-0.08863900	2.55499500
C	-1.89134800	-2.51024100	2.50623000

SUPPORTING INFORMATION

C	-2.43583700	-0.12380300	3.85300600
H	-1.73750400	0.86651800	2.07857300
C	-2.40730900	-2.54089500	3.80282100
H	-1.67749600	-3.44332400	1.99504900
C	-2.67796200	-1.34868900	4.47958700
H	-2.63964600	0.80701200	4.37458500
H	-2.59218400	-3.49660700	4.28471900
H	-3.07192400	-1.37465700	5.49147900
C	3.54671900	1.54844400	-0.71040300
C	3.76527100	1.70587400	-2.08941200
C	4.21199600	2.39340900	0.18992000
C	4.63476500	2.69231600	-2.55648400
H	3.25777100	1.06033100	-2.80044800
C	5.08043400	3.38058200	-0.28239100
H	4.05794300	2.28545600	1.25834900
C	5.29210600	3.53397000	-1.65407900
H	4.79920600	2.80161600	-3.62460900
H	5.59069300	4.02777100	0.42514200
H	5.96746500	4.30238200	-2.01892900
C	2.77425900	-0.07584800	1.57997300
C	4.07407200	-0.48104300	1.92771700
C	1.79575800	0.02695700	2.58069600
C	4.37068200	-0.81926900	3.24839800
H	4.85675700	-0.51842000	1.17703600
C	2.09607700	-0.31094000	3.90177800
H	0.79559200	0.35815900	2.32394600
C	3.38131000	-0.74351800	4.23492500
H	5.37618000	-1.13672900	3.50870800
H	1.32419200	-0.23816100	4.66260600
H	3.61721400	-1.01102000	5.26086500
C	-2.30388800	-1.64040500	-0.99343000
C	-3.46492200	-2.30864300	-0.58346400
C	-2.13014000	-1.32889700	-2.35123800
C	-4.43653600	-2.66539400	-1.52243400
H	-3.61981600	-2.55107800	0.46255500
C	-3.09593900	-1.69877200	-3.28797200
H	-1.24675500	-0.78615300	-2.67343900
C	-4.25196000	-2.36864800	-2.87436400
H	-5.33738400	-3.17527700	-1.19352000
H	-2.95069700	-1.45458900	-4.33638600
H	-5.00835800	-2.64905000	-3.60159100
C	-5.24835300	2.16076700	0.67879300
C	-6.63884500	2.09245300	0.73609500
C	-7.35599300	1.43677300	-0.27037200
C	-6.67382800	0.84621800	-1.33957900
C	-5.28419500	0.91004900	-1.40834100
C	-4.55180900	1.56967700	-0.39740300
H	-4.68932800	2.66564100	1.46108700
H	-7.16492000	2.55043000	1.56888400
H	-8.43977500	1.38445900	-0.22033700

SUPPORTING INFORMATION

H	-7.22596400	0.33048200	-2.12019100
H	-4.75136800	0.44126400	-2.22907700
C	-3.13011500	1.60460100	-0.45061900
C	-1.90160900	1.56922300	-0.48205400
C	0.62598100	2.96138400	-0.73667700
C	1.02492700	3.79205300	0.48689400
C	-1.15368000	4.27463200	0.07897900
C	-0.74199200	3.27611700	-0.97800200
H	1.30730500	2.85725300	-1.57749000
H	-1.16613900	3.28825500	-1.97542400
C	-0.29678000	3.83841400	1.28537700
H	-0.28328600	4.58796100	2.08190000
H	-0.59614700	2.87167400	1.69957600
C	1.09906900	5.25692900	-0.03895100
H	1.48876100	5.91693300	0.74263700
H	1.75336600	5.34594000	-0.91088900
C	-0.39338700	5.57817500	-0.36013000
H	-0.76499100	6.41476800	0.23831100
H	-0.56472600	5.82145500	-1.41274000
H	1.91448100	3.45413700	1.01522400
H	-2.22671800	4.39556400	0.22034000

Br⁻

B3LYP-D3/BSI SCF energy in acetonitrile: -13.55754918 a.u.

M06/BSII SCF energy in acetonitrile: -13.51974309 a.u.

M06/BSII free energy in acetonitrile: -13.53591909 a.u.

Br	0.00000000	0.00000000	0.00000000
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INT4

B3LYP-D3/BSI SCF energy in acetonitrile: -2681.860166 a.u.

M06/BSII SCF energy in acetonitrile: -2680.736829 a.u.

M06/BSII free energy in acetonitrile: -2680.190317 a.u.

Pd	-0.32272700	-0.84050100	0.39112600
P	2.08365100	-0.60068600	0.62245000
P	-0.76738100	1.36694900	-0.35964700
Fe	2.24289000	1.67277300	-1.90298000
C	0.69193700	2.93385600	-2.37714200
C	1.41778100	1.23971100	-3.77396300
C	1.43317300	2.65109400	-3.55964600
C	2.98425500	2.09558700	-0.03854200
C	4.32874000	1.70621000	-1.87823300
C	3.80807700	2.71949600	-1.01790000
H	0.55882100	3.90978400	-1.93466400
H	1.92789100	0.71159000	-4.56858900
H	1.96240600	3.38088100	-4.15818200
H	2.42994500	2.59289900	0.74348200
H	4.95481600	1.86717600	-2.74577300
H	3.96864100	3.78474700	-1.11840900

SUPPORTING INFORMATION

C	0.66848100	0.63535700	-2.72720000
C	0.21824600	1.68256000	-1.84534900
C	3.83807100	0.44637300	-1.43143800
C	3.00088600	0.67727500	-0.28556500
H	0.47126000	-0.42292100	-2.59995200
H	4.02965300	-0.51401800	-1.88891400
C	2.45121200	-0.28278900	2.39449400
C	1.60774700	-0.82681200	3.37901600
C	3.56185300	0.48004500	2.78805500
C	1.86713000	-0.60056900	4.73095900
H	0.73853100	-1.41333000	3.09784600
C	3.81594600	0.70413500	4.14282400
H	4.22911000	0.90170000	2.04482700
C	2.96861800	0.16915400	5.11554100
H	1.20371000	-1.01969800	5.48173200
H	4.67648900	1.29899700	4.43454400
H	3.16496800	0.35074300	6.16819800
C	-2.48375800	1.73205000	-0.88847700
C	-2.88403100	1.45216500	-2.20317000
C	-3.41159000	2.25723500	0.02391300
C	-4.19791300	1.70735100	-2.60206300
H	-2.17740000	1.04038400	-2.91669500
C	-4.72279500	2.50921500	-0.38066800
H	-3.11517000	2.47149900	1.04571800
C	-5.11767000	2.23748100	-1.69378300
H	-4.49896500	1.49370000	-3.62348500
H	-5.43518900	2.91579200	0.33102400
H	-6.13922900	2.43430300	-2.00580700
C	-0.38388900	2.63767700	0.89451000
C	-0.53599800	4.00564400	0.60883000
C	0.06535200	2.24203900	2.16176900
C	-0.18506800	4.95880300	1.56427300
H	-0.93900300	4.32679100	-0.34576700
C	0.41377500	3.20000900	3.11638600
H	0.14609000	1.18956600	2.40298400
C	0.30102100	4.55819400	2.81398800
H	-0.29644800	6.01447100	1.33499400
H	0.77212400	2.87958900	4.09010900
H	0.57657300	5.30494800	3.55294000
C	3.01627000	-2.12410300	0.20036700
C	4.18973000	-2.46586400	0.89149500
C	2.58405500	-2.91403200	-0.87463100
C	4.91765800	-3.59376800	0.51156200
H	4.53684900	-1.85977100	1.72196400
C	3.32274900	-4.03831700	-1.25245600
H	1.67106800	-2.67305400	-1.41385900
C	4.48690300	-4.38059800	-0.56132400
H	5.82085500	-3.85713500	1.05442900
H	2.98120900	-4.64732900	-2.08468400
H	5.05611400	-5.25855600	-0.85335500

SUPPORTING INFORMATION

C	-5.40145700	-1.88687700	2.28185800
C	-6.77638600	-1.99369200	2.48629300
C	-7.67248600	-1.56717000	1.50094500
C	-7.18410500	-1.03224500	0.30459100
C	-5.81123900	-0.91966200	0.09174300
C	-4.89898400	-1.34577200	1.08048400
H	-4.70636100	-2.21787100	3.04798400
H	-7.14964700	-2.41062500	3.41756700
H	-8.74308700	-1.65106500	1.66463300
H	-7.87450100	-0.69826900	-0.46501400
H	-5.43120800	-0.49870000	-0.83313300
C	-3.49131300	-1.21400700	0.86464400
C	-2.29981100	-1.04201300	0.63673100
Br	-0.73641900	-3.00295400	-2.55904500
C	-0.24189900	-2.75722300	0.82565900
O	-0.29570500	-3.85825600	1.11440500

TS3

B3LYP-D3/BSI SCF energy in acetonitrile: -2681.842133 a.u.

M06/BSII SCF energy in acetonitrile: -2680.720258 a.u.

M06/BSII free energy in acetonitrile: -2680.176375 a.u.

Pd	-0.28494900	-0.82522600	0.32059300
P	2.06566800	-0.79148600	0.58607100
P	-0.64592600	1.44041600	-0.33027900
Fe	2.40687200	1.75077400	-1.74692900
C	0.97455600	3.20754900	-2.02315800
C	1.62261600	1.72967100	-3.67941000
C	1.74613000	3.07411500	-3.21327900
C	3.19519400	1.86395100	0.14764600
C	4.47697500	1.53401700	-1.74730700
C	4.07978900	2.49794200	-0.77155700
H	0.90105500	4.09339900	-1.40913400
H	2.12367900	1.30758900	-4.54066900
H	2.36167800	3.84687100	-3.65480600
H	2.70708300	2.32990000	0.99121300
H	5.11121100	1.71908000	-2.60414800
H	4.35908300	3.54330700	-0.75800800
C	0.77946900	1.01925500	-2.77929900
C	0.37067200	1.93331700	-1.74455900
C	3.84864200	0.29530900	-1.43006400
C	3.05546300	0.48777500	-0.24914700
H	0.49401200	-0.02483900	-2.83877800
H	3.92998300	-0.62714600	-1.98801600
C	2.47770700	-0.58756100	2.36789400
C	1.56206300	-1.04216700	3.33201500
C	3.67661800	0.00943000	2.79016300
C	1.83808800	-0.89552900	4.69211100
H	0.62603200	-1.49611100	3.02066900
C	3.94732300	0.15610900	4.15201200

SUPPORTING INFORMATION

H	4.39755400	0.36608300	2.06284700
C	3.02893800	-0.29175000	5.10465100
H	1.11881800	-1.24558900	5.42681500
H	4.87602200	0.62350900	4.46626200
H	3.23954100	-0.16938800	6.16318000
C	-2.38330800	1.71514700	-0.85078400
C	-2.75458200	1.62322200	-2.19943500
C	-3.37369500	1.89326800	0.12901800
C	-4.10080400	1.71655600	-2.56208200
H	-2.00153600	1.47360100	-2.96626200
C	-4.71652600	1.98195800	-0.23815900
H	-3.09917300	1.95617200	1.17797800
C	-5.08301200	1.89188100	-1.58437300
H	-4.37958100	1.64960100	-3.60992600
H	-5.47605900	2.10834900	0.52789400
H	-6.12954600	1.95435000	-1.86837300
C	-0.35212300	2.69066200	0.97312300
C	-0.71714900	4.03427200	0.78153800
C	0.24836400	2.30533600	2.18005600
C	-0.45353800	4.97859600	1.77410500
H	-1.20948900	4.34125200	-0.13632400
C	0.51145300	3.25342700	3.17165400
H	0.51485800	1.26880000	2.34715900
C	0.16589000	4.59101000	2.96745800
H	-0.73461200	6.01599300	1.61754400
H	0.98345100	2.94133500	4.09886100
H	0.36884500	5.32950800	3.73765000
C	2.88672700	-2.34907400	0.06410400
C	4.13367800	-2.72281900	0.59267600
C	2.27581100	-3.15000200	-0.91122300
C	4.75735200	-3.88941400	0.15041900
H	4.61730100	-2.11233600	1.34885000
C	2.91019800	-4.31458700	-1.35307700
H	1.31322500	-2.87129500	-1.33358400
C	4.14723800	-4.68695100	-0.82368200
H	5.71878900	-4.17598900	0.56694400
H	2.43110100	-4.93081000	-2.10896900
H	4.63539000	-5.59545600	-1.16494300
C	-5.38560400	-1.18651800	2.32092800
C	-6.76718600	-1.10738900	2.47477100
C	-7.60805900	-1.25371300	1.36617000
C	-7.06530100	-1.48108800	0.09679900
C	-5.68572000	-1.56189300	-0.07035000
C	-4.83092400	-1.41537900	1.04369100
H	-4.72627300	-1.06765700	3.17508700
H	-7.19005800	-0.92940900	3.45900200
H	-8.68498500	-1.18904800	1.49127600
H	-7.71876000	-1.59105500	-0.76340300
H	-5.25542000	-1.72489700	-1.05318200
C	-3.42281900	-1.44694600	0.86562400

SUPPORTING INFORMATION

C	-2.20913400	-1.42862900	0.66538100
Br	-0.95547400	-2.37361700	-2.74184600
C	-0.83733900	-2.59880000	0.83638400
O	-0.92119500	-3.72201900	1.13290700

INT5

B3LYP-D3/BSI SCF energy in acetonitrile: -2681.867464 a.u.

M06/BSII SCF energy in acetonitrile: -2680.75241 a.u.

M06/BSII free energy in acetonitrile: -2680.205601 a.u.

Pd	0.00654000	0.44813500	-1.12772700
P	-1.95750100	0.78365300	0.08057200
P	1.01067000	-1.32968300	0.18215300
Fe	-1.97877800	-2.61003000	0.92534100
C	-0.29871100	-3.77045200	1.23107500
C	-1.81443900	-4.14752400	-0.47530200
C	-1.37459100	-4.60200700	0.80532100
C	-2.11269900	-1.08914500	2.30742400
C	-3.89347800	-2.43735000	1.72079300
C	-2.91605000	-2.18600800	2.73029000
H	0.21592400	-3.83826400	2.17856600
H	-2.64333500	-4.54961900	-1.04264600
H	-1.81351700	-5.40788800	1.37900700
H	-1.27455400	-0.66998200	2.84321400
H	-4.62640600	-3.23343000	1.72611000
H	-2.77191800	-2.76028700	3.63606200
C	-1.01667300	-3.02940500	-0.84517000
C	-0.06827900	-2.78390900	0.21241000
C	-3.70435100	-1.48971800	0.67356900
C	-2.59942800	-0.64306500	1.02910500
H	-1.11680400	-2.43193400	-1.74163500
H	-4.27588400	-1.42920000	-0.24152500
C	-1.98733200	2.12996500	1.33072500
C	-1.01856700	3.14378800	1.27928100
C	-2.95149700	2.15488400	2.35315600
C	-1.01118400	4.16397600	2.23298900
H	-0.25605200	3.13098600	0.50948900
C	-2.94187500	3.17657100	3.30381400
H	-3.70805300	1.37876500	2.40972500
C	-1.97088400	4.18077800	3.24768400
H	-0.25002400	4.93748800	2.18544200
H	-3.69159200	3.18542600	4.08981500
H	-1.96140800	4.97006400	3.99397700
C	2.65207800	-1.90890200	-0.39840100
C	2.88751700	-3.21495800	-0.84200200
C	3.70105800	-0.97395500	-0.40901000
C	4.16026900	-3.58305200	-1.29079500
H	2.08549400	-3.94718800	-0.83860000
C	4.96892300	-1.34470400	-0.85294600
H	3.52857000	0.04472800	-0.07207500

SUPPORTING INFORMATION

C	5.20125200	-2.65166400	-1.29710600
H	4.33667400	-4.59997900	-1.63046100
H	5.77165900	-0.61252400	-0.85581300
H	6.18911300	-2.94153800	-1.64403300
C	1.38802300	-0.89171300	1.92800500
C	2.00539400	-1.80258500	2.80207400
C	1.10255600	0.40315600	2.38148200
C	2.28556700	-1.43265500	4.11815300
H	2.27699000	-2.79448600	2.45330400
C	1.38842000	0.77506600	3.69756500
H	0.65536800	1.12152500	1.70605300
C	1.97185200	-0.14541700	4.57002700
H	2.75499100	-2.14601800	4.78955400
H	1.15554900	1.78186800	4.03286100
H	2.19386500	0.13898500	5.59464700
C	-3.34358600	1.11591800	-1.08053200
C	-4.32318100	2.08923400	-0.84538400
C	-3.41327700	0.33188600	-2.24408700
C	-5.36366800	2.26941500	-1.76131900
H	-4.28196300	2.70874200	0.04441500
C	-4.46175600	0.50377700	-3.14709400
H	-2.64059300	-0.40542100	-2.44409600
C	-5.43811100	1.47628700	-2.90845600
H	-6.11665000	3.02971600	-1.57427500
H	-4.50907000	-0.11113900	-4.04135400
H	-6.24929800	1.61809600	-3.61681100
C	3.22391200	2.94093300	1.03946000
C	4.39274500	2.83757300	1.78848800
C	5.62554500	2.66172500	1.15069100
C	5.68942300	2.59692100	-0.24521900
C	4.52804300	2.69944900	-1.00839800
C	3.28296700	2.86643300	-0.36897600
H	2.26293700	3.06200300	1.52833000
H	4.33991700	2.88388000	2.87220600
H	6.53388400	2.57498000	1.73953400
H	6.64591100	2.46169300	-0.74127500
H	4.57034100	2.63656000	-2.09099900
C	2.07273500	2.85404200	-1.11326700
C	1.00031000	2.76594500	-1.69981400
Br	1.12584700	-0.42382100	-3.38167400
C	-0.26464900	2.18582100	-2.11982100
O	-1.10334800	2.66400200	-2.84816400

INT6

B3LYP-D3/BSI SCF energy in acetonitrile: -2954.634492 a.u.

M06/BSII SCF energy in acetonitrile: -2953.339426 a.u.

M06/BSII free energy in acetonitrile: -2952.640686 a.u.

Pd	0.00295000	0.44461800	0.83286100
P	-0.35776100	-1.86890000	0.34963300

SUPPORTING INFORMATION

P	2.08126800	0.72138600	-0.51588200
Fe	1.37686200	-1.83578600	-2.63757000
C	2.85163000	-0.48539500	-3.11155100
C	0.78849400	-0.52702200	-4.15520200
C	2.16854800	-0.86305100	-4.30397500
C	1.91169200	-3.01658700	-1.04534500
C	0.98019000	-3.85568300	-2.98366300
C	2.19696400	-3.71384600	-2.25220700
H	3.89920000	-0.65175700	-2.90959200
H	0.00481700	-0.72133800	-4.87563400
H	2.61555300	-1.36122000	-5.15452000
H	2.62746500	-2.74023200	-0.28656100
H	0.87117000	-4.31094900	-3.95921000
H	3.17792700	-4.03621700	-2.57606500
C	0.60977300	0.05754500	-2.87053700
C	1.88545000	0.07942300	-2.20634300
C	-0.06620400	-3.25162400	-2.22954000
C	0.50488800	-2.71380400	-1.02272500
H	-0.31088500	0.43698400	-2.44730100
H	-1.10113300	-3.18328200	-2.52877100
C	0.06274600	-2.99912900	1.73980600
C	0.49022200	-2.50393400	2.97897300
C	0.00396400	-4.38999200	1.53820500
C	0.86165400	-3.38455400	3.99847100
H	0.52040200	-1.43692600	3.15614000
C	0.36755900	-5.26553200	2.56058200
H	-0.32592100	-4.78876200	0.58355500
C	0.80206400	-4.76382100	3.79178100
H	1.19711000	-2.98857600	4.95275400
H	0.31727300	-6.33760800	2.39375700
H	1.09281300	-5.44666400	4.58499000
C	2.79702700	2.38900300	-0.85148000
C	2.20638900	3.19075200	-1.84292500
C	3.87089600	2.90263800	-0.10765100
C	2.69058800	4.47693200	-2.08784200
H	1.35000100	2.82719500	-2.40085400
C	4.34903000	4.19175600	-0.35439600
H	4.34364500	2.30075200	0.66073400
C	3.76143900	4.98185200	-1.34501400
H	2.22585700	5.08573300	-2.85859100
H	5.18285100	4.57410900	0.22762200
H	4.13484900	5.98378800	-1.53702400
C	3.47225000	-0.19886400	0.25145700
C	4.75203300	-0.26629500	-0.32588200
C	3.23640400	-0.86642800	1.46166200
C	5.75591400	-1.02379000	0.27835900
H	4.97314000	0.28483400	-1.23363300
C	4.24154400	-1.62350600	2.06730100
H	2.25675500	-0.80321600	1.91923500
C	5.50090500	-1.71043800	1.47084900

SUPPORTING INFORMATION

H	6.73965300	-1.07417200	-0.17941100
H	4.03448700	-2.14566400	2.99710000
H	6.28509400	-2.30116400	1.93558200
C	-2.11902900	-2.19307200	-0.06109800
C	-2.95247000	-2.96800500	0.75500600
C	-2.65398800	-1.57514500	-1.20501800
C	-4.29984900	-3.13557100	0.42167300
H	-2.56277900	-3.43541000	1.65282400
C	-3.99296400	-1.76045400	-1.54276200
H	-2.02742700	-0.94206800	-1.82473400
C	-4.82089900	-2.53884500	-0.72730400
H	-4.93938400	-3.73353900	1.06461200
H	-4.39624700	-1.27698400	-2.42745100
H	-5.86923700	-2.66580000	-0.98098700
C	-6.39898600	0.56283700	0.67042300
C	-7.56510400	0.77966400	-0.05915500
C	-7.51210500	1.45456000	-1.28394500
C	-6.28820500	1.91720900	-1.77937900
C	-5.11272200	1.70540600	-1.06188400
C	-5.16288700	1.02360100	0.17229800
H	-6.42895400	0.03056700	1.61599200
H	-8.51549000	0.41989100	0.32385100
H	-8.42411800	1.61942800	-1.85065700
H	-6.25043800	2.44088500	-2.73046600
H	-4.15082300	2.05473700	-1.43024300
Br	-1.50138800	2.89549100	-1.58567500
C	0.59727000	2.67872900	1.44189500
C	1.62336000	2.77950700	2.56251900
C	-0.40878200	2.56850600	3.54246900
C	-0.63609500	2.54730100	2.04195600
H	0.71936800	3.11014400	0.45689600
H	-1.56702200	2.79801400	1.54628100
C	0.97769000	1.89797600	3.65279200
H	1.43800400	2.03295700	4.63670900
H	0.95921800	0.83458300	3.39957700
C	1.37906900	4.20491100	3.16325900
H	2.15414800	4.43322300	3.90128900
H	1.40888000	4.98283500	2.39484400
C	-0.02277100	4.06232400	3.83521600
H	0.03551200	4.21656600	4.91702600
H	-0.76172700	4.76368800	3.43737300
H	2.65738000	2.57183100	2.29277500
H	-1.21391400	2.17123300	4.15902400
C	-1.65564200	0.17263800	2.04860100
C	-2.91445900	0.49837700	1.45069000
C	-3.95823900	0.75489700	0.87787300
O	-1.56908800	-0.26845400	3.18686700

TS4

B3LYP-D3/BSI SCF energy in acetonitrile: -2954.623034 a.u.

SUPPORTING INFORMATION

M06/BSII SCF energy in acetonitrile: -2953.32919 a.u.

M06/BSII free energy in acetonitrile: -2952.630265 a.u.

Pd	-0.16306200	-0.56642600	0.73788600
P	0.42517300	1.77460700	0.42343800
P	-2.20961500	-0.61947400	-0.47571700
Fe	-1.45503200	2.03339200	-2.46902000
C	-3.05142900	0.82134100	-2.91594800
C	-1.06923400	0.79678800	-4.10647800
C	-2.42830800	1.23470200	-4.12919000
C	-1.81807700	3.15787000	-0.79070300
C	-0.92739300	4.03146700	-2.73372900
C	-2.11403900	3.93566700	-1.94639500
H	-4.06673300	1.04379400	-2.62359700
H	-0.32538800	0.98851300	-4.86873100
H	-2.89593300	1.82347100	-4.90759900
H	-2.51481000	2.88556200	-0.01146100
H	-0.83567200	4.52521800	-3.69225700
H	-3.08505900	4.33754200	-2.20439000
C	-0.84257700	0.11216000	-2.87965100
C	-2.06786700	0.12736900	-2.12646200
C	0.11011500	3.32137800	-2.06203300
C	-0.43579700	2.76530700	-0.85476200
H	0.07992900	-0.34815000	-2.55073800
H	1.12291000	3.19313900	-2.41510900
C	0.14918500	2.85832600	1.88749700
C	-0.26540900	2.31141200	3.11008500
C	0.27861400	4.25429400	1.77092600
C	-0.54483200	3.14417300	4.19747800
H	-0.36553700	1.23870500	3.21891900
C	0.00728000	5.08197100	2.85997800
H	0.58889700	4.69452800	0.82792900
C	-0.40846000	4.52803300	4.07532900
H	-0.87095800	2.70773500	5.13733300
H	0.11364700	6.15818300	2.75797800
H	-0.62794300	5.17420400	4.92056900
C	-2.91175400	-2.27495100	-0.87777600
C	-2.24048100	-3.05728000	-1.83361200
C	-4.03197300	-2.80663900	-0.22168700
C	-2.69443400	-4.34201200	-2.13371100
H	-1.34281600	-2.68219700	-2.31676400
C	-4.48109000	-4.09465100	-0.52601200
H	-4.55882600	-2.22535700	0.52709200
C	-3.81609800	-4.86425700	-1.48262100
H	-2.16649900	-4.93715400	-2.87379200
H	-5.35162100	-4.49297400	-0.01251400
H	-4.16648400	-5.86529000	-1.71770800
C	-3.54984600	0.27721500	0.39425800
C	-4.85160900	0.37649900	-0.12700600
C	-3.25261800	0.90508000	1.61269400

SUPPORTING INFORMATION

C	-5.82185400	1.11979100	0.54616900
H	-5.11388000	-0.13735800	-1.04589600
C	-4.22450000	1.64897200	2.28496400
H	-2.25384200	0.82195200	2.02531000
C	-5.50878500	1.76321300	1.74839900
H	-6.82376500	1.19327900	0.13337600
H	-3.97304900	2.13943600	3.22096600
H	-6.26674700	2.34335600	2.26680400
C	2.17792500	2.00321700	-0.08457700
C	3.08107000	2.83518500	0.58943800
C	2.60888700	1.29469900	-1.22007300
C	4.38906100	2.97954300	0.11618300
H	2.77585200	3.37170100	1.48131400
C	3.90633300	1.46191600	-1.70176800
H	1.94309400	0.59109600	-1.70993900
C	4.79981200	2.30678700	-1.03591100
H	5.08341100	3.62261800	0.64969400
H	4.22836200	0.90976000	-2.57944800
H	5.81648000	2.41980200	-1.40089200
C	6.38289300	-0.44568700	0.77358100
C	7.57489600	-0.51984000	0.05777900
C	7.61081700	-1.16994100	-1.18110500
C	6.45072300	-1.75005300	-1.70629200
C	5.25103100	-1.68372700	-1.00173100
C	5.21184100	-1.02763600	0.24684500
H	6.34201800	0.06552200	1.73014700
H	8.47598500	-0.06883400	0.46262700
H	8.54259900	-1.22267700	-1.73698800
H	6.48205200	-2.25060300	-2.66982700
H	4.33252800	-2.10809300	-1.39997700
Br	1.57650700	-2.60041700	-1.84478100
C	-0.52619000	-2.59422200	1.19993700
C	-1.56238300	-2.93128500	2.26604900
C	0.42996600	-2.88138400	3.34055200
C	0.74935200	-2.49996500	1.88741900
H	-0.55342900	-3.09770700	0.23807200
H	1.60401100	-2.92948400	1.36945600
C	-0.96687300	-2.25482600	3.51844600
H	-1.45576400	-2.56860600	4.44581300
H	-0.95182400	-1.16288600	3.46650200
C	-1.30778500	-4.43490900	2.58739400
H	-2.08745200	-4.80830200	3.25941800
H	-1.31844300	-5.05420700	1.68553400
C	0.08340500	-4.40095400	3.29318100
H	0.02225800	-4.78789500	4.31505700
H	0.84626200	-4.97997500	2.76435900
H	-2.59434600	-2.69549800	2.01104900
H	1.19608400	-2.61092600	4.06652700
C	1.62567000	-0.76394500	2.13828500
C	2.89891800	-0.83067200	1.49702900

SUPPORTING INFORMATION

C	3.97798500	-0.92355400	0.94136400
O	1.46081100	-0.21898000	3.22336100

INT7

B3LYP-D3/BSI SCF energy in acetonitrile: -2841.329922 a.u.

M06/BSII SCF energy in acetonitrile: -2840.061051 a.u.

M06/BSII free energy in acetonitrile: -2839.365485 a.u.

Pd	-0.23664300	-0.84969800	0.15449700
P	1.46611800	0.91150000	0.17137500
P	-2.15129100	0.43683500	0.11362600
Fe	-0.62955900	3.19170100	-1.23748600
C	-2.67880400	3.03183400	-1.19563200
C	-1.42551400	2.78574900	-3.12325900
C	-2.28639400	3.67175400	-2.40704400
C	0.16098900	3.46775400	0.63750700
C	0.79369000	4.71367200	-1.20227000
C	0.02195100	4.73367300	-0.00121000
H	-3.29706100	3.46875700	-0.42601100
H	-0.92915400	2.99986000	-4.06067700
H	-2.55629400	4.67714000	-2.70330400
H	-0.32385000	3.15971600	1.55237700
H	0.86365900	5.51294800	-1.92859200
H	-0.60181300	5.54866300	0.34221600
C	-1.28085600	1.59247700	-2.36145100
C	-2.05249200	1.73570400	-1.15609000
C	1.42117600	3.43770100	-1.30499600
C	1.02932900	2.65275400	-0.16816400
H	-0.69493400	0.72078200	-2.62246400
H	2.05226000	3.10031900	-2.11503300
C	2.24655900	1.05800800	1.83235500
C	2.00077900	0.05519400	2.78298300
C	3.01729500	2.17300000	2.20315200
C	2.52724100	0.15386000	4.07300300
H	1.39259400	-0.80330100	2.51350500
C	3.55203600	2.26552100	3.48904500
H	3.19276600	2.97467200	1.49222200
C	3.30843700	1.25655900	4.42608800
H	2.32689400	-0.63059100	4.79720700
H	4.15125700	3.12969700	3.76132100
H	3.71910700	1.33478600	5.42869400
C	-3.72757600	-0.40618000	-0.31275200
C	-3.87925400	-0.87313000	-1.62997700
C	-4.73139600	-0.66917500	0.63081700
C	-5.02918300	-1.57233500	-1.99700400
H	-3.08471900	-0.72845000	-2.35674000
C	-5.88030800	-1.37112500	0.25681400
H	-4.62515000	-0.33198600	1.65591100
C	-6.03371500	-1.82081200	-1.05640300
H	-5.13622500	-1.92960800	-3.01751000

SUPPORTING INFORMATION

H	-6.65316200	-1.56510500	0.99505400
H	-6.92771700	-2.36671700	-1.34418900
C	-2.44591200	1.27876200	1.71570900
C	-3.54869000	2.12417900	1.92838700
C	-1.51658700	1.09521900	2.75085900
C	-3.69347400	2.79575500	3.14318700
H	-4.30166300	2.24830000	1.15723100
C	-1.66311500	1.76847400	3.96508900
H	-0.66954500	0.43589000	2.59733700
C	-2.74791900	2.62615700	4.16001100
H	-4.54738800	3.44916500	3.29630000
H	-0.92729000	1.62340600	4.75091200
H	-2.86349100	3.15401600	5.10226600
C	2.80193400	0.66664000	-1.06996800
C	4.11062700	1.14224900	-0.90057400
C	2.43616400	0.06738600	-2.28610200
C	5.03550300	1.03415500	-1.94041400
H	4.41662300	1.59120600	0.03804600
C	3.36319700	-0.02728700	-3.32723200
H	1.43885000	-0.34446400	-2.42478000
C	4.66131500	0.45965200	-3.15922800
H	6.04922000	1.39748500	-1.79751300
H	3.06945300	-0.49129100	-4.26480000
H	5.38316200	0.38111400	-3.96734600
C	4.25617200	-2.04798800	1.48462100
C	5.62338300	-1.78504200	1.43601000
C	6.31649300	-1.88497500	0.22598100
C	5.63805400	-2.25206400	-0.94097100
C	4.26999900	-2.50607500	-0.90561000
C	3.56244100	-2.40002400	0.30988700
H	3.71842000	-1.97767800	2.42239000
H	6.14862400	-1.50527300	2.34451600
H	7.38223800	-1.67812900	0.19173800
H	6.17365100	-2.32767500	-1.88220100
H	3.73572200	-2.77173100	-1.81121200
C	2.16448100	-2.68062700	0.33663700
C	0.97671100	-2.97213300	0.29470500
Br	-0.63136600	-2.08324700	-3.33688100
C	-1.45338500	-2.53041000	0.32706000
C	-2.15958100	-2.74547500	1.67741800
C	-0.61363100	-4.40221600	1.62903700
C	-0.35604800	-3.62289200	0.30684700
H	-2.10078900	-2.55691000	-0.54712100
H	-0.42349300	-4.25810700	-0.58231800
C	-1.01985600	-3.26046700	2.58336800
H	-1.37492900	-3.62259500	3.55395900
H	-0.22420700	-2.52582500	2.74753800
C	-3.02426600	-4.02634700	1.52872100
H	-3.67346600	-4.14774600	2.40327600
H	-3.66593500	-3.98728300	0.64326500

SUPPORTING INFORMATION

C	-1.95226700	-5.16230300	1.45728600
H	-2.08220100	-5.88317400	2.27044300
H	-1.98671600	-5.71866900	0.51516700
H	-2.71725500	-1.88604900	2.05116800
H	0.22908300	-5.02766500	1.93398400

INT8

B3LYP-D3/BSI SCF energy in acetonitrile: -2954.65149 a.u.

M06/BSII SCF energy in acetonitrile: -2953.355021 a.u.

M06/BSII free energy in acetonitrile: -2952.654912 a.u.

Pd	0.12467700	0.37998300	-0.91544900
P	-0.10868400	-2.04355300	-0.20811300
P	0.81549200	1.11168400	1.29391900
Fe	2.53795600	-1.79251300	1.89494600
C	3.01897100	-0.05351700	2.88569500
C	4.31821900	-0.95035500	1.19839100
C	4.21527000	-0.77486600	2.61141900
C	0.74407700	-2.56681300	2.53518700
C	2.63890100	-3.84988600	2.21657300
C	1.80703400	-3.23913100	3.20263300
H	2.65884000	0.20922300	3.86877200
H	5.09671900	-1.49349900	0.67899300
H	4.89994300	-1.16361100	3.35403600
H	-0.04080500	-1.99298500	3.00339900
H	3.55007200	-4.40242600	2.40445000
H	1.97705400	-3.24320200	4.27127500
C	3.18847400	-0.33812800	0.58885600
C	2.36244700	0.21469600	1.63245400
C	2.08959100	-3.56556700	0.93351200
C	0.91010700	-2.76481900	1.11984600
H	2.97586800	-0.30293900	-0.47364600
H	2.50317300	-3.86857200	-0.01781800
C	-1.83186000	-2.51090800	0.21634100
C	-2.88449400	-1.82955600	-0.41635700
C	-2.12846400	-3.52927000	1.13554800
C	-4.20950600	-2.15807600	-0.12985600
H	-2.67619600	-1.02422300	-1.11381800
C	-3.45652300	-3.84956600	1.42574300
H	-1.32928400	-4.07242600	1.62775200
C	-4.49811400	-3.16445800	0.79591900
H	-5.01255200	-1.61548500	-0.61611800
H	-3.67394200	-4.63538800	2.14345000
H	-5.53083800	-3.40937100	1.02717700
C	1.24238400	2.80821900	1.86922300
C	2.56656800	3.27120100	1.80233300
C	0.24699000	3.65020400	2.38784300
C	2.88544400	4.55702300	2.24149200
H	3.34973000	2.63213900	1.40671800
C	0.57052600	4.93431800	2.82861900

SUPPORTING INFORMATION

H	-0.78079600	3.30723100	2.45083100
C	1.88876700	5.39151100	2.75456500
H	3.91349000	4.90298500	2.18581600
H	-0.20872100	5.57578800	3.22997300
H	2.13902100	6.39108600	3.09809000
C	-0.45174000	0.61750100	2.52837400
C	-0.19153800	0.63838700	3.91011700
C	-1.72182200	0.23412600	2.08005700
C	-1.16475900	0.21310400	4.81287300
H	0.76082000	0.99411000	4.28542900
C	-2.69902000	-0.18725700	2.98652100
H	-1.95122100	0.26073700	1.02134300
C	-2.41608500	-0.21443300	4.35179600
H	-0.94922800	0.22062900	5.87742000
H	-3.67293000	-0.49230800	2.61671200
H	-3.16955700	-0.55037200	5.05835400
C	0.32836500	-3.13657400	-1.62455500
C	-0.35345700	-4.33853400	-1.87101900
C	1.40908600	-2.77281100	-2.44269000
C	0.04139300	-5.16246200	-2.92668200
H	-1.18941700	-4.63475200	-1.24542000
C	1.80504300	-3.60676600	-3.49058700
H	1.93805100	-1.83540200	-2.28966600
C	1.12259700	-4.80051100	-3.73610400
H	-0.49600100	-6.08766900	-3.11510300
H	2.64118800	-3.31133700	-4.11798200
H	1.42679300	-5.44427200	-4.55668100
C	-4.75629100	1.36966400	0.51076600
C	-5.95116300	0.89051900	1.04485400
C	-6.95604900	0.40464500	0.20246300
C	-6.75908400	0.39951400	-1.18239000
C	-5.56384400	0.87014400	-1.72512900
C	-4.54540400	1.36078300	-0.88252800
H	-3.97655400	1.74516900	1.16436700
H	-6.09731200	0.89717500	2.12116100
H	-7.88625200	0.03233800	0.62155700
H	-7.53648300	0.02447600	-1.84181700
H	-5.40807200	0.86191900	-2.79964300
C	-3.31886700	1.84533500	-1.43365100
C	-2.27922400	2.26057100	-1.90846200
Br	3.28823900	0.34537700	-3.30419700
C	0.29842800	2.27694200	-1.96620800
C	0.93894600	3.50530300	-1.30111300
C	-0.96739300	4.36217500	-2.16404900
C	-1.07556800	2.83954100	-2.50506500
H	0.93653200	1.93583600	-2.78153900
H	-1.13537400	2.68874700	-3.59091000
C	-0.27454200	4.30296500	-0.78894900
H	-0.01018400	5.28771800	-0.39055700
H	-0.86445800	3.76587100	-0.04219600

SUPPORTING INFORMATION

C	1.44296800	4.42521500	-2.44899500
H	2.05937500	5.23043100	-2.03257100
H	2.05551200	3.87763300	-3.17123600
C	0.12283000	4.98593300	-3.06227800
H	0.08610000	6.07830200	-2.99990000
H	-0.00867500	4.71259200	-4.11455000
H	1.72423500	3.27934800	-0.58656100
H	-1.93281000	4.87210600	-2.20583700
C	-0.44171200	-0.16935900	-2.69255200
O	-0.80109400	-0.47035900	-3.73454700

TS5

B3LYP-D3/BSI SCF energy in acetonitrile: -2954.639912 a.u.

M06/BSII SCF energy in acetonitrile: -2953.342304 a.u.

M06/BSII free energy in acetonitrile: -2952.640855 a.u.

Pd	0.12379600	0.36586300	-0.81055500
P	-0.13966600	-1.98987000	-0.50613000
P	0.87124200	0.89969700	1.47927300
Fe	2.46312300	-2.09908700	1.73363100
C	2.93841300	-0.56479900	3.01936000
C	4.31448500	-1.24239900	1.28966100
C	4.12232800	-1.29170500	2.70369200
C	0.61740800	-2.88409300	2.16886400
C	2.47985200	-4.18204800	1.73407700
C	1.62373400	-3.69462500	2.76758700
H	2.51356100	-0.45884700	4.00640000
H	5.10565500	-1.73265400	0.73775300
H	4.73760700	-1.83089900	3.41223000
H	-0.16983400	-2.35644900	2.68627600
H	3.36323100	-4.79124500	1.87313200
H	1.74406200	-3.86748400	3.82897800
C	3.25098500	-0.48750400	0.72125900
C	2.38080600	-0.06697200	1.79018000
C	2.00141700	-3.68377300	0.48832200
C	0.84038600	-2.87660200	0.74696600
H	3.10798200	-0.27243300	-0.33178800
H	2.44606200	-3.85364200	-0.48212500
C	-1.87491200	-2.47543000	-0.15019400
C	-2.91553200	-1.68474400	-0.66272900
C	-2.18773600	-3.62180000	0.59819000
C	-4.24589500	-2.03381100	-0.42768400
H	-2.69045400	-0.78475100	-1.22655500
C	-3.52059800	-3.96390900	0.83536000
H	-1.39817500	-4.24857000	0.99748100
C	-4.55088000	-3.17049000	0.32535400
H	-5.04013500	-1.40747100	-0.81818200
H	-3.75044900	-4.85033100	1.41958100
H	-5.58747400	-3.43260300	0.51697300
C	1.38125400	2.58466100	2.01855100

SUPPORTING INFORMATION

C	2.66575200	3.05353200	1.69682300
C	0.49389500	3.43274200	2.69831200
C	3.05232300	4.34789800	2.04793500
H	3.36626200	2.40950900	1.17350900
C	0.88692700	4.72440500	3.05475000
H	-0.50413700	3.08974800	2.95219000
C	2.16436100	5.18633400	2.72820500
H	4.04864300	4.69791200	1.79328600
H	0.19211600	5.36896800	3.58562600
H	2.46764200	6.19215200	3.00435400
C	-0.37727100	0.40304000	2.72739300
C	-0.12145000	0.43534200	4.10907700
C	-1.63252800	-0.02889800	2.27675200
C	-1.08567100	-0.01369400	5.01156300
H	0.81974100	0.82406900	4.48239900
C	-2.59969500	-0.47454200	3.18132100
H	-1.85541800	-0.02275600	1.21651100
C	-2.32166900	-0.48088000	4.54890200
H	-0.87499000	0.00634100	6.07695400
H	-3.56314000	-0.81086300	2.81069900
H	-3.06786700	-0.83298700	5.25535800
C	0.30256600	-2.90837500	-2.03792700
C	-0.33852000	-4.10957900	-2.37929100
C	1.34760000	-2.42655000	-2.84014500
C	0.06079200	-4.81691300	-3.51451700
H	-1.14590900	-4.49645200	-1.76602900
C	1.74795400	-3.14505900	-3.96925000
H	1.84768800	-1.48998100	-2.60382900
C	1.10590300	-4.33786600	-4.31008600
H	-0.44521400	-5.74203200	-3.77568200
H	2.55759300	-2.76341200	-4.58506200
H	1.41405000	-4.89057500	-5.19316500
C	-4.60497200	1.32446100	0.75179500
C	-5.74035200	0.80125700	1.36749000
C	-6.86695200	0.47273300	0.60706900
C	-6.85359100	0.67241900	-0.77723300
C	-5.71934800	1.18891400	-1.40312700
C	-4.57863400	1.51871800	-0.64361200
H	-3.73053600	1.57659400	1.34142600
H	-5.74328400	0.64863100	2.44286000
H	-7.75012800	0.06421500	1.08948400
H	-7.72702300	0.42122800	-1.37209400
H	-5.70574900	1.33877400	-2.47837200
C	-3.40960600	2.04374800	-1.27683000
C	-2.42030400	2.49864200	-1.81634300
Br	3.27334900	0.81611800	-2.92627400
C	0.10300400	2.38488800	-2.23531700
C	0.92622600	3.33274800	-1.32658300
C	-0.96217500	4.51330000	-1.74033900
C	-1.26036400	3.14091900	-2.43097800

SUPPORTING INFORMATION

H	0.64903300	2.23652400	-3.16461000
H	-1.46138500	3.27263000	-3.50064200
C	-0.15772100	4.05587000	-0.50841100
H	0.24052000	4.88691700	0.08010900
H	-0.72408500	3.39475200	0.15166700
C	1.41439400	4.47893300	-2.25237100
H	2.12545200	5.10651900	-1.70285900
H	1.92610100	4.09648900	-3.13934000
C	0.10259900	5.26106500	-2.57427200
H	0.17031700	6.30477200	-2.25195000
H	-0.14183700	5.26218100	-3.64163100
H	1.73983900	2.85495100	-0.79138900
H	-1.87194100	5.08693000	-1.54953400
C	-0.40054500	0.44430300	-2.60390800
O	-0.79766200	0.19097200	-3.66609900

INT9

B3LYP-D3/BSI SCF energy in acetonitrile: -2954.678209 a.u.

M06/BSII SCF energy in acetonitrile: -2953.391778 a.u.

M06/BSII free energy in acetonitrile: -2952.692418 a.u.

Pd	0.09760400	-0.37354400	0.13553500
P	-2.16750500	-1.39488100	0.37421900
P	-0.56106400	1.67061000	-0.75943800
Fe	-3.51307000	0.51364900	-2.07895400
C	-1.68498800	0.21793000	-2.96799600
C	-3.29157600	1.63624400	-3.82513500
C	-2.67324100	0.35908400	-3.98269700
C	-4.41325000	-1.25419200	-1.49974800
C	-5.29373600	0.83310600	-1.04842300
C	-5.41497600	-0.31628200	-1.88634600
H	-1.06144300	-0.64822200	-2.79508900
H	-4.11154200	2.02378900	-4.41571600
H	-2.93941200	-0.39184400	-4.71471900
H	-4.22718100	-2.21341700	-1.96183100
H	-5.88805300	1.73522300	-1.11268700
H	-6.12076500	-0.44335900	-2.69673600
C	-2.68957000	2.29095200	-2.71186100
C	-1.68968500	1.41206500	-2.16461500
C	-4.21054100	0.61456000	-0.14940700
C	-3.65369000	-0.68320800	-0.42212200
H	-2.97305400	3.25720800	-2.32166000
H	-3.84964500	1.31175200	0.59201800
C	-2.26677700	-3.12704200	-0.23725500
C	-3.12310100	-4.08490900	0.32316400
C	-1.50093800	-3.46360800	-1.36348500
C	-3.21223300	-5.36137900	-0.23770500
H	-3.72254900	-3.84062800	1.19473000
C	-1.60331600	-4.73430100	-1.93253700
H	-0.81446600	-2.73575100	-1.78410100

SUPPORTING INFORMATION

C	-2.45771200	-5.68640800	-1.36863500
H	-3.87446700	-6.09920400	0.20662600
H	-1.00818100	-4.98356600	-2.80672900
H	-2.53186600	-6.67821400	-1.80576700
C	-1.44272000	2.71407100	0.46358500
C	-1.94358100	3.98809900	0.14759200
C	-1.63347800	2.20475200	1.75797300
C	-2.65005500	4.72058700	1.10292300
H	-1.76881600	4.41753600	-0.83331900
C	-2.34041300	2.93931300	2.71166200
H	-1.24182800	1.22550600	2.01328800
C	-2.85558300	4.19543500	2.38301600
H	-3.03509400	5.70376100	0.84852300
H	-2.48759300	2.52677500	3.70569900
H	-3.40739000	4.76845700	3.12262500
C	0.71486700	2.75489400	-1.51972900
C	1.27260100	2.35270400	-2.74466500
C	1.20150400	3.91208900	-0.89461200
C	2.29259700	3.09835500	-3.33462600
H	0.91331000	1.45526100	-3.23943800
C	2.22633500	4.65453000	-1.48657500
H	0.78691700	4.24233800	0.05141700
C	2.77556500	4.24949400	-2.70509900
H	2.71225100	2.77785000	-4.28404400
H	2.59228600	5.55003900	-0.99249100
H	3.57258600	4.82791200	-3.16349900
C	-2.66836900	-1.43563700	2.14814400
C	-4.01619200	-1.48288200	2.54163900
C	-1.67300300	-1.36220100	3.13750100
C	-4.35960800	-1.45761500	3.89484400
H	-4.80091800	-1.53210900	1.79353500
C	-2.01964500	-1.33445000	4.49000600
H	-0.62719700	-1.33222800	2.84942600
C	-3.36314600	-1.37922300	4.87147000
H	-5.40606700	-1.49459400	4.18431800
H	-1.23928900	-1.27366400	5.24365000
H	-3.63253100	-1.35217000	5.92355300
C	7.84754600	-1.47922600	-0.25639100
C	8.70114000	-2.09813100	-1.16875700
C	8.19152100	-2.66231200	-2.34224200
C	6.81828700	-2.60347300	-2.60083000
C	5.95724200	-1.98563200	-1.69542200
C	6.46189900	-1.41457700	-0.50805200
H	8.24372400	-1.04208800	0.65527300
H	9.76695800	-2.14048100	-0.96245300
H	8.85959500	-3.14406700	-3.05040900
H	6.41618600	-3.03965800	-3.51100100
H	4.89123100	-1.93840800	-1.89686100
C	5.57738400	-0.78166900	0.41974500
C	4.77713600	-0.24732300	1.16085100

SUPPORTING INFORMATION

C	2.38879400	0.62630500	1.72991300
C	2.20917400	2.15132500	2.00009400
C	4.38069300	1.82922400	2.53524300
C	3.90461000	0.38759400	2.14182500
H	1.73689700	0.04129900	2.37830800
H	3.90365400	-0.25332400	3.03154000
C	3.57518600	2.71070700	1.56054900
H	3.68271900	3.78195900	1.76075600
H	3.80122600	2.51546900	0.50898700
C	2.23262500	2.38040000	3.52897500
H	1.89555300	3.39576700	3.76160100
H	1.57208800	1.68441100	4.05592600
C	3.73940800	2.18639300	3.89450300
H	4.17271800	3.11306400	4.28443700
H	3.89908700	1.40565200	4.64496800
H	1.32687700	2.56945500	1.51783700
H	5.46745800	1.93461500	2.50999300
C	2.00058900	0.32696400	0.27882200
O	2.73720400	0.50050600	-0.66356900
Br	1.19507200	-2.62482600	0.95428900

OMe⁻

B3LYP-D3/BSI SCF energy in acetonitrile: -115.176612 a.u.

M06/BSII SCF energy in acetonitrile: -115.1727077 a.u.

M06/BSII free energy in acetonitrile: -115.1601287 a.u.

O	0.79147600	0.00009600	0.00001700
C	-0.52509400	0.00020800	-0.00004800
H	-1.06174900	1.01072600	-0.15360700
H	-1.05951200	-0.63950000	-0.79862400
H	-1.05998400	-0.37323900	0.95237800

INT10

B3LYP-D3/BSI SCF energy in acetonitrile: -3056.361528 a.u.

M06/BSII SCF energy in acetonitrile: -3055.065263 a.u.

M06/BSII free energy in acetonitrile: -3054.323592 a.u.

Pd	-0.12790100	0.23346800	0.13619200
P	1.80391600	1.70816500	0.50971500
P	0.87679500	-1.67248900	-0.71125700
Fe	3.97702400	-0.27882000	-1.16013600
C	2.50936800	-0.23667000	-2.59469200
C	4.42331200	-1.51190300	-2.78170600
C	3.77807900	-0.32225800	-3.23555900
C	4.56211000	1.59519600	-0.51543900
C	5.30381800	-0.37400500	0.44116400
C	5.66746500	0.69841100	-0.42885700
H	1.79386300	0.56520300	-2.70131300
H	5.41994300	-1.83769300	-3.04990700
H	4.19643800	0.41321400	-3.90991400

SUPPORTING INFORMATION

H	4.51303700	2.49147400	-1.11772500
H	5.91415500	-1.23452000	0.68211500
H	6.60340800	0.79525500	-0.96346800
C	3.55472800	-2.16833700	-1.86139200
C	2.35799000	-1.37975100	-1.73429000
C	3.96929600	-0.14950300	0.88639900
C	3.49719900	1.07404900	0.29477800
H	3.78186900	-3.07245300	-1.31633600
H	3.39296900	-0.80391900	1.52539700
C	1.78117200	3.18092900	-0.59424100
C	2.51032300	4.34465900	-0.30180800
C	1.02716600	3.12379600	-1.77665400
C	2.49402100	5.42592200	-1.18444000
H	3.09066200	4.40664600	0.61417000
C	1.01563900	4.20526000	-2.66142600
H	0.43942100	2.23739200	-1.99816900
C	1.74990700	5.35640300	-2.36696800
H	3.06159800	6.32202700	-0.94973000
H	0.42690000	4.15001500	-3.57278100
H	1.73808800	6.19947900	-3.05202100
C	1.40446300	-2.86241700	0.58090600
C	1.91838500	-4.13445100	0.27753800
C	1.28288500	-2.47741500	1.92597400
C	2.31583800	-4.99550700	1.30193800
H	1.99554600	-4.46078200	-0.75448000
C	1.68164400	-3.34015400	2.94899000
H	0.87050300	-1.50152800	2.16750900
C	2.20080700	-4.59921100	2.63785800
H	2.70980100	-5.97729200	1.05573900
H	1.58124100	-3.02990100	3.98499300
H	2.50880400	-5.27250700	3.43265800
C	-0.19323600	-2.62146300	-1.87799900
C	-0.50060700	-2.01764300	-3.10869700
C	-0.78941900	-3.84911700	-1.55696400
C	-1.37372700	-2.63550500	-4.00390000
H	-0.06451100	-1.05788800	-3.37070400
C	-1.67024900	-4.46232100	-2.45199200
H	-0.57456500	-4.33546600	-0.61238000
C	-1.96480800	-3.85946300	-3.67653000
H	-1.59715900	-2.15690400	-4.95333100
H	-2.12380100	-5.41361900	-2.18814600
H	-2.64986900	-4.33799900	-4.37056500
C	1.86585200	2.41811300	2.21101300
C	3.07621300	2.65035000	2.88437200
C	0.65028800	2.72916400	2.84649200
C	3.07202200	3.19017700	4.17294900
H	4.02180000	2.41330200	2.40707600
C	0.65537300	3.27065800	4.13421400
H	-0.28484900	2.54229800	2.31733600
C	1.86272100	3.50094500	4.80039500

SUPPORTING INFORMATION

H	4.01388900	3.36749000	4.68504600
H	-0.28699900	3.50890700	4.62079200
H	1.86203000	3.91873200	5.80338700
C	-7.67847400	1.51182200	-0.14362400
C	-8.51839800	2.30903300	-0.91983300
C	-7.99197800	3.09845300	-1.94700000
C	-6.61553000	3.08670100	-2.19382900
C	-5.76766200	2.29271200	-1.42321900
C	-6.28924400	1.49198800	-0.38572400
H	-8.08775500	0.89896800	0.65398400
H	-9.58661700	2.31416700	-0.72171800
H	-8.64924500	3.71868100	-2.54971900
H	-6.19994600	3.69874400	-2.98954700
H	-4.69898900	2.28699100	-1.61239000
C	-5.42615600	0.67483300	0.40921700
C	-4.67321500	-0.01909400	1.06258500
C	-2.36290500	-1.12617600	1.51084500
C	-2.29306400	-2.68324200	1.56126600
C	-4.43694000	-2.28219700	2.15617800
C	-3.85948300	-0.83950100	1.95336800
H	-1.67742600	-0.68354500	2.23456600
H	-3.82588800	-0.32118900	2.91931400
C	-3.69697100	-3.07763600	1.06294600
H	-3.88232200	-4.15581800	1.11731400
H	-3.90636600	-2.72258400	0.05062300
C	-2.33203200	-3.12474300	3.04119800
H	-2.07860900	-4.18657300	3.12632600
H	-1.61693400	-2.56647400	3.65340800
C	-3.81836200	-2.86264600	3.44824300
H	-4.32236900	-3.79491300	3.72216900
H	-3.91328900	-2.17523100	4.29506800
H	-1.44696600	-3.08882800	1.00863700
H	-5.52864800	-2.30801600	2.13046500
C	-1.94349000	-0.65342000	0.11905100
O	-2.65339800	-0.74639900	-0.85977600
O	-1.46317900	1.72396500	0.84267900
C	-2.11848200	2.48039300	-0.13450500
H	-2.95178400	3.04759500	0.31846000
H	-1.46110400	3.22315000	-0.62541200
H	-2.55908900	1.86470300	-0.93974800

TS6

B3LYP-D3/BSI SCF energy in acetonitrile: -3056.356638 a.u.

M06/BSII SCF energy in acetonitrile: -3055.061998 a.u.

M06/BSII free energy in acetonitrile: -3054.322815 a.u.

Pd	0.09681500	-0.17973500	0.06156600
P	-1.61858300	-1.92035300	0.39626700
P	-1.06472800	1.69775900	-0.61321300
Fe	-4.15425400	0.11507900	-0.48971500

SUPPORTING INFORMATION

C	-3.03798300	0.32333900	-2.20088700
C	-4.98673700	1.49757700	-1.80729100
C	-4.42098800	0.40521400	-2.53293100
C	-4.54624800	-1.85191400	-0.00734500
C	-5.10655000	-0.06902600	1.35451300
C	-5.62578100	-1.03177000	0.43640900
H	-2.33536600	-0.41511100	-2.56026600
H	-6.02861400	1.79050000	-1.80851600
H	-4.95751700	-0.27592300	-3.18044900
H	-4.60987200	-2.64934300	-0.73424300
H	-5.66920000	0.71867500	1.83817700
H	-6.65233600	-1.10211900	0.10090100
C	-3.95320900	2.09883100	-1.03092500
C	-2.73586900	1.37236400	-1.26594100
C	-3.70362700	-0.28484600	1.47389400
C	-3.34365100	-1.39168500	0.62840800
H	-4.06765200	2.93165900	-0.35162900
H	-3.01653900	0.30379800	2.06560700
C	-1.70940400	-3.13872600	-0.98306700
C	-2.41626700	-4.34791100	-0.87794600
C	-1.03007600	-2.84576100	-2.17637400
C	-2.45812000	-5.23567700	-1.95412300
H	-2.93266600	-4.59825700	0.04397800
C	-1.07340300	-3.73530500	-3.25342500
H	-0.46305300	-1.92196200	-2.25879200
C	-1.78861500	-4.92997000	-3.14393600
H	-3.00925100	-6.16748500	-1.86300800
H	-0.54293400	-3.49727100	-4.17114500
H	-1.81997900	-5.62454800	-3.97869300
C	-1.37927500	2.90998800	0.73776000
C	-1.74040900	4.23984700	0.47014200
C	-1.25388200	2.48886400	2.07052900
C	-1.98039100	5.12855100	1.52022900
H	-1.83133600	4.58236900	-0.55638100
C	-1.50055800	3.37703300	3.11956500
H	-0.94485700	1.46929300	2.28413900
C	-1.86336000	4.69846900	2.84566000
H	-2.25677800	6.15642000	1.30290700
H	-1.39611000	3.04001400	4.14683400
H	-2.04675000	5.39277200	3.66071600
C	-0.35845700	2.74429800	-1.96718700
C	-1.07899700	3.03614600	-3.13737400
C	0.93637100	3.27089300	-1.82429600
C	-0.51853400	3.83799100	-4.13552400
H	-2.08162400	2.64772800	-3.27502400
C	1.48932500	4.07932100	-2.81760200
H	1.52219900	3.04237900	-0.94548100
C	0.76504100	4.36448500	-3.97841000
H	-1.09203100	4.05415200	-5.03274900
H	2.49090400	4.47956000	-2.68563600

SUPPORTING INFORMATION

H	1.19840400	4.98983100	-4.75389300
C	-1.32915100	-2.97415500	1.88304700
C	-2.37845700	-3.56843400	2.60323200
C	-0.00334400	-3.18430500	2.29962700
C	-2.10555700	-4.36796400	3.71532000
H	-3.40819000	-3.40858200	2.29781600
C	0.26361300	-3.98849400	3.41076300
H	0.81204900	-2.70329300	1.76310800
C	-0.78450700	-4.58201400	4.11944900
H	-2.92474600	-4.82379800	4.26468700
H	1.29180800	-4.14486900	3.72636100
H	-0.57447700	-5.20325500	4.98573600
C	7.81261500	-1.32756300	-0.22345100
C	8.67704900	-1.98438000	-1.09827400
C	8.21034300	-2.46094300	-2.32723100
C	6.86930200	-2.27602400	-2.67853600
C	5.99775000	-1.61995500	-1.81090600
C	6.45888700	-1.13661800	-0.56833400
H	8.17550000	-0.95811000	0.73104400
H	9.71778500	-2.12469300	-0.81968100
H	8.88667400	-2.97238000	-3.00618200
H	6.50070400	-2.64369900	-3.63217400
H	4.95656400	-1.47735000	-2.08176400
C	5.56477400	-0.46533500	0.32275700
C	4.76133300	0.09660200	1.03943200
C	2.38591800	1.03142500	1.53166200
C	2.24697900	2.57322300	1.66001900
C	4.39064100	2.23997100	2.29443300
C	3.89186000	0.78782100	1.98450100
H	1.71630400	0.52247000	2.22654900
H	3.87665700	0.19528200	2.90676600
C	3.64308900	3.06181800	1.22579700
H	3.77696300	4.14238000	1.34434100
H	3.89729300	2.77217100	0.20254100
C	2.22785100	2.93656500	3.16247500
H	1.92688500	3.98056600	3.29646600
H	1.52100000	2.31787100	3.72377300
C	3.71177300	2.71346900	3.59907100
H	4.16716700	3.64712800	3.94478000
H	3.81280700	1.97905800	4.40487800
H	1.39353800	2.97000200	1.11133000
H	5.48016600	2.31879100	2.30207100
C	2.03415300	0.56082600	0.12008300
O	2.66663800	0.82409700	-0.88794100
O	1.92033900	-1.31040800	0.51503100
C	2.38596200	-2.11227500	-0.54747600
H	3.30985200	-2.62791200	-0.24608400
H	1.64477300	-2.87405500	-0.83606900
H	2.61752800	-1.50898700	-1.43955200

SUPPORTING INFORMATION

product

B3LYP-D3/BSI SCF energy in acetonitrile: -809.1117285 a.u.

M06/BSII SCF energy in acetonitrile: -808.6968878 a.u.

M06/BSII free energy in acetonitrile: -808.4319628 a.u.

C	3.41763300	-1.51372300	-0.76797800
C	4.77611100	-1.38780900	-0.47988700
C	5.21734100	-0.43332200	0.44185800
C	4.29109800	0.39851700	1.07948200
C	2.93103300	0.27969200	0.79983700
C	2.47854900	-0.67882200	-0.13118900
H	3.07395500	-2.25371300	-1.48435200
H	5.49227600	-2.03628100	-0.97663200
H	6.27667700	-0.33863100	0.66257600
H	4.62901200	1.14090200	1.79693500
H	2.20628900	0.92035400	1.29312000
C	1.08152300	-0.78083500	-0.41489100
C	-0.11357600	-0.80600200	-0.62672700
C	-2.22585900	0.61368500	-0.41997500
C	-3.19371700	0.21897900	0.72000200
C	-2.30587700	-1.77707300	0.12618300
C	-1.55973200	-0.78356800	-0.82252900
H	-2.75483000	1.01979000	-1.28570800
H	-1.78187500	-1.00861100	-1.87069700
C	-2.44128300	-0.93759200	1.41091500
H	-3.03786500	-1.43318300	2.18393800
H	-1.48206200	-0.63088500	1.83624500
C	-4.39377000	-0.52062500	0.08757700
H	-5.18315300	-0.66593700	0.83182100
H	-4.82792900	0.03557500	-0.74928100
C	-3.77333300	-1.88791400	-0.34822000
H	-4.26884300	-2.72562900	0.15222800
H	-3.84267800	-2.06203200	-1.42686000
H	-3.46549100	1.06485700	1.35413000
H	-1.78868700	-2.73463300	0.21610800
C	-1.18978700	1.63476300	0.00225300
O	-0.87964900	1.90423900	1.14783700
O	-0.62784000	2.21603400	-1.07374600
C	0.44818800	3.13653600	-0.80222700
H	1.27765800	2.62221400	-0.30890700
H	0.76591500	3.51478900	-1.77429800
H	0.10428500	3.95953300	-0.17000600

TS2a

B3LYP-D3/BSI SCF energy in acetonitrile: -2841.256679 a.u.

M06/BSII SCF energy in acetonitrile: -2839.99592 a.u.

M06/BSII free energy in acetonitrile: -2839.30935 a.u.

Pd	-2.16963000	0.31266600	0.72250800
P	-1.43059600	-1.91603200	0.37969000

SUPPORTING INFORMATION

P	3.96230600	0.26481900	0.65175800
Fe	1.25881300	-0.37821000	-1.46836500
C	2.79443200	0.88064500	-2.00894700
C	0.70221900	1.63354400	-1.38404700
C	1.55871100	1.39381800	-2.50120300
C	1.27851400	-2.30248600	-0.68112800
C	0.97252600	-1.82154600	-2.91693600
C	1.92156900	-2.27535800	-1.95244400
H	3.63408600	0.56698900	-2.61320000
H	-0.31553200	1.99297200	-1.42045000
H	1.29791400	1.52412900	-3.54378700
H	1.74033600	-2.57441600	0.25477500
H	1.16447400	-1.64790800	-3.96767600
H	2.96338200	-2.50179600	-2.13265200
C	1.40931800	1.27100800	-0.20273400
C	2.71158800	0.79996500	-0.57523000
C	-0.25356500	-1.55436400	-2.24228500
C	-0.08413700	-1.88691400	-0.85130700
H	1.01193900	1.29927000	0.80124000
H	-1.15695500	-1.17928600	-2.69879800
C	-0.81820200	-2.93776200	1.78495400
C	-1.19982100	-2.61661800	3.09444600
C	-0.10869700	-4.12894500	1.54998000
C	-0.84496500	-3.45255500	4.15721200
H	-1.76220700	-1.71162500	3.28724900
C	0.25586000	-4.95299100	2.61434800
H	0.14856500	-4.42399300	0.53810500
C	-0.10717300	-4.61372700	3.92171900
H	-1.14494000	-3.19102600	5.16815100
H	0.81274400	-5.86540000	2.42074600
H	0.17454000	-5.25851100	4.74944200
C	5.27167800	1.55415700	0.41297300
C	4.95579300	2.85703300	-0.00518600
C	6.60337800	1.26369000	0.75995500
C	5.94788200	3.83781500	-0.09044000
H	3.93355200	3.11084700	-0.27062100
C	7.59367000	2.24300800	0.66975100
H	6.87259800	0.26303600	1.08816500
C	7.26995500	3.53455000	0.24286000
H	5.68464400	4.83891600	-0.42157300
H	8.61894800	1.99603900	0.93213800
H	8.04101800	4.29662600	0.17230200
C	4.73735000	-1.20997800	-0.15414100
C	5.49742100	-1.14408100	-1.33469700
C	4.51575400	-2.46297400	0.43718600
C	5.99363500	-2.30766900	-1.92440800
H	5.70899500	-0.18152300	-1.79009200
C	5.01197800	-3.62938400	-0.15247600
H	3.94548600	-2.52975200	1.36017100
C	5.74626000	-3.55406000	-1.33775600

SUPPORTING INFORMATION

H	6.57525500	-2.24259200	-2.83998100
H	4.82747900	-4.59191100	0.31649400
H	6.13374700	-4.45868800	-1.79797300
C	-2.66431000	-3.10565800	-0.31436700
C	-2.47885500	-3.82596600	-1.50152500
C	-3.84064600	-3.30285800	0.42916900
C	-3.46458400	-4.71174300	-1.94791500
H	-1.57399800	-3.70150700	-2.08480300
C	-4.82037500	-4.18894300	-0.01728400
H	-3.99186900	-2.76091800	1.35961500
C	-4.63698700	-4.89195300	-1.21244900
H	-3.31009300	-5.26119300	-2.87233100
H	-5.72651200	-4.32825400	0.56545500
H	-5.40212900	-5.57807900	-1.56413300
C	-1.76693100	5.53757500	-0.65937400
C	-1.63252900	6.92230800	-0.73479500
C	-2.03466900	7.73092700	0.33353700
C	-2.57465700	7.14371800	1.48246300
C	-2.71208900	5.75967500	1.56863400
C	-2.30922500	4.93298900	0.49691800
H	-1.45563400	4.91038400	-1.48959900
H	-1.21220100	7.37244900	-1.62986500
H	-1.92758100	8.81005500	0.27149000
H	-2.88812700	7.76667200	2.31560500
H	-3.12884700	5.30460700	2.46229200
C	-2.44265900	3.51615800	0.57364400
C	-2.52607600	2.29033300	0.62316200
Br	-0.60931300	0.78671700	2.77142700
C	-3.92046300	-0.07366800	-0.51730600
C	-3.76250100	-0.31216900	-2.01865800
C	-4.17275900	1.90402900	-1.76914300
C	-4.21420100	1.30828300	-0.38396000
H	-4.43710700	-0.80161400	0.10164100
H	-4.85988300	1.70018300	0.39284800
C	-3.12697100	1.01687500	-2.47641200
H	-3.13346800	1.14359700	-3.56291400
H	-2.11434900	1.16160800	-2.09523900
C	-5.20405700	-0.16677700	-2.59710100
H	-5.20942700	-0.44276700	-3.65620600
H	-5.92050800	-0.81044600	-2.07853300
C	-5.50058100	1.35200100	-2.40523600
H	-5.66376300	1.85667500	-3.36165200
H	-6.37314000	1.54571700	-1.77460600
H	-3.26080700	-1.23682400	-2.29527100
H	-4.05730800	2.98546300	-1.81760300

TS2b

B3LYP-D3/BSI SCF energy in acetonitrile: -2841.273591 a.u.

M06/BSII SCF energy in acetonitrile: -2840.014983 a.u.

M06/BSII free energy in acetonitrile: -2839.326603 a.u.

SUPPORTING INFORMATION

Pd	-2.53433100	0.96492900	0.28409200
P	-1.68962400	-1.26863500	0.57746000
P	3.07522100	-0.25512400	-0.01328700
Fe	0.44167500	-1.08378700	-2.19748400
C	2.30058300	-0.49310200	-2.87232000
C	0.43103200	0.86725200	-2.90369600
C	1.28243400	0.04921900	-3.71041100
C	0.18139300	-2.80288300	-1.06672100
C	-0.69861700	-2.50859800	-3.18047000
C	0.34426300	-3.14392900	-2.43864700
H	3.07971200	-1.17552900	-3.18164000
H	-0.45947400	1.38483300	-3.23493300
H	1.14787400	-0.16508200	-4.76290600
H	0.82878600	-3.10807700	-0.26027600
H	-0.82749100	-2.54155100	-4.25442200
H	1.14736100	-3.74252900	-2.84821100
C	0.92531400	0.82947500	-1.56907400
C	2.08966300	-0.01205900	-1.53421500
C	-1.50296600	-1.76495100	-2.27003700
C	-0.96836400	-1.94849600	-0.94729100
H	0.48383800	1.32026400	-0.71476500
H	-2.36267500	-1.15804100	-2.51490300
C	-0.48384100	-1.78500000	1.87995100
C	0.28005800	-0.84429100	2.58007000
C	-0.33585500	-3.15016600	2.19097200
C	1.17740500	-1.25365100	3.57168100
H	0.17431700	0.20578800	2.35333300
C	0.56207100	-3.55689700	3.17713400
H	-0.92246800	-3.89673100	1.66511100
C	1.32066300	-2.60808100	3.87261800
H	1.76266600	-0.50701600	4.10065400
H	0.66728400	-4.61383400	3.40489400
H	2.01750200	-2.92690400	4.64250400
C	4.55434100	0.80224500	-0.36421600
C	4.59355200	1.75482200	-1.39361100
C	5.64091800	0.72936000	0.52636000
C	5.68988500	2.61271500	-1.52890200
H	3.76647100	1.83769300	-2.09155300
C	6.73721300	1.58021100	0.38714300
H	5.62858000	0.00446800	1.33718300
C	6.76408100	2.52946300	-0.64057300
H	5.70200600	3.34523400	-2.33175900
H	7.56786700	1.50741600	1.08401700
H	7.61438400	3.19742000	-0.74569900
C	3.76861000	-1.95512900	-0.23747400
C	4.72830600	-2.28855000	-1.20829100
C	3.29016700	-2.96179900	0.61605700
C	5.17450400	-3.60520100	-1.33928100
H	5.12989600	-1.51742700	-1.85929800

SUPPORTING INFORMATION

C	3.73414200	-4.28022700	0.48357500
H	2.56515800	-2.71556900	1.38613100
C	4.67418400	-4.60475400	-0.49727400
H	5.91418500	-3.85161700	-2.09630500
H	3.35004500	-5.04707300	1.15081400
H	5.02379600	-5.62825800	-0.60066800
C	-3.09707600	-2.39041900	0.96870700
C	-3.36355200	-3.56117300	0.24934700
C	-3.91392600	-2.04707600	2.05726800
C	-4.43733200	-4.37913200	0.61485900
H	-2.74053200	-3.83775400	-0.59520900
C	-4.97954900	-2.86785100	2.42454400
H	-3.72036400	-1.13240200	2.61283900
C	-5.24565900	-4.03554400	1.70083700
H	-4.63805600	-5.28600200	0.05102500
H	-5.60604100	-2.59424900	3.26905900
H	-6.07884000	-4.67298400	1.98317700
C	2.26529400	3.26062300	1.10888400
C	3.56127600	3.56366100	1.51884700
C	3.94823600	3.35539700	2.84645500
C	3.02735700	2.84937200	3.77039700
C	1.72667100	2.54691700	3.37327400
C	1.32856500	2.74427900	2.03234200
H	1.96957300	3.39927900	0.07376700
H	4.27792500	3.94064400	0.79587700
H	4.96419000	3.58112000	3.15689400
H	3.32519100	2.68593800	4.80220500
H	1.01270300	2.14540700	4.08576800
C	0.02598500	2.37922400	1.59823000
C	-1.06829000	2.00630200	1.17027000
Br	-4.51175300	0.06837600	-1.13022700
C	-3.47334500	2.90498800	0.05641900
C	-3.35760500	3.55930500	-1.31838500
C	-1.73324000	4.48846200	-0.03531900
C	-2.44920900	3.49552000	0.85481500
H	-4.44857000	2.68665300	0.48551400
H	-2.57704700	3.67417200	1.91665000
C	-1.83575700	3.81334000	-1.41922200
H	-1.57184700	4.49141400	-2.23628000
H	-1.23947600	2.90084400	-1.49567600
C	-3.87765300	5.01591800	-1.11156600
H	-3.93583500	5.53286300	-2.07500200
H	-4.87308100	5.03792700	-0.65851200
C	-2.78143000	5.64412900	-0.19614600
H	-2.29242100	6.49631600	-0.67706200
H	-3.17026000	5.98601900	0.76764200
H	-3.83253800	3.00829900	-2.12937300
H	-0.75064500	4.80415200	0.31357900

TS3a

SUPPORTING INFORMATION

B3LYP-D3/BSI SCF energy in acetonitrile: -2681.822046 a.u.

M06/BSII SCF energy in acetonitrile: -2680.710147 a.u.

M06/BSII free energy in acetonitrile: -2680.167344 a.u.

Pd	-2.51345300	-0.38125700	0.27411200
P	-0.66667900	-1.84706600	0.42660000
P	3.58600400	1.25071000	0.76991600
Fe	1.20248000	0.19130300	-1.58787000
C	2.36053100	1.87725400	-1.86885900
C	0.12366600	1.93941800	-1.28497100
C	1.04396200	2.10354200	-2.36656900
C	1.81624000	-1.72225600	-1.10433500
C	1.03783600	-1.12128300	-3.19346800
C	2.21231700	-1.41970000	-2.43713800
H	3.26850600	1.90044000	-2.45443100
H	-0.95473400	2.00634200	-1.34418900
H	0.78372000	2.31257800	-3.39624300
H	2.47871800	-1.95417900	-0.28678500
H	1.00988000	-0.81136600	-4.22982600
H	3.23258800	-1.37575400	-2.79383300
C	0.87670900	1.61398600	-0.11998900
C	2.26928700	1.56901000	-0.46685600
C	-0.08896300	-1.23351200	-2.33154300
C	0.38602300	-1.61025200	-1.02602600
H	0.47700300	1.40147300	0.85972600
H	-1.12108500	-1.05228200	-2.59464900
C	0.48133200	-1.73992500	1.85788200
C	0.41826900	-0.67757100	2.76797700
C	1.45091700	-2.74239300	2.03919500
C	1.32358500	-0.60230300	3.82995700
H	-0.33433700	0.09179700	2.66042200
C	2.35659600	-2.66184600	3.09696400
H	1.49897700	-3.58517700	1.35683300
C	2.29661600	-1.58954700	3.99311400
H	1.26365900	0.22795600	4.52749500
H	3.10494400	-3.43878600	3.22303500
H	3.00126400	-1.52978800	4.81741800
C	4.51985600	2.84913300	0.69613000
C	3.86241500	4.06487500	0.44406600
C	5.89004900	2.87945400	1.01122300
C	4.55969400	5.27482600	0.48788000
H	2.80235300	4.07164500	0.20686300
C	6.58575900	4.08914700	1.05170400
H	6.42174200	1.95314400	1.21198500
C	5.92385000	5.29198600	0.78835500
H	4.03441500	6.20391200	0.28277600
H	7.64673200	4.09068100	1.28699800
H	6.46609800	6.23287000	0.81811600
C	4.73596000	0.09582300	-0.10467000
C	5.45363100	0.43372900	-1.26512100

SUPPORTING INFORMATION

C	4.87046200	-1.19897000	0.42003700
C	6.25844700	-0.51255000	-1.90144000
H	5.39347700	1.44053200	-1.66637100
C	5.67571100	-2.14784500	-0.21703100
H	4.33323000	-1.47187900	1.32474000
C	6.36578200	-1.80793300	-1.38229400
H	6.80495400	-0.23937700	-2.80002600
H	5.76408600	-3.14751800	0.19926800
H	6.99273000	-2.54299000	-1.87922100
C	-1.14647300	-3.61554500	0.42608500
C	-0.59969500	-4.53776500	-0.47439600
C	-2.08429600	-4.04356400	1.37877100
C	-0.98757600	-5.87977000	-0.41977800
H	0.12395200	-4.21581200	-1.21658700
C	-2.46358000	-5.38400500	1.43378900
H	-2.52242800	-3.32813600	2.07055400
C	-1.91696900	-6.30422300	0.53233100
H	-0.56109800	-6.59119500	-1.12125900
H	-3.18961500	-5.70992200	2.17316800
H	-2.21646500	-7.34761700	0.57254300
C	-6.73297700	3.13271700	1.07360300
C	-7.67817100	4.14997300	0.97618500
C	-7.52473900	5.16452000	0.02505600
C	-6.42007400	5.16371700	-0.83353900
C	-5.46690100	4.15308700	-0.74649000
C	-5.61590400	3.12536500	0.21018000
H	-6.84508000	2.34123500	1.80800100
H	-8.53617200	4.15268500	1.64172400
H	-8.26598700	5.95511800	-0.04721500
H	-6.30303600	5.95180100	-1.57130200
H	-4.60747400	4.14443700	-1.40961300
C	-4.64565600	2.09323800	0.30383400
C	-3.80534700	1.19621500	0.37916100
Br	-3.70162600	-1.86264800	-1.45800800
C	-2.28730100	1.12994500	1.38518700
O	-1.93367700	1.94198600	2.14287500

TS3b

B3LYP-D3/BSI SCF energy in acetonitrile: -2681.820182 a.u.

M06/BSII SCF energy in acetonitrile: -2680.707794 a.u.

M06/BSII free energy in acetonitrile: -2680.164963 a.u.

Pd	2.39153700	0.44019100	1.53777200
P	1.34114300	1.36849400	-0.41461100
P	-3.60409100	0.15334400	0.70647300
Fe	-0.77710400	-1.30950000	-0.86869300
C	-2.42491600	-2.39218000	-0.25784700
C	-0.40898100	-2.38590200	0.87066800
C	-1.23599900	-3.14051600	-0.01695900
C	-0.76440000	0.33426700	-2.13268100

SUPPORTING INFORMATION

C	0.06084100	-1.73947800	-2.72124200
C	-1.04170200	-0.84475300	-2.87988200
H	-3.23723700	-2.68813000	-0.90654500
H	0.58062500	-2.65583400	1.20913000
H	-0.98065300	-4.09025300	-0.46912000
H	-1.41493800	1.18773500	-2.03064800
H	0.13732900	-2.73734500	-3.13279200
H	-1.95261900	-1.04072400	-3.42948500
C	-1.08825200	-1.17326000	1.17848000
C	-2.34732000	-1.16321600	0.48512500
C	1.01787100	-1.12008100	-1.86819200
C	0.51220900	0.17316300	-1.49541100
H	-0.70820100	-0.37650200	1.80378200
H	1.94954200	-1.55243400	-1.53929400
C	0.06868300	2.67189900	-0.18620000
C	-0.70795000	2.68180100	0.98041700
C	-0.16302000	3.63751200	-1.17933800
C	-1.70153400	3.64827600	1.15469700
H	-0.52648900	1.94997600	1.75867100
C	-1.15659200	4.60162300	-1.00187000
H	0.42877400	3.63878000	-2.08959300
C	-1.92415400	4.61112000	0.16740400
H	-2.29793600	3.64734400	2.06218700
H	-1.32825300	5.34568300	-1.77430100
H	-2.69360400	5.36515700	0.30599800
C	-5.02608900	-0.83066700	1.37014500
C	-4.81901100	-1.94988500	2.19389400
C	-6.34388100	-0.38604400	1.16124000
C	-5.90008400	-2.61501300	2.77797600
H	-3.81118600	-2.30952000	2.38029100
C	-7.42299400	-1.05371800	1.74305600
H	-6.53147700	0.47953900	0.53159700
C	-7.20581000	-2.17256800	2.55258700
H	-5.71911500	-3.48292200	3.40657900
H	-8.43450800	-0.70033000	1.56135800
H	-8.04587400	-2.69249300	3.00439500
C	-4.15958900	0.51868300	-1.01950900
C	-4.81777400	-0.40749000	-1.84715500
C	-3.86589000	1.79273400	-1.52957900
C	-5.14423900	-0.07366000	-3.16278500
H	-5.08637400	-1.38611200	-1.46149000
C	-4.19157900	2.12717700	-2.84738100
H	-3.36665300	2.52330100	-0.89965300
C	-4.82551300	1.19221800	-3.66796600
H	-5.64984600	-0.79976400	-3.79370400
H	-3.94903500	3.11589400	-3.22719500
H	-5.07999600	1.44860100	-4.69260100
C	2.62198700	2.15262900	-1.47184300
C	2.67209600	1.95775500	-2.85945100
C	3.58007500	2.97339200	-0.85205500

SUPPORTING INFORMATION

C	3.66900400	2.57793500	-3.61745600
H	1.93726000	1.32718000	-3.34998100
C	4.56929900	3.59506300	-1.61451100
H	3.54885700	3.12600900	0.22402600
C	4.61662200	3.39619400	-2.99808900
H	3.70176100	2.42156400	-4.69195500
H	5.30546900	4.22899900	-1.12843200
H	5.39075500	3.87609000	-3.58999700
C	4.83828500	-3.89541500	-0.84098200
C	5.07245800	-5.08032500	-1.53212700
C	4.06271400	-6.04319300	-1.64083900
C	2.81171400	-5.82372800	-1.05347300
C	2.56353500	-4.64523300	-0.35612100
C	3.57883500	-3.66817100	-0.24406000
H	5.61321300	-3.14010200	-0.75622600
H	6.04140800	-5.25380000	-1.99032000
H	4.25096700	-6.96467300	-2.18399500
H	2.03021200	-6.57274000	-1.13919600
H	1.59576900	-4.46575800	0.09978000
C	3.31339800	-2.45240700	0.43199600
C	3.02612500	-1.38953100	0.98730600
Br	2.21313100	2.48487300	3.05053600
C	3.34472900	-0.82922100	2.61744800
O	3.88768400	-1.37237600	3.49573900

TS4a

B3LYP-D3/BSI SCF energy in acetonitrile: -2954.602048 a.u.

M06/BSII SCF energy in acetonitrile: -2953.317152 a.u.

M06/BSII free energy in acetonitrile: -2952.622155 a.u.

Pd	-1.78913100	1.53510700	-0.26164300
P	-1.20671200	-0.77192900	-0.72966800
P	3.84486100	-0.43855600	1.14590500
Fe	1.98695800	0.04861000	-1.81582600
C	3.86715800	0.85310500	-1.51889100
C	1.91157800	2.08149200	-1.42724700
C	3.04862200	1.77321000	-2.23607600
C	1.32656400	-1.91898400	-1.65105800
C	1.62967600	-0.82421200	-3.66024500
C	2.19711500	-1.78750000	-2.77057700
H	4.78473800	0.40868200	-1.87770600
H	1.07534300	2.70560300	-1.71192200
H	3.22863000	2.13035700	-3.24201100
H	1.48361600	-2.55889100	-0.79750800
H	2.07154900	-0.47222700	-4.58343400
H	3.14077900	-2.30099700	-2.89897600
C	2.03206900	1.35604700	-0.20621400
C	3.24598800	0.58774300	-0.24954500
C	0.41683000	-0.34613300	-3.08540200
C	0.21793500	-1.02520200	-1.83403100

SUPPORTING INFORMATION

H	1.31937000	1.36552600	0.60804000
H	-0.23278300	0.41797600	-3.48790300
C	-0.82770900	-1.91411900	0.66656900
C	0.26775000	-1.61687800	1.49340200
C	-1.60062100	-3.05102000	0.94478900
C	0.58848500	-2.44229500	2.57070200
H	0.87476900	-0.74397600	1.29521100
C	-1.28119400	-3.87314500	2.02906500
H	-2.45583400	-3.29873700	0.32558100
C	-0.18770900	-3.57271900	2.84443300
H	1.44530300	-2.19874400	3.19246100
H	-1.89225500	-4.74730500	2.23494300
H	0.05828300	-4.21333100	3.68655800
C	5.38946200	0.46559900	1.62074800
C	5.53305000	1.84707000	1.41341300
C	6.40449000	-0.21988100	2.31261600
C	6.66734000	2.52204300	1.87327300
H	4.76111700	2.40157500	0.88787300
C	7.53912900	0.45454200	2.76560300
H	6.31510500	-1.28911500	2.48749900
C	7.67548900	1.82904900	2.54709200
H	6.76280700	3.59043800	1.69853000
H	8.31765500	-0.09416300	3.28885400
H	8.55874700	2.35384600	2.90010900
C	4.51992800	-1.93153400	0.28500700
C	5.66306400	-1.90894800	-0.53212300
C	3.81773000	-3.13818400	0.43228100
C	6.07296200	-3.05804300	-1.21046400
H	6.23712700	-0.99324700	-0.63383300
C	4.22662100	-4.28895400	-0.24797800
H	2.94060200	-3.17635100	1.07297700
C	5.35122400	-4.24924900	-1.07526000
H	6.95621100	-3.02510700	-1.84262700
H	3.66935500	-5.21379600	-0.12711700
H	5.67112800	-5.14258600	-1.60436500
C	-2.59777500	-1.61324900	-1.58611800
C	-2.39353500	-2.57584500	-2.58475000
C	-3.90716300	-1.30464700	-1.18504500
C	-3.48551700	-3.21478100	-3.17774600
H	-1.38613600	-2.82929600	-2.90081400
C	-4.99533700	-1.95614400	-1.76650900
H	-4.07454300	-0.55849300	-0.41469200
C	-4.78630700	-2.90879200	-2.76838900
H	-3.31876200	-3.95490300	-3.95540100
H	-6.00360100	-1.71663700	-1.44066700
H	-5.63339100	-3.40992800	-3.22829000
C	-4.30217300	-2.50200200	3.32415800
C	-5.31879300	-3.45132300	3.38616200
C	-6.53598800	-3.22319400	2.73521200
C	-6.74102100	-2.03729400	2.02163200

SUPPORTING INFORMATION

C	-5.73196900	-1.08073500	1.95064600
C	-4.49988800	-1.30695800	2.60126800
H	-3.35182600	-2.67582500	3.81706300
H	-5.16107800	-4.37215800	3.93962900
H	-7.32407300	-3.96904100	2.78357500
H	-7.68584400	-1.86114600	1.51621000
H	-5.87937900	-0.16215300	1.39146000
C	-3.45183600	-0.35650400	2.47766300
C	-2.54822800	0.44616500	2.31709900
Br	-2.37787400	2.08482100	-2.72914100
C	-2.45420900	3.45501400	0.21021200
C	-1.53798700	4.62936500	-0.08367200
C	-1.09434800	4.03693600	2.05880000
C	-2.16167000	3.03615500	1.58672000
H	-3.48213800	3.48624000	-0.14613900
H	-3.03879900	2.88313400	2.21701900
C	-0.29487500	4.28095900	0.76581300
H	0.40935000	5.11408500	0.85282600
H	0.23823300	3.39414000	0.41873900
C	-2.13332200	5.81544900	0.74008800
H	-1.60960000	6.74115200	0.48046400
H	-3.19800300	5.96552000	0.53775000
C	-1.84682500	5.39122700	2.21367400
H	-1.19464800	6.11214500	2.71575300
H	-2.75547500	5.29155700	2.81480700
H	-1.39080400	4.83632800	-1.14394700
H	-0.53567000	3.71342700	2.93656700
C	-1.49439900	1.34186500	1.92115200
O	-0.35273400	1.29359600	2.36857000

TS4b

B3LYP-D3/BSI SCF energy in acetonitrile: -2954.599296 a.u.

M06/BSII SCF energy in acetonitrile: -2953.319051 a.u.

M06/BSII free energy in acetonitrile: -2952.625472 a.u.

Pd	2.54561100	0.25733400	-0.89395900
P	0.84605200	0.49840500	0.71858400
P	-4.12112500	-0.88932600	0.14677800
Fe	-2.00318000	1.67451100	-0.98566400
C	-3.86902000	1.34224700	-1.80004300
C	-1.89069300	0.76290300	-2.84580000
C	-2.95290800	1.71808300	-2.82575700
C	-1.62869200	2.01829500	1.01534900
C	-1.38166000	3.62274700	-0.62790700
C	-2.22617000	3.17220100	0.43443200
H	-4.75839100	1.88745300	-1.51771100
H	-1.00876600	0.78279800	-3.47047700
H	-3.02400200	2.60508200	-3.44228600
H	-2.03554100	1.43409500	1.82541200
H	-1.58237200	4.45349700	-1.29162800

SUPPORTING INFORMATION

H	-3.18017700	3.59765500	0.71715100
C	-2.15243600	-0.20431000	-1.83359000
C	-3.38106600	0.14166000	-1.17435000
C	-0.25994300	2.74863100	-0.70539700
C	-0.40539400	1.74454100	0.31272200
H	-1.50659600	-1.03244600	-1.58159100
H	0.55188000	2.80379900	-1.41754200
C	-0.06079200	-1.00947900	1.26364200
C	-0.02303700	-2.17991800	0.49370100
C	-0.75971900	-1.01297900	2.48427700
C	-0.68145300	-3.33287800	0.93168800
H	0.51840100	-2.18978100	-0.44584000
C	-1.41310400	-2.16644900	2.91848200
H	-0.78169600	-0.12296000	3.10457200
C	-1.37447500	-3.33010600	2.14333700
H	-0.64068600	-4.23474400	0.32744900
H	-1.94772400	-2.15665200	3.86391600
H	-1.87895300	-4.22895100	2.48612500
C	-5.60097700	-1.57390200	-0.73495000
C	-5.59672100	-1.79358300	-2.12201800
C	-6.71921000	-1.99263900	0.00840000
C	-6.68751800	-2.40077400	-2.75045100
H	-4.74185200	-1.48813200	-2.71854800
C	-7.80949900	-2.59482400	-0.62122600
H	-6.74537600	-1.83461200	1.08353200
C	-7.79866000	-2.80030600	-2.00433100
H	-6.66815800	-2.55692100	-3.82583900
H	-8.66900500	-2.90154500	-0.03104300
H	-8.64778700	-3.26835300	-2.49437400
C	-4.90238200	0.36042300	1.26690300
C	-5.97132700	1.19063600	0.88745100
C	-4.37548300	0.48868400	2.56159700
C	-6.47358400	2.14852300	1.76976700
H	-6.41844400	1.08076300	-0.09562800
C	-4.87695500	1.44811400	3.44613200
H	-3.56382000	-0.16120300	2.87654200
C	-5.92244000	2.28424300	3.04883900
H	-7.29726500	2.78671000	1.46143100
H	-4.45438200	1.53685200	4.44317900
H	-6.31514800	3.03021000	3.73419000
C	1.52320300	1.11125600	2.32200900
C	1.38109900	2.44582300	2.72386200
C	2.29888300	0.23875400	3.10538700
C	2.00181200	2.90060300	3.89176900
H	0.79242500	3.13616800	2.12898200
C	2.91266400	0.69424900	4.27164700
H	2.42659500	-0.79719300	2.80380900
C	2.76733900	2.02849400	4.66745600
H	1.88218700	3.93758200	4.19273500
H	3.50560200	0.00854500	4.87044100

SUPPORTING INFORMATION

H	3.24776000	2.38338800	5.57471700
C	5.21421600	-4.62172800	0.41015500
C	5.00493000	-5.62219200	1.35706000
C	3.95238700	-5.51900400	2.27296500
C	3.10307900	-4.40736200	2.24695500
C	3.30778000	-3.39517500	1.31393800
C	4.36757100	-3.49650200	0.38546400
H	6.02495700	-4.69870300	-0.30733800
H	5.66102500	-6.48715400	1.37814100
H	3.79288100	-6.30595300	3.00427600
H	2.27962300	-4.32973000	2.95080300
H	2.65103800	-2.53221300	1.27857800
C	4.53313400	-2.44889600	-0.56136500
C	4.56904700	-1.50768700	-1.33809000
Br	1.27472200	-1.14534700	-2.76448500
C	3.72648200	1.65234500	0.13169500
C	3.39213000	3.11042400	-0.17705400
C	4.95566800	2.50555900	-1.70556100
C	4.72792800	1.27149600	-0.84203600
H	3.83264000	1.34275100	1.16768800
H	5.58766100	0.70419900	-0.48655600
C	3.55714700	3.15635700	-1.71384200
H	3.56872100	4.17742200	-2.10720600
H	2.80871400	2.56994700	-2.25676400
C	4.64964300	3.91356100	0.27596400
H	4.44413700	4.98740700	0.22250300
H	4.93508300	3.67857600	1.30577700
C	5.72998500	3.48806400	-0.76910500
H	6.07975600	4.34515900	-1.35210000
H	6.60594700	3.01845800	-0.31168100
H	2.44947400	3.46552500	0.23893400
H	5.42976300	2.31288300	-2.66744200
C	4.36334500	-0.28039700	-2.05388900
O	4.65254000	-0.03378900	-3.20387600

TS7

B3LYP-D3/BSI SCF energy in acetonitrile: -2841.247912 a.u.

M06/BSII SCF energy in acetonitrile: -2839.992925 a.u.

M06/BSII free energy in acetonitrile: -2839.303321 a.u.

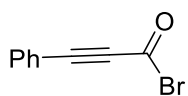
Pd	0.24522800	0.56603100	-0.51788000
P	-1.37699200	-1.01311400	0.09468600
P	2.35189000	-0.29980700	-0.03499400
Fe	1.04976500	-3.39413700	-0.79208900
C	3.08784500	-3.12147500	-0.59653400
C	2.03031700	-3.43662600	-2.62821100
C	2.82995200	-4.07062000	-1.62935100
C	0.09247400	-3.36661400	1.03411000
C	-0.32357500	-4.93474500	-0.60943700
C	0.34112100	-4.71387800	0.63494300

SUPPORTING INFORMATION

H	3.62871500	-3.31635300	0.31822700
H	1.63551200	-3.90510600	-3.52032300
H	3.14394800	-5.10673500	-1.62862600
H	0.47489100	-2.88565600	1.92283600
H	-0.29455600	-5.84401100	-1.19598400
H	0.96472800	-5.42518900	1.16102100
C	1.79043200	-2.09520700	-2.21244400
C	2.44646500	-1.88530900	-0.94846700
C	-0.99315200	-3.72652400	-0.97128500
C	-0.75056100	-2.74903000	0.04880300
H	1.19035400	-1.35976400	-2.73154300
H	-1.56854100	-3.56310400	-1.87217700
C	-1.97981300	-0.91996000	1.84449800
C	-1.88430600	0.31688100	2.50107200
C	-2.47455200	-2.02494800	2.55846600
C	-2.27590100	0.45055500	3.83548500
H	-1.49584500	1.17689400	1.96439200
C	-2.87019000	-1.89142700	3.89093600
H	-2.54046600	-2.99684600	2.08011000
C	-2.76989000	-0.65378000	4.53383700
H	-2.19213800	1.41611000	4.32683800
H	-3.25072700	-2.75573100	4.42836700
H	-3.07073200	-0.55332500	5.57297200
C	3.92930500	0.51934000	-0.54766200
C	4.33375900	0.47745200	-1.89480100
C	4.65200100	1.33546900	0.34234900
C	5.43451700	1.21532900	-2.33282600
H	3.78853900	-0.13712400	-2.60570600
C	5.75248400	2.07443400	-0.09889200
H	4.35669000	1.39548000	1.38542700
C	6.14937200	2.01757300	-1.43711000
H	5.73668100	1.16015400	-3.37530100
H	6.29908800	2.69424600	0.60689200
H	7.00579900	2.59143700	-1.77935900
C	2.70791500	-0.78435500	1.71268000
C	3.93334900	-1.33688400	2.12400600
C	1.69696600	-0.60111800	2.66759000
C	4.12762700	-1.71942800	3.45259800
H	4.74048800	-1.46180400	1.40862400
C	1.88865600	-0.98537800	3.99736100
H	0.75144700	-0.16640200	2.36343200
C	3.10424700	-1.54902000	4.39158700
H	5.07882900	-2.14806300	3.75598000
H	1.08842200	-0.84211300	4.71847500
H	3.25850700	-1.84792200	5.42466700
C	-2.90596600	-1.23778900	-0.92937000
C	-4.08255400	-1.85564500	-0.47740800
C	-2.83083700	-0.81432100	-2.26611700
C	-5.15374000	-2.05871500	-1.34949400
H	-4.17094500	-2.17916600	0.55428000

SUPPORTING INFORMATION

C	-3.89900200	-1.03005600	-3.14132600
H	-1.93945800	-0.29859200	-2.61180100
C	-5.06171300	-1.65577600	-2.68562600
H	-6.06112800	-2.53269700	-0.98507500
H	-3.82516900	-0.70045300	-4.17430700
H	-5.89566800	-1.81923000	-3.36251200
C	-4.60401400	2.05054600	1.48067800
C	-5.84946500	1.42456200	1.46457200
C	-6.45854800	1.09840700	0.24924200
C	-5.81335700	1.39663500	-0.95505100
C	-4.56354700	2.01231100	-0.94918500
C	-3.94469200	2.34859600	0.27205200
H	-4.12944700	2.30333200	2.42255500
H	-6.34546800	1.19237300	2.40272400
H	-7.42874200	0.61010100	0.23988900
H	-6.27744600	1.13495900	-1.90074100
H	-4.05187800	2.22919800	-1.88106700
C	-2.66769600	2.98895400	0.27174900
C	-1.58028600	3.52249000	0.21182600
Br	-0.33659900	2.13249600	-2.68806900
C	0.78059400	3.75711000	-0.73717600
C	1.94687800	3.48117000	0.13183000
C	0.40425500	4.34425000	1.55485400
C	-0.33815500	4.28401400	0.16692500
H	0.92758000	4.18193700	-1.71821900
H	-0.58653800	5.29660500	-0.18598000
C	1.31608900	3.10466600	1.48681700
H	2.04717300	3.06737500	2.29935000
H	0.77072000	2.15659600	1.43962700
C	2.45786900	4.95699100	0.43840000
H	3.46270500	4.85116600	0.85982700
H	2.53765700	5.57223200	-0.46180900
C	1.42729600	5.49543200	1.47039000
H	1.89544000	5.65491100	2.44595800
H	0.96844100	6.43796100	1.15815200
H	2.72920600	2.85955900	-0.29068100
H	-0.29121900	4.40205200	2.39313500



B3LYP-D3/BSI SCF energy in acetonitrile: -434.5338761 a.u.

M06/BSII SCF energy in acetonitrile: -434.2969957 a.u.

M06/BSII free energy in acetonitrile: -434.2257177 a.u.

C	2.95031200	1.21076500	0.00035700
C	4.30191200	0.88345200	0.00041300
C	4.69897200	-0.45866100	0.00001900
C	3.74459400	-1.48254300	-0.00039200
C	2.38906200	-1.17213700	-0.00039400

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C	1.98335400	0.18113600	0.00002700
H	2.62854600	2.24696700	0.00064000
H	5.04782900	1.67215900	0.00075700
H	5.75611800	-0.70759300	0.00003500
H	4.05977200	-2.52125600	-0.00073100
H	1.63868500	-1.95617300	-0.00073400
C	0.60677900	0.50185600	-0.00001100
C	-0.58415900	0.76731300	-0.00004700
C	-1.94240500	1.07958600	-0.00025400
O	-2.53210100	2.11428600	-0.00061400
Br	-3.07899100	-0.70608500	0.00019000

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