

Electronic Supplementary Information
for
Unexpected Iron(III) Chloride-Catalyzed Dimerization of 1,1,3-
Trisubstituted-prop-2-yn-1-ols as an Expedient to Route to Highly
Conjugated Indenes

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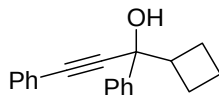
Representative Procedure for the Synthesis of 1,1,3-Trisubstituted-prop-2-yn-1-ols (1):

To a solution of ethynylbenzene (0.37 mL, 3.3 mmol, 1.1 equiv.) in THF was added LDA (2.0 M in THF, 2.25 mL, 1.5 equiv) at -78 °C. The resulting solution was stirred for 1 h at -78 °C. The cyclobutyl phenyl ketone (0.467 mL, 3 mmol, 1.0 equiv.) in THF (2 mL) was subsequently slowly added to the resulting solution at -78 °C and the reaction mixture was slowly warmed up to room temperature stirred for 10 h. The reaction mixture was quenched by addition of saturated NH₄Cl (10 mL) and extracted with diethyl ether (2 x 30 mL). The combined organic layers were washed with brine (20 mL), dried over Mg₂SO₄, concentrated under reduced pressure and purified by flash column chromatography on silica gel (eluent: *n*-hexane: ethyl acetate = 9: 1) to give **1a** (653 mg, 83 % yield) as a colorless oil.

Experimental Procedure for the Synthesis of Enantioenriched 1,3-Diphenylpent-1-yn-3-ol (1f):^{S1}

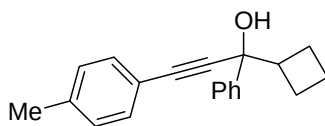
To a toluene (1 mL) solution containing phenylacetylene (3 mmol) was added a solution of Me₂Zn in toluene (2 M, 3 mmol) at room temperature and the resulting reaction mixture was stirred for 1 h. The Jacobsen chiral *R,R*-Schiff base ligand (0.2 mmol) was added at room temperature. The resulting yellow reaction solution was stirred for a further 1 h. On completion, propiophenone (1 mmol) was added and the reaction mixture was stirred for 48 h, quenched with water (5 mL), diluted with Et₂O and filtered through Celite®. The collected phases were separated and the aqueous phase was extracted with Et₂O (3 x 3 mL). The combined organic layers were dried over sodium sulfate, concentrated under reduced pressure and purified quickly by flash column chromatography (eluent: *n*-hexane: ethyl acetate = 9: 1 with 1% Et₃N by volume) on deactivated silica gel with 1% Et₃N by volume during the preparation of the column to furnish the enantioriched starting alcohol **1f** in 48% yield and 59% ee.

1-Cyclobutyl-1,3-diphenylprop-2-yn-1-ol (1a)



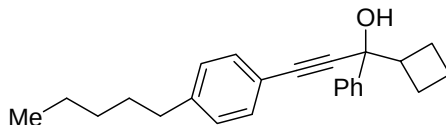
Colorless oil; R_f = 0.58 (eluent: *n*-hexane:CH₂Cl₂ = 4:1); ¹H NMR (CDCl₃, 400 MHz): δ 1.77-2.00 (m, 4H, CH₂), 2.10-2.19 (m, 1H, CH₂), 2.27-2.37 (m, 1H, CH₂), 2.45 (s, 1H, OH), 2.80-2.86 (m, 1H, CH), 7.29-7.39 (m, 6H, Ar-H), 7.52-7.54 (m, 2H, Ar-H), 7.67(d, 2H, J = 7.6 Hz, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 16.7 (CH₂), 23.3 (CH₂), 23.9 (CH₂), 47.2 (CH), 75.5 (C-OH), 86.6 (C $\equiv$ C), 90.4 (C $\equiv$ C), 122.7 (Ar-C), 125.5 (Ar-C), 127.6 (Ar-C), 128.1(Ar-C), 128.4 (Ar-C), 128.5 (Ar-C), 131.9 (Ar-C), 143.5(Ar-C); IR (NaCl, neat) ν : 3420, 2978, 2940, 1599, 1489, 1447, 754, 691 cm⁻¹; MS (ESI) m/z 245 [M-OH]⁺; HRMS (ESI) calcd. for C₁₉H₁₇ (M⁺-OH): 245.1330, found: 245.1328.

1-Cyclobutyl-1-phenyl-3-p-tolylprop-2-yn-1-ol (1b)



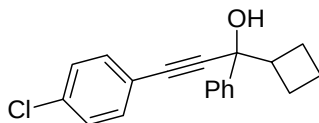
Pale yellow oil; R_f = 0.57 (eluent: *n*-hexane:CH₂Cl₂ = 5:1); ¹H NMR (CDCl₃, 400 MHz): δ 1.76-1.95 (m, 4H, CH₂), 2.12-2.17 (m, 1H, CH₂), 2.30-2.34 (m, 1H, CH₂), 2.50 (s, 4H, Ar-CH₃, OH), 2.80-2.84 (m, 1H, CH), 7.12-7.36 (m, 6H, Ar-H), 7.47 (d, 1H, J = 7.5 Hz, Ar-H), 7.65 (d, 2H, J = 7.3 Hz, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 16.7 (CH₂), 21.6 (Ar-CH₃), 23.3 (CH₂), 23.9 (CH₂), 47.2 (CH), 75.6 (C-OH), 86.8 (C $\equiv$ C), 89.6 (C $\equiv$ C), 119.6 (Ar-C), 125.6 (Ar-C), 127.6 (Ar-C), 128.1 (Ar-C), 129.1 (Ar-C), 131.8 (Ar-C), 138.7 (Ar-C), 143.6 (Ar-C); IR (NaCl, neat) ν : 3428, 2978, 2940, 1508, 1489, 1447, 815, 700 cm⁻¹; MS (ESI) m/z 259 [M-OH]⁺; HRMS (ESI) calcd. for C₂₀H₁₉ (M⁺-OH): 259.1487, found: 259.1485.

1-Cyclobutyl-3-(4-pentylphenyl)-1-phenylprop-2-yn-1-ol (1c)



Pale yellow oil; R_f = 0.69 (eluent: *n*-hexane:CH₂Cl₂ = 5:1); ¹H NMR (CDCl₃, 400 MHz): δ 0.92 (t, 3H, J = 7.0 Hz, CH₃), 1.30-1.39 (m, 4H, CH₂), 1.60-1.67 (m, 2H, CH₂), 1.77-1.99 (m, 4H, CH₂), 2.12-2.19 (m, 1H, CH₂), 2.28-2.37 (m, 1H, CH₂), 2.47 (s, 1H, OH), 2.63 (t, 1H, J = 7.8 Hz, Ar-CH₂), 2.80-2.88 (m, 1H, CH), 7.17 (d, 2H, J = 8.1 Hz, Ar-H), 7.28-7.46 (m, 5H, Ar-H), 7.66-7.69 (m, 2H, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 14.1 (CH₃), 16.7 (CH₂), 22.6 (CH₂), 23.3 (CH₂), 23.9 (CH₂), 31.0 (CH₂), 31.4 (CH₂), 35.9 (Ar-CH₂), 47.2 (CH), 75.6 (C-OH), 86.8 (C $\equiv$ C), 89.6 (C $\equiv$ C), 119.8 (Ar-C), 125.6 (Ar-C), 127.6 (Ar-C), 128.1 (Ar-C), 128.5 (Ar-C), 131.8 (Ar-C), 143.6 (Ar-C), 143.7 (Ar-C); IR (NaCl, neat) ν : 3435, 3026, 2930, 2857, 2224, 1601, 1508, 1447, 1265, 1011, 980, 839, 741 cm⁻¹; MS (ESI) m/z 315 [M-OH]⁺; HRMS (ESI) calcd. for C₂₄H₂₇ (M⁺-OH): 315.2113, found: 315.2108.

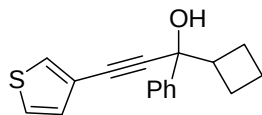
3-(4Chlorophenyl)-1-cyclobutyl-1-phenylprop-2-yn-1-ol (1d)



Pale yellow oil; R_f = 0.60 (eluent: *n*-hexane:CH₂Cl₂ = 5:1); ¹H NMR (CDCl₃, 400 MHz): δ 1.76-1.98 (m, 4H, CH₂), 2.05-2.17 (m, 1H, CH₂), 2.23-2.32 (m, 1H, CH₂), 2.43 (s, H, OH), 2.78-2.87 (m, 1H, CH), 7.30-7.45 (m, 7H, Ar-H), 7.62-7.64 (m, 2H, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 16.7 (CH₂), 23.2 (CH₂), 23.9 (CH₂), 47.1 (CH), 75.5 (C-OH), 85.4 (C $\equiv$ C), 91.4 (C $\equiv$ C), 121.2 (Ar-C), 125.4 (Ar-C), 127.7(Ar-C), 128.2 (Ar-C), 128.7 (Ar-C), 133.1 (Ar-C), 134.6(Ar-C), 143.2 (Ar-C); IR (NaCl, neat) ν : 3420, 2978, 2940, 2231, 1489, 1447, 1092, 1015, 827, 752

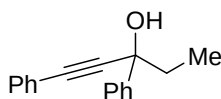
cm^{-1} ; MS (ESI) m/z 279 $[\text{M}-\text{OH}]^+$; HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{16}\text{Cl}$ (M^+-OH): 279.0941, found: 279.0931.

1-Cyclobutyl-1-phenyl-3-(thiophen-3-yl)prop-2-yn-1-ol (1e)



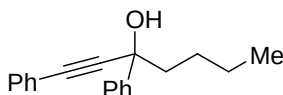
Pale yellow oil; R_f = 0.58 (eluent: n -hexane: CH_2Cl_2 = 5:1); ^1H NMR (CDCl_3 , 400 MHz): δ 1.75-1.97 (m, 4H, CH_2), 2.05-2.17 (m, 1H, CH_2), 2.23-2.33 (m, 1H, CH_2), 2.40 (s, 1H, OH), 2.78-2.86 (m, 1H, CH), 7.17-7.38 (m, 5H, Ar-H), 7.50-7.52 (m, 1H, Ar-H), 7.63-7.65 (m, 2H, Ar-H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 16.7 (CH_2), 23.2 (CH_2), 23.9 (CH_2), 47.1 (CH), 75.5 (C-OH), 81.6 ($\text{C}\equiv\text{C}$), 90.0 ($\text{C}\equiv\text{C}$), 121.7 (Ar-C), 125.4 (Ar-C), 125.5 (Ar-C), 127.6 (Ar-C), 128.1 (Ar-C), 129.1 (Ar-C), 130.1 (Ar-C), 143.4 (Ar-C); IR (NaCl, neat) ν : 3422, 2977, 2938, 2223, 1601, 1489, 1358, 1015, 781 cm^{-1} ; MS (ESI) m/z 251 $[\text{M}-\text{OH}]^+$; HRMS (ESI) calcd. for $\text{C}_{17}\text{H}_{15}\text{S}$ (M^+-OH): 251.0894, found: 251.0884.

1,3-Diphenylpent-1-yn-3-ol (1f)^{S2-S4}



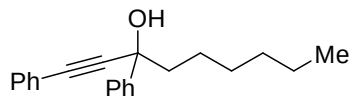
Pale yellow oil; R_f = 0.70 (eluent: n -hexane: CH_2Cl_2 = 5:1); ^1H NMR (CDCl_3 , 400 MHz): δ 1.04 (t, 3H, J = 7.4 Hz), 1.97-2.15 (m, 4H), 2.53 (s, 1H), 7.30-7.41 (m, 6H), 7.50-7.53 (m, 2H), 7.70-7.72 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 9.2, 38.5, 74.4, 86.2, 91.3, 122.7, 125.6, 127.7, 128.2, 128.4, 128.5, 131.8, 144.6; MS (ESI) m/z 219 $[\text{M}-\text{OH}]^+$.

1,3-Diphenylhept-1-yn-3-ol (**1g**)^{S1}



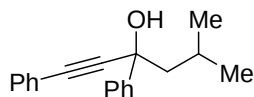
Pale yellow oil; R_f = 0.65 (eluent: *n*-hexane:CH₂Cl₂ = 5:1); ¹H NMR (CDCl₃, 400 MHz): δ 0.90 (t, 3H, J = 7.2 Hz), 1.27-1.59 (m, 4H), 1.94-2.10 (m, 2H), 2.49 (s, 1H), 7.30-7.52 (m, 8H), 7.70-7.72 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 14.0, 22.7, 27.0, 45.3, 73.8, 86.0, 91.6, 122.7, 125.5, 127.7, 128.2, 128.3, 128.5, 131.8, 144.9; MS (ESI) m/z 247 [M-OH]⁺.

1,3-Diphenylnon-1-yn-3-ol (**1h**)



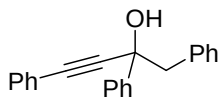
Pale yellow solid; R_f = 0.64 (eluent: *n*-hexane:CH₂Cl₂ = 5:1); m.p. 55-56 °C; ¹H NMR (CDCl₃, 400 MHz): δ 0.86 (t, 3H, J = 6.5 Hz, CH₃), 1.28-1.58 (m, 8H, CH₃CH₂CH₂CH₂CH₂CH₂), 1.94-2.09 (m, 2H, CH₃CH₂CH₂CH₂CH₂CH₂), 2.50 (s, 1H, OH), 7.30-7.41 (m, 6H, Ar-H), 7.50-7.52 (m, 2H, Ar-H), 7.71 (m, 2H, J = 8.0 Hz, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 14.1 (CH₃), 22.6 (CH₃CH₂CH₂CH₂CH₂CH₂), 24.8 (CH₃CH₂CH₂CH₂CH₂CH₂), 29.2 (CH₃CH₂CH₂CH₂CH₂CH₂), 31.7 (CH₃CH₂CH₂CH₂CH₂CH₂), 45.6 (CH₃CH₂CH₂CH₂CH₂), 73.8 (C-OH), 86.0 (C≡C), 91.7 (C≡C), 122.7 (Ar-C), 125.5 (Ar-C), 127.7 (Ar-C), 128.2 (Ar-C), 128.3 (Ar-C), 128.5 (Ar-C), 131.8 (Ar-C), 144.9 (Ar-C); IR (NaCl, neat) ν : 3383, 3059, 2951, 2926, 2857, 1599, 1489, 1447, 1265, 1030, 756, 691 cm⁻¹; MS (ESI) m/z 275 [M-OH]⁺; HRMS (ESI) calcd. for C₂₁H₂₃: 275.1800, found: 275.1795.

5-Methyl-1,3-diphenylhex-1-yn-3-ol (1i)



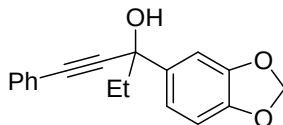
Pale yellow solid; R_f = 0.62 (eluent: *n*-hexane:CH₂Cl₂ = 5:1); m.p. 59-60 °C; ¹H NMR (CDCl₃, 400 MHz): δ 0.91(d, 3H, J = 6.2 Hz, CH₃), 1.04 (d, 3H, J = 6.2 Hz, CH₃), 1.90-2.05 (m, 3H, CH₂, CH), 2.47 (s, 1H, OH), 7.30-7.52 (m, 8H, Ar-H), 7.71-7.73 (m, 2H, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 24.1 (CH₃), 24.2 (CH₃), 25.3 (CH), 53.8 (CH₂), 73.7 (C-OH), 86.3 (C≡C), 92.0 (C≡C), 122.7 (Ar-C), 125.5 (Ar-C), 127.7 (Ar-C), 128.2 (Ar-C), 128.4 (Ar-C), 128.5 (Ar-C), 131.7 (Ar-C), 145.4 (Ar-C); IR (NaCl, neat) ν : 3406, 3059, 2953, 1599, 1490, 1445, 754 cm⁻¹; MS (ESI) m/z 247 [M-OH]⁺; HRMS (ESI) calcd. for C₁₉H₁₉ (M⁺-OH): 247.1487, found: 247.1477.

1,2,4-Triphenylbut-3-yn-2-ol (1j)



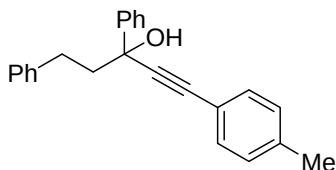
Pale yellow oil; R_f = 0.71 (eluent: *n*-hexane:CH₂Cl₂ = 5:1); ¹H NMR (CDCl₃, 400 MHz): δ 2.53 (s, 1H, OH), 3.24 (s, 2H, CH₂), 7.24-7.43 (m, 13H, Ar-H), 7.67 (m, 2H, J = 7.4 Hz, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 52.0 (CH₂), 73.7 (C-OH), 87.4 (C≡C), 91.1 (C≡C), 122.5 (Ar-C), 125.7 (Ar-C), 127.1 (Ar-C), 127.8 (Ar-C), 127.9 (Ar-C), 128.2 (Ar-C), 128.3 (Ar-C), 128.6 (Ar-C), 131.0 (Ar-C), 131.7 (Ar-C), 135.9 (Ar-C), 144.2 (Ar-C); IR (NaCl, neat) ν : 3428, 3059, 3028, 2924, 1599, 1491, 1449, 1030, 756, 700 cm⁻¹; MS (ESI) m/z 281 [M-OH]⁺; HRMS (ESI) calcd. for C₂₂H₁₇ (M⁺-OH): 281.1330, found: 281.1327.

3-(Benzo[d][1,3]dioxol-5-yl)-1-phenylpent-1-yn-3-ol (1k)



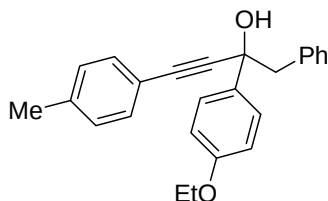
Pale yellow oil; R_f = 0.55 (eluent: *n*-hexane:CH₂Cl₂ = 5:1); ¹H NMR (CDCl₃, 400 MHz): δ 1.01 (t, 3H, J = 7.4 Hz, CH₃CH₂), 1.91-2.10 (m, 2H, CH₃CH₂), 2.50 (s, 1H, OH), 5.96 (s, 2H, OCH₂O), 6.79 (d, 2H, J = 8.0 Hz, Ar-H), 7.17-7.49 (m, 7H, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 9.3 (CH₃CH₂), 38.5 (CH₃CH₂), 74.2 (C-OH), 86.1 (C $\equiv$ C), 91.3 (C $\equiv$ C), 101.1 (OCH₂O), 106.5 (Ar-C), 107.7 (Ar-C), 119.1 (Ar-C), 122.6 (Ar-C), 128.3 (Ar-C), 128.5 (Ar-C), 131.8 (Ar-C), 138.7 (Ar-C), 147.0 (Ar-C), 147.6 (Ar-C); IR (NaCl, neat) ν : 3433, 2971, 1624, 1498, 1179 cm⁻¹; MS (ESI) m/z 263 [M-OH]⁺; HRMS (ESI) calcd. for C₁₈H₁₅O₂ (M⁺-OH): 263.1067, found: 263.1061.

3,5-Diphenyl-1-*p*-tolylpent-1-yn-3-ol (1l)



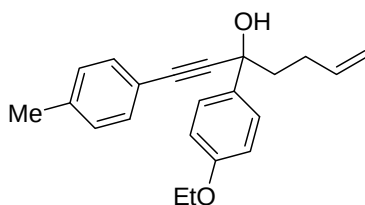
Pale yellow oil; R_f = 0.70 (eluent: *n*-hexane:CH₂Cl₂ = 5:1); ¹H NMR (CDCl₃, 400 MHz): δ 2.22-2.38 (m, 5H, Ar-CH₃, PhCH₂CH₂), 2.52 (s, 1H, OH), 2.75-2.94 (m, 2H, PhCH₂CH₂), 7.13-7.40 (m, 12H, Ar-H), 7.73 (d, 2H, J = 7.6 Hz, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 21.5 (Ar-CH₃), 31.4 (PhCH₂CH₂), 47.2 (PhCH₂CH₂), 73.7 (C-OH), 86.7 (C $\equiv$ C), 90.5 (C $\equiv$ C), 119.5 (Ar-C), 125.6 (Ar-C), 125.9 (Ar-C), 127.8 (Ar-C), 128.3 (Ar-C), 128.4 (Ar-C), 128.5 (Ar-C), 129.2 (Ar-C), 131.7 (Ar-C), 138.8 (Ar-C), 141.8 (Ar-C), 144.7 (Ar-C); IR (NaCl, neat) ν : 3430, 3051, 2965, 1612, 1498, 1035 cm⁻¹; MS (ESI) m/z 309 [M-OH]⁺; HRMS (ESI) calcd. for C₂₄H₂₁ (M⁺-OH): 309.1638, found: 309.1633.

2-(4-Ethoxyphenyl)-1-phenyl-4-p-tolylbut-3-yn-2-ol (1m)



Yellow oil; R_f = 0.48 (eluent: *n*-hexane:CH₂Cl₂ = 5:1); ¹H NMR (CDCl₃, 400 MHz): δ 1.42 (t, 3H, J = 7.0 Hz, CH₃CH₂), 2.34 (s, 3H, Ar-CH₃), 2.50 (s, 1H, OH), 3.18-3.26 (m, 2H, PhCH₂), 4.04 (q, 2H, J = 7.0 Hz, CH₃CH₂O), 6.85-6.89 (m 2H, Ar-H), 7.11 (d, 2H, J = 7.9 Hz, Ar-H), 7.21-7.31 (m, 7H, Ar-H), 7.53-7.57 (m, 2H, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 14.9 (CH₃CH₂), 21.5 (Ar-CH₃), 52.0 (PhCH₂), 63.5 (CH₃CH₂O), 73.4 (C-OH), 87.4 (C≡C), 90.6 (C≡C), 114.0 (Ar-C), 119.5 (Ar-C), 126.9 (Ar-C), 127.0 (Ar-C), 127.8 (Ar-C), 129.1 (Ar-C), 131.1 (Ar-C), 131.6 (Ar-C), 136.2 (Ar-C), 136.3 (Ar-C), 138.6 (Ar-C), 158.5 (Ar-C); IR (NaCl, neat) ν : 3410, 2978, 2922, 1609, 1508, 1246, 1175, 818, 700 cm⁻¹; MS (ESI) m/z 339 [M-OH]⁺; HRMS (ESI) calcd. for C₂₅H₂₃O (M⁺-OH): 339.1749, found: 339.1740.

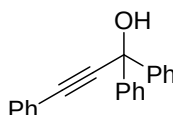
3-(4-Ethoxyphenyl)-1-p-tolylhept-6-en-1-yn-3-ol (1n)



Pale yellow oil; R_f = 0.52 (eluent: *n*-hexane:CH₂Cl₂ = 5:1); ¹H NMR (CDCl₃, 500 MHz): δ 1.43 (t, 3H, J = 6.9 Hz, CH₃CH₂), 2.06-2.37 (m, 7H, CH₂CH₂ Ar-CH₃), 2.54 (s, 1H, OH), 4.05 (q, 2H, J = 6.9 Hz, CH₃CH₂O), 4.96 (d, 1H, J = 10.1 Hz, CH₂CH), 5.04 (d, 1H, J = 17.1 Hz, CH₂CH), 5.81-5.88 (m, 1H, CH₂CH₂CH), 6.90 (d, 2H, J = 8.3 Hz, Ar-H), 7.14 (d, 2H, J = 7.7 Hz, Ar-H), 7.39 (d, 2H, J = 7.7 Hz, Ar-H), 7.60 (d, 2H, J = 8.3 Hz, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 14.9 (CH₃CH₂), 21.5 (Ar-CH₃), 29.5 (CH₂CH₂CH), 44.5 (CH₂CH₂CH), 63.5 (CH₃CH₂O), 73.3 (C-OH), 86.4 (C≡C), 90.7 (C≡C), 114.1 (Ar-C), 114.7 (Ar-C), 119.5 (Ar-

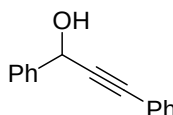
C), 126.8 (Ar-C), 129.1 (Ar-C), 131.7 (Ar-C), 136.7(Ar-C), 138.3(Ar-C), 138.7 (Ar-C), 158.5(Ar-C); IR (NaCl, neat) ν : 3435, 2924, 2226, 1609, 1508, 1246, 1047, 914, 756 cm^{-1} ; MS (ESI) m/z 303 $[\text{M-OH}]^+$; HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{23}\text{O}$ ($\text{M}^+ - \text{OH}$): 303.1743, found: 303.1739.

1,1,3-Triphenylprop-2-yn-1-ol (1o)^{S5}



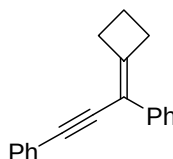
White solid; R_f = 0.31 (eluent: *n*-hexane: CH_2Cl_2 = 8:1); ^1H NMR (CDCl_3 , 400 MHz): δ 2.96 (s, 1H), 7.26-7.40 (m, 9H), 7.54-7.72 (m, 6H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 74.9, 87.3, 91.8, 122.5, 126.1, 127.8, 128.4, 128.7, 131.8, 145.1; MS (ESI) m/z 267 $[\text{M-OH}]^+$.

1,3-Diphenylprop-2-yn-1-ol (1p)^{S6}



Pale yellow oil; R_f = 0.31 (eluent: *n*-hexane: CH_2Cl_2 = 8:1); ^1H NMR (CDCl_3 , 400 MHz): δ 3.01 (s, 1H), 5.72 (s, 1H), 7.33-7.46 (m, 6H), 7.52 (dd, 2H, J = 7.1, 2.1 Hz), 7.66 (d, 2H, J = 7.9 Hz); ^{13}C NMR (CDCl_3 , 100 MHz): δ 65.1, 86.7, 89.0, 122.5, 126.9, 128.4, 128.5, 128.7, 128.7, 131.9, 140.8; MS (ESI) m/z 191 $[\text{M-OH}]^+$.

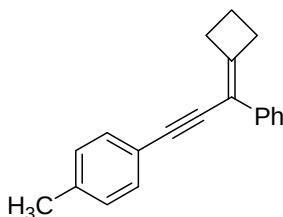
(3-Cyclobutylideneprop-1-yne-1,3-diyl)dibenzene (7a)



Pale yellow oil; R_f = 0.33 (eluent: *n*-hexane: CH_2Cl_2 = 6:1); ^1H NMR (CDCl_3 , 400 MHz): δ 2.18-2.16 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.07-3.11 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.20-7.36 (m, 5H, Ar-H), 7.47-7.55 (m, 4H, Ar-H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 17.5 ($\text{CH}_2\text{CH}_2\text{CH}_2$), 33.3

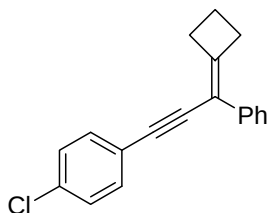
(CH₂CH₂CH₂), 33.6 (CH₂CH₂CH₂), 87.1 (C≡C), 93.2 (C≡C), 115.7 (Ar-C), 124.0 (Ar-C), 126.7 (Ar-C), 126.9 (Ar-C), 127.9 (Ar-C), 128.3 (Ar-C), 128.3 (Ar-C), 131.5 (Ar-C), 137.0 (Ar-C), 153.7 (Ar-C); IR (NaCl, neat) ν : 2968, 2884, 2199, 1597, 1491, 1447, 1217, 1111, 756, 656 cm⁻¹; MS (ESI) m/z 245 [M+1]⁺; HRMS (ESI) calcd. For C₁₉H₁₇ (M⁺+H): 245.1330, found: 245.1334.

1-(3-Cyclobutylidene-3-phenylprop-1-ynyl)-4-methylbenzene (7b)



Pale yellow oil; R_f = 0.63 (eluent: *n*-hexane:CH₂Cl₂ = 4:1); ¹H NMR (CDCl₃, 400 MHz): δ 2.08-2.16 (m, 2H, CH₂CH₂CH₂), 2.34 (s, 3H, Ar-CH₃), 3.06-3.11 (m, 4H, CH₂CH₂CH₂), 7.12 (d, 2H, J = 7.9, Ar-H), 7.20-7.39 (m, 5H, Ar-H), 7.54 (d, 2H, J = 7.6 Hz, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 17.5 (CH₂CH₂CH₂), 21.5 (Ar-CH₃), 33.2 (CH₂CH₂CH₂), 33.6 (CH₂CH₂CH₂), 86.3 (C≡C), 93.3 (C≡C), 115.8 (Ar-C), 120.9 (Ar-C), 126.7 (Ar-C), 126.9 (Ar-C), 128.2 (Ar-C), 129.1 (Ar-C), 131.4 (Ar-C), 137.0 (Ar-C), 137.9 (Ar-C), 153.2 (Ar-C); IR (NaCl, neat) ν : 2963, 2922, 2195, 1603, 1508, 1447, 1107, 818, 754 cm⁻¹; MS (ESI) m/z 259 [M+1]⁺; HRMS (ESI) calcd. For C₂₀H₁₉ (M⁺+H): 259.1487, found: 259.1497.

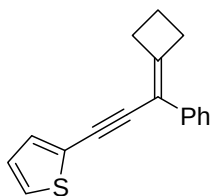
1-Chloro-4-(3-cyclobutylidene-3-phenylprop-1-ynyl)benzene (7d)



Pale yellow oil; R_f = 0.51 (eluent: *n*-hexane:CH₂Cl₂ = 6:1); ¹H NMR (CDCl₃, 400 MHz): δ 2.14-2.22 (m, 2H, CH₂CH₂CH₂), 3.10-3.16 (m, 4H, CH₂CH₂CH₂), 7.26-7.57 (m, 9H, Ar-H); ¹³C

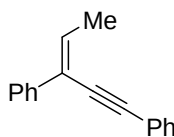
NMR (CDCl₃, 100 MHz): δ 17.5 (CH₂CH₂CH₂), 33.2 (CH₂CH₂CH₂), 33.6 (CH₂CH₂CH₂), 88.0 (C $\equiv$ C), 91.9 (C $\equiv$ C), 115.5 (Ar-C), 122.4 (Ar-C), 126.8 (Ar-C), 126.8 (Ar-C), 128.3 (Ar-C), 128.6 (Ar-C), 132.6 (Ar-C), 133.8 (Ar-C), 136.7 (Ar-C), 154.2 (Ar-C); IR (NaCl, neat) ν : 2966, 2884, 2199, 1593, 1489, 1400, 1092, 1015, 829, 780, 698 cm⁻¹; MS (ESI) m/z 279 [M+1]⁺; HRMS (ESI) calcd. For C₁₉H₁₅Cl (M⁺+H): 279.0941, found: 279.0937.

2-(3-Cyclobutylidene-3-phenylprop-1-ynyl)thiophene (7e)



Brown oil; R_f = 0.48 (eluent: *n*-hexane:CH₂Cl₂ = 6:1); ¹H NMR (CDCl₃, 400 MHz): δ 2.09-2.16 (m, 2H, CH₂CH₂CH₂), 3.05-3.11(m, 4H, CH₂CH₂CH₂), 7.15 (d, 1H, J = 4.9 Hz, Ar-H), 7.21-7.36 (m, 4H, Ar-H), 7.43 (d, 1H, J = 2.7 Hz, Ar-H), 7.52 (d, 2H, J = 7.8 Hz, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 17.5 (CH₂CH₂CH₂), 33.2 (CH₂CH₂CH₂), 33.5 (CH₂CH₂CH₂), 86.4 (C $\equiv$ C), 88.0 (C $\equiv$ C), 115.6 (Ar-C), 122.9 (Ar-C), 125.2 (Ar-C), 126.7 (Ar-C), 126.9 (Ar-C), 127.8 (Ar-C), 128.2 (Ar-C), 130.0 (Ar-C), 136.9 (Ar-C), 153.5 (Ar-C); IR (NaCl, neat) ν : 2965, 2884, 1493, 1447, 1110, 783, 754, 627 cm⁻¹; MS (ESI) m/z 251 [M+1]⁺; HRMS (ESI) calcd. For C₁₇H₁₅S (M⁺+H): 251.0894, found: 251.0891.

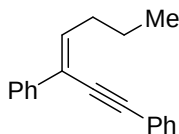
(Z)-Pent-3-en-1-yne-1,3-diylidibenzene (7f)^{S7}



Pale yellow oil; R_f = 0.53 (eluent: *n*-hexane:CH₂Cl₂ = 4:1); ¹H NMR (CDCl₃, 400 MHz): δ 2.15 (d, 3H, J = 7.0 Hz), 6.54 (q, 1H, J = 7.0 Hz), 7.25-7.37 (m, 6H), 7.53-7.65 (m, 4H); ¹³C NMR

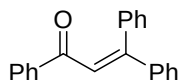
(CDCl₃, 100 MHz): δ 17.1, 86.7, 95.6, 123.6, 124.5, 125.9, 127.4, 128.2, 128.3, 131.5, 133.2, 138.3; MS (ESI) m/z 219 [M+1]⁺.

(Z)-Hept-3-en-1-yne-1,3-diylidibenzene (7g)



Yellow oil; R_f = 0.55 (eluent: *n*-hexane:CH₂Cl₂ = 4:1); ¹H NMR (CDCl₃, 400 MHz): δ 1.02 (t, 3H, J = 7.4 Hz, CH₃), 1.54-1.61(m, 2H, CH₃CH₂), 2.56 (dt, 2H, J = 7.4, 7.4 Hz, CHCH₂), 6.47 (t, 1H, J = 7.4 Hz, CHCH₂), 7.26-7.37 (m, 6H, Ar-H), 7.52-7.74 (m, 2H, Ar-H), 7.66 (d, 2H, J = 7.5 Hz, Ar-H); ¹³C NMR (CDCl₃, 100 MHz): δ 14.0 (CH₃), 22.4 (CH₃CH₂), 33.4 (CHCH₂), 86.9 (C≡C), 95.0 (C≡C), 123.6 (C=CH), 123.6 (Ar-C), 126.0 (Ar-C), 127.4 (Ar-C), 128.2 (Ar-C), 128.3 (Ar-C), 128.4 (Ar-C), 131.5 (Ar-C), 138.3 (C=CH), 138.8 (Ar-C); IR (NaCl, neat) ν : 2961, 2872, 1491, 1449, 1271, 1026, 756, 700 cm⁻¹; MS (ESI) m/z 247 [M+1]⁺; HRMS (ESI) calcd. For C₁₉H₁₉ (M⁺+H): 247.1487, found: 247.1491.

1,3,3-Triphenylprop-2-en-1-one (8)^{S8}



Pale yellow oil; R_f = 0.48 (eluent: *n*-hexane:CH₂Cl₂ = 5:1); ¹H NMR (CDCl₃, 500 MHz): δ 7.11-7.48 (m, 14H), 7.90 (d, 2H, J = 7.8 Hz); ¹³C NMR (CDCl₃, 125 MHz): δ 124.1, 128.1, 128.4, 128.5, 128.6, 128.8, 129.4, 129.8, 132.7, 138.3, 139.1, 141.4, 154.8, 192.7; MS (ESI) m/z 285 [M+1]⁺

Figure S1. ^1H and ^{13}C NMR Spectra of 1-Cyclobutyl-1,3-diphenylprop-2-yn-1-ol (**1a**)

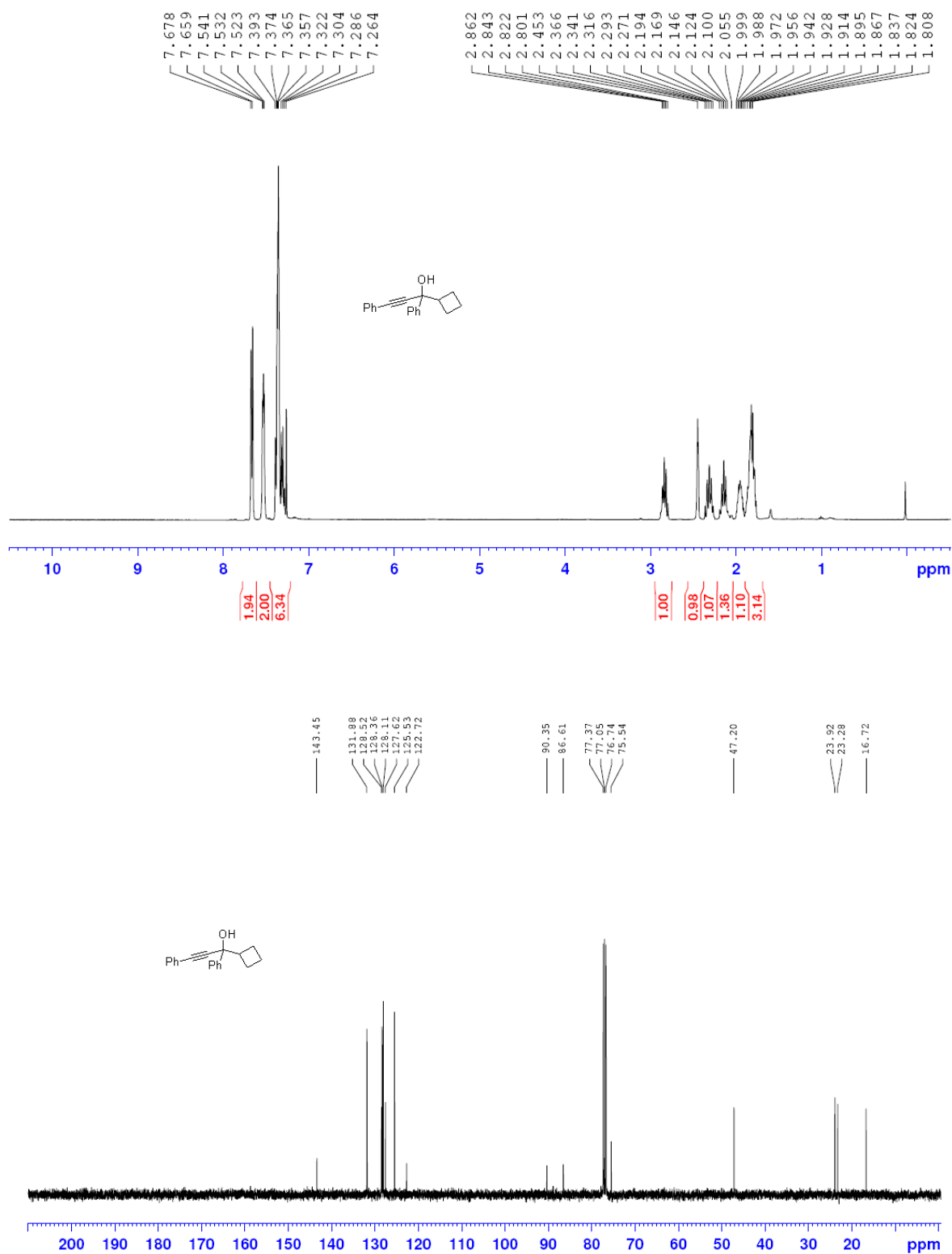


Figure S2. ^1H and ^{13}C NMR Spectra of 1-Cyclobutyl-1-phenyl-3-*p*-tolylprop-2-yn-1-ol (**1b**)

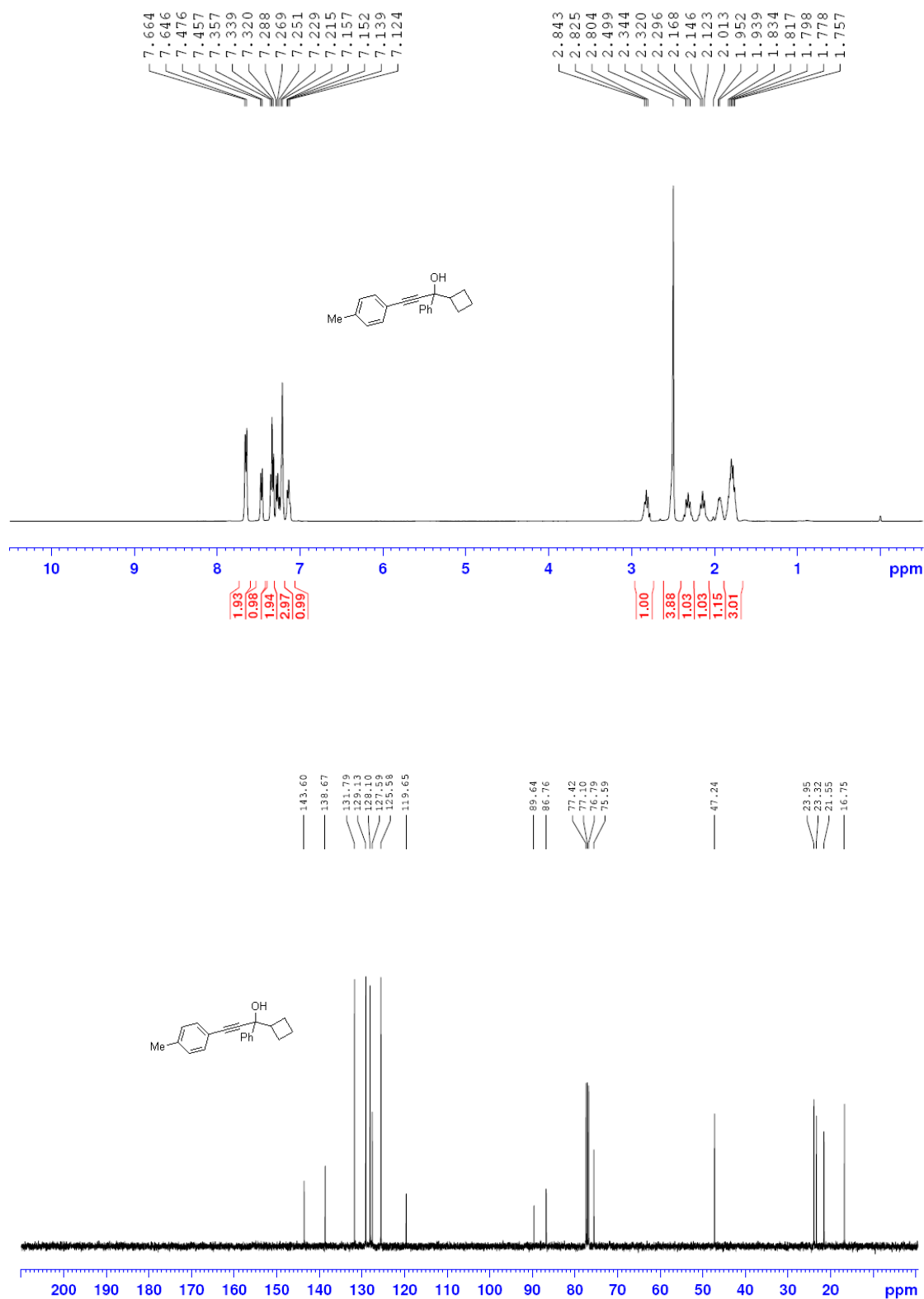


Figure S3. ^1H and ^{13}C NMR Spectra of 1-Cyclobutyl-3-(4-pentylphenyl)-1-phenyl prop-2-yn-1-ol (**1c**)

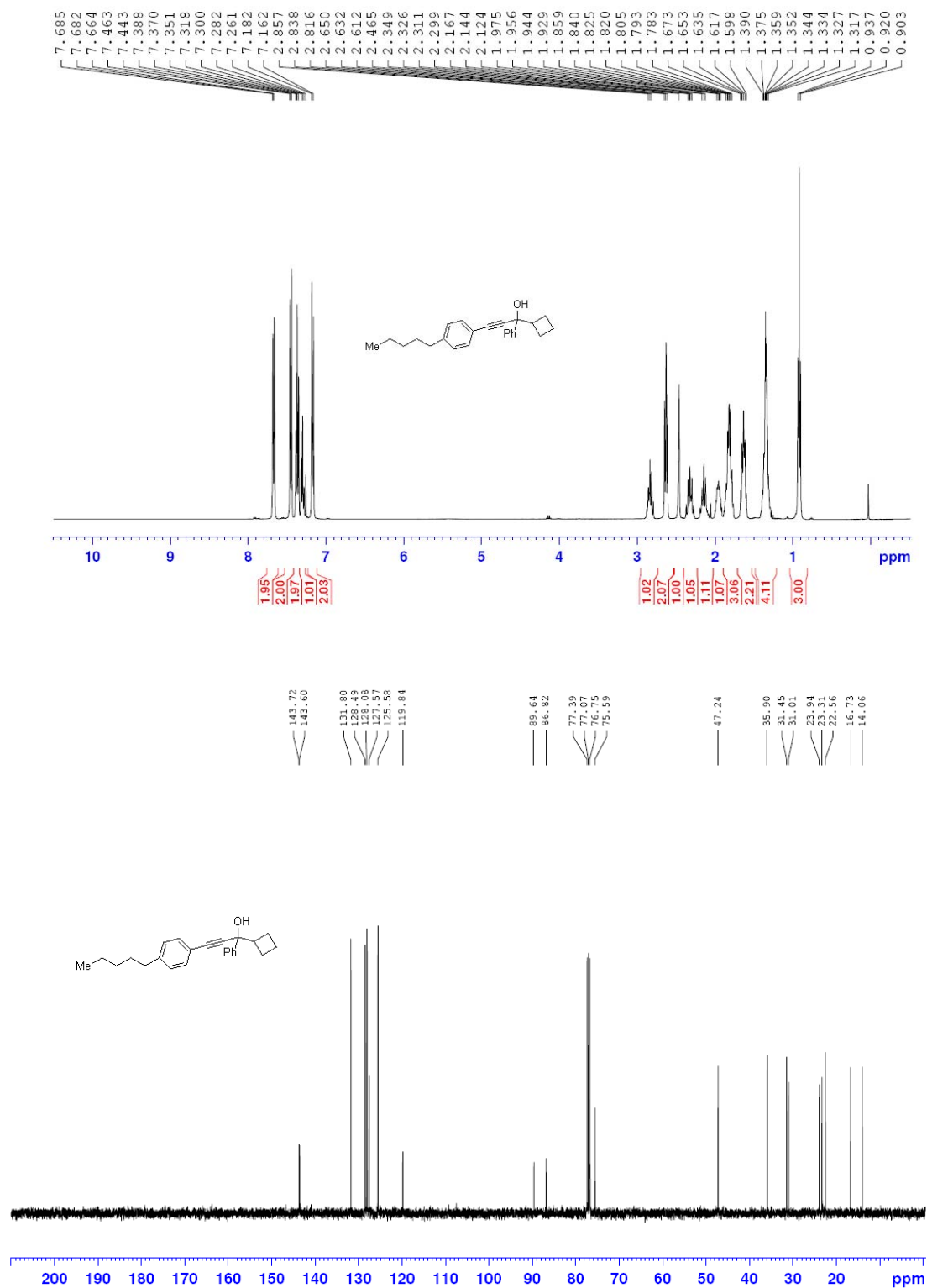


Figure S4. ^1H and ^{13}C NMR Spectra of 3-(4-Chlorophenyl)-1-cyclobutyl-1-phenyl prop-2-yn-1-ol (**1d**)

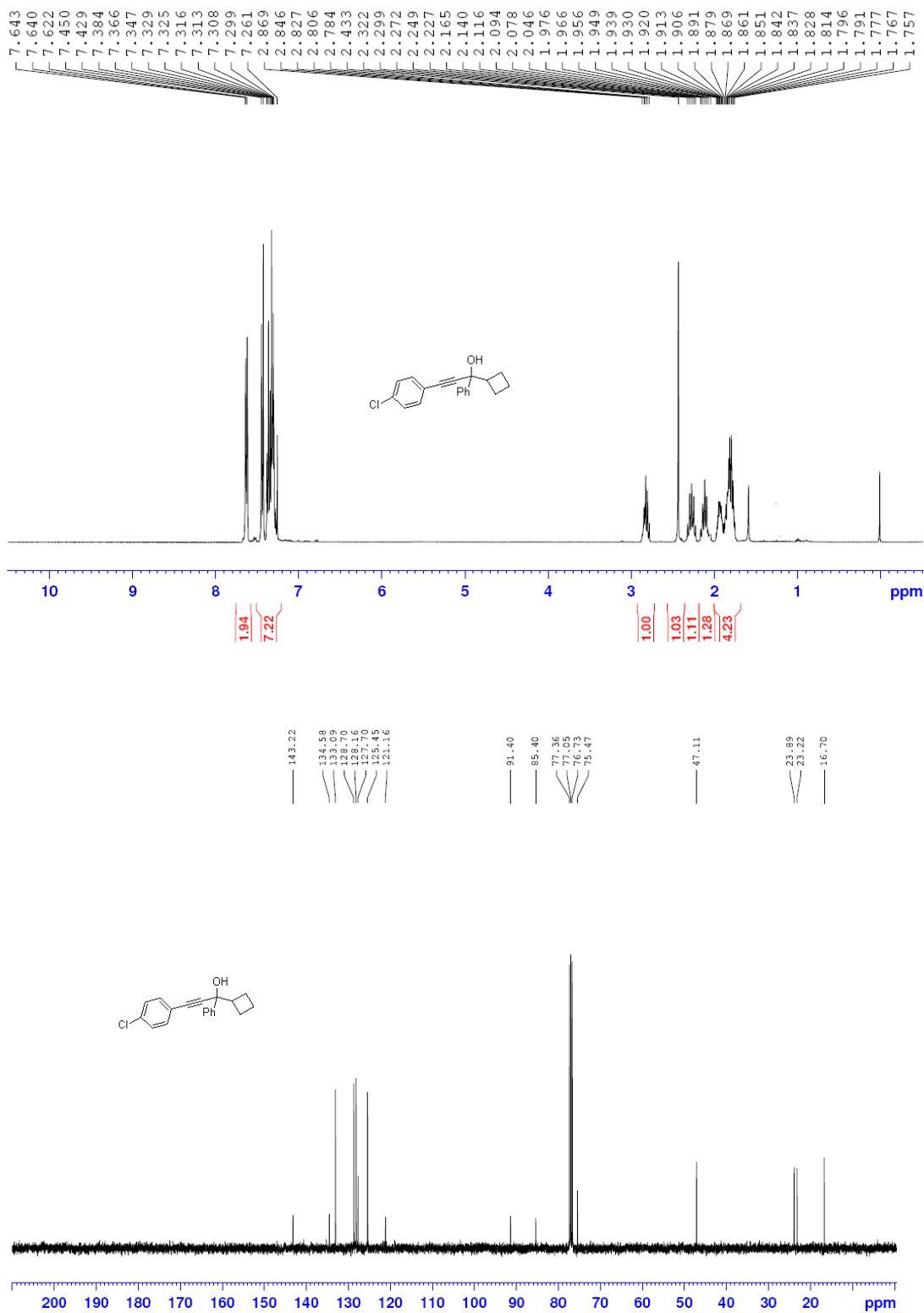


Figure S5. ^1H and ^{13}C NMR Spectra of 1-Cyclobutyl-1-phenyl-3-(thiophen-3-yl)prop-2-yn-1-ol (**1e**)

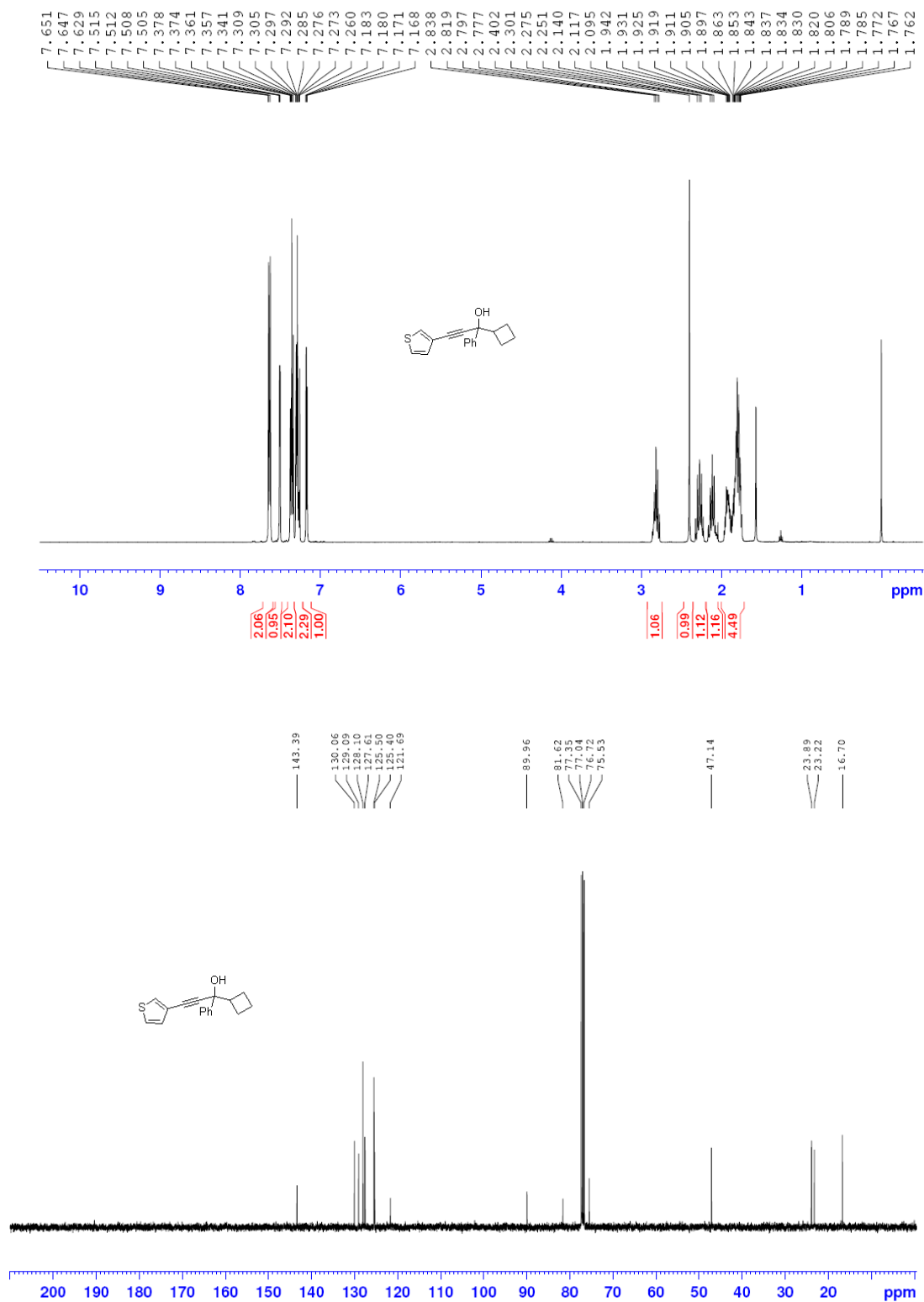


Figure S6. ^1H and ^{13}C NMR Spectra of 1,3-Diphenylpent-1-yn-3-ol (**1f**)

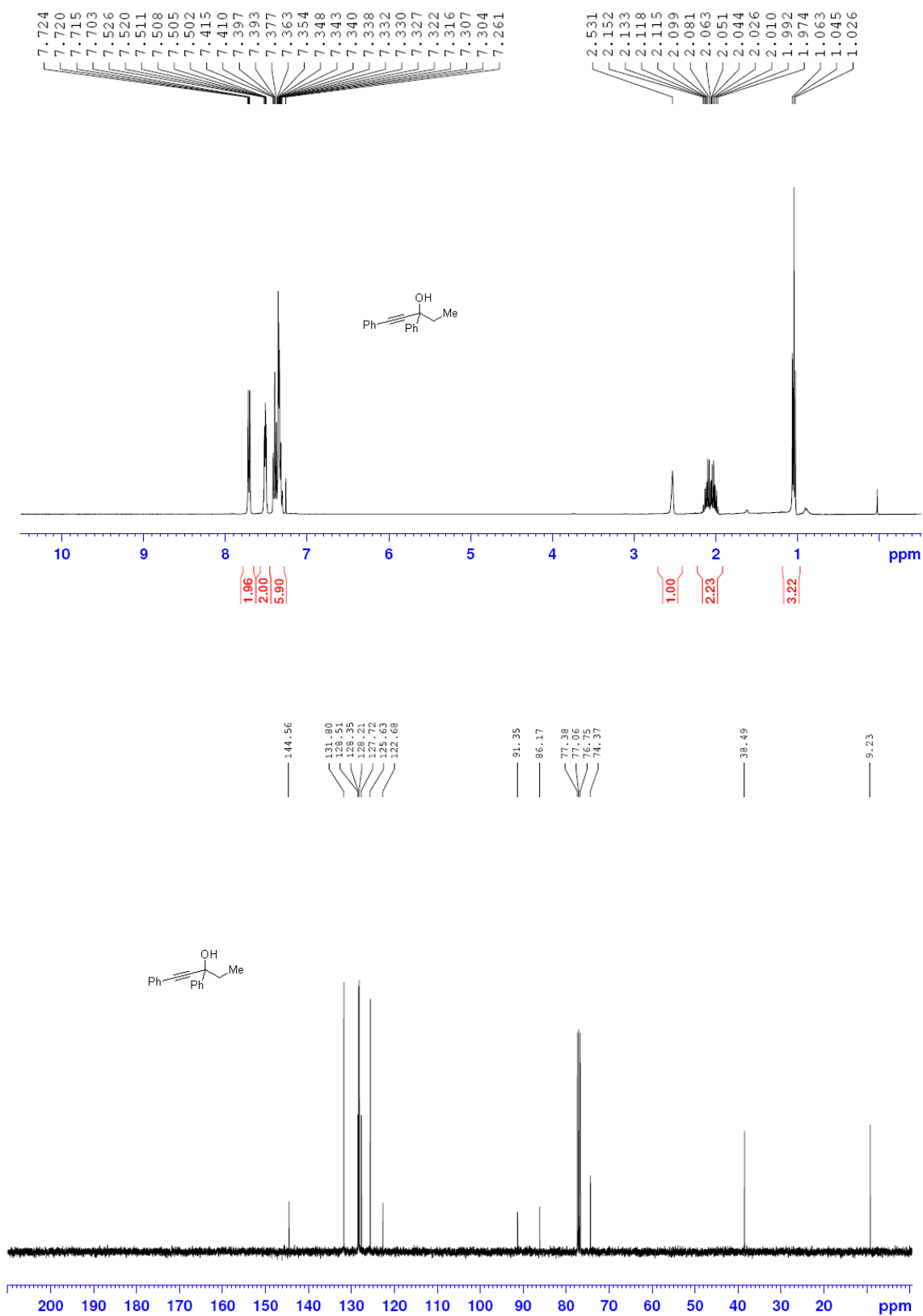


Figure S7. ^1H and ^{13}C NMR Spectra of 1,3-Diphenylhept-1-yn-3-ol (**1g**)

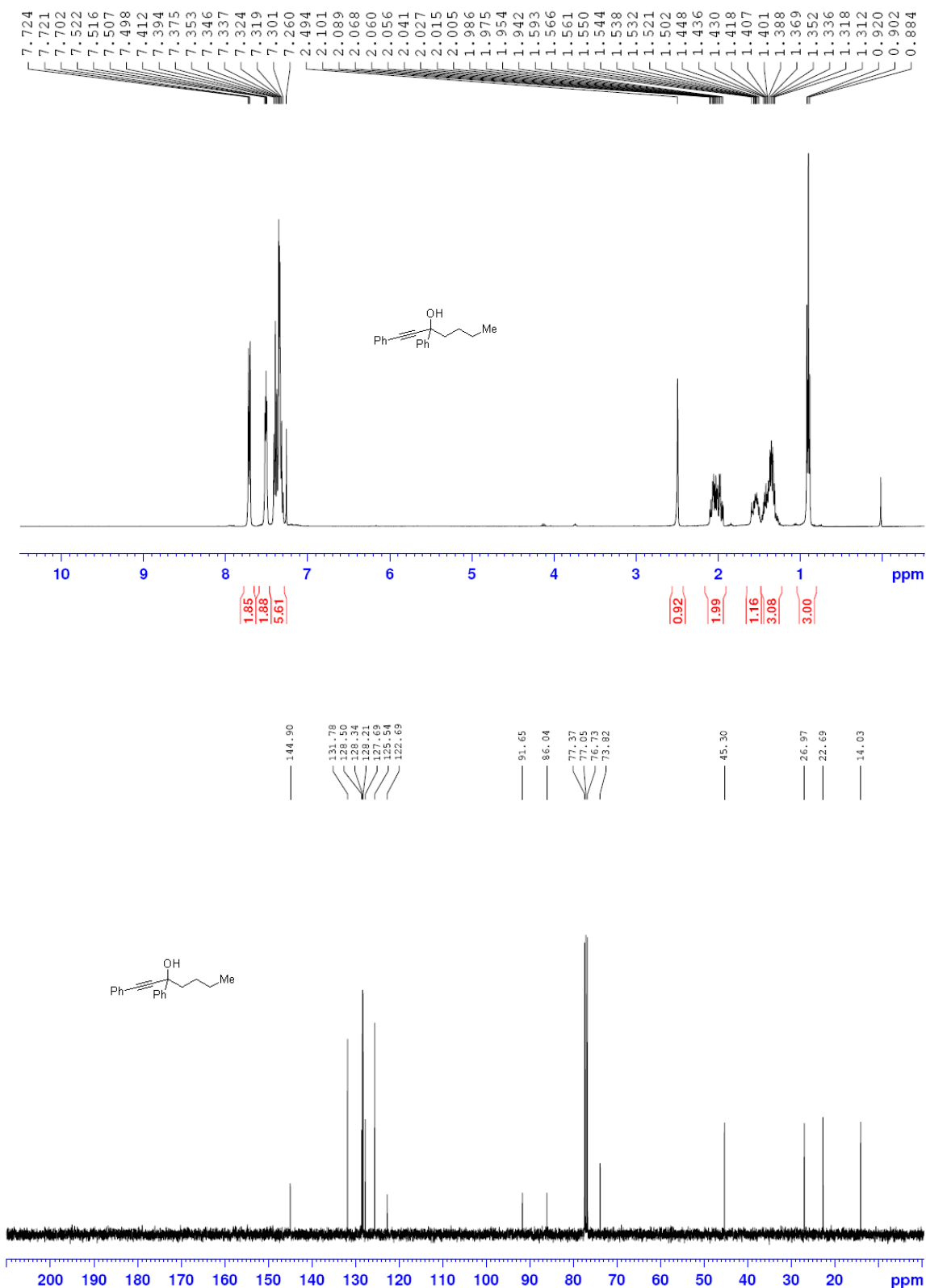


Figure S8. ^1H and ^{13}C NMR Spectra of 1,3-Diphenylnon-1-yn-3-ol (**1h**)

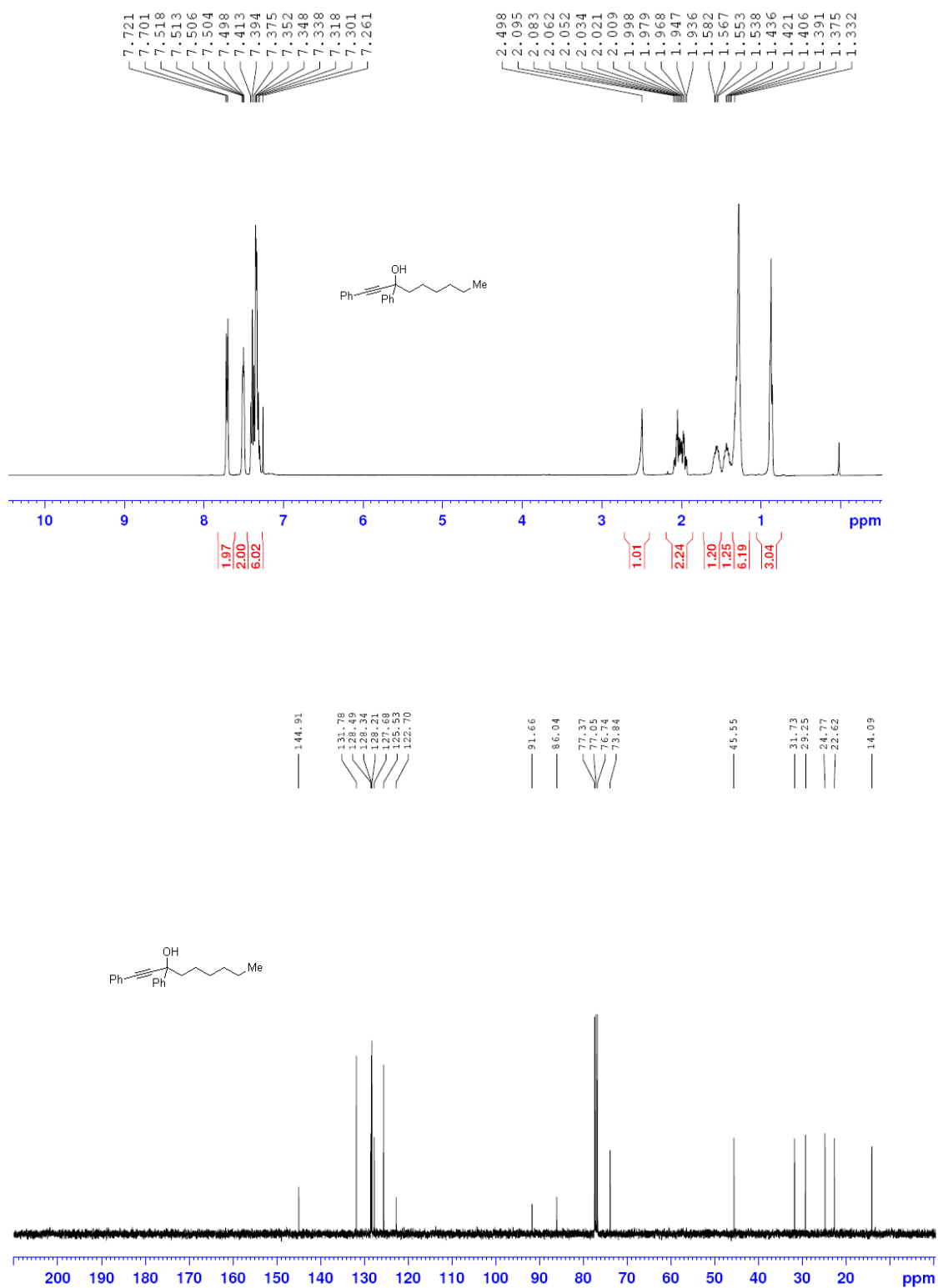


Figure S9. ^1H and ^{13}C NMR Spectra of 5-Methyl-1,3-diphenylhex-1-yn-3-ol (**1i**)

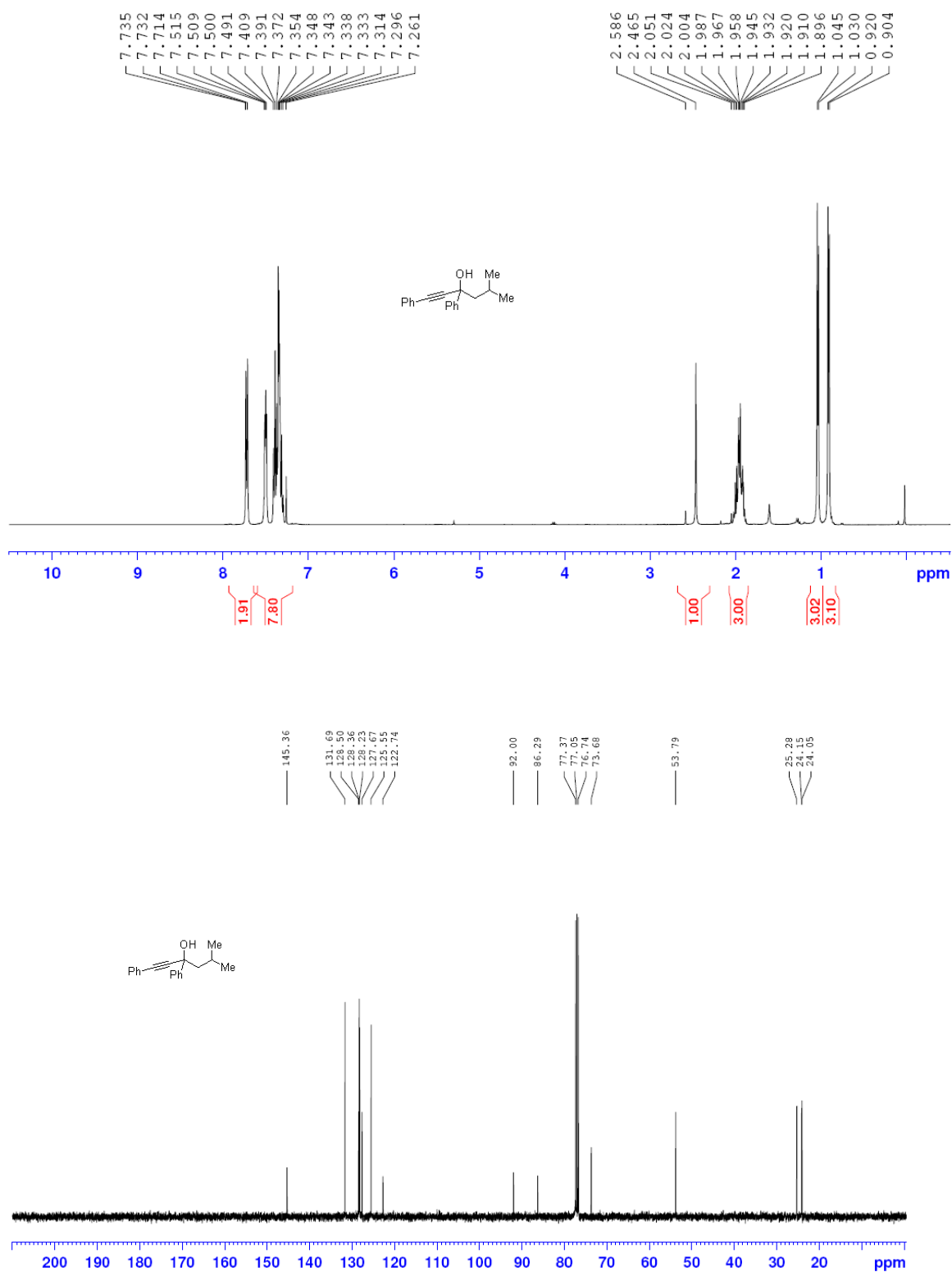


Figure S10. ^1H and ^{13}C NMR Spectra of 1,2,4-Triphenylbut-3-yn-2-ol (**1j**)

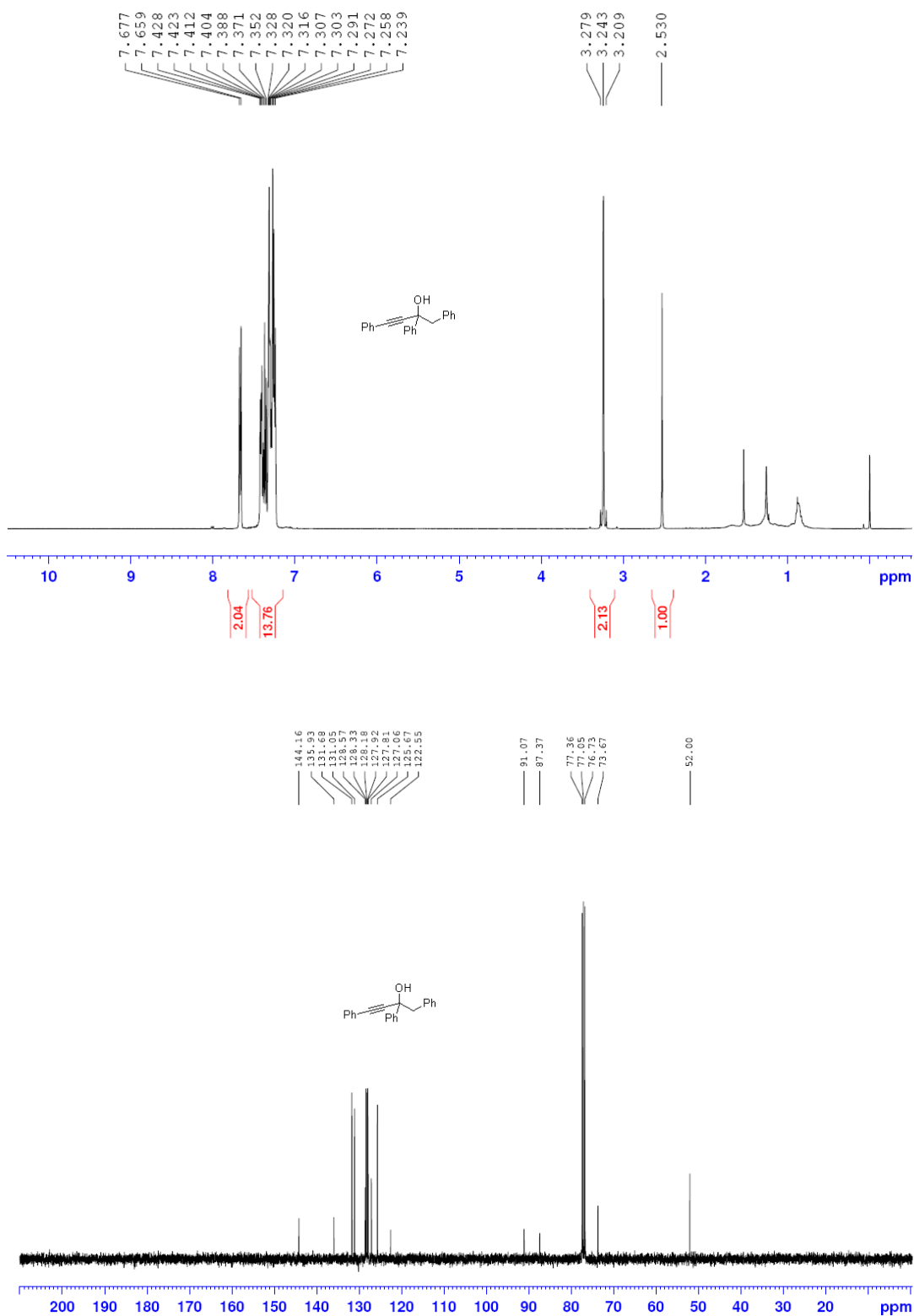


Figure S11. ^1H and ^{13}C NMR Spectra of 3-(Benzo[*d*][1,3]dioxol-5-yl)-1-phenylpent-1-yn-3-ol
(1k)

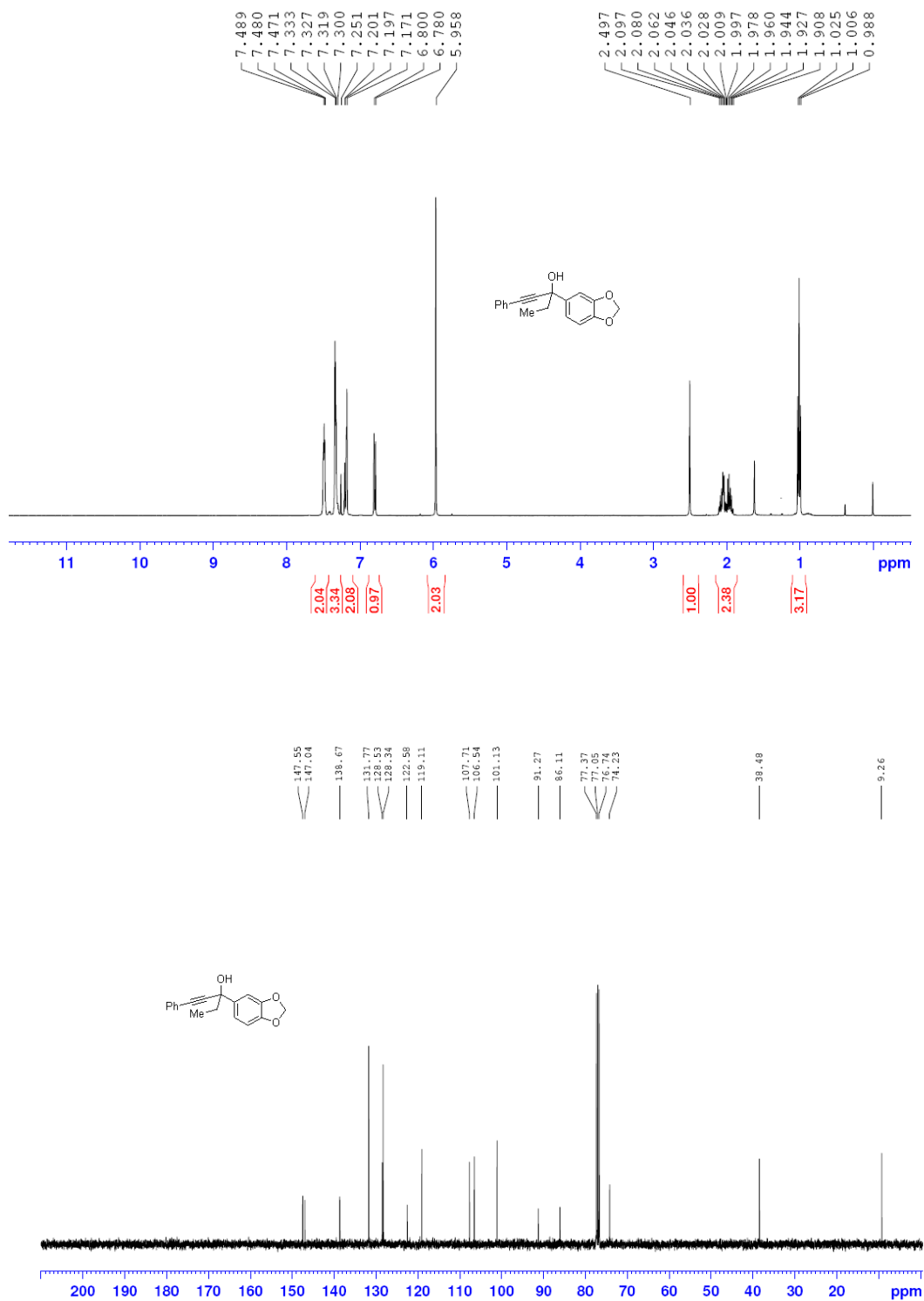


Figure S12. ^1H and ^{13}C NMR Spectra of 3,5-Diphenyl-1-*p*-tolylpent-1-yn-3-ol (**11**)

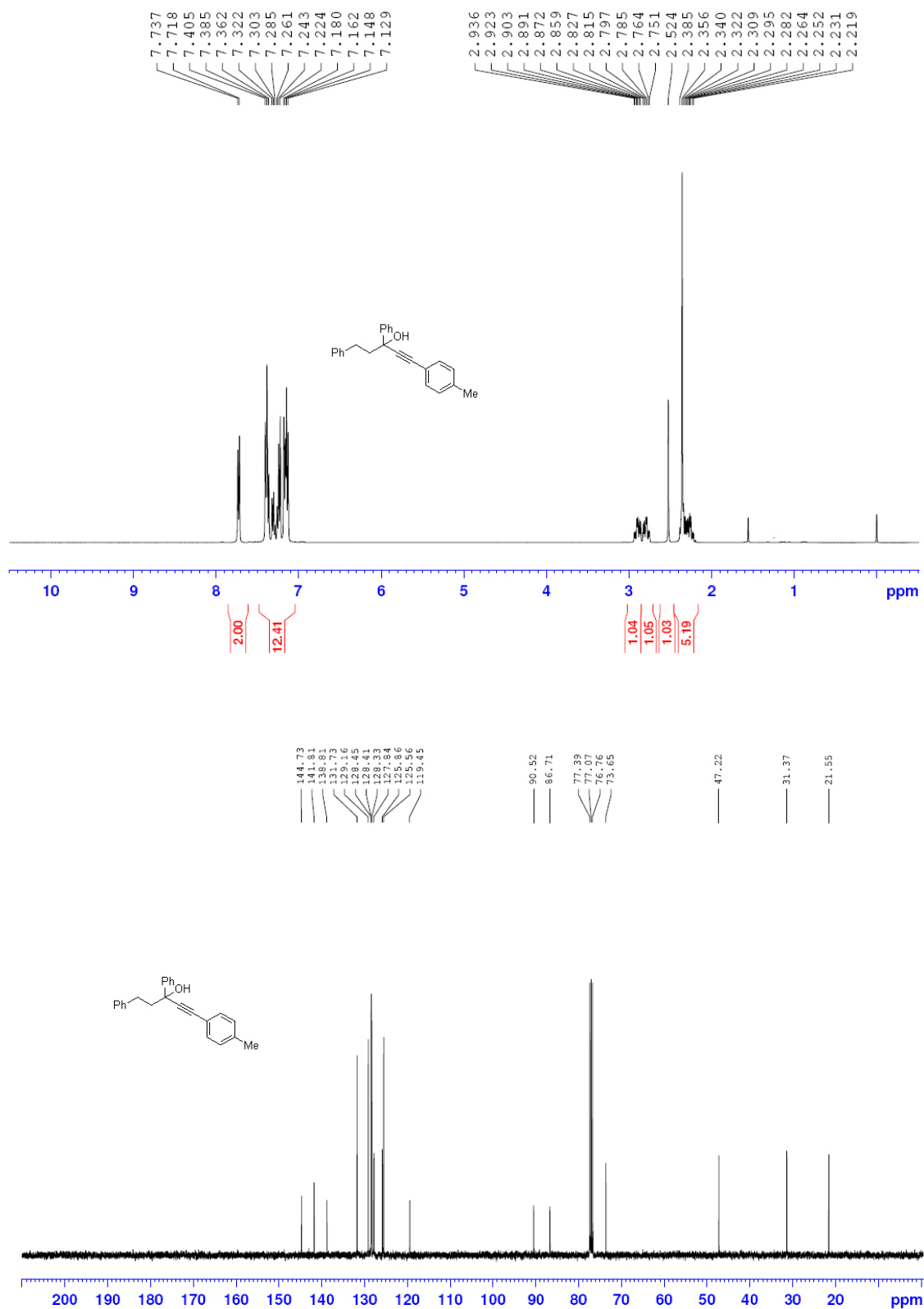


Figure S13. ^1H and ^{13}C NMR Spectra of 2-(4-Ethoxyphenyl)-1-phenyl-4-*p*-tolylbut-3-yn-2-ol
(1m)

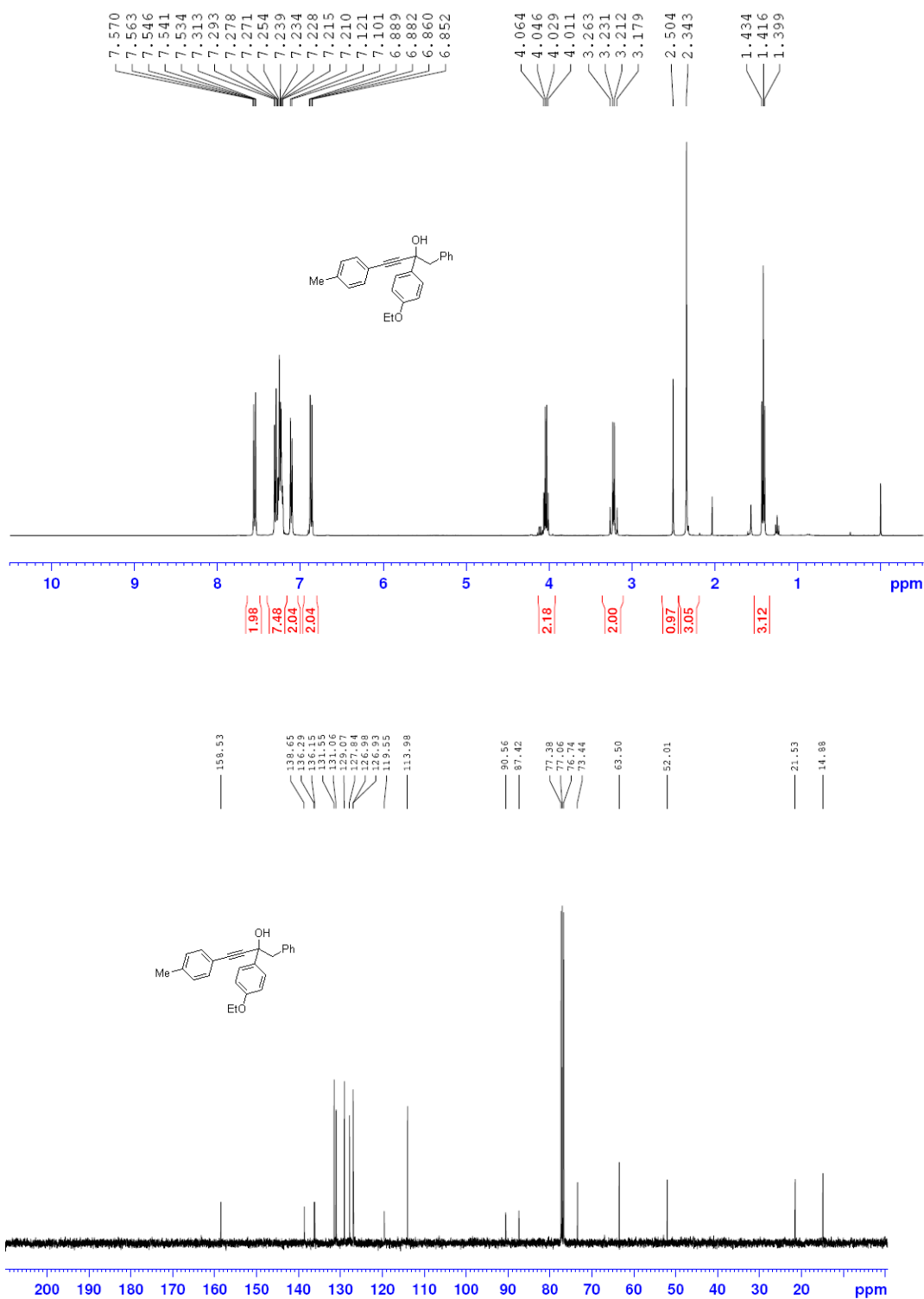


Figure S14. ^1H and ^{13}C NMR Spectra of 3-(4-Ethoxyphenyl)-1-p-tolylhept-6-en-1-yn-3-ol (**1n**)

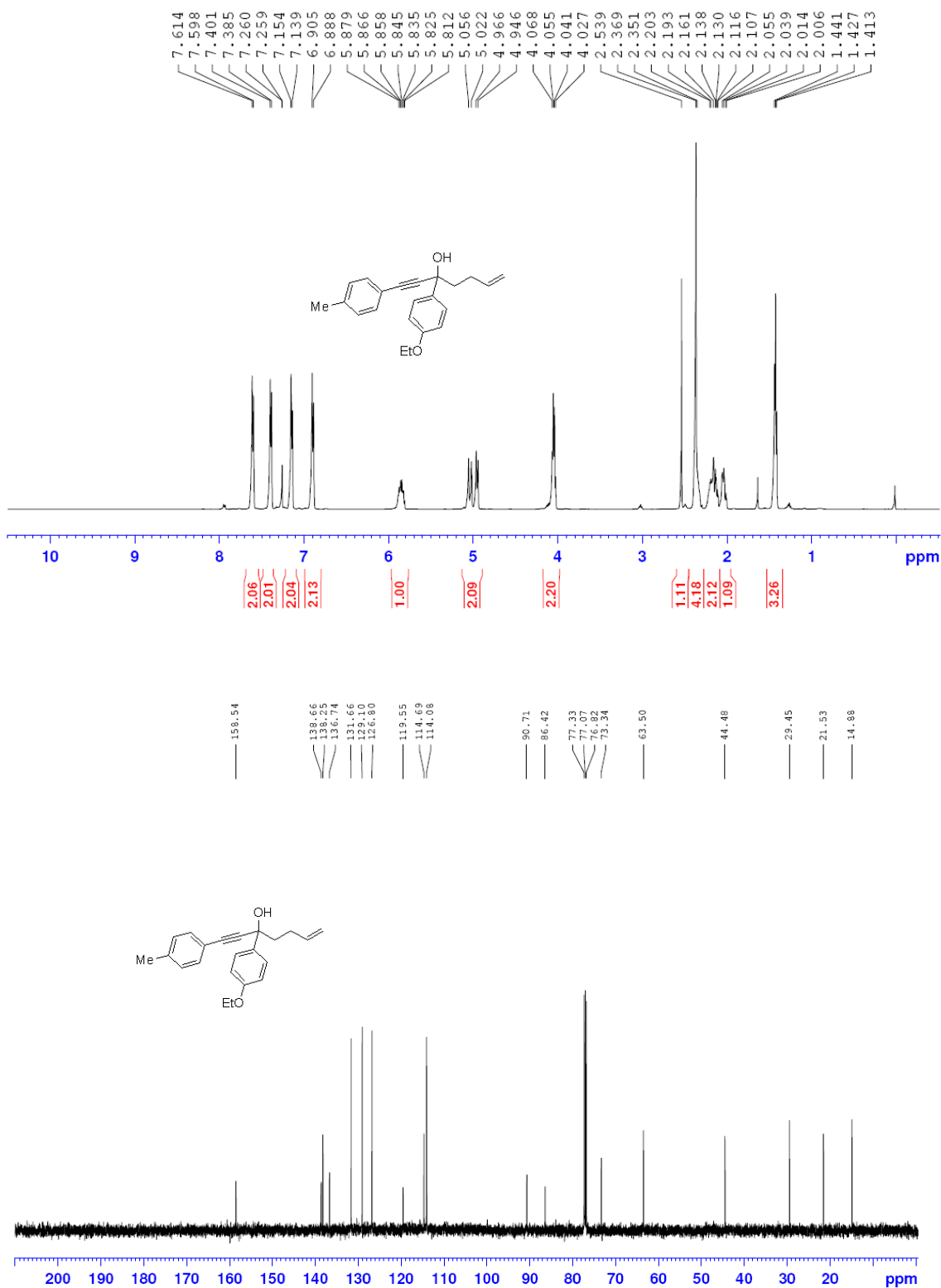


Figure S15. ^1H and ^{13}C NMR Spectra of 1,1,3-Triphenylprop-2-yn-1-ol (**1o**)^{S5}

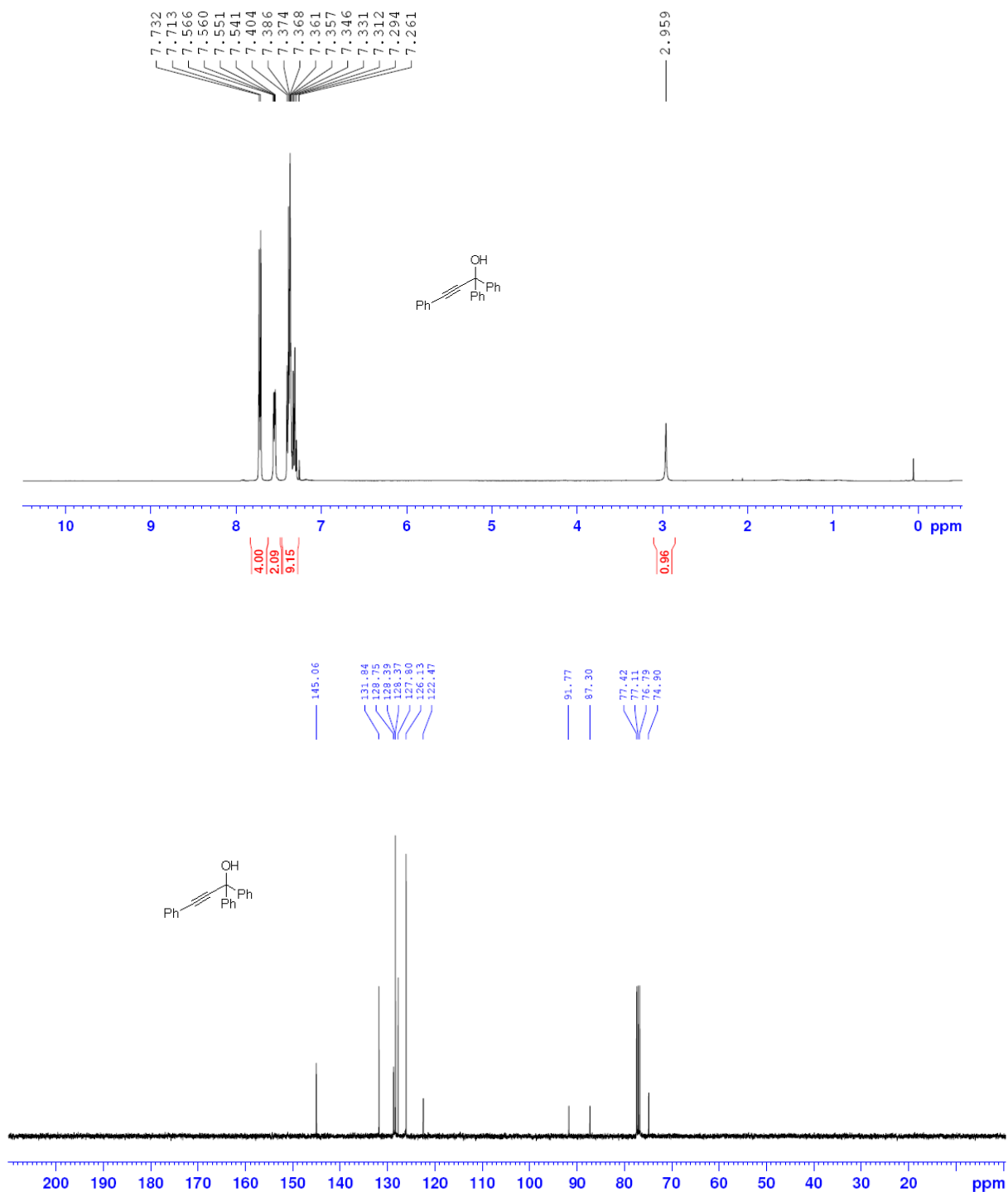


Figure S16. ^1H and ^{13}C NMR Spectra of 1,3-Diphenylprop-2-yn-1-ol (**1p**)^{S6}

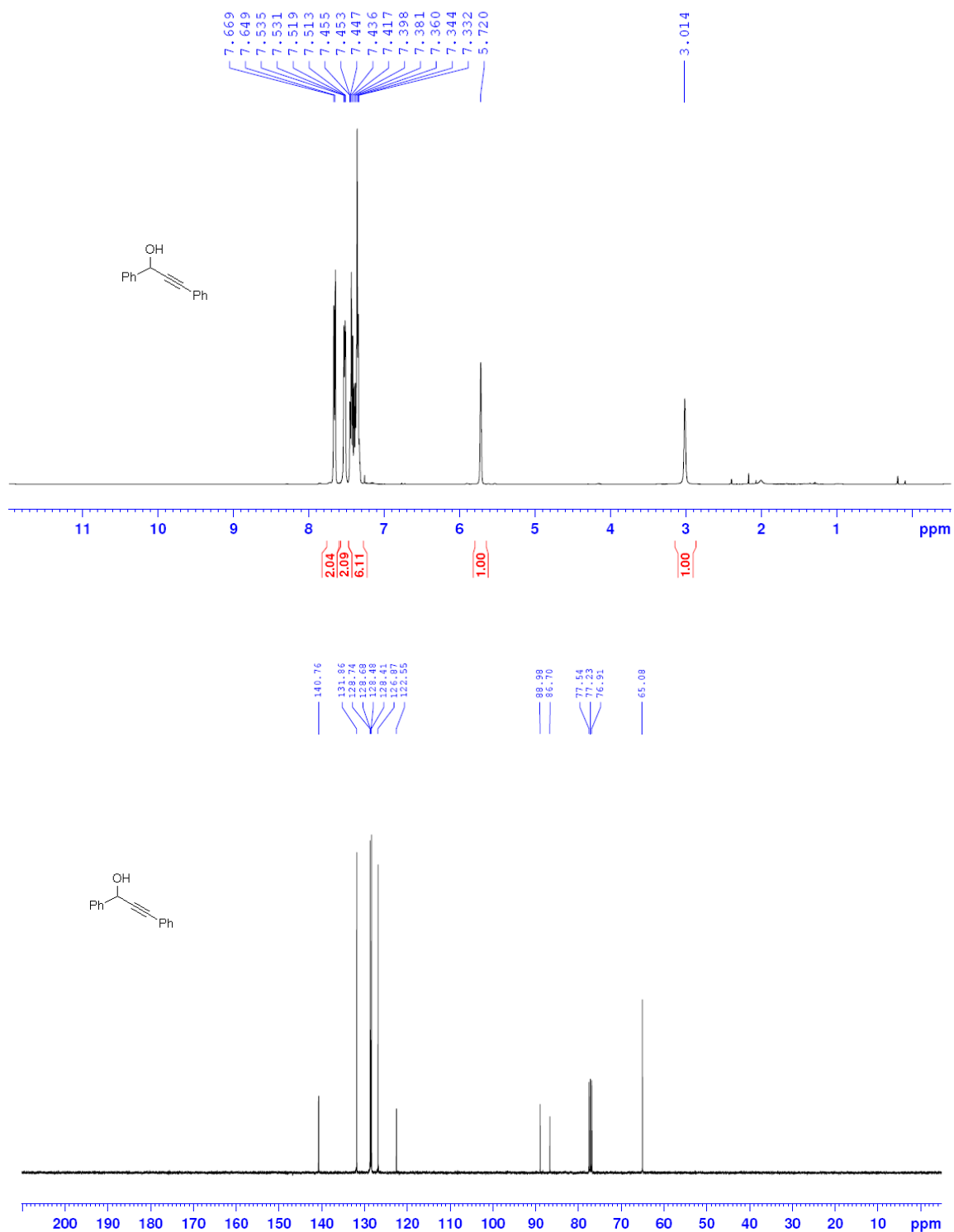


Figure S17. ^1H and ^{13}C NMR Spectra of 1-Cyclobutyl-2-(cyclobutylidene(phenyl) methyl)-1-phenyl-3-(phenylethynyl)-1H-indene (**2a**)

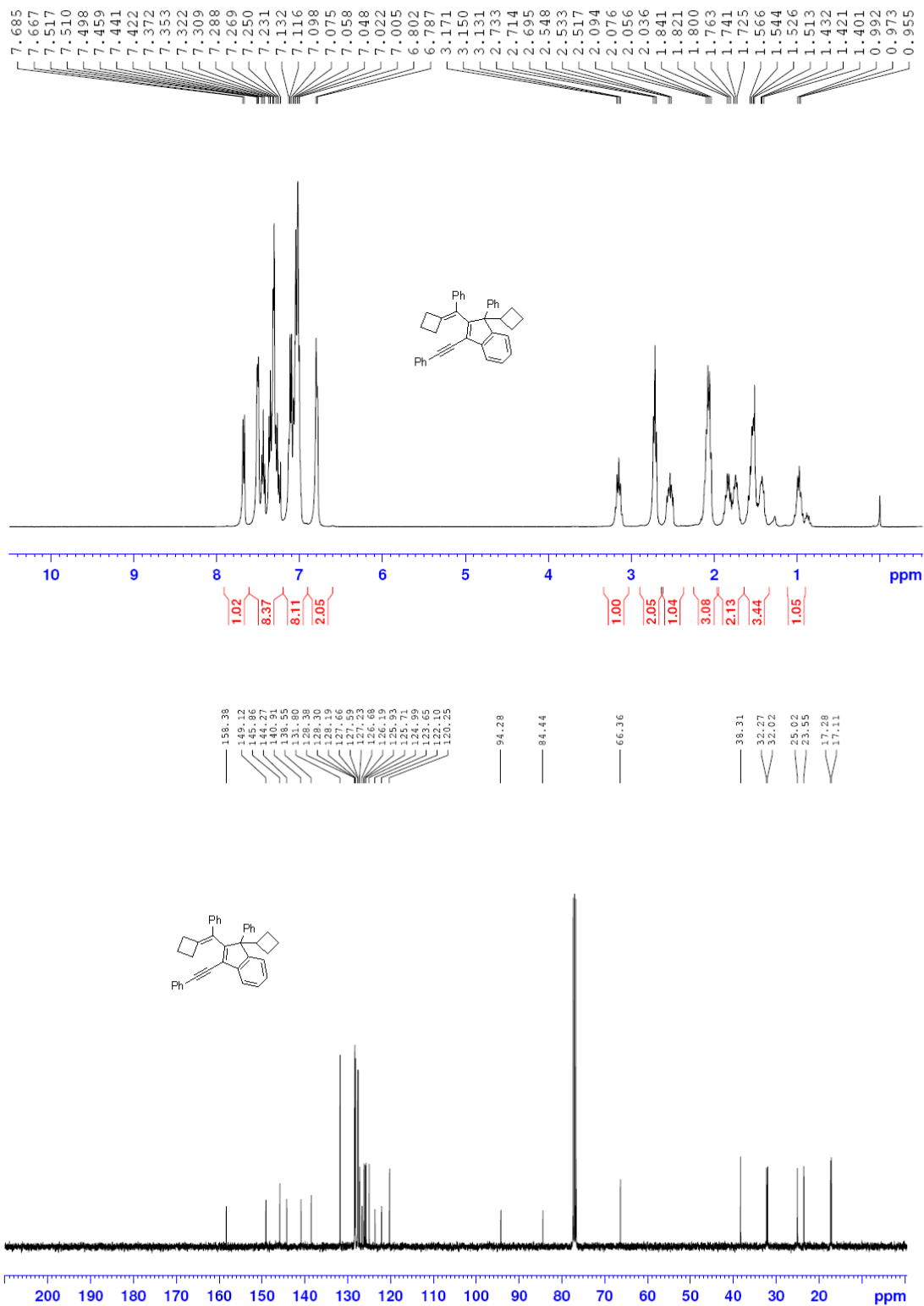


Figure S18. ^1H and ^{13}C NMR Spectra of 3-Cyclobutyl-2-(cyclobutylidene(phenyl) methyl)-1-phenyl-1-(phenylethynyl)-1*H*-indene (**3a**)

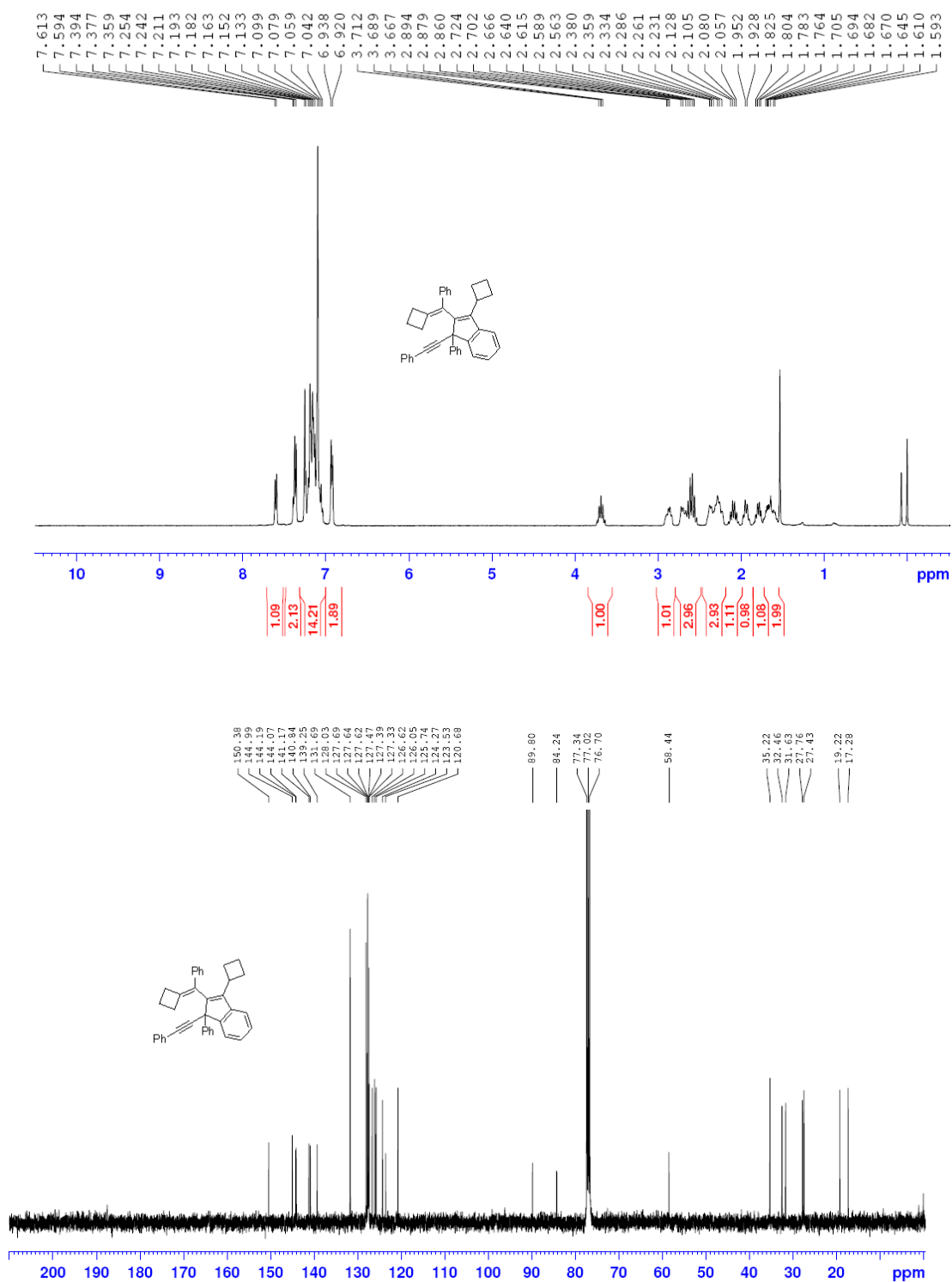


Figure S19. ^1H and ^{13}C NMR Spectra of 1-Cyclobutyl-2-(cyclobutylidene(*p*-tolyl) methyl)-1-phenyl-3-(*p*-tolylethynyl)-1*H*-indene (**2b**)

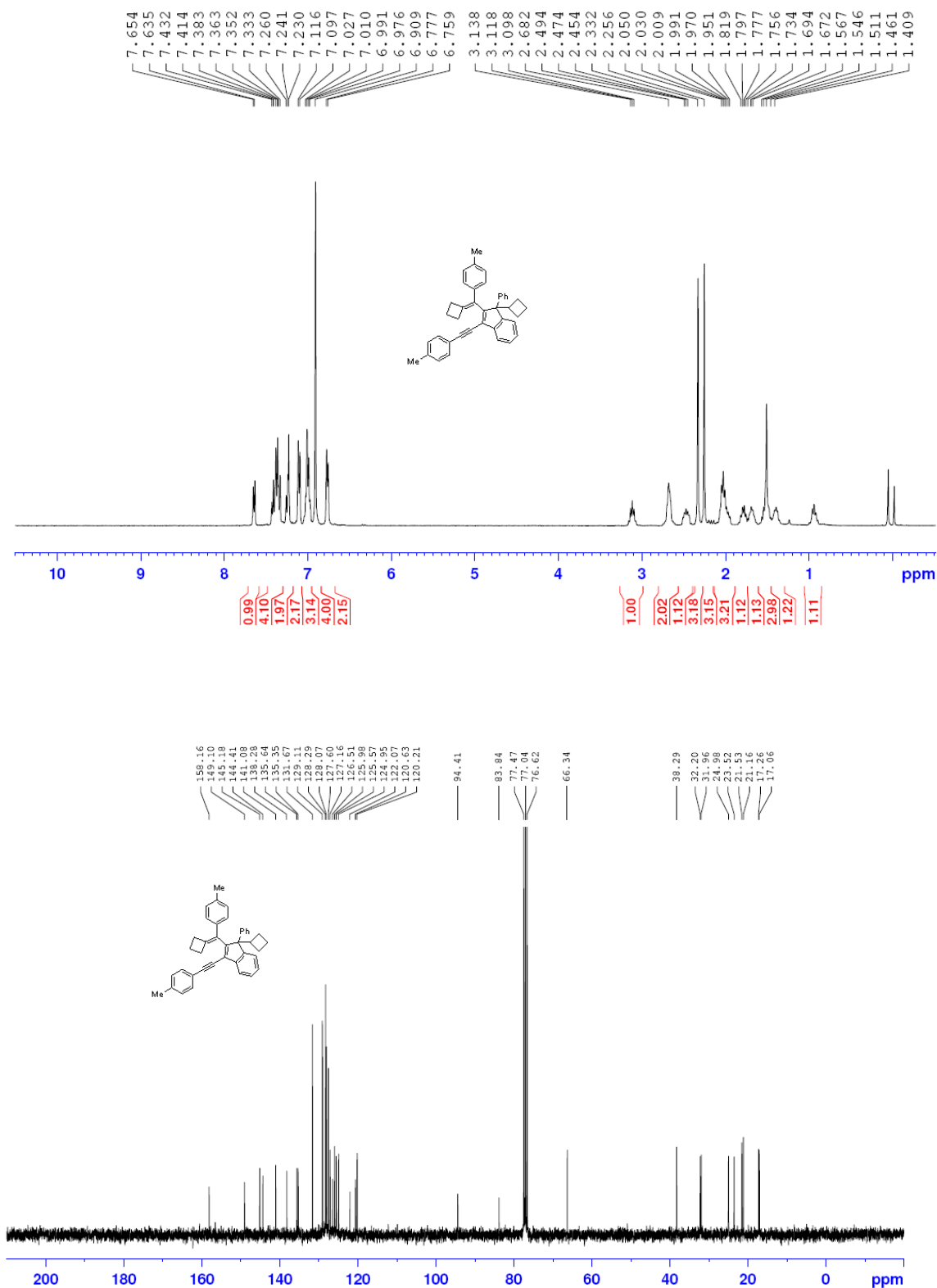


Figure S20. ^1H and ^{13}C NMR Spectra of 3-Cyclobutyl-2-(cyclobutylidene(*p*-tolyl) methyl)-1-phenyl-1-(*p*-tolylethynyl)-1*H*-indene (**3b**)

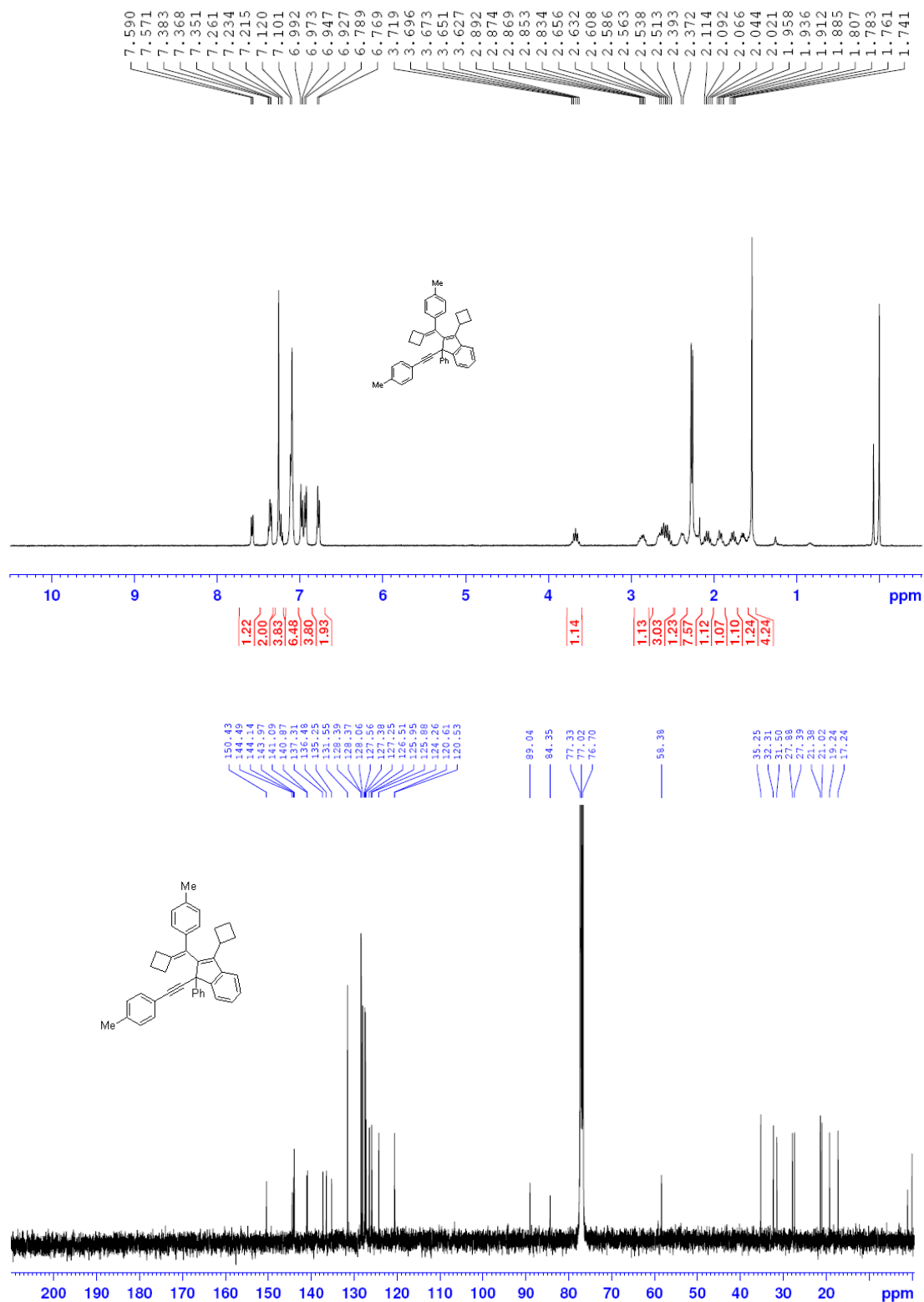


Figure S21. ^1H and ^{13}C NMR Spectra of 1-Cyclobutyl-2-(cyclobutylidene(4-pentylphenyl)methyl)-3-((4-pentylphenyl)ethynyl)-1-phenyl-1*H*-indene (**2c**)

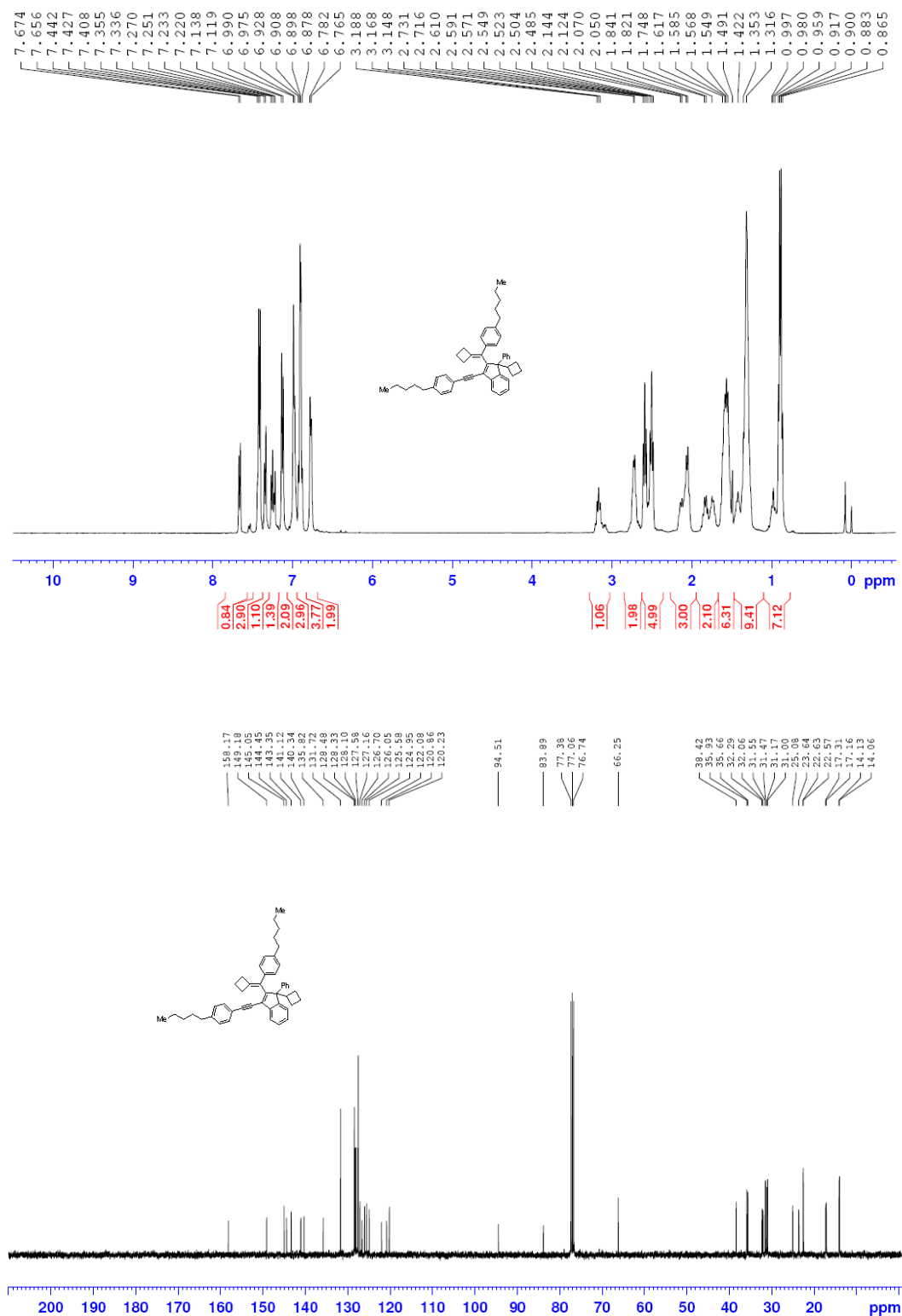


Figure S22. ^1H and ^{13}C NMR Spectra of 3-Cyclobutyl-2-(cyclobutylidene(4-pentylphenyl)methyl)-1-((4-pentylphenyl)ethynyl)-1-phenyl-1*H*-indene (**3c**)

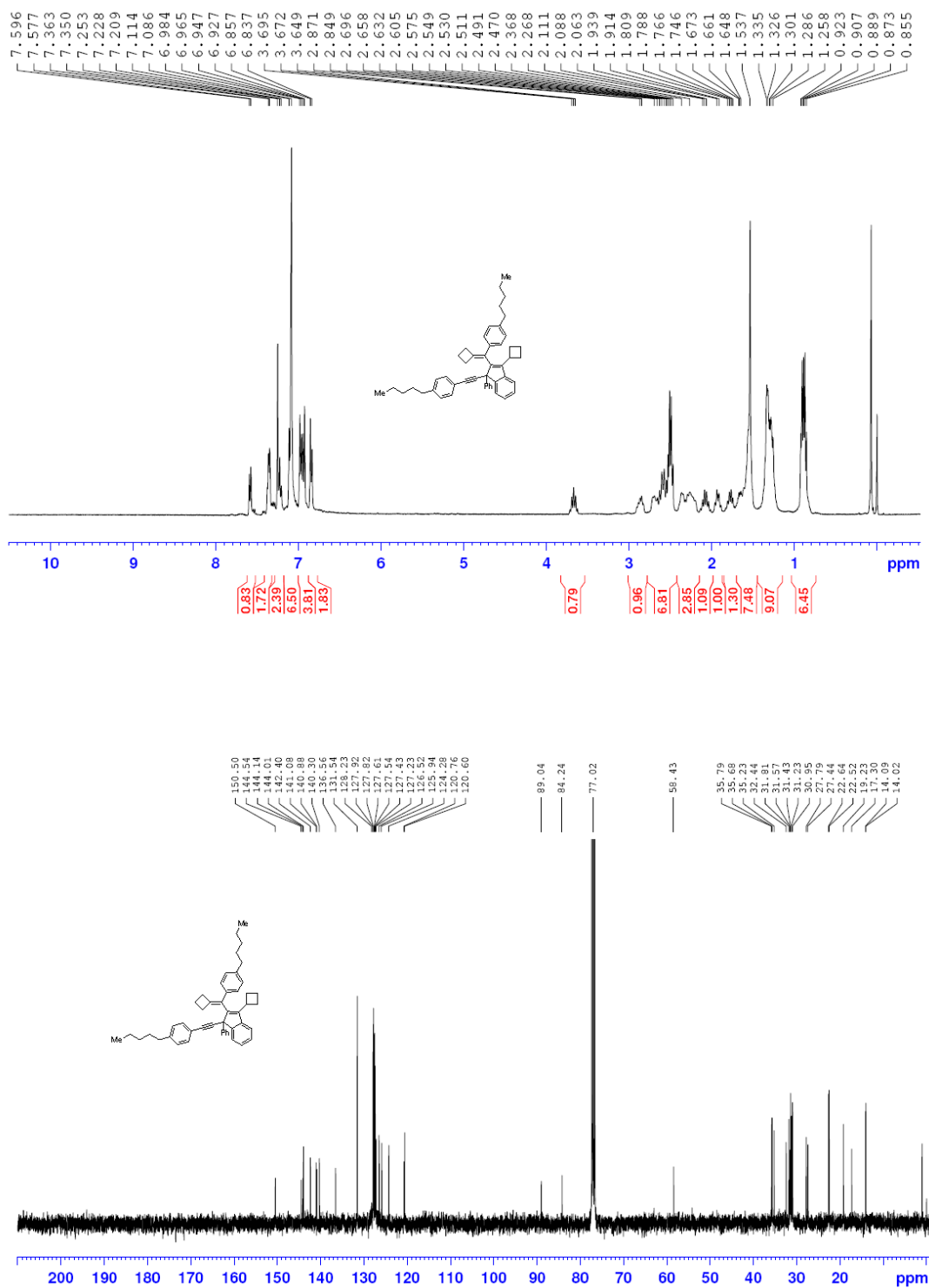


Figure S23. ^1H and ^{13}C NMR Spectra of 2-((4-Chlorophenyl)(cyclobutylidene) methyl)-3-((4-chlorophenyl)ethynyl)-1-cyclobutyl-1-phenyl-1*H*-indene (**2d**)

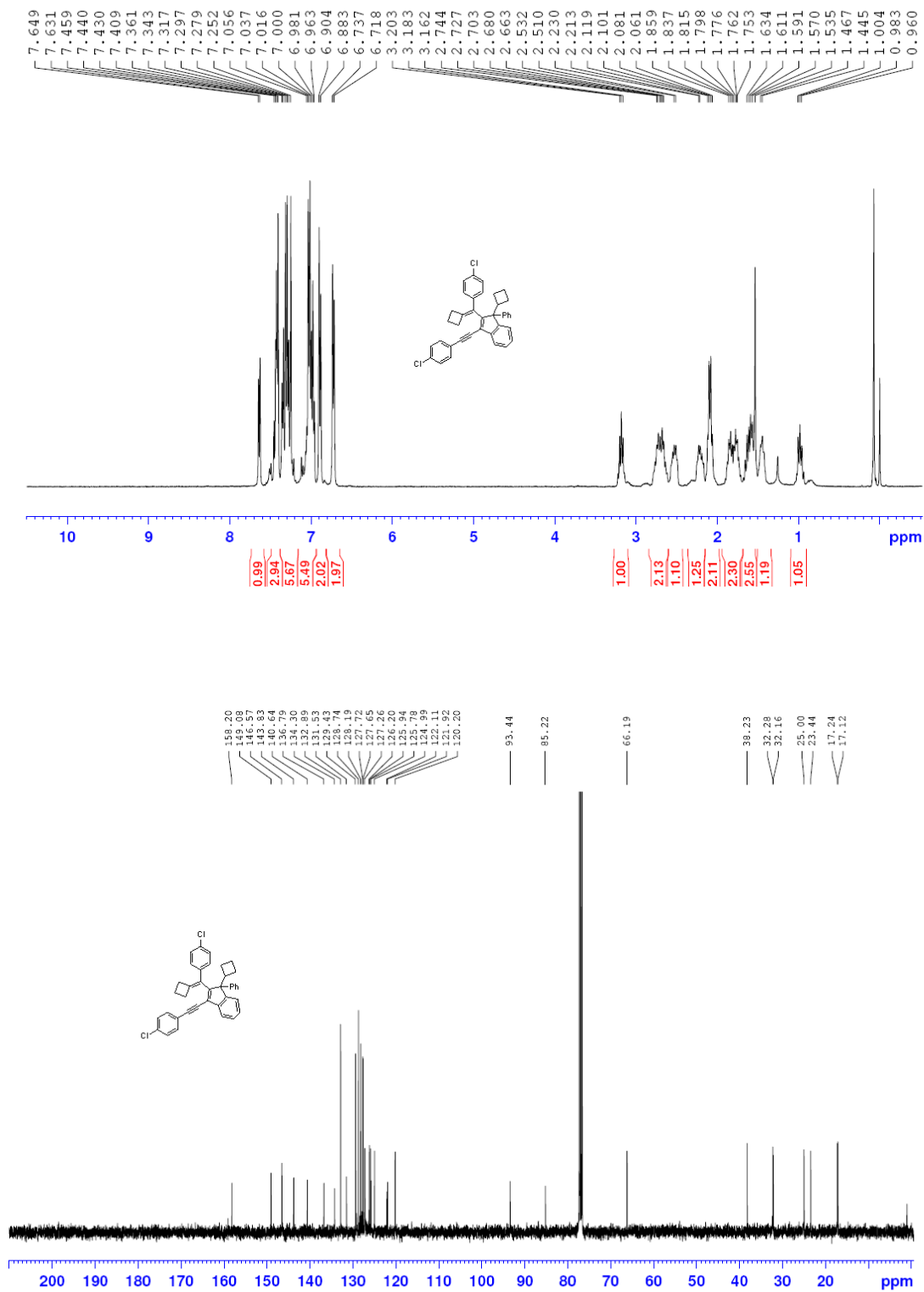


Figure S24. ^1H and ^{13}C NMR Spectra of 1-Chloro-4-(3-cyclobutylidene-3-phenyl prop-1-ynyl) benzene (**7d**)

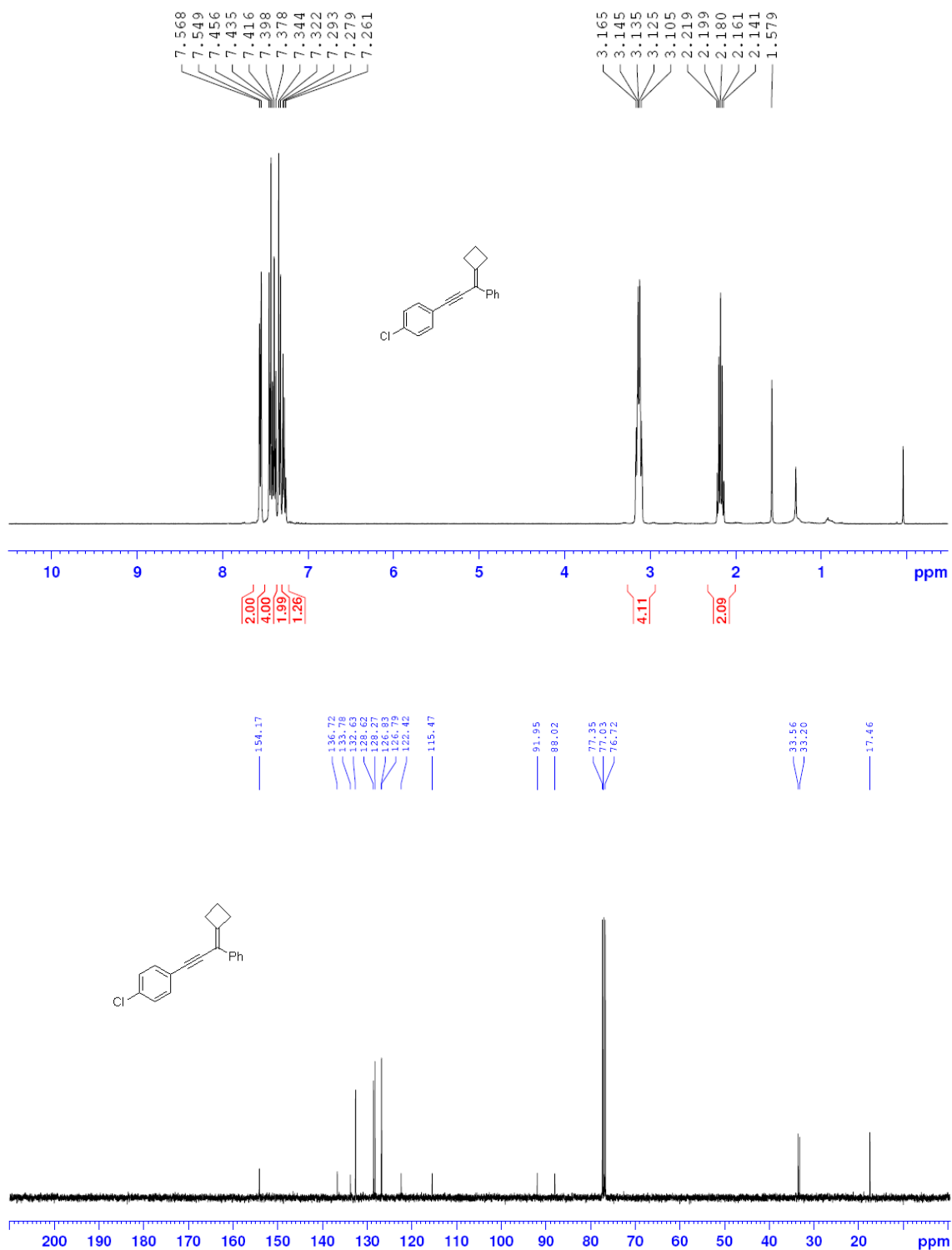


Figure S25. ^1H and ^{13}C NMR Spectra of 3-((1-Cyclobutyl-1-phenyl-3-(thiophen-3-yl ethynyl)-1*H*-inden-2-yl)(cyclobutylidene)methyl)thiophene (**2e**)

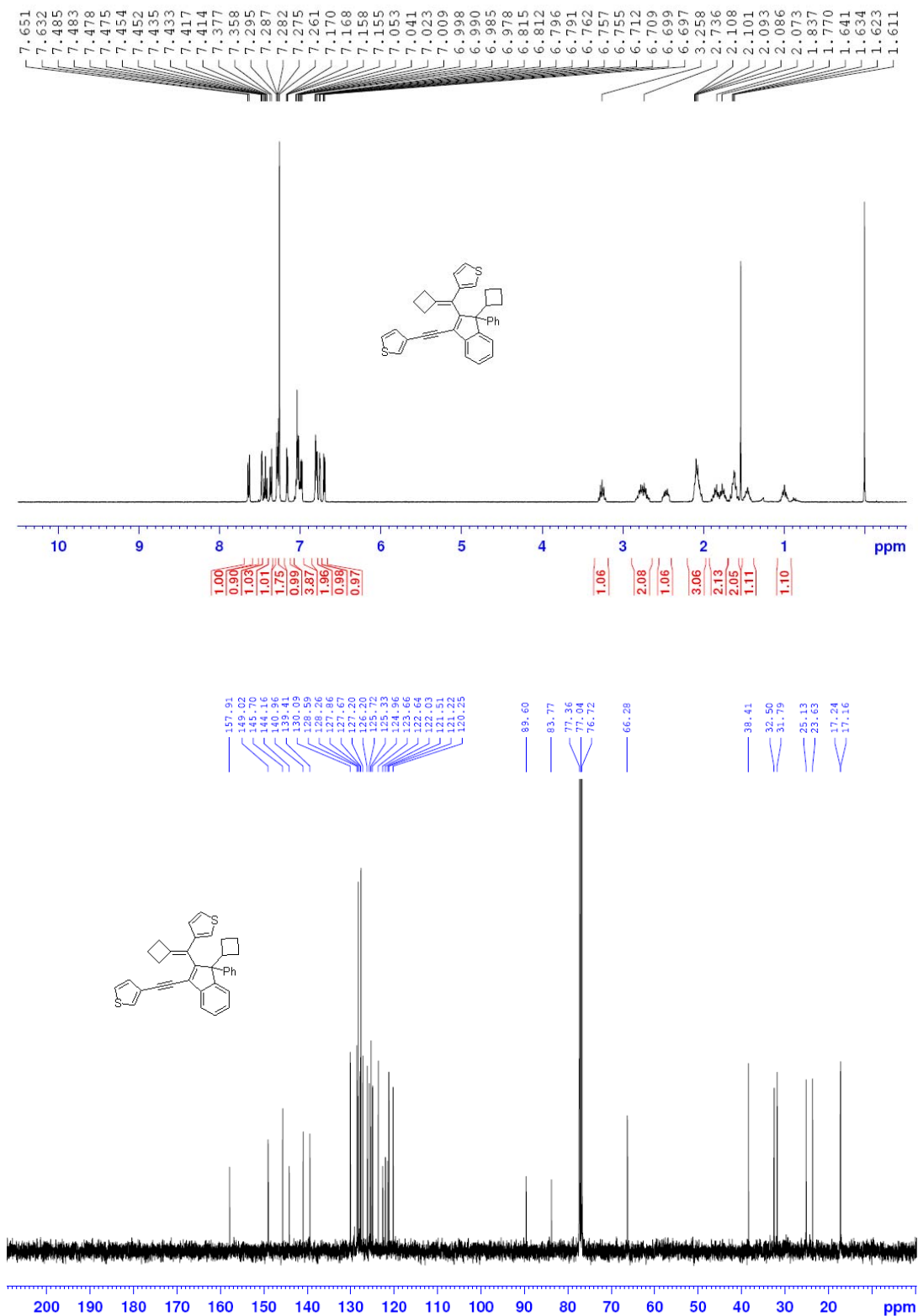


Figure S26. ^1H and ^{13}C NMR Spectra of (*E*)-1-Ethyl-1-phenyl-3-(phenylethynyl)-2-(1-phenylprop-1-enyl)-1*H*-indene (**2f**)

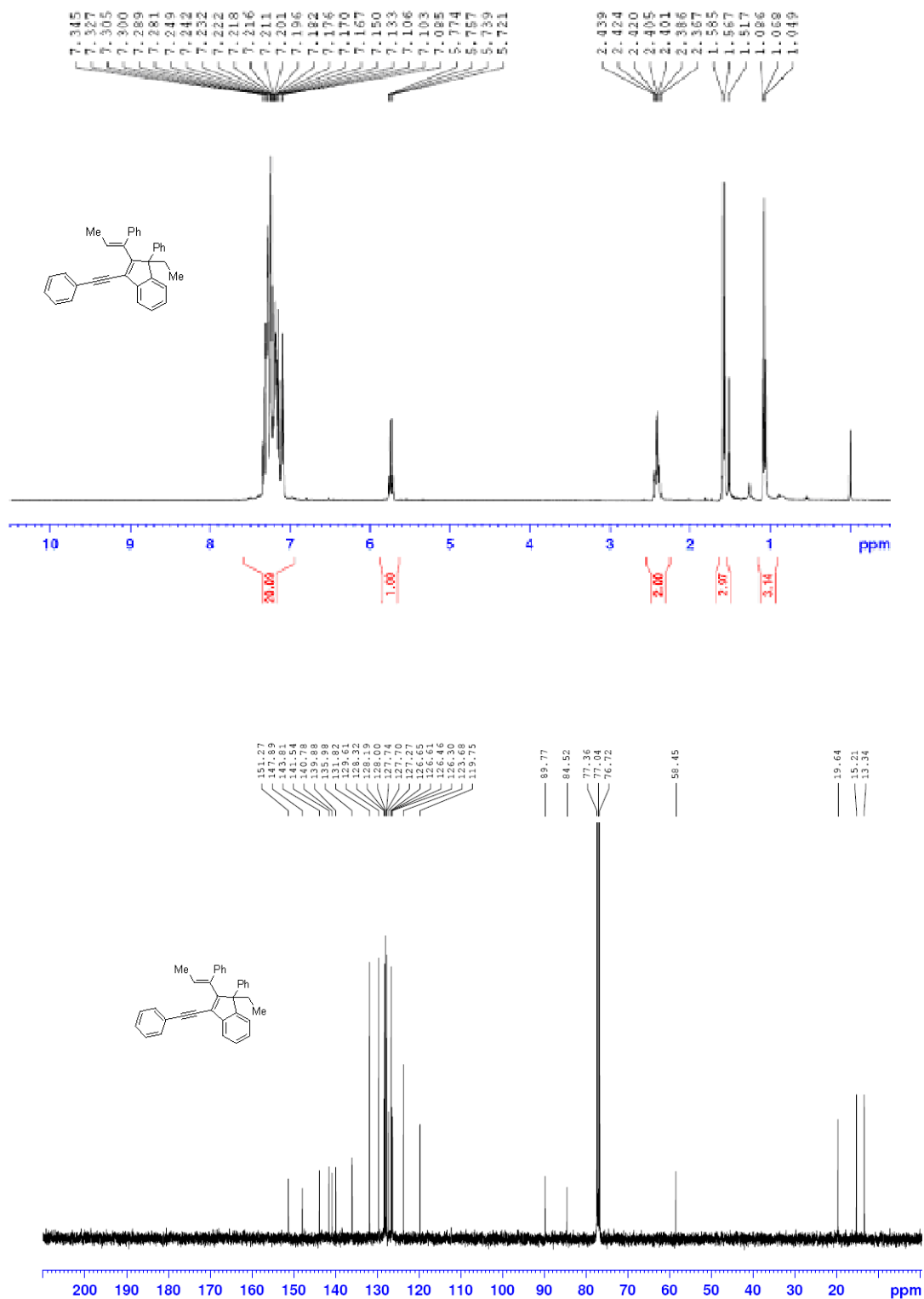


Figure S28. ^1H and ^{13}C NMR Spectra of (*E*)-1-Butyl-1-phenyl-3-(phenylethynyl)-2-(1-phenylpent-1-enyl)-1*H*-indene (**2g**)

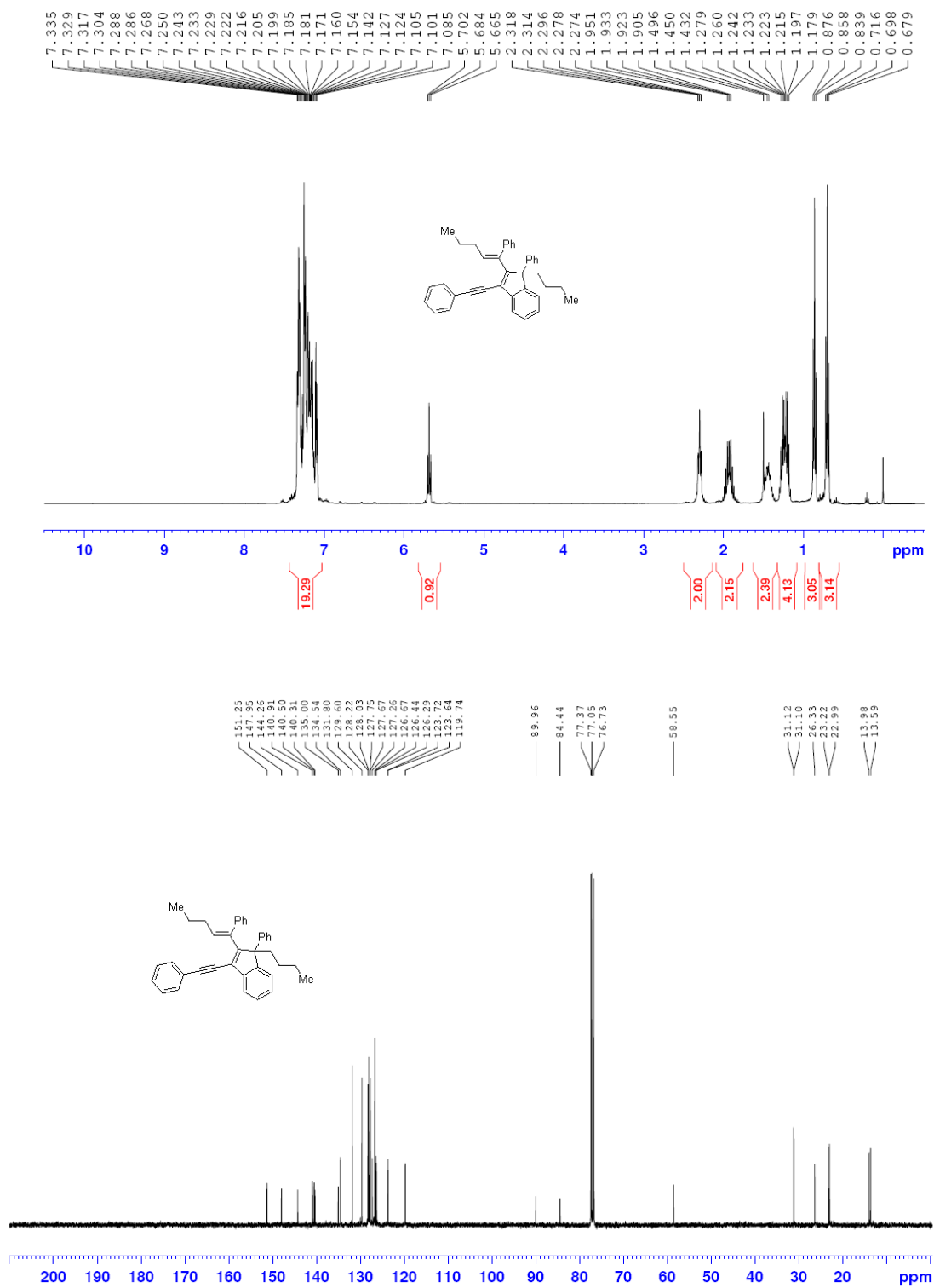


Figure S29. ^1H and ^{13}C NMR Spectra of (*E*)-3-Butyl-1-phenyl-1-(phenylethynyl)-2-(1-phenylpent-1-enyl)-1*H*-indene (**3g**)

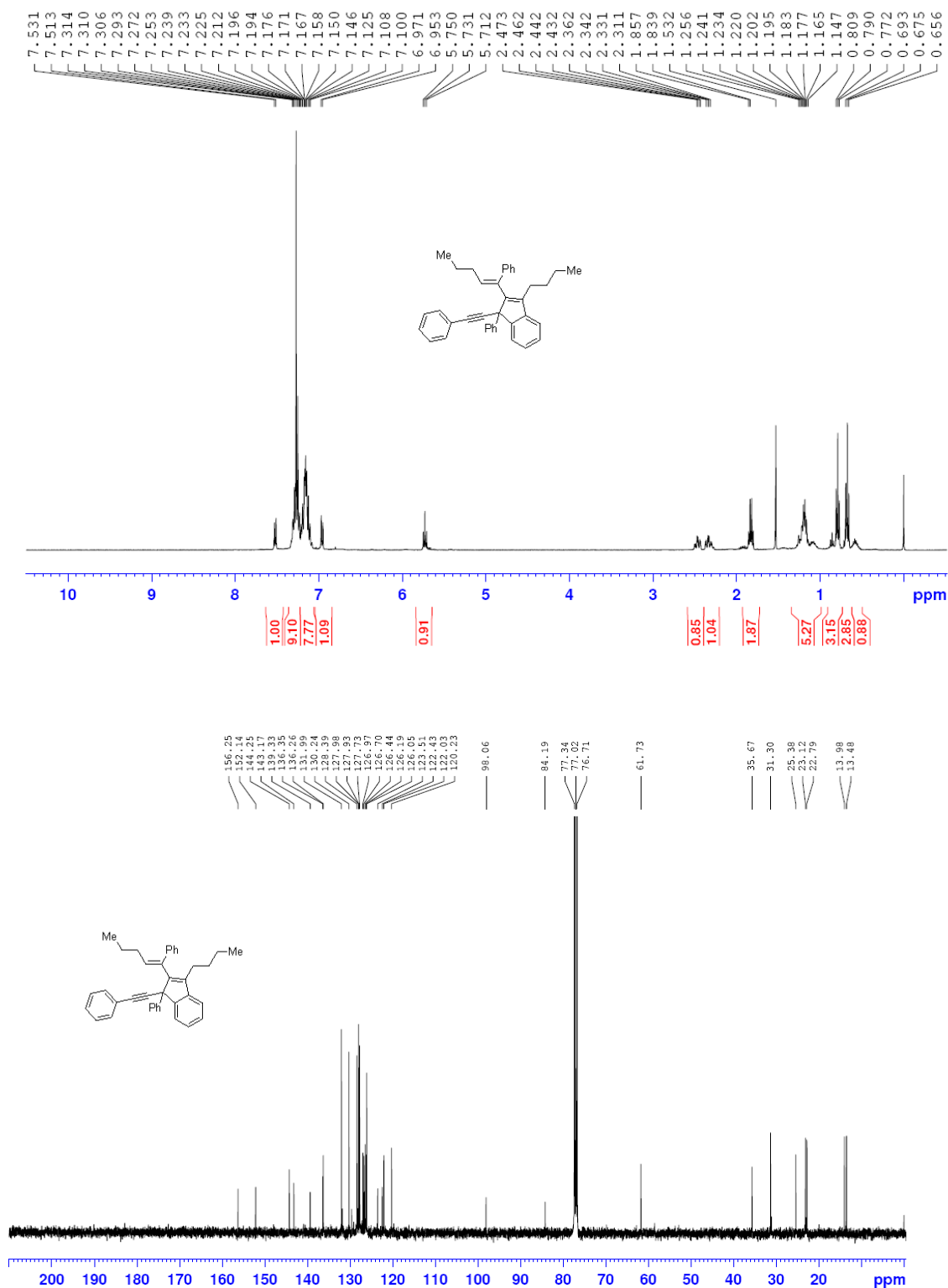


Figure S30. ^1H and ^{13}C NMR Spectra of (*E*)-1-Hexyl-1-phenyl-3-(phenylethynyl)-2-(1-phenylhept-1-enyl)-1*H*-indene (**2h**)

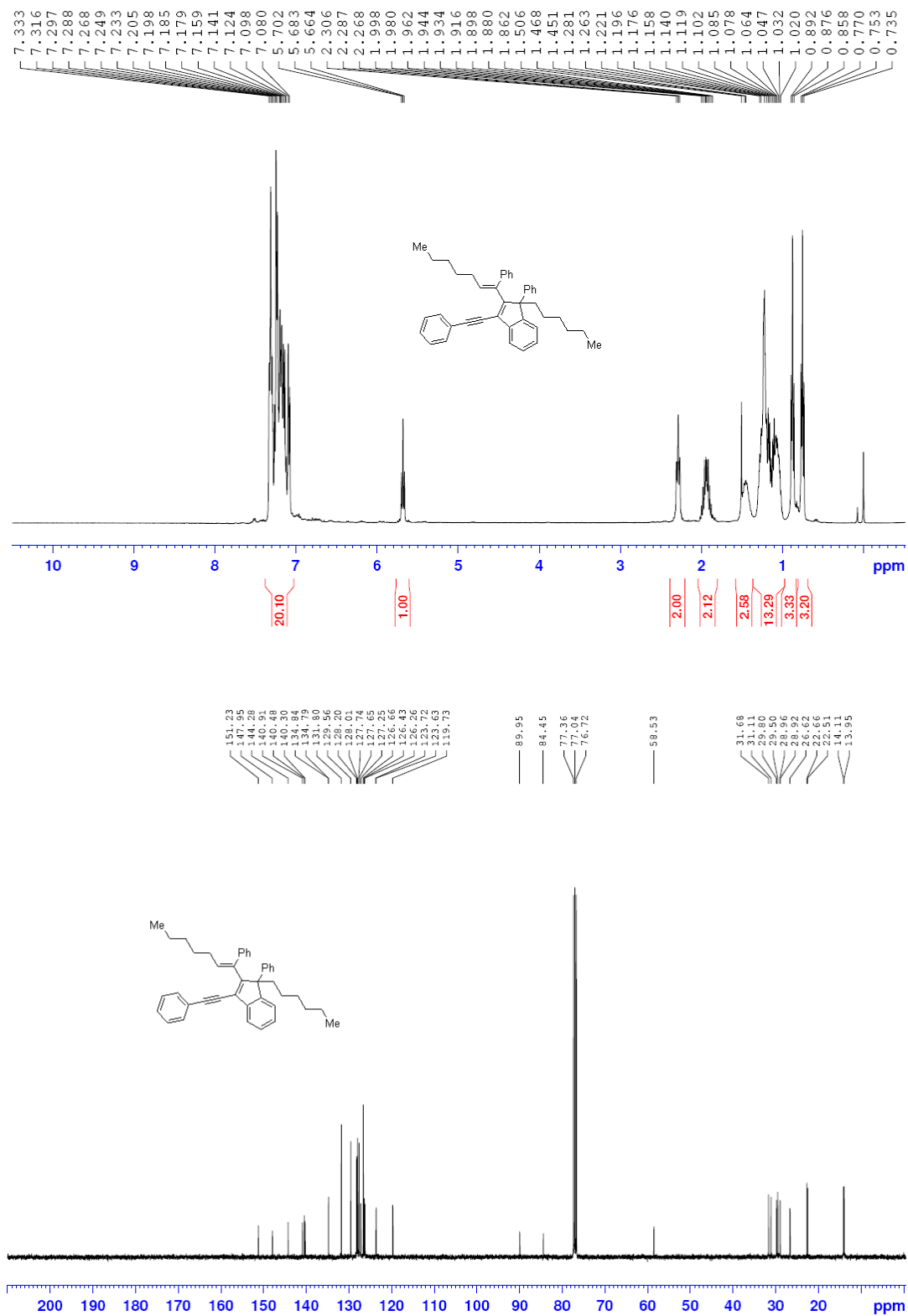


Figure S31. ^1H and ^{13}C NMR Spectra of (*E*)-3-Hexyl-1-phenyl-1-(phenylethynyl)-2-(1-phenylhept-1-enyl)-1*H*-indene (**3h**)

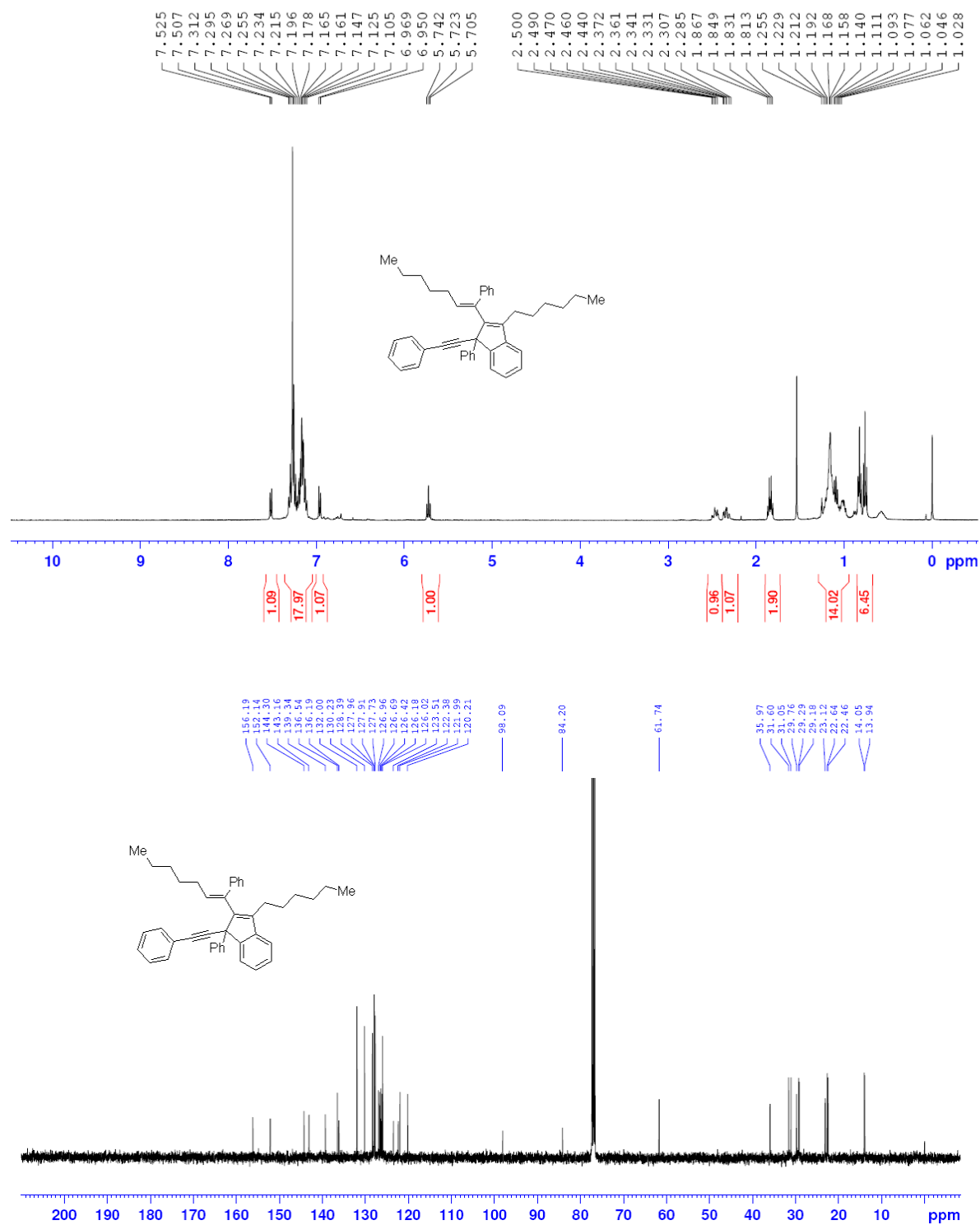


Figure S32. ^1H and ^{13}C NMR Spectra of (*E*)-1-Isobutyl-2-(3-methyl-1-phenylbut-1-enyl)-1-phenyl-3-(phenylethynyl)-1*H*-indene (**2i**)

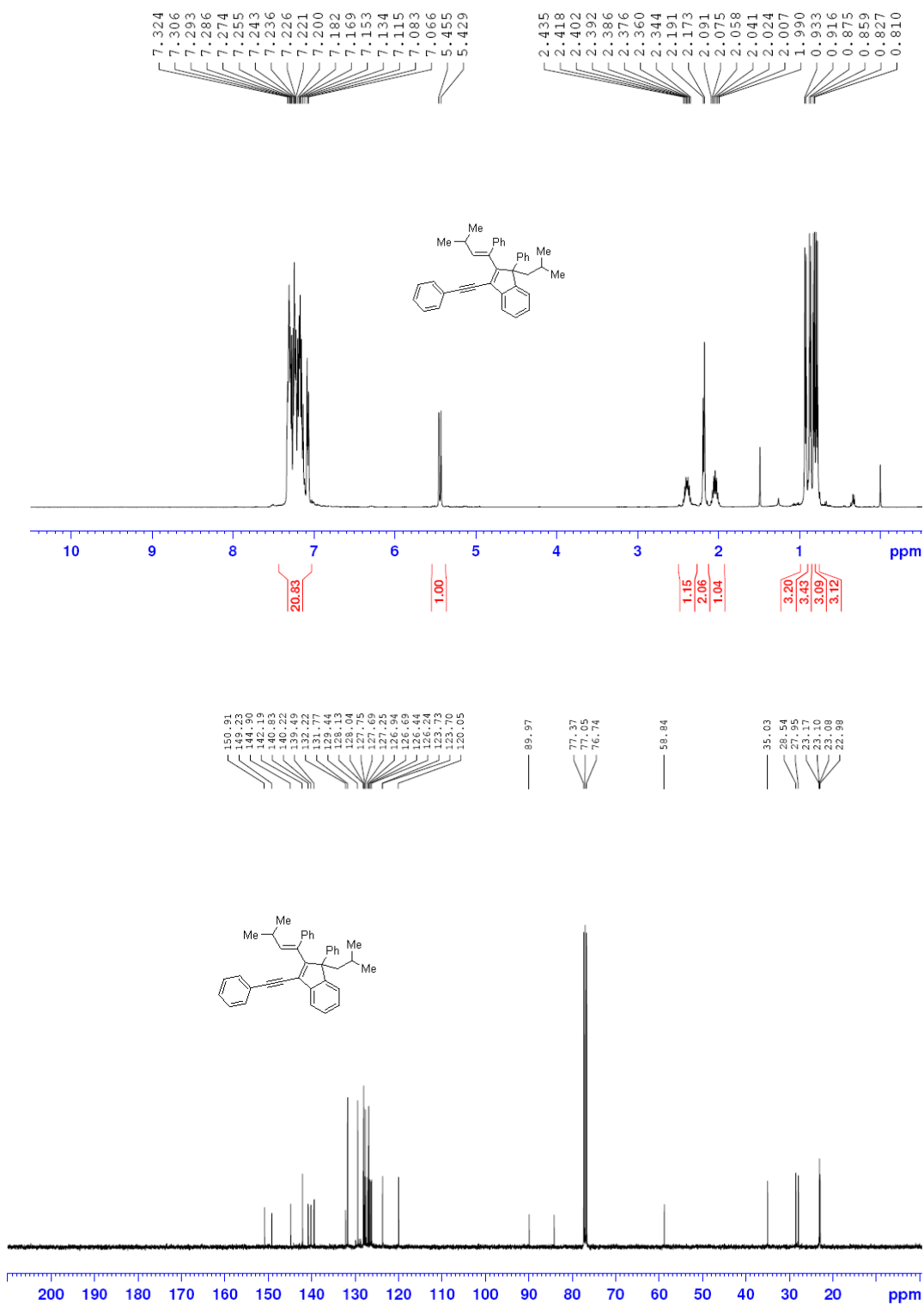


Figure S33. ^1H and ^{13}C NMR Spectra of (*E*)-1-Benzyl-2-(1,2-diphenylvinyl)-1-phenyl-3-(phenylethynyl)-1*H*-indene (**2j**)

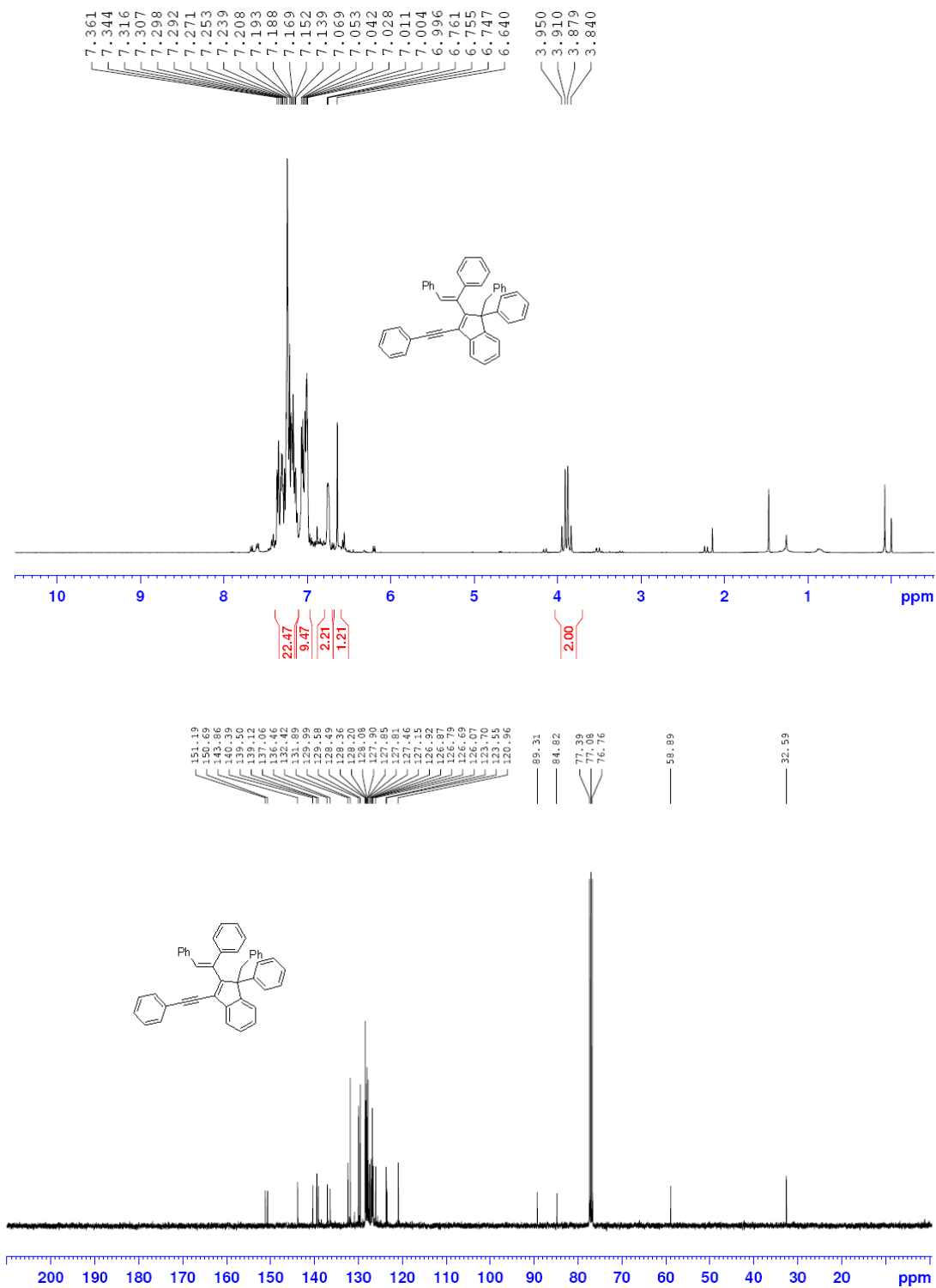


Figure S34. ^1H and ^{13}C NMR Spectra of (*E*)-5-(Benzo[*d*][1,3]dioxol-5-yl)-5-ethyl-7-(phenylethynyl)-6-(1-phenylprop-1-enyl)-5H-indeno[5,6-*d*][1,3]dioxole (**2k**)

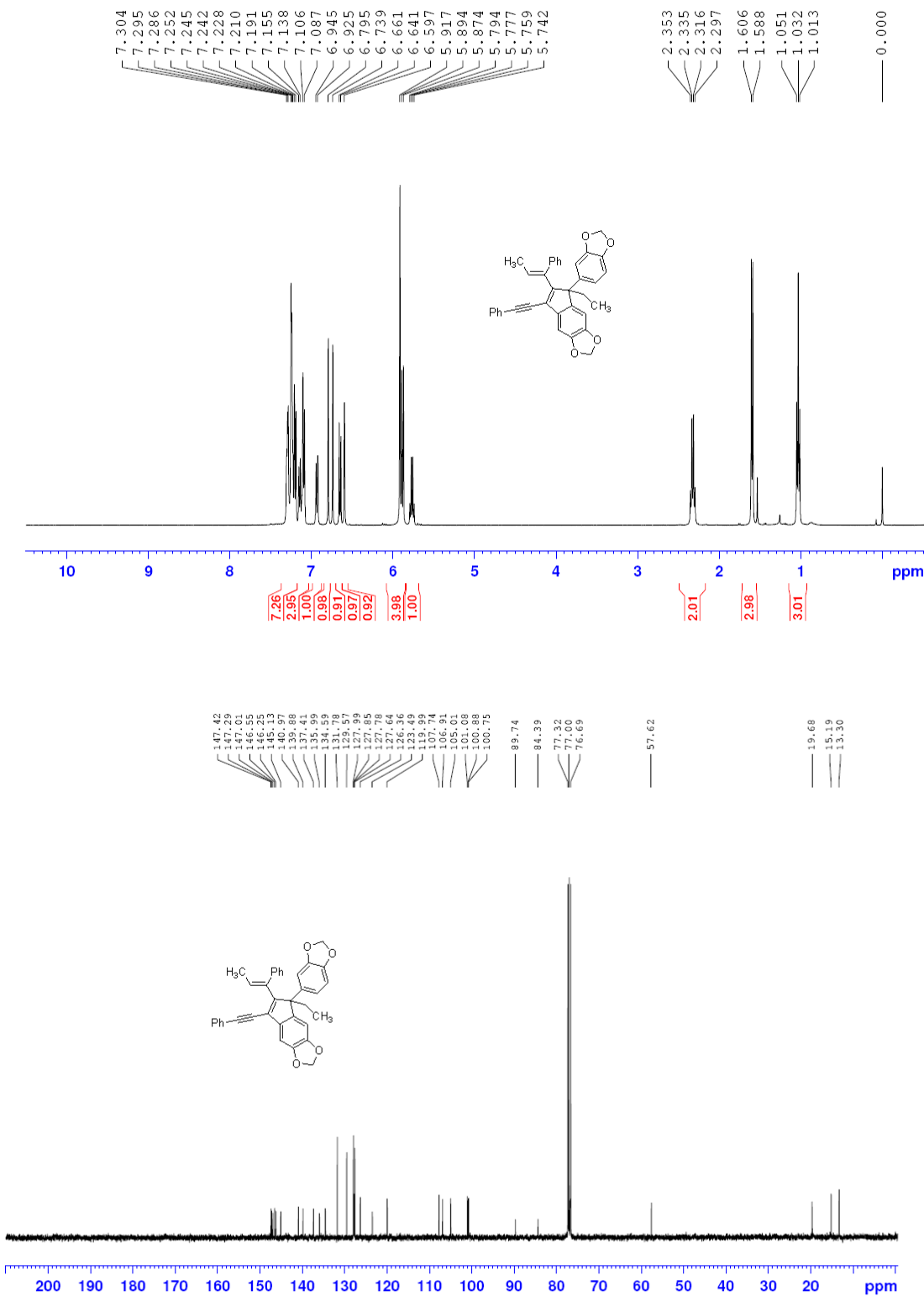


Figure S35. ^1H and ^{13}C NMR Spectra of (*E*)-5-(Benzo[*d*][1,3]dioxol-5-yl)-7-ethyl-5-(phenylethynyl)-6-(1-phenylprop-1-enyl)-5H-indeno[5,6-*d*][1,3]dioxole (**3k**)

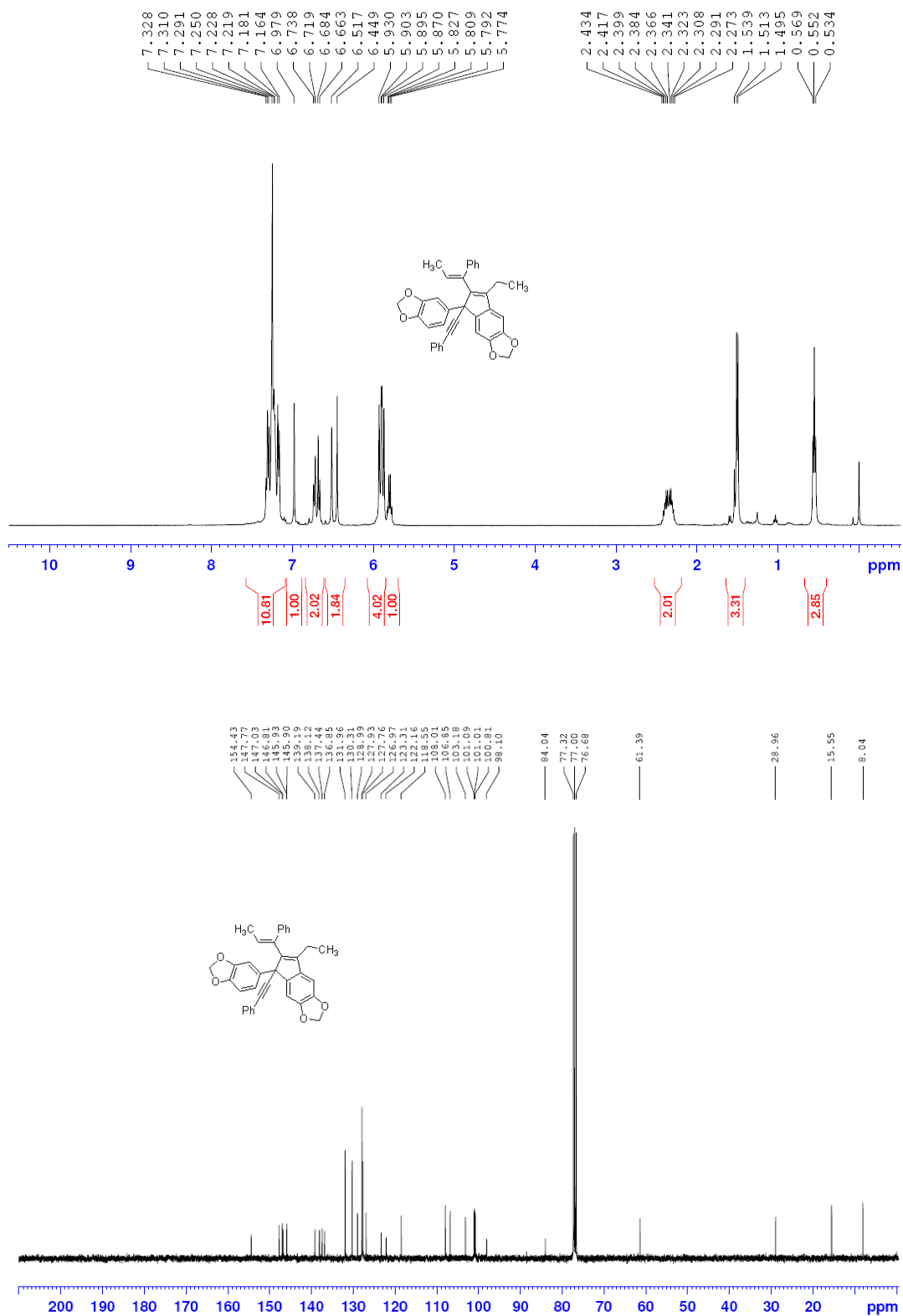


Figure S36. ^1H and ^{13}C NMR Spectra of (*E*)-1-Phenethyl-1-phenyl-2-(3-phenyl-1-*p*-tolylprop-1-enyl)-3-(*p*-tolylethynyl)-1*H*-indene (**2I**)

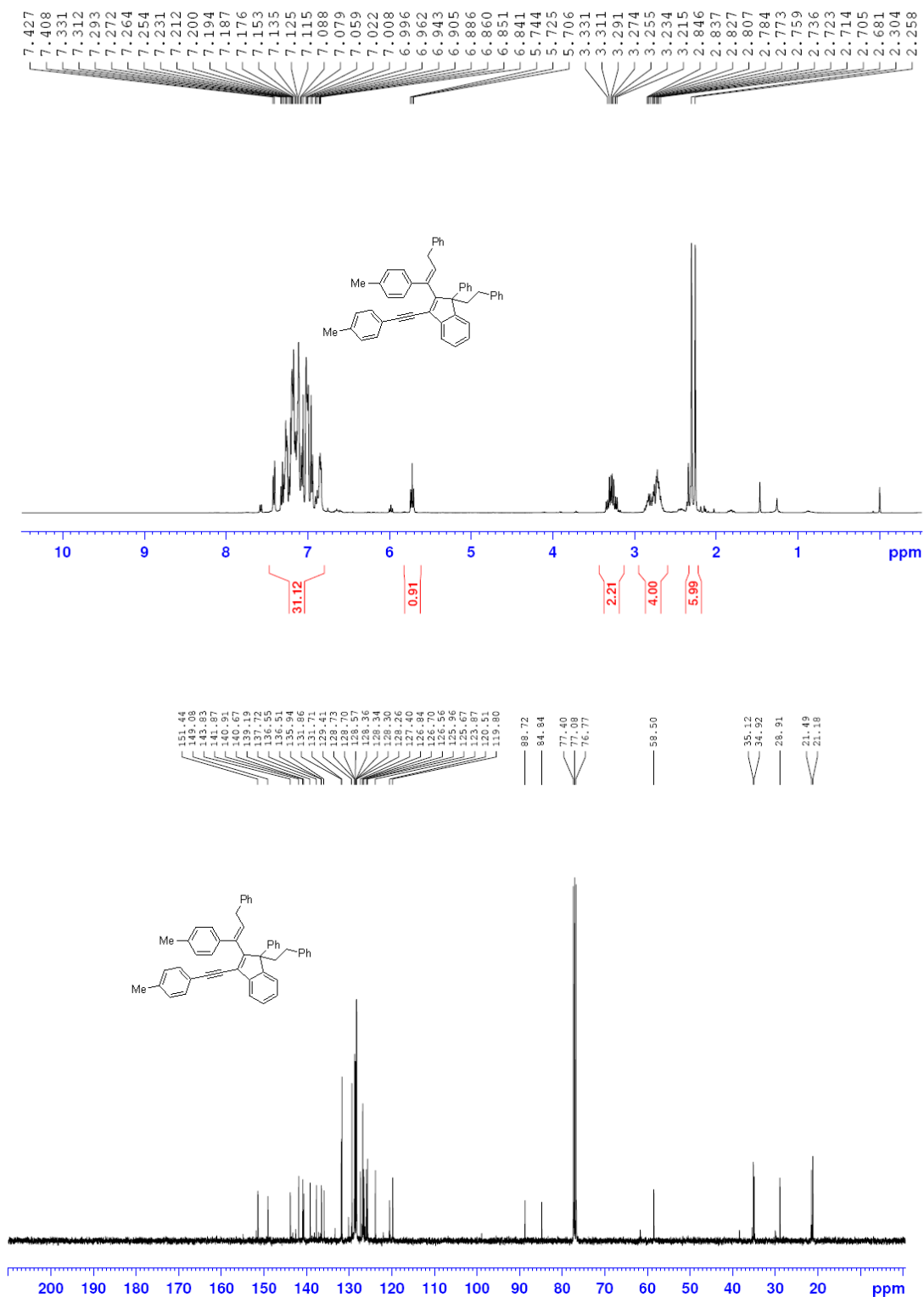


Figure S37. ^1H and ^{13}C NMR Spectra of (*E*)-1-Benzyl-6-ethoxy-1-(4-ethoxy phenyl)-2-(2-phenyl-1-*p*-tolylvinyl)-3-(*p*-tolylethynyl)-1*H*-indene (**2m**)

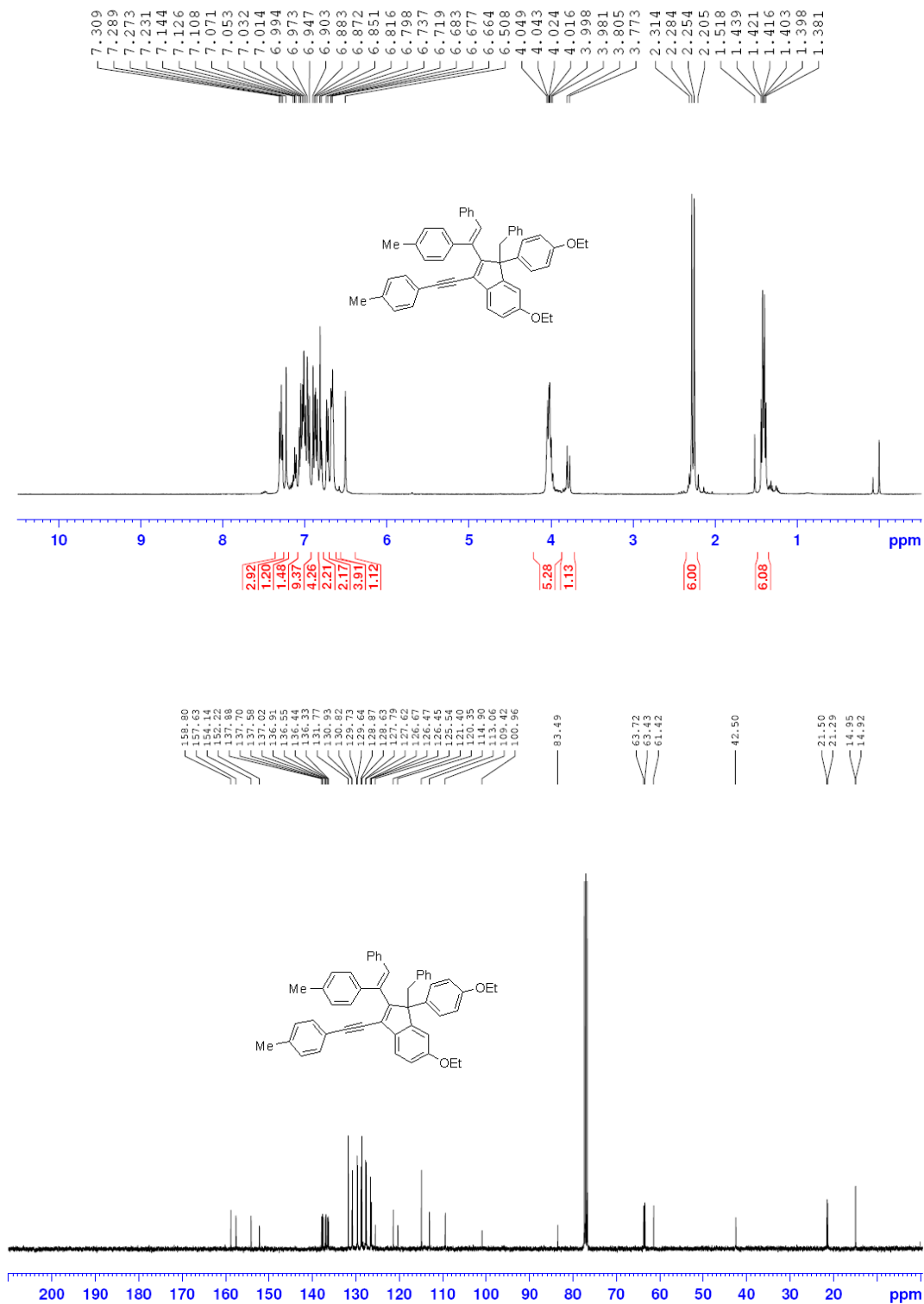


Figure S38. ^1H and ^{13}C NMR Spectra of (E)-1-(But-3-enyl)-6-ethoxy-1-(4-ethoxyphenyl)-3-(*p*-tolylethynyl)-2-(1-*p*-tolylpenta-1,4-dienyl)-1*H*-indene (**2n**)

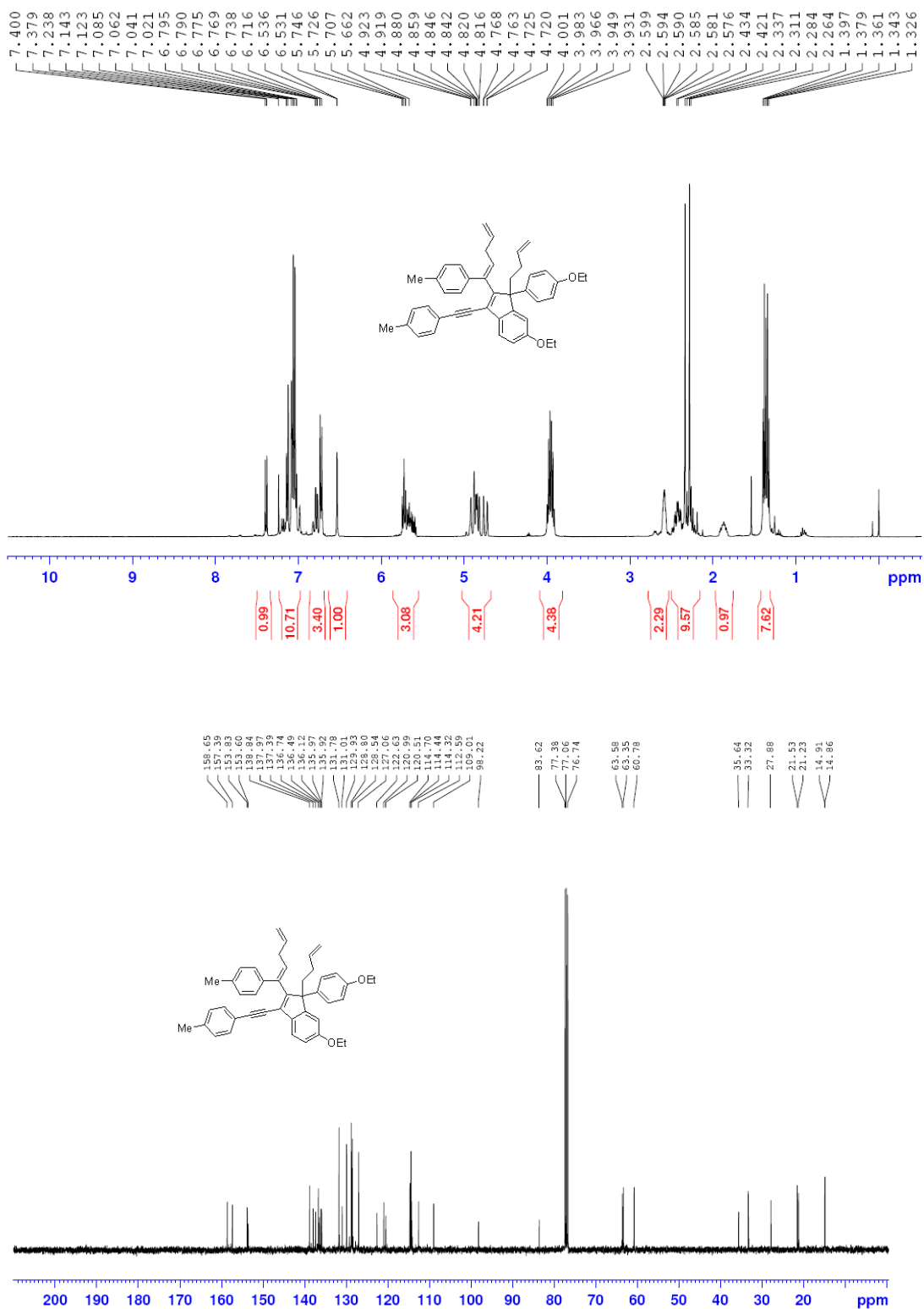


Figure S39. ^1H and ^{13}C NMR Spectra of (3-Cyclobutylideneprop-1-yne-1,3-diyl) dibenzene

(7a)

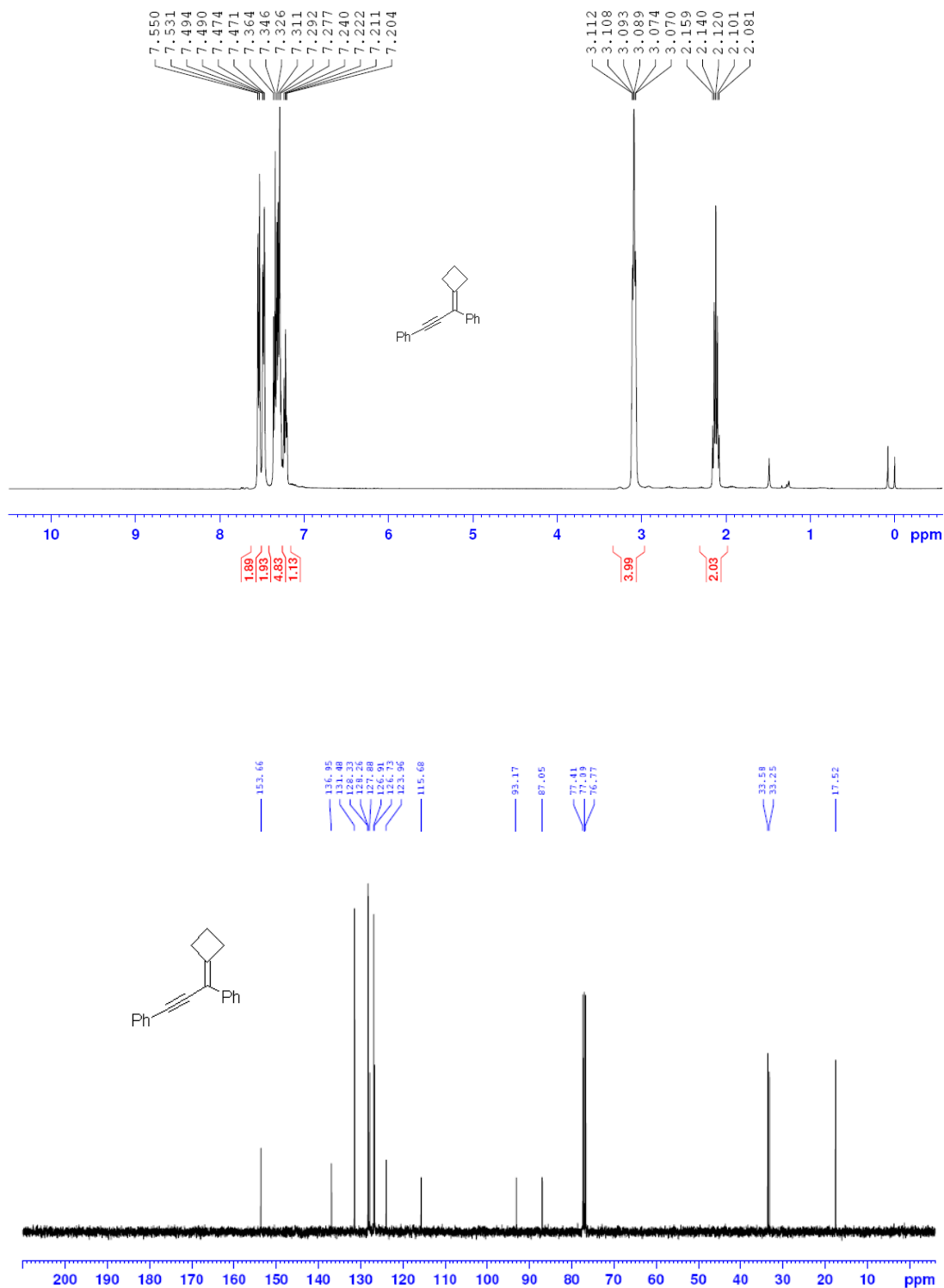


Figure S40. ^1H and ^{13}C NMR Spectra of 1-(3-Cyclobutylidene-3-phenylprop-1-ynyl)-4-methyl benzene (**7b**)

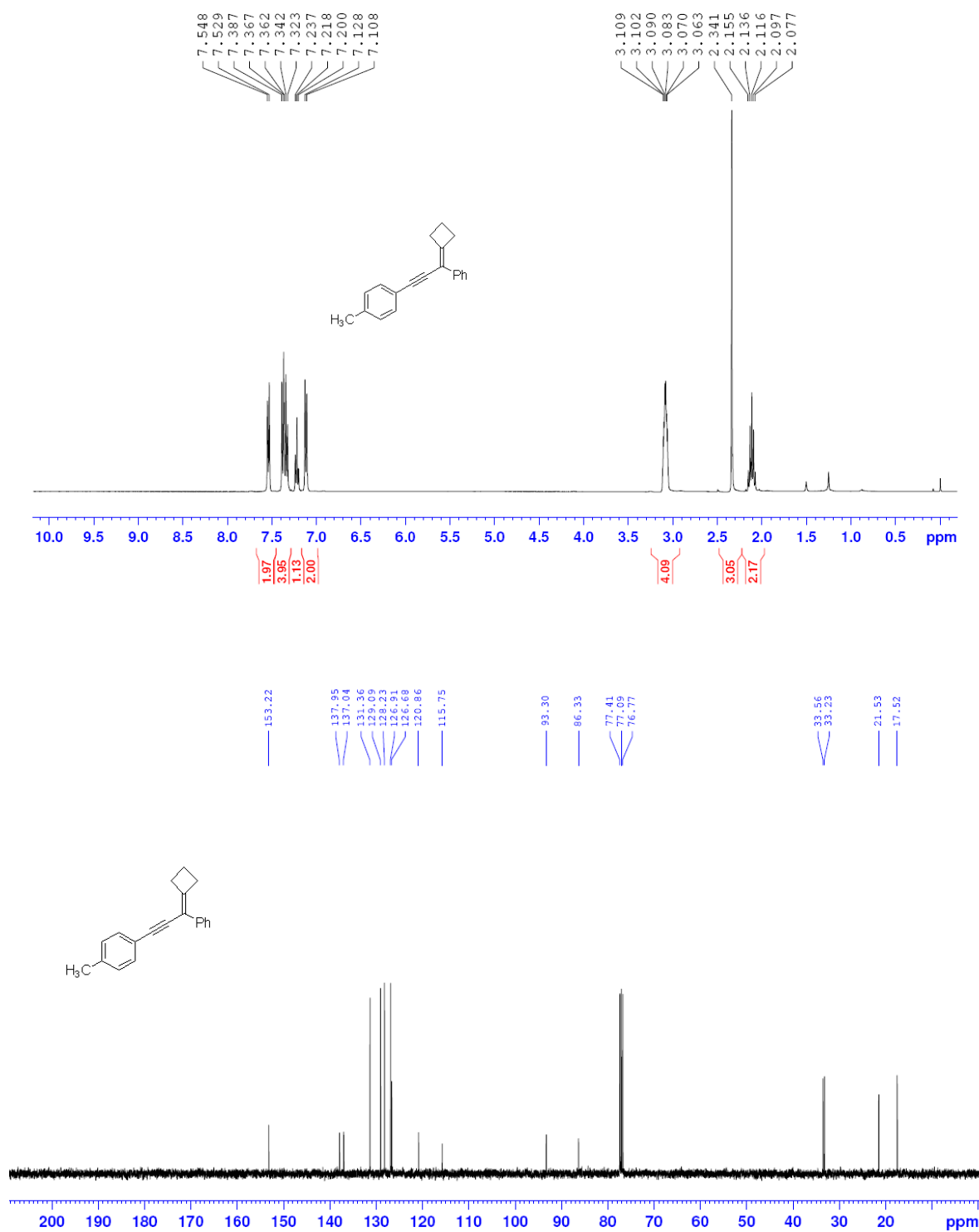


Figure S41. ^1H and ^{13}C NMR Spectra of 1-Chloro-4-(3-cyclobutylidene-3-phenylprop-1-ynyl)benzene (**7d**)

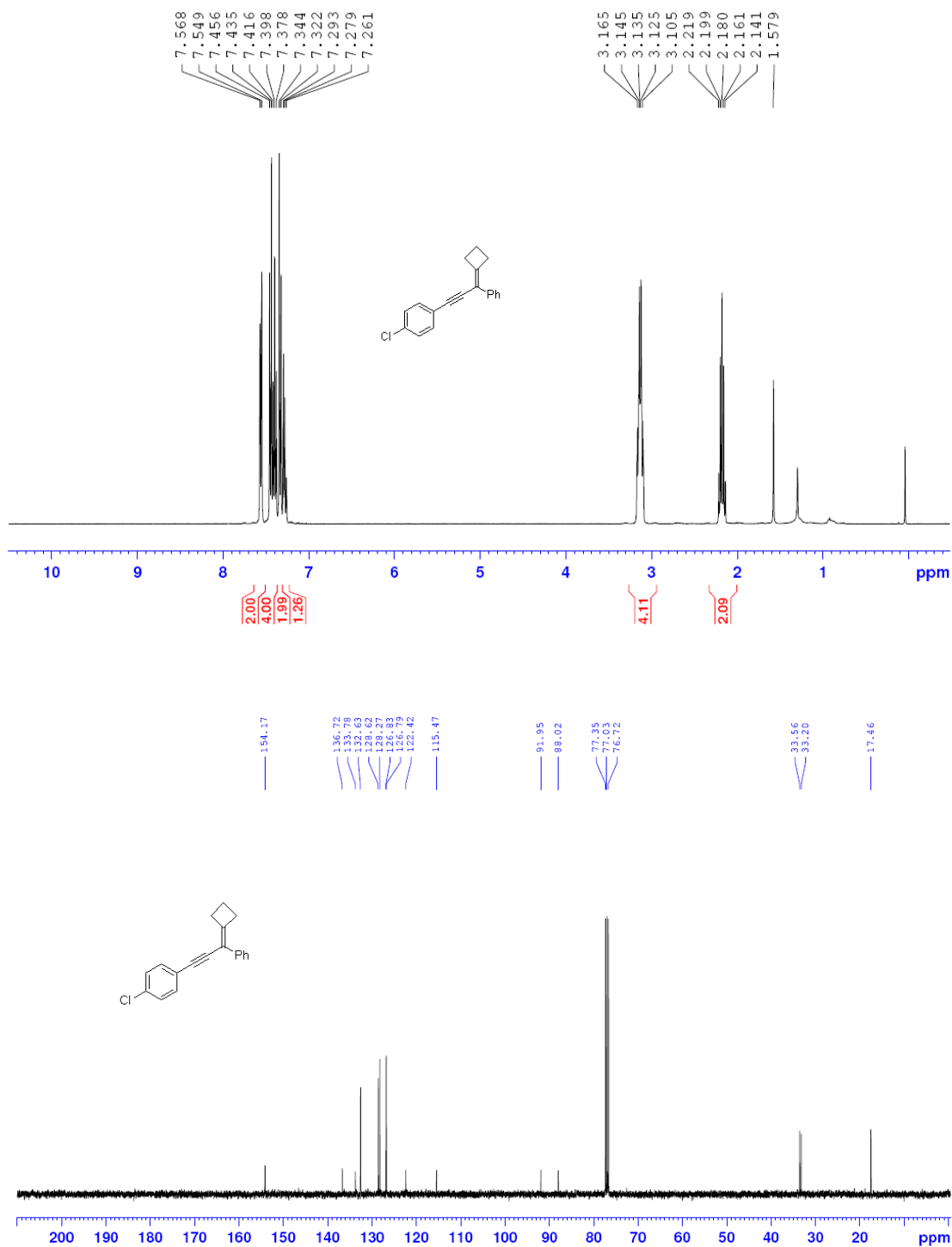


Figure S42. ^1H and ^{13}C NMR Spectra of 2-(3-Cyclobutylidene-3-phenylprop-1-ynyl) thiophene
(7e)

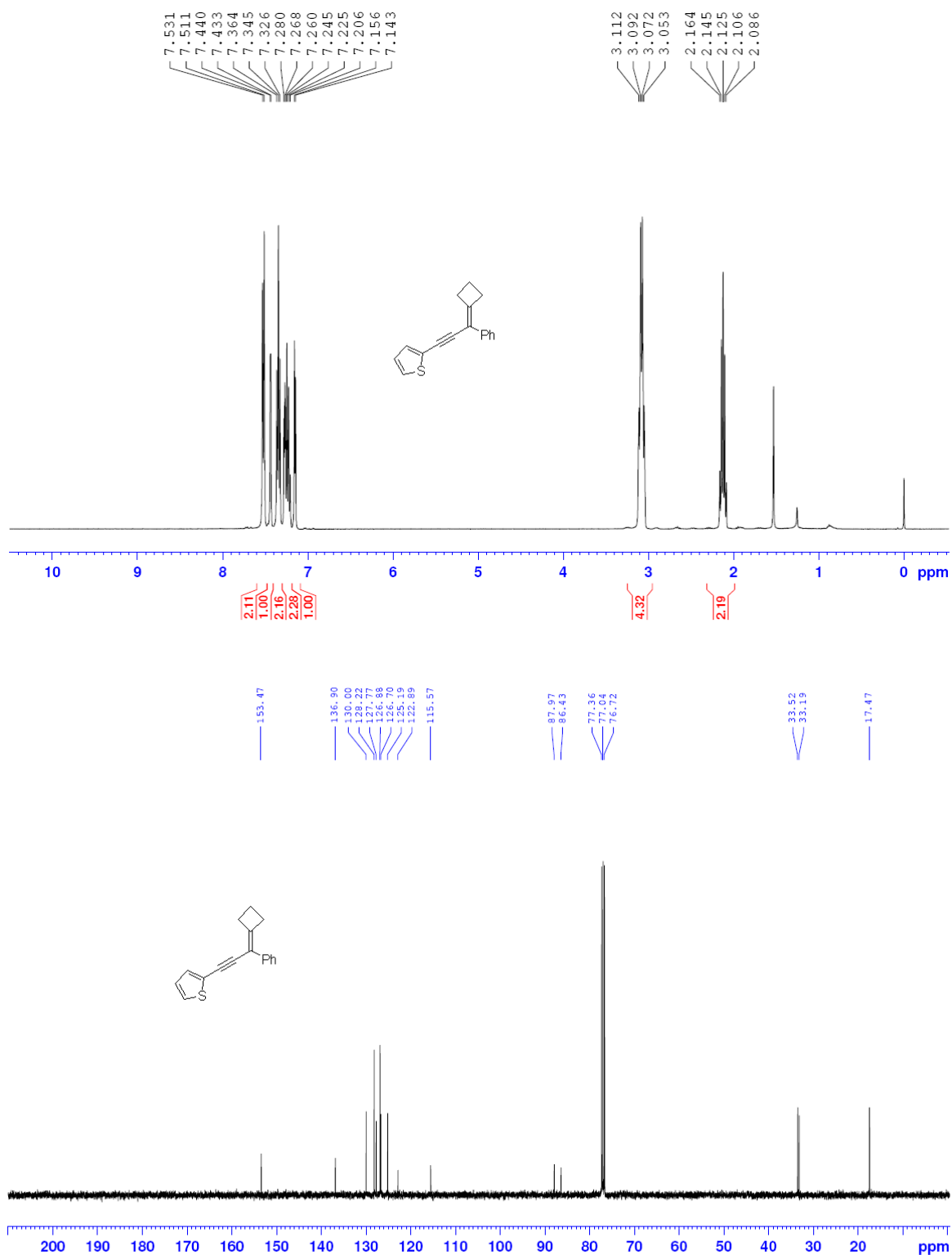


Figure S43. ^1H and ^{13}C NMR Spectra of (Z)-Pent-3-en-1-yne-1,3-diylidibenzene (**7f**)^{S7}

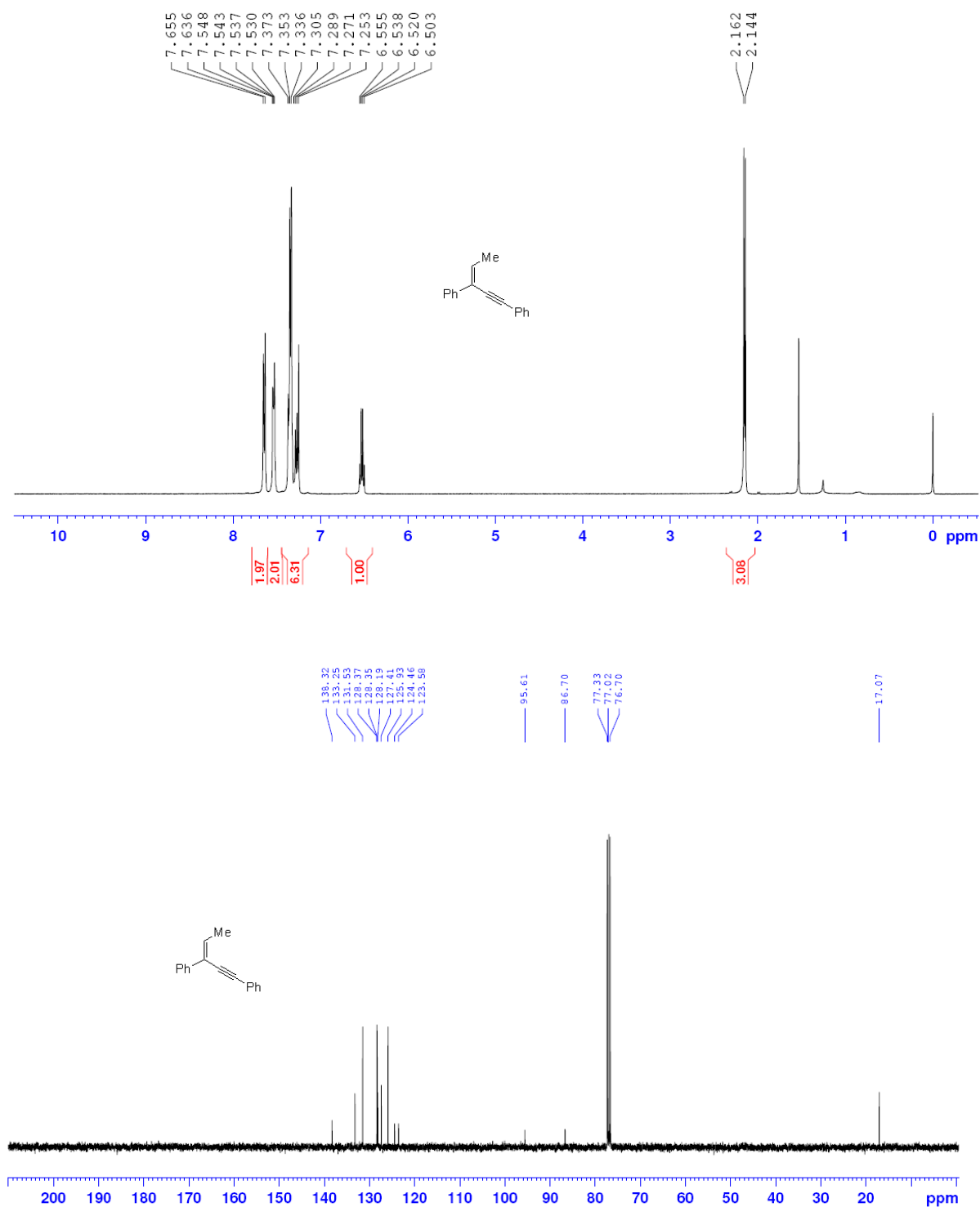


Figure S44. ^1H and ^{13}C NMR Spectra of (Z)-hept-3-en-1-yne-1,3-diylidibenzene (**7g**)

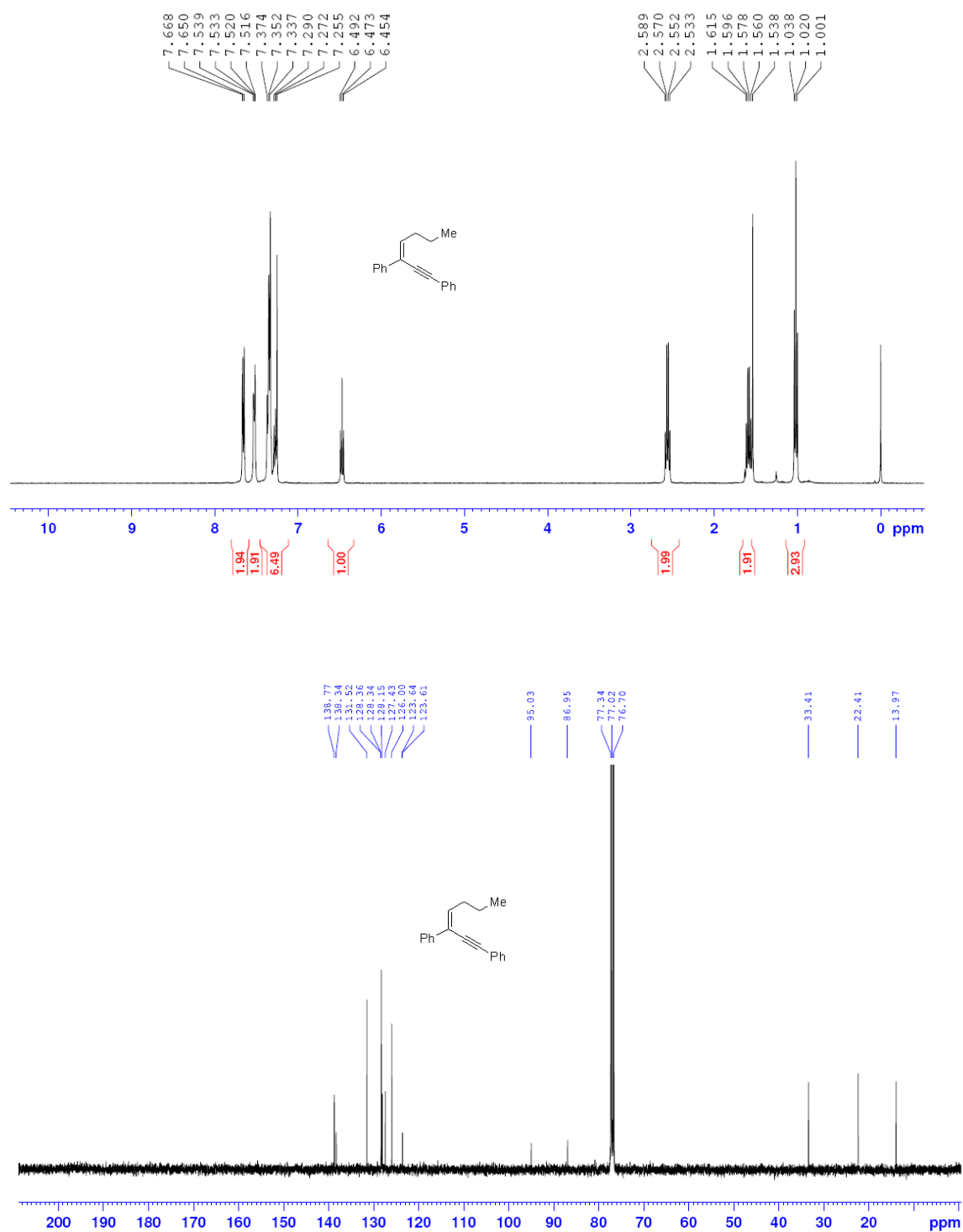


Figure S45. ^1H and ^{13}C NMR Spectra of 1,3,3-Triphenylprop-2-en-1-one (**8**)^{S8}

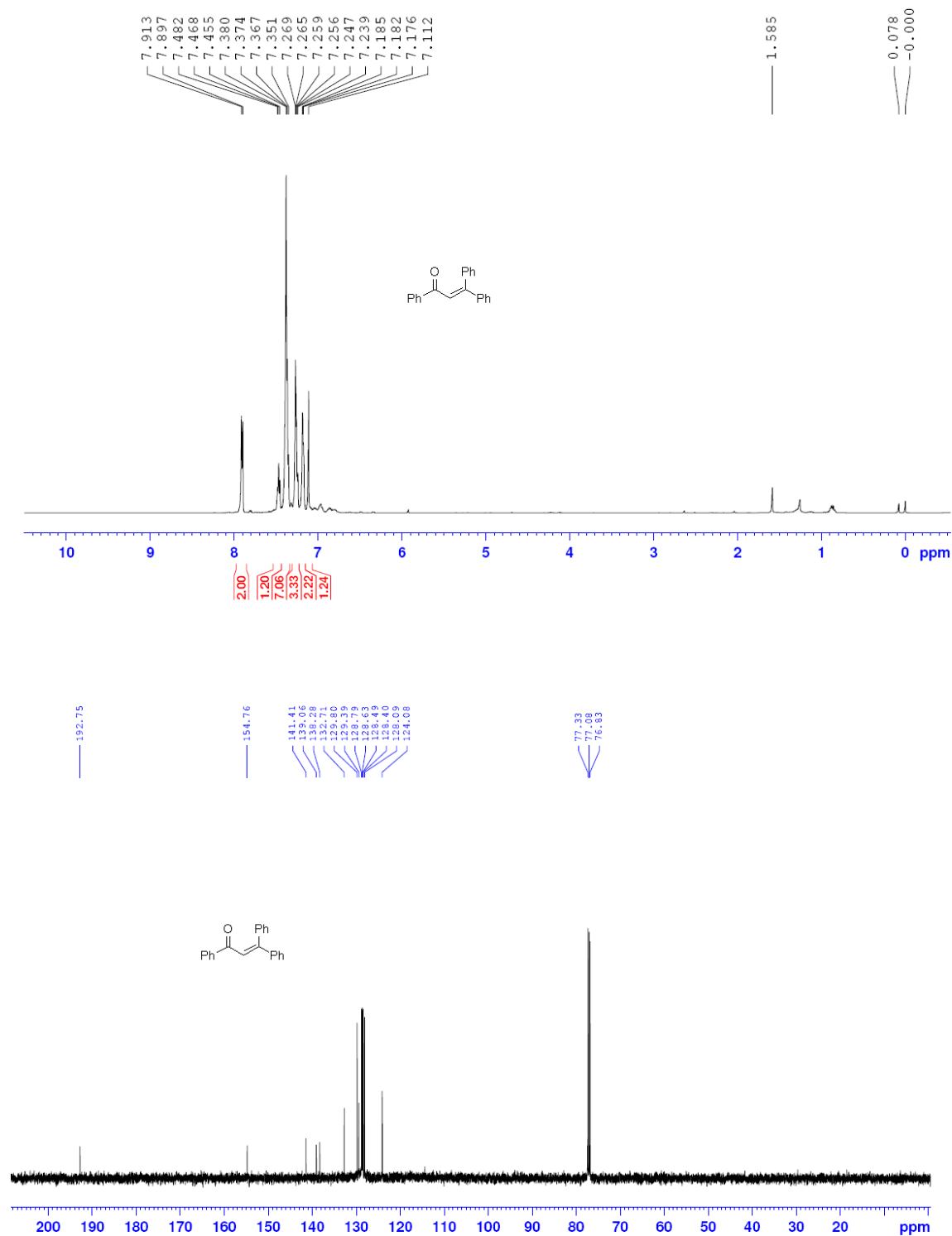


Figure S46. HPLC Spectrum of *rac*-1,3-Diphenylpent-1-yn-3-ol (**1f**)

OD-Column, HEX:IPA=96:4, 0.5 ml/min

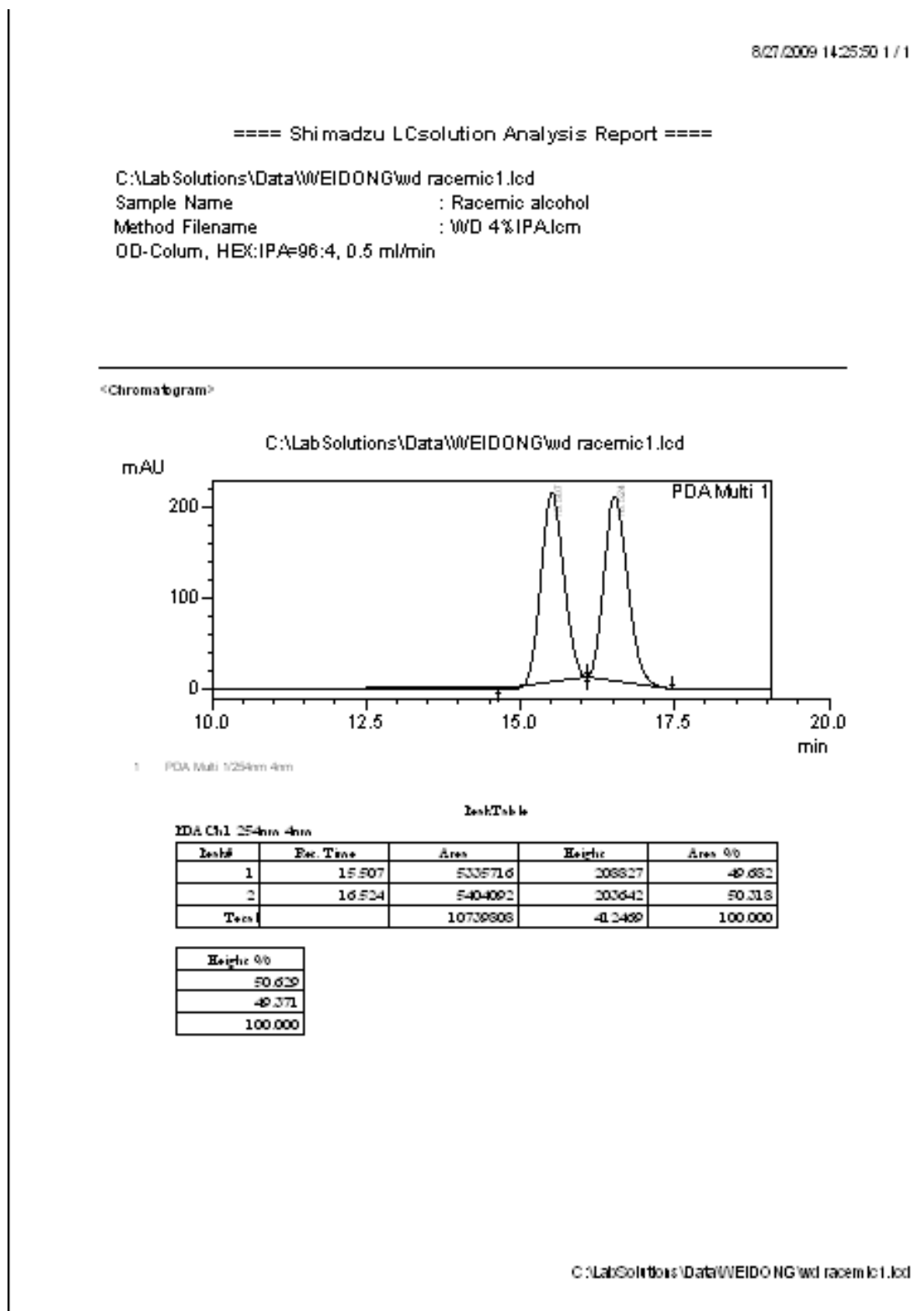


Figure S47. HPLC Spectrum of Enantioenriched 1,3-Diphenylpent-1-yn-3-ol (**1f**)

OD-Column, HEX:IPA=96:4, 0.5 ml/min

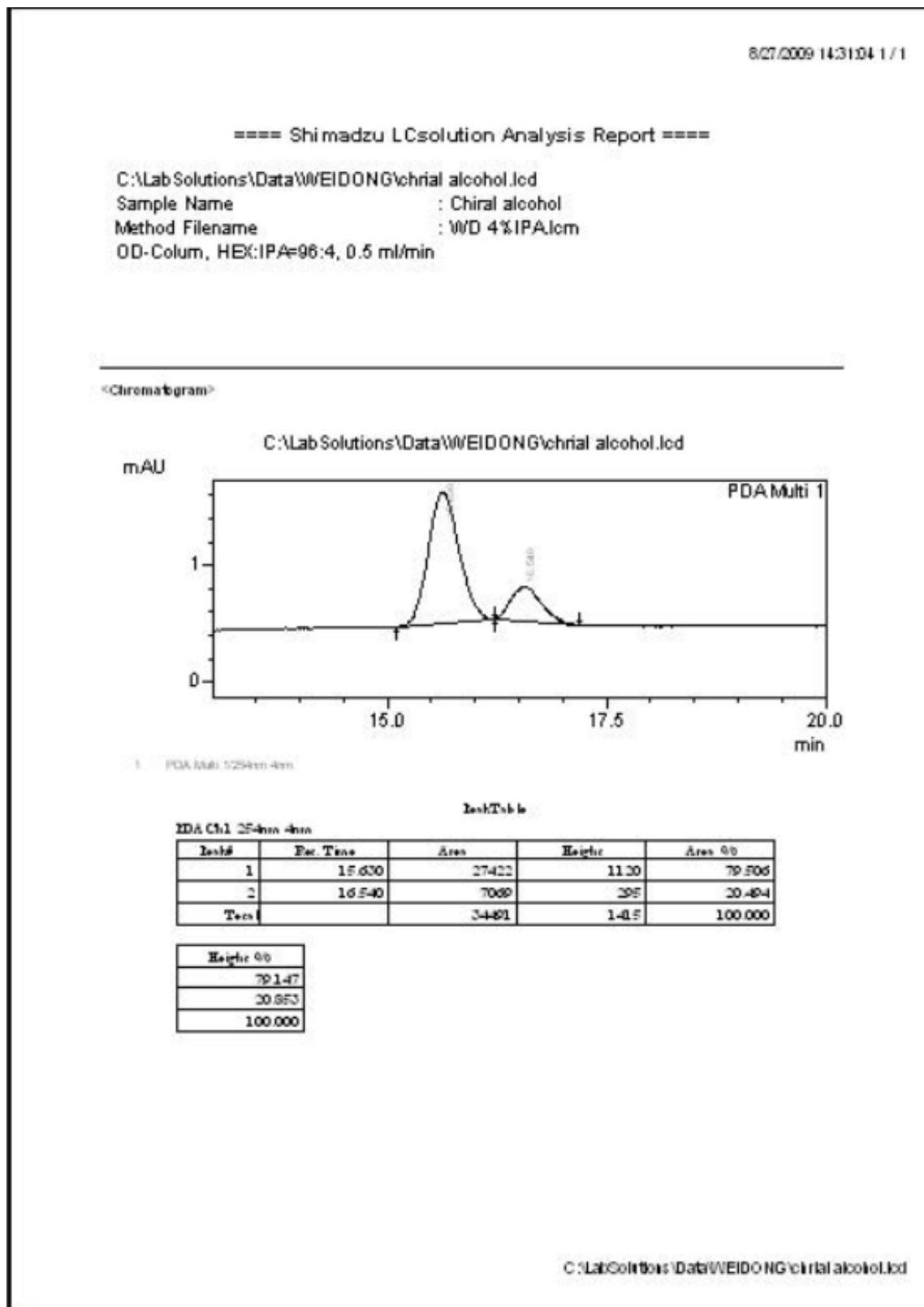


Figure S48. HPLC Spectrum of HPLC Spectrum of *rac*-(*E*)-1-Ethyl-1-phenyl-3-(phenylethynyl)-2-(1-phenylprop-1-enyl)-1*H*-indene (**2f**) Obtained from *rac*-1,3-Diphenylpent-1-yn-3-ol (**1f**)
OD-Column, HEX:IPA=99.7:0.3, 0.5 ml/min

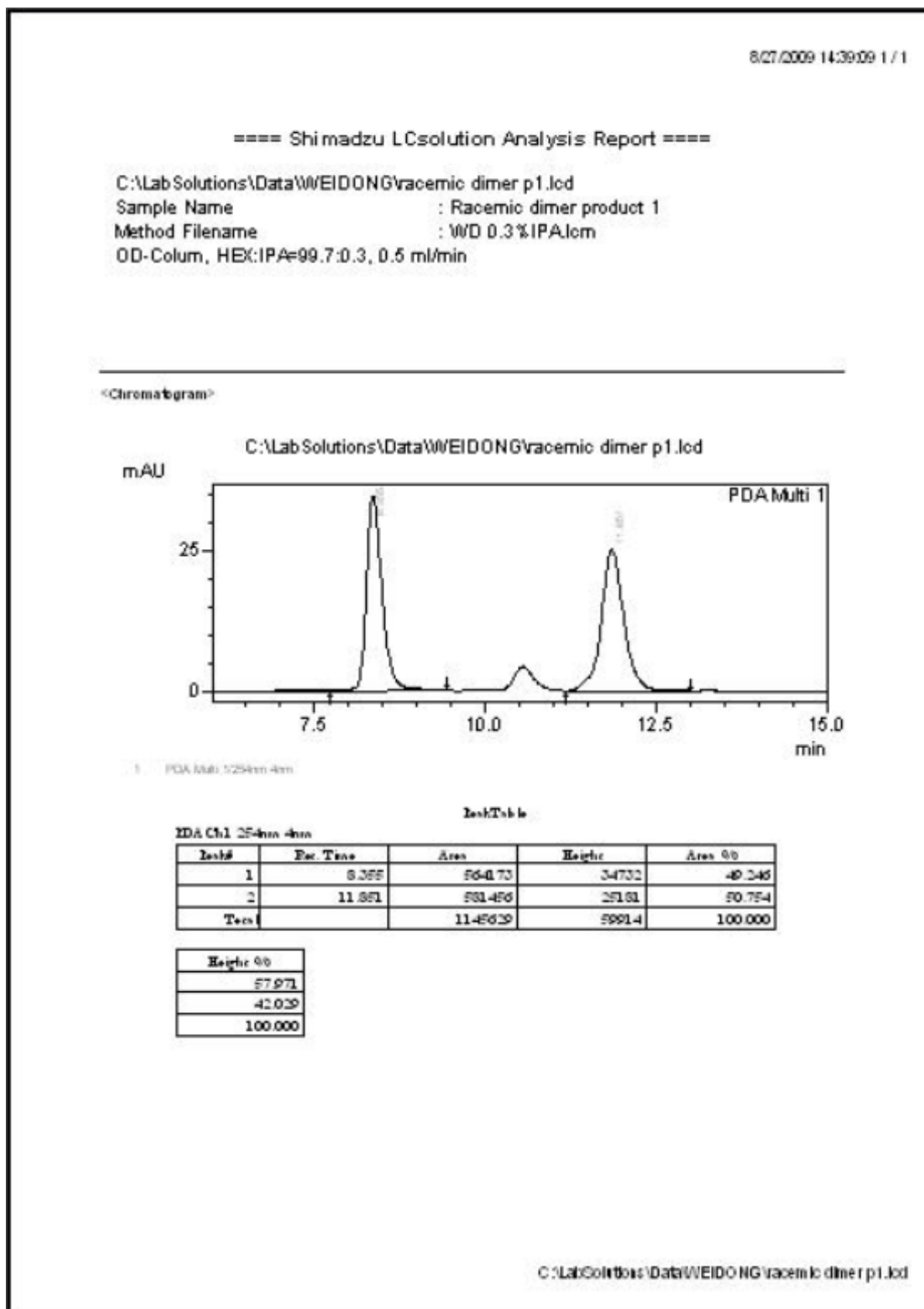


Figure S49. HPLC Spectrum of HPLC Spectrum of *rac*-(*E*)-3-Ethyl-1-phenyl-1-(phenylethynyl)-2-(1-phenylprop-1-enyl)-1*H*-indene (**3f**) Obtained from *rac*-1,3-Diphenylpent-1-yn-3-ol (**1f**)
OD-Column, HEX:IPA=99.7:0.3, 0.5 ml/min

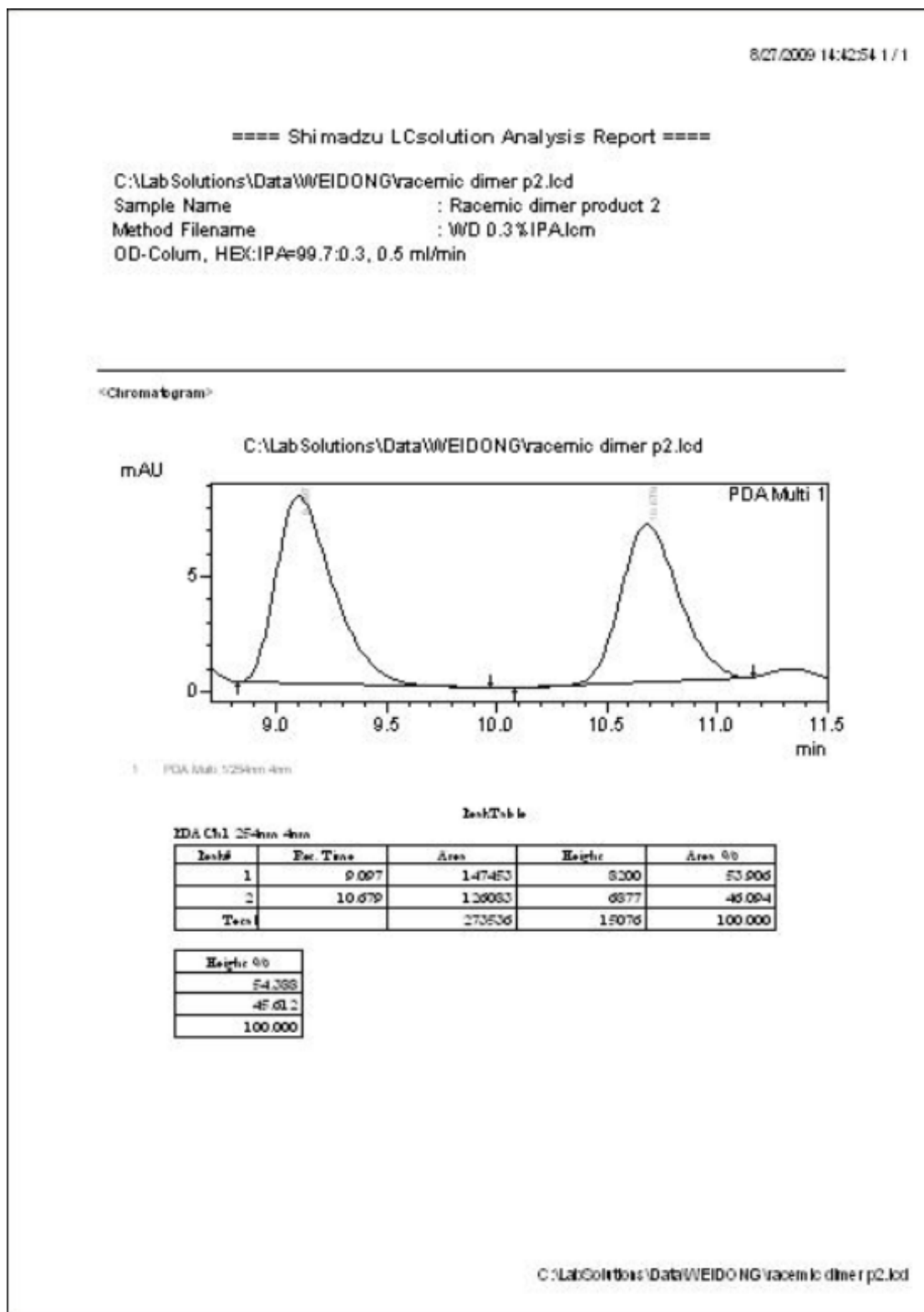


Figure S50. HPLC Spectrum of HPLC Spectrum of *rac*-(*E*)-1-Ethyl-1-phenyl-3-(phenylethynyl)-2-(1-phenylprop-1-enyl)-1*H*-indene (**2f**) Obtained from Enantioenriched 1,3-Diphenylpent-1-yn-3-ol (**1f**)

OD-Column, HEX:IPA=99.7:0.3, 0.5 ml/min

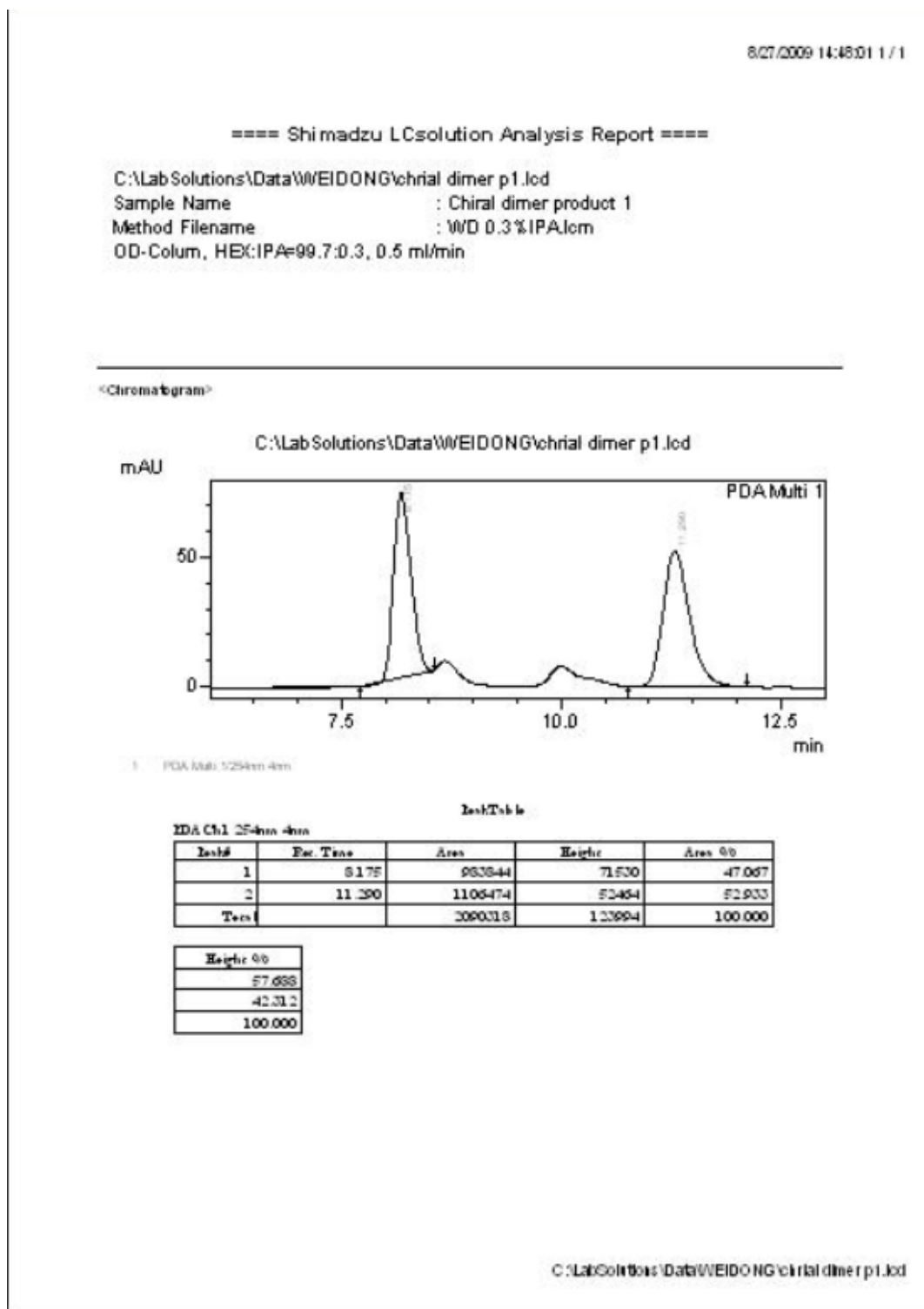
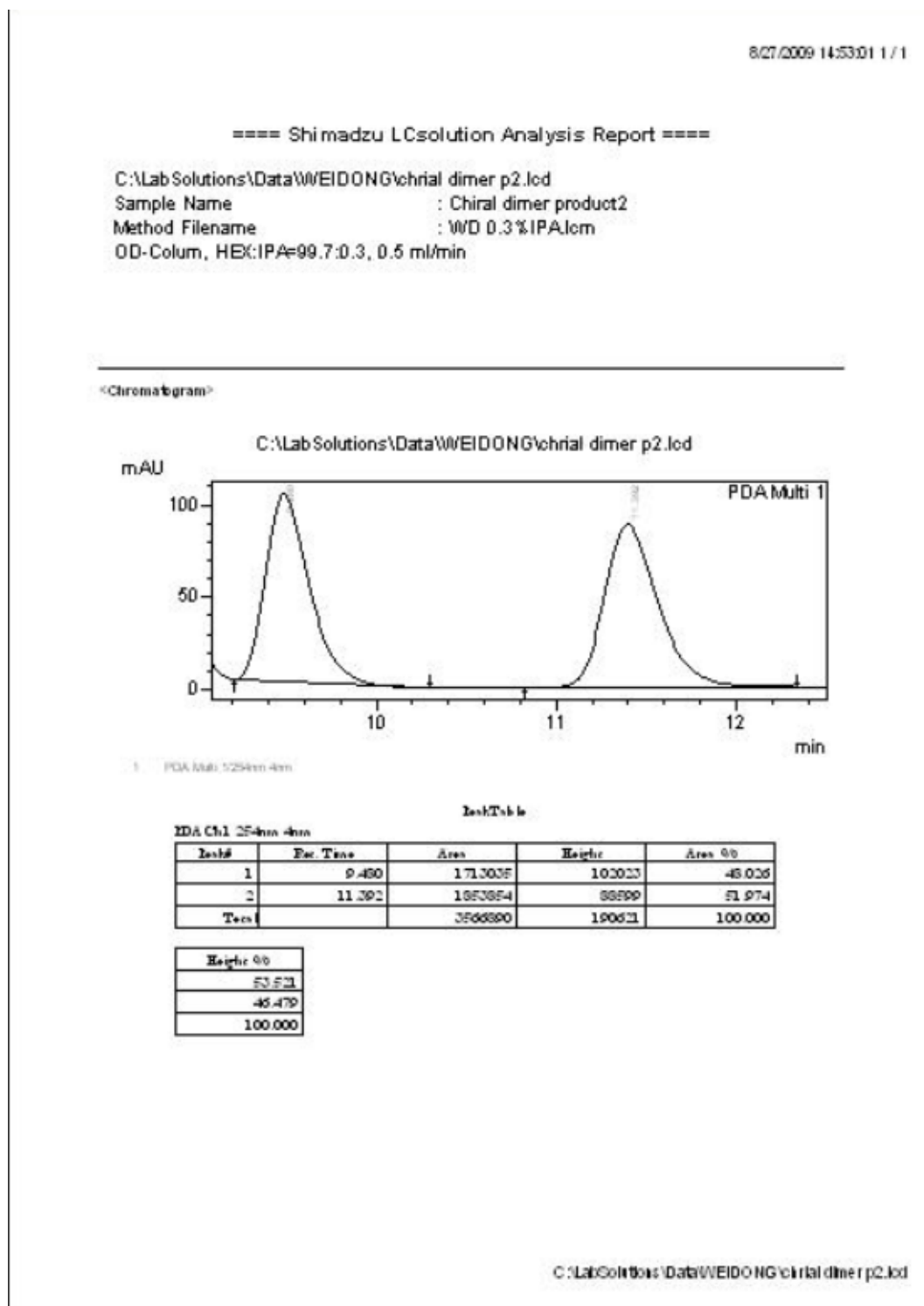


Figure S51. HPLC Spectrum of HPLC Spectrum of *rac*-(*E*)-3-Ethyl-1-phenyl-1-(phenylethynyl)-2-(1-phenylprop-1-enyl)-1*H*-indene (**3f**) Obtained from Enantioenriched 1,3-Diphenylpent-1-yn-3-ol (**1f**)

OD-Column, HEX:IPA=99.7:0.3, 0.5 ml/min



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