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α-Perfluoroalkyl-β-alkynylation of Alkenes *via* Radical Alkynyl Migration

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Supporting information

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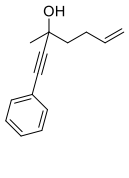
1. Instrumentation and chemicals

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in heat-gun-dried glassware under an argon atmosphere. For reactions with visible light a *Philips Master HPI-T Plus* (400 W) bulb was used. THF was freshly distilled from potassium under argon. All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich, Acros Organics, Alfa Aesar. Propargylic alcohols **1** were synthesized according to literature procedures.[1] ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 300, a Bruker AV 300, a Bruker AV 400 at 300 K. The solvents residual proton resonance and the respective carbon resonance ($CHCl_3$, δ = 7.26 ppm for ^{1}H NMR, δ = 77.0 ppm for ^{13}C NMR) was used for calibration. Merck silica gel 60 F 254 plates were used for TLC, detection with UV light and dipping into a solution of $KMnO_4$ (1.5 g in 400 mL H_2O, 5 g of $NaHCO_3$), followed by heating. Flash column chromatography (FC) was performed using Merck or Fluka silica gel 60 (40-63 μm) with a pressure of 0.3 bar. IR spectra were recorded on a Digilab Varian 3100 FT-IR Excalibur Series. Melting points (M.P.) were determined on a *SMP 10 apparatus* (*Stuart Scientific*). Mass spectra were recorded on a Bruker MicroTof or an Orbitrap LTQ XL (Nanospray) of Thermo Scientific.

2. Preparation of propargylic alcohols 1



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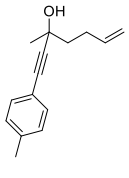

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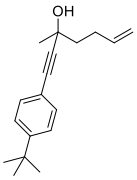

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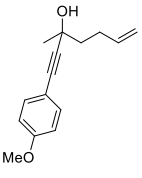

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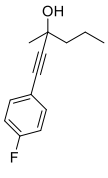

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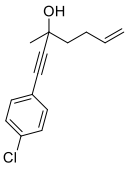

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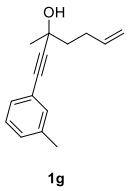

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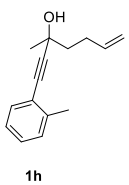

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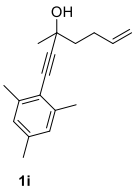

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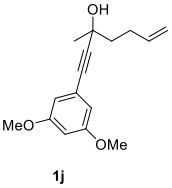

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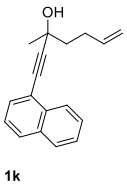

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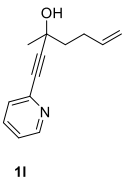

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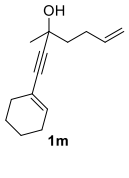

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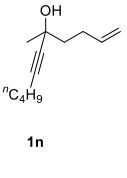

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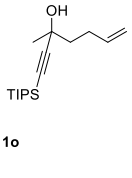

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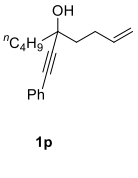

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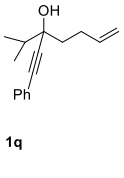

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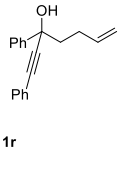

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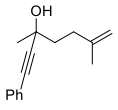

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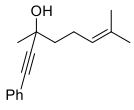

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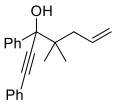

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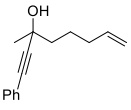
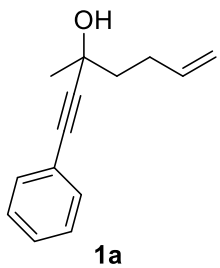


1v

General procedure (GP1): Propargylic alcohols **1** were synthesized according to literature procedures.[1] To a flame-dried flask equipped with a magnetic stir bar were added alkyne (5 mmol) and THF (35 mL). The mixture was then cooled to -78 °C. *n*BuLi (1.2 equiv) was added to it dropwise and the mixture maintained at this temperature for 15 min. Then the ketone (1 equiv) in 5 mL of THF was added dropwise at -78 °C. The reaction was allowed to warm to rt and stirring was continued overnight and then the reaction quenched with 50 mL of H_2O. The aqueous phase was extracted with 50 mL of ethyl acetate three times. The organic phase was combined and washed with 50 mL of brine, dried over Na_2SO_4, and concentrated. The residual was then purified by flash column chromatography (SiO_2) to obtain product **1**.

3-Methyl-1-phenylhept-6-en-1-yn-3-ol (1a)

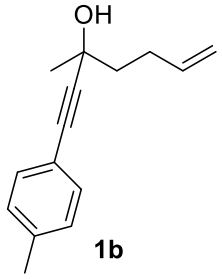


1a

1a[1] was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 2H), 7.37 – 7.31 (m, 3H), 6.04 – 5.84 (m, 1H), 5.24 – 4.97 (m, 2H), 2.52 – 2.31 (m, 2H), 2.15 (s, 1H), 1.94 – 1.83 (m, 2H), 1.62 (s, 3H). **^{13}C NMR**

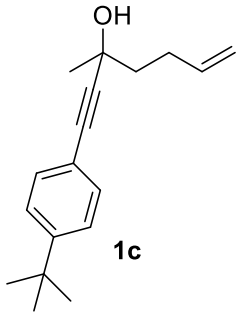
(100 MHz, $CDCl_3$) δ 138.37, 131.62, 128.29, 128.24, 114.92, 92.44, 83.69, 68.56, 42.67, 30.04, 29.36. **FTIR (neat)**: $\tilde{\nu}$ = 3376, 2978, 2933, 1641, 1598, 1490, 1443, 1370, 1109 cm^{-1}.

3-Methyl-1-(p-tolyl)hept-6-en-1-yn-3-ol (1b)



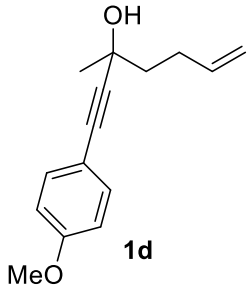
1b was synthesized according to GP1: **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.35 – 7.29 (m, 2H), 7.15 – 7.07 (m, 2H), 5.99 – 5.83 (m, 1H), 5.16 – 4.96 (m, 2H), 2.47 – 2.32 (m, 5H), 2.09 (brs, 1H), 1.92 – 1.79 (m, 2H), 1.59 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.42, 138.36, 131.50, 128.98, 114.84, 91.75, 68.55, 42.71, 30.06, 29.36, 21.43. **FTIR (neat)**: $\tilde{\nu}$ = 3363, 2978, 2928, 1641, 1510, 1449, 1370, 1106 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{17}H_{14}OSNa$ ($[M+Na]^+$): 237.1250, mass found: 237.1260.

1-(4-(Tert-butyl)phenyl)-3-methylhept-6-en-1-yn-3-ol (1c)



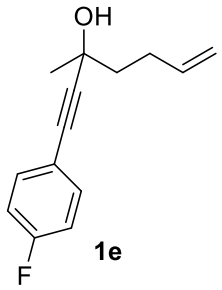
1c was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.29 – 7.12 (m, 4H), 5.88 – 5.62 (m, 1H), 5.10 – 4.77 (m, 2H), 2.35 – 2.11 (m, 3H), 1.85 – 1.61 (m, 2H), 1.46 (s, 3H), 1.17 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 151.44, 138.40, 131.32, 125.17, 119.66, 114.75, 91.90, 83.72, 68.47, 42.76, 34.66, 31.10, 30.02, 29.32. **FTIR (neat)**: $\tilde{\nu}$ = 3358, 2964, 1641, 1507, 1462, 1364, 1267, 1105 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for C14H15ClONa ($[M+Na]^+$): 279.1719, mass found: 279.1722.

3-Methyl-1-(p-tolyl)hept-6-en-1-yn-3-ol (1d)



1d was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.46 – 7.34 (m, 2H), 6.92 – 6.79 (m, 2H), 6.06 – 5.82 (m, 1H), 5.23 – 4.98 (m, 2H), 3.83 (s, 3H), 2.52 – 2.31 (m, 2H), 2.19 (s, 1H), 1.96 – 1.78 (m, 2H), 1.61 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.52, 138.43, 133.05, 114.83, 114.72, 113.84, 91.03, 83.54, 68.55, 55.25, 42.71, 30.09, 29.36. **FTIR (neat)**: $\tilde{\nu}$ = 3370, 2933, 1641, 1606, 1509, 1445, 1288, 1245, 1169, 1106, 1030 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{17}H_{14}OSNa$ ($[M+Na]^+$): 253.1199, mass found: 253.1201.

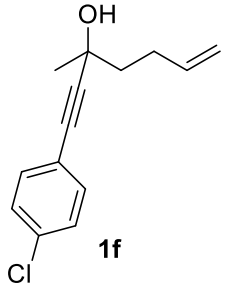
1-(4-Fluorophenyl)-3-methylhept-6-en-1-yn-3-ol (1e)



1e

1e was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 – 7.37 (m, 2H), 7.13 – 6.94 (m, 2H), 6.06 – 5.77 (m, 1H), 5.24 – 4.97 (m, 2H), 2.50 – 2.30 (m, 2H), 2.21 (s, 1H), 1.95 – 1.83 (m, 2H), 1.61 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 164.14, 138.30, 133.56, 133.45, 115.65, 115.36, 114.90, 82.64, 68.51, 42.69, 29.99, 29.30. **FTIR (neat)**: $\tilde{\nu}$ = 3376, 3080, 2989, 2934, 1641, 1601, 1506, 1450, 1222, 1155, 1093 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{14}H_{15}OFNa$ ($[M+Na]^+$): 241.0999, mass found: 241.1009.

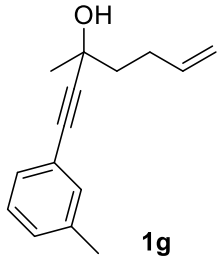
1-(4-Chlorophenyl)-3-methylhept-6-en-1-yn-3-ol (1f)



1f

1f was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.33 – 7.28 (m, 2H), 6.00 – 5.86 (m, 1H), 5.19 – 4.99 (m, 2H), 2.48 – 2.30 (m, 2H), 2.15 (s, 1H), 1.95 – 1.82 (m, 2H), 1.61 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.24, 134.32, 132.85, 128.59, 121.14, 115.00, 93.42, 82.60, 68.55, 42.58, 29.96, 29.31. **FTIR (neat)**: $\tilde{\nu}$ = 3353, 2977, 2930, 1641, 1488, 1452, 1370, 1265, 1089, 1015 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{14}H_{15}{}^{35}ClONa$ ($[M+Na]^+$): 257.0704, mass found: 257.0744.

3-Methyl-1-(m-tolyl)hept-6-en-1-yn-3-ol (1g)

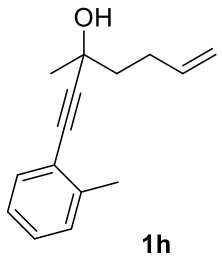


1g

1g was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.31 – 7.13 (m, 4H), 6.05 – 5.85 (m, 1H), 5.23 – 4.99 (m, 2H), 2.47 – 2.31 (m, 5H), 2.21 (s, 1H), 1.98 – 1.81 (m, 2H), 1.63 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.40, 137.91, 132.21, 129.14, 128.68, 128.13, 122.48, 114.84, 92.15, 83.85, 68.53, 42.74, 30.05, 29.34, 21.14. **FTIR (neat)**: $\tilde{\nu}$ = 3374, 2970, 2927, 2856, 1641, 1601, 1582, 1481, 1449, 1369, 1111 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{15}H_{18}ONa$ ($[M+Na]^+$): 237.1250, mass found: 237.1254.

3-Methyl-1-(*o*-tolyl)hept-6-en-1-yn-3-ol (1h)

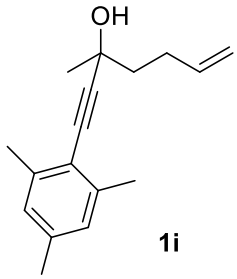
1h was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 (d, J = 7.2 Hz, 1H), 7.30 – 7.12 (m, 3H), 6.05 – 5.86 (m, 1H), 5.22 – 4.99 (m, 2H), 2.54 – 2.36 (m, 5H), 2.29 (s, 1H), 2.00 – 1.83



1h

(m, 2H), 1.66 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 140.04, 138.37, 131.90, 129.36, 128.28, 125.47, 122.42, 114.84, 96.59, 82.52, 68.69, 42.80, 30.17, 29.41, 20.65. **FTIR (neat)**: $\tilde{\nu}$ = 3349, 2977, 2926, 1641, 1485, 1452, 1370, 1117 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{15}H_{18}ONa$ ($[M+Na]^+$): 237.1250, mass found: 237.1258.

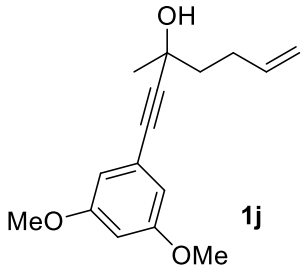
1-Mesityl-3-methylhept-6-en-1-yn-3-ol (1i)



1i

1i was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.89 (s, 2H), 6.05 – 5.87 (m, 1H), 5.20 – 4.98 (m, 2H), 2.51 – 2.37 (m, 8H), 2.31 (s, 3H), 2.21 (s, 1H), 2.00 – 1.84 (m, 2H), 1.67 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 140.06, 138.47, 137.71, 127.54, 119.36, 114.80, 100.38, 81.37, 68.92, 42.92, 30.41, 29.53, 21.24, 20.93. **FTIR (neat)**: $\tilde{\nu}$ = 3388, 2976, 2917, 2856, 1641, 1611, 1480, 1450, 1375, 1106, 1034 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{17}H_{22}ONa$ ($[M+Na]^+$): 265.1563, mass found: 265.1572.

1-(3,5-Dimethoxyphenyl)-3-methylhept-6-en-1-yn-3-ol (1j)

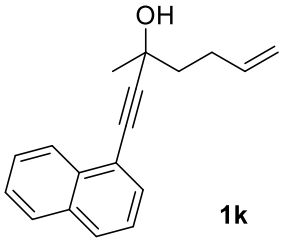


1j

1j was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.57 (d, *J* = 2.3 Hz, 2H), 6.43 (t, *J* = 2.3 Hz, 1H), 6.01 – 5.81 (m, 1H), 5.18 – 4.94 (m, 2H), 3.77 (s, 6H), 2.47 – 2.30 (m, 2H), 2.24 (brs, 1H), 1.90 – 1.79 (m, 2H), 1.59 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.42, 138.32, 123.92, 114.92, 109.39, 101.69, 92.01, 83.63, 68.51, 55.39, 42.61, 29.98, 29.31. **FTIR (neat)**: $\tilde{\nu}$ = 3381, 2976, 2936, 2841, 1641, 1587, 1453, 1420, 1350, 1204, 1153, 1060 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{16}H_{20}O_3Na$ ($[M+Na]^+$): 283.1305, mass found: 283.1317.

3-Methyl-1-(naphthalen-1-yl)hept-6-en-1-yn-3-ol (1k)

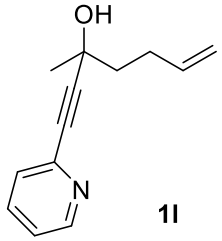
1k was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.34 – 8.26 (m, 1H), 7.90 – 7.79 (m, 2H), 7.67 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.63 – 7.49 (m, 2H), 7.42 (dd, *J* = 8.3, 7.1 Hz, 1H), 6.05 – 5.88 (m, 1H), 5.21 – 4.99 (m, 2H), 2.58 – 2.40 (m, 2H), 2.28 (brs, 1H), 2.03 – 1.93 (m, 2H), 1.72 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.34 , 133.19 , 133.09 , 130.46 , 128.78 , 128.27 , 126.77 , 126.36 ,



1k

125.94 , 125.12 , 120.22 , 115.01 , 97.46 , 81.73 , 68.86 , 42.78 , 30.22 , 29.50 . **FTIR (neat)**: $\tilde{\nu}$ = 3352, 3059, 2977, 2930, 2856, 1641, 1587, 1508, 1395, 1371, 1116 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{18}ONa$ ($[M+Na]^+$): 273.1250, mass found: 273.1256.

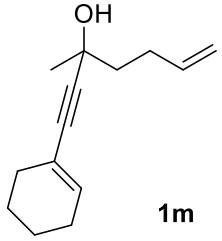
3-Methyl-1-(pyridin-2-yl)hept-6-en-1-yn-3-ol (1l)



1l

1l was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δδ 8.60 (d, *J* = 4.5 Hz, 2H), 7.67 (td, *J* = 7.7, 1.8 Hz, 1H), 7.44 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.25 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 6.03 – 5.81 (m, 1H), 5.21 – 4.92 (m, 2H), 2.76 (s, 1H), 2.53 – 2.28 (m, 1H), 1.98 – 1.85 (m, 2H), 1.65 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 149.87 , 142.92 , 138.24 , 136.15 , 127.09 , 122.88 , 114.88 , 92.78 , 82.95 , 68.29 , 42.43 , 29.79 , 29.17 . **FTIR (neat)**: $\tilde{\nu}$ = 3309, 2976, 2934, 1641, 1583, 1564, 1464, 1428, 1369, 1272, 1150 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{13}H_{15}NONa$ ($[M+Na]^+$): 224.1046, mass found: 224.1056.

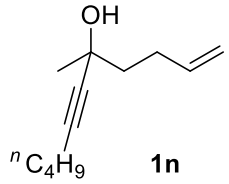
1-Cyclohexyl-3-methylhept-6-en-1-yn-3-ol (1m)



1m

1m was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.15 – 6.08 (m, 1H), 6.00 – 5.82 (m, 1H), 5.17 – 4.94 (m, 2H), 2.44 – 2.22 (m, 2H), 2.19 – 2.04 (m, 5H), 1.87 – 1.74 (m, 2H), 1.71 – 1.56 (m, 4H), 1.53 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.49 , 134.90 , 120.13 , 114.68 , 89.82 , 85.46 , 68.42 , 42.79 , 30.13 , 29.33 , 29.25 , 25.57 , 22.26 , 21.46 . **FTIR (neat)**: $\tilde{\nu}$ = 3397, 2929, 1641, 1437, 1369, 1136, 1110 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{14}H_{20}ONa$ ($[M+Na]^+$): 227.1406, mass found: 227.1414.

5-Methylundec-1-en-6-yn-5-ol (1n)

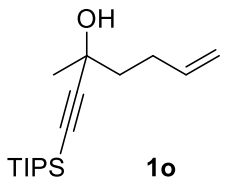


1n

1n was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.02 – 5.76 (m, 1H), 5.19 – 4.91 (m, 2H), 2.42 – 2.16 (m, 4H), 2.06 (s, 1H), 1.85 – 1.65 (m, 2H), 1.60 – 1.35 (m, 7H), 0.93 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.57 , 114.56 , 84.09 , 83.70 , 68.16 , 42.90 , 30.77 , 30.26 , 29.33 , 21.87 , 18.24 , 13.53 . **FTIR (neat)**: $\tilde{\nu}$ = 3350, 2959, 2932, 1642, 1455, 1369, 1125 cm^{-1}. **HRMS (ESI)**:

Exact mass calculated for $C_{12}H_{20}ONa$ ([M+Na]$^+$): 203.1406, mass found: 203.1413.

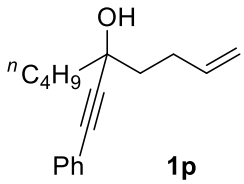
3-Methyl-1-(triisopropylsilyl)hept-6-en-1-yn-3-ol (1o)



1o

1o was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.99 – 5.76 (m, 1H), 5.17 – 4.91 (m, 2H), 2.45 – 2.21 (m, 2H), 2.02 (s, 1H), 1.85 – 1.66 (m, 2H), 1.50 (s, 3H), 1.12 – 1.01 (m, 21H). **^{13}C NMR** (75 MHz, $CDCl_3$) 13C NMR (75 MHz, $CDCl_3$) δ 138.50, 114.79, 111.41, 83.80, 68.51, 42.77, 30.17, 29.47, 18.58, 11.15. **FTIR (neat)**: $\tilde{\nu}$ = 3381, 2943, 2865, 1642, 1463, 1367, 1119, 1073 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{17}H_{32}OSiNa$ ([M+Na]$^+$): 303.2115, mass found: 303.2124.

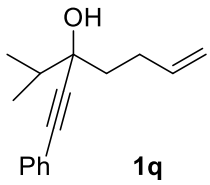
5-(Phenylethynyl)non-1-en-5-ol (1p)



1p

1p was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 2H), 7.40 – 7.30 (m, 3H), 6.06 – 5.84 (m, 1H), 5.21 – 4.99 (m, 2H), 2.52 – 2.33 (m, 2H), 2.14 (s, 1H), 1.93 – 1.73 (m, 4H), 1.68 – 1.52 (m, 2H), 1.51 – 1.35 (m, 2H), 0.99 (t, J = 7.3 Hz, 3H).. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.57 , 131.65 , 128.24 , 122.82 , 114.79 , 91.82 , 84.72 , 71.60 , 42.10 , 41.14 , 28.97 , 26.51 , 22.88 , 14.05 . **FTIR (neat)**: $\tilde{\nu}$ = 3374, 2956, 2934, 2862, 1641, 1599, 1490, 1443, 1379, 1340, 1256, 1135 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{17}H_{22}ONa$ ([M+Na]$^+$): 265.1563, mass found: 265.1566.

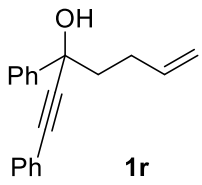
3-Isopropyl-1-phenylhept-6-en-1-yn-3-ol (1q)



1q

1q was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.35 – 7.28 (m, 3H), 6.01 – 5.85 (m, 1H), 5.20 – 4.96 (m, 2H), 2.52 – 2.35 (m, 2H), 2.11 (s, 1H), 2.01 – 1.70 (m, 3H), 1.12 (d, J = 5.1 Hz, 3H), 1.09 (d, J = 5.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.77 , 131.64 , 128.22 , 128.19 , 122.86 , 114.73 , 90.86 , 85.38 , 74.96 , 38.37 , 37.88 , 28.87 , 17.97 , 17.09 . **FTIR (neat)**: $\tilde{\nu}$ = 3424, 2864, 1641, 1598, 1490, 1444, 1369, 1140, 1029 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{16}H_{20}ONa$ ([M+Na]$^+$): 251.1406, mass found: 251.1410.

1,3-Diphenylhept-6-en-1-yn-3-ol (1r)

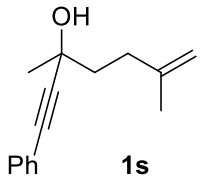


1r

1r was synthesized according to GP1: yellow solid, **MP**: 69 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.77 – 7.67 (m, 2H), 7.56 – 7.45 (m, 2H), 7.47 – 7.27 (m, 6H), 5.94 – 5.76 (m, 1H), 5.11 – 4.92 (m, 2H), 2.50 (s, 1H), 2.45 – 2.31 (m, 1H), 2.31 – 2.00 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.62 , 138.09 , 131.74 , 128.54 , 128.32 , 128.25 , 127.77 , 125.47 , 122.54 , 114.77 , 91.24 , 86.38 , 73.60 , 44.52 , 29.30 . **FTIR (neat)**: $\tilde{\nu}$ = 3273, 3070, 2945, 1641, 1489, 1449, 1388, 1306, 1014 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{18}ONa$ ($[M+Na]^+$): 285.1250, mass found: 285.1256.

Chiral **1r** was synthesized according to GP1 and literature[2]: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 2H), 7.55 – 7.46 (m, 2H), 7.44 – 7.29 (m, 6H), 5.96 – 5.76 (m, 1H), 5.12 – 4.93 (m, 2H), 2.54 (s, 1H), 2.45 – 2.32 (m, 1H), 2.31 – 2.01 (m, 3H). The pure product was analyzed by chiral HPLC. Chiral HPLC (Chiralcel OD-H column with guard, 25 °C, 1 mL/min, cyclohexane:isopropanol = 90:10); Elution time: t_{major} = 14.6 min and t_{minor} = 23.0 min, enantiomeric excess (25%).

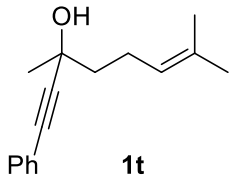
3,6-Dimethyl-1-phenylhept-6-en-1-yn-3-ol (1s)



1s

1s was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 2H), 7.35 – 7.27 (m, 3H), 4.83 – 4.73 (m, 2H), 2.45 – 2.22 (m, 3H), 2.02 – 1.84 (m, 2H), 1.79 (s, 3H), 1.61 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 145.72 , 131.61 , 128.21 , 122.71 , 110.17 , 92.53 , 83.65 , 68.63 , 41.61 , 33.13 , 29.97 , 22.58 . **FTIR (neat)**: $\tilde{\nu}$ = 3355, 2978, 2931, 1649, 1599, 1490, 1444, 1374, 1341, 1261, 1201, 1118, 1099 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{15}H_{18}ONa$ ($[M+Na]^+$): 237.1250, mass found: 237.1271.

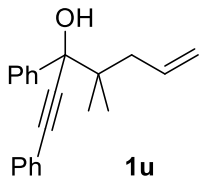
3,7-Dimethyl-1-phenyloct-6-en-1-yn-3-ol (1t)



1t

1t was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 2H), 7.35 – 7.27 (m, 3H), 5.27 – 5.16 (m, 1H), 2.46 – 2.14 (m, 3H), 1.84 – 1.76 (m, 2H), 1.73 – 1.70 (m, 3H), 1.68 (s, 3H), 1.59 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 132.44 , 131.62 , 128.21 , 128.17 , 123.87 , 122.84 , 92.78 , 83.53 , 68.82 , 43.49 , 29.92 , 25.69 , 23.83 , 17.71 . **FTIR (neat)**: $\tilde{\nu}$ = 3363, 2971, 2919, 2854, 1598, 1490, 1444, 1375, 1267, 1186, 1117 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{16}H_{20}ONa$ ($[M+Na]^+$): 251.1406, mass found: 251.1405.

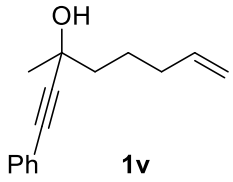
4,4-Dimethyl-1,3-diphenylhept-6-en-1-yn-3-ol (1u)



1u

1u was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.74 – 7.66 (m, 2H), 7.55 – 7.47 (m, 2H), 7.40 – 7.30 (m, 6H), 5.98 – 5.81 (m, 1H), 5.13 – 5.00 (m, 2H), 2.50 (s, 1H), 2.40 – 2.27 (m, 2H), 1.05 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.88 , 135.95 , 131.65 , 128.42 , 128.31 , 127.90 , 127.46 , 127.13 , 122.77 , 117.38 , 92.18 , 86.36 , 79.72 , 42.63 , 41.92 , 28.25 , 22.48 , 21.60 . **FTIR (neat)**: $\tilde{\nu}$ = 3472, 3065, 2971, 2938, 1727, 1683, 1599, 1491, 1444, 1385, 1364, 1312, 1255, 1171, 1162, 1046 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{21}H_{22}ONa$ ($[M+Na]^+$): 313.1563, mass found: 313.1568.

3-Methyl-1-phenyloct-7-en-1-yn-3-ol (1v)



1v

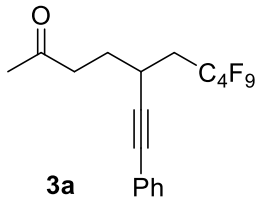
1v was synthesized according to GP1: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 2H), 7.39 – 7.30 (m, 3H), 5.97 – 5.77 (m, 1H), 5.15 – 4.96 (m, 2H), 2.24 – 2.11 (m, 2H), 2.06 (s, 1H), 1.87 – 1.67 (m, 4H), 1.61 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.51 , 131.64 , 128.23 , 122.77 , 114.76 , 92.83 , 83.40 , 68.55 , 43.19 , 33.70 , 29.94 , 24.07 . **FTIR (neat)**: $\tilde{\nu}$ = 3383, 3079, 2977, 2935, 2865, 2203, 1676, 1641, 1599, 1490, 1444, 1370, 1157 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{15}H_{18}ONa$ ($[M+Na]^+$): 237.1250, mass found: 237.1256.

3. Reaction of propargylic alcohols 1 with perfluoroalkyl iodides 2

General procedure 2 (GP2): To a flame-dried Schlenk tube equipped with a magnetic stir bar LiOH (0.42 equiv), LiHMDS (1.2 equiv), **1** (0.1 mmol), and 1.25 mL of DME were added sequentially under Ar atmosphere. The mixture was allowed to stir at room temperature for 0.5 h. After that DABCO (1.5 equiv), and **2** (1.8 equiv) were added to the reaction mixture under Ar atmosphere. Then the reaction mixture was stirred under visible-light irradiation (temperature up to 50 °C) for 18 h. After that, the solvent was removed and the residue was purified by flash column chromatography (SiO_2) to obtain product **3**.

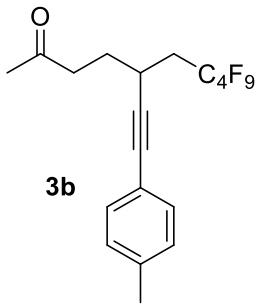
7,7,8,8,9,9,10,10,10-Nonafluoro-5-(phenylethynyl)decan-2-one (3a)

3a was synthesized according to GP2 with **1a** (20 mg, 0.100 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL,



0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 10/1) provided **3a** as a liquid (33 mg, 79%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 6.6, 3.2 Hz, 2H), 7.34 – 7.27 (m, 3H), 3.10 (ddd, *J* = 10.2, 5.0, 3.1 Hz, 1H), 2.83 – 2.65 (m, 2H), 2.58 – 2.22 (m, 2H), 2.19 (s, 3H), 2.11 – 1.96 (m, 1H), 1.89 – 1.74 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.44 , 131.59 , 128.28 , 128.18 , 89.26 , 40.89 , 36.21 (t, *J* = 20.9 Hz), 30.09 , 29.10 , 24.71 (t, *J* = 3.0 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.02 (tt, *J* = 9.7, 3.4 Hz, 3F), -113.32 – -113.51 (m, 2F), -124.38 – -124.58 (m, 2F), -125.73 – -125.95 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2947, 1718, 1599, 1491, 1443, 1356, 1217, 1131, 1110 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{15}OF_9Na$ ($[M+Na]^+$): 441.0871, mass found: 441.0887.

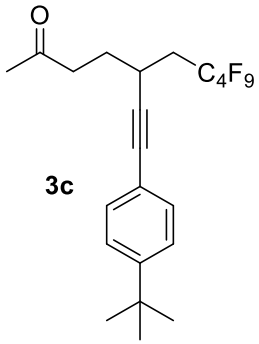
7,7,8,8,9,9,10,10,10-Nonafluoro-5-(p-tolylethynyl)decan-2-one (3b)



3b was synthesized according to GP2 with **1b** (21 mg, 0.098 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 10/1) provided **3b** as a liquid (32 mg, 76%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.08 (m, 2H), 3.08 (ddd, *J* = 10.2, 5.0, 3.0 Hz, 1H), 2.84 – 2.63 (m, 2H), 2.34 (brs, 5H), 2.19 (s, 3H), 2.11 – 1.95 (m, 1H), 1.88 – 1.71 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.52 , 138.27 , 131.45 , 129.02 , 88.50 , 40.90 , 36.50 (d, *J* = 21.2 Hz), 36.22 , 35.95 , 30.07 , 29.13 , 24.76 (d, *J* = 3.0 Hz), 24.71 , 24.67 , 21.39 . **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.04 (tt, *J* = 9.7, 3.4 Hz, 3F), -113.34 – -113.55 (m, 2F), -124.37 – -124.64 (m, 2F), -125.73 – -125.99 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2946, 1719, 1511, 1356, 1217,1131, 1021 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{17}OF_9Na$ ($[M+Na]^+$): 455.1028, mass found: 455.1044.

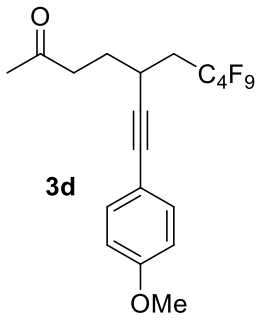
5-((4-(*Tert*-butyl)phenyl)ethynyl)-7,7,8,8,9,9,10,10,10-nonafluorodecan-2-one (3c)

3c was synthesized according to GP2 with **1c** (26 mg, 0.101 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column



chromatography (pentane/ethyl ether = 10/1) provided **3c** as a liquid (27 mg, 56%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33 (s, 4H), 3.15 – 3.01 (m, 1H), 2.84 – 2.64 (m, 2H), 2.55 – 2.22 (m, 2H), 2.19 (s, 3H), 2.09 – 1.96 (m, 1H), 1.87 – 1.73 (m, 1H), 1.31 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.51 , 151.48 , 131.31 , 125.27 , 119.93 , 88.54 , 83.36 , 40.90 , 36.25 (t, J = 21.0 Hz), 34.73 , 31.15 , 30.08 , 29.14 , 24.71 (t, J = 3.0 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.03 (tt, J = 9.7, 3.4 Hz, 3F), -113.33 – -113.54 (m, 2F), -124.39 – -124.62 (m, 2F), -125.76 – -125.98 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2965, 1719, 1355, 1217, 1163, 1131, 1107, 1017 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{22}H_{23}OF_9Na$ ([M+Na]$^+$): 497.1497, mass found: 497.1504.

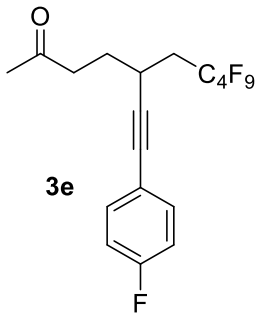
7,7,8,8,9,9,10,10,10-Nonafluoro-5-((4-methoxyphenyl)ethynyl)decan-2-one (3d)



3d was synthesized according to GP2 with **1f** (23 mg, 0.100 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 10/1) provided **3f** as a liquid (30 mg, 67%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.32 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H), 3.14 – 3.00 (m, 1H), 2.74 (dt, J = 8.4, 3.5 Hz, 2H), 2.55 – 2.21 (m, 2H), 2.19 (s, 3H), 2.01 (ddd, J = 8.6, 6.8, 3.9 Hz, 1H), 1.80 (ddd, J = 10.2, 5.9, 3.8 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.55 , 159.54 , 132.96 , 115.07 , 113.92 , 87.75 , 83.10 , 55.27 , 40.93 , 36.24 (t, J = 20.9 Hz), 30.08 , 29.16 , 24.72 (t, J = 2.9 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.04 (tt, J = 9.7, 3.3 Hz, 3F), -113.37 – -113.56 (m, 2F), -124.42 – -124.60 (m, 2F), -125.76 – -125.98 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2938, 1718, 1608, 1511, 1444, 1365, 1290, 1232, 1219, 1172, 1132, 1107, 1031 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{17}O_2F_9Na$ ([M+Na]$^+$): 471.0977, mass found: 471.0991.

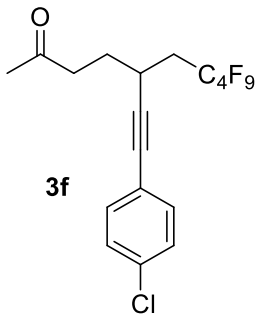
7,7,8,8,9,9,10,10,10-Nonafluoro-5-((4-fluorophenyl)ethynyl)decan-2-one (3e)

3e was synthesized according to GP2 with **1e** (23 mg, 0.100 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column



chromatography (pentane/ethyl ether = 10/1) provided **3e** as a liquid (30 mg, 68%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 6.97 – 6.87 (m, 2H), 3.00 (ddt, *J* = 9.9, 8.2, 4.9 Hz, 1H), 2.77 – 2.55 (m, 2H), 2.50 – 2.15 (m, 2H), 2.12 (s, 3H), 2.02 – 1.88 (m, 1H), 1.81 – 1.65 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.36 , 162.43 (d, *J* = 249.2 Hz), 133.43 (d, *J* = 8.3 Hz), 118.99 (d, *J* = 3.5 Hz), 115.52 (d, *J* = 22.2 Hz), 88.92 (d, *J* = 1.5 Hz), 82.25 , 40.84 , 36.14 (t, *J* = 21.0 Hz), 30.06 , 29.04 , 24.65 (t, *J* = 3.0 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.04 (tt, *J* = 9.7, 3.3 Hz, 3F), -111.14 – -111.24 (m, 1F), -113.36 – -113.59 (m, 2F), -124.41 – -124.62 (m, 2F), -125.76 – -125.99 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2949, 1718, 1603, 1508, 1356, 1218, 1157, 1132, 1015 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{14}OF_{10}Na$ ($[M+Na]^+$): 459.0777, mass found: 459.0788.

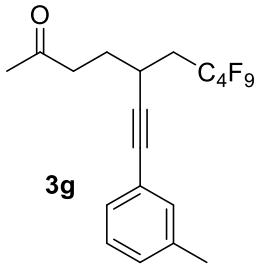
5-((4-Chlorophenyl)ethynyl)-7,7,8,8,9,9,10,10,10-nonafluorodecan-2-one (3f)



3f was synthesized according to GP2 with **1c** (23 mg, 0.098 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 10/1) provided **3c** as a liquid (37 mg, 83%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 4H), 3.01 (ddt, *J* = 9.9, 8.2, 4.9 Hz, 1H), 2.75 – 2.54 (m, 2H), 2.48 – 2.15 (m, 2H), 2.12 (s, 3H), 1.94 (dq, *J* = 10.9, 3.9, 3.4 Hz, 1H), 1.80 – 1.68 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.30 , 134.22 , 132.80 , 128.60 , 121.40 , 90.28 , 82.23 , 40.81 , 36.08 (t, *J* = 21.0 Hz), 30.07 , 28.98 , 24.69 (t, *J* = 3.3 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.03 (tt, *J* = 9.7, 3.3 Hz, 3F), -113.28 – -113.65 (m, 2F), -124.39 – -124.59 (m, 2F), -125.77 – -125.96 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2947, 1718, 1491, 1357, 1234, 1222, 1165, 1134, 10921016 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{14}O^{35}ClF_9Na$ ($[M+Na]^+$): 475.0482, mass found: 475.0484.

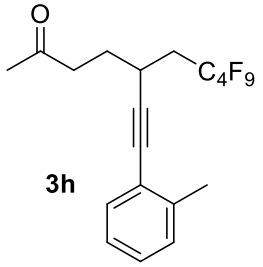
7,7,8,8,9,9,10,10,10-Nonafluoro-5-(*m*-tolylethynyl)decan-2-one (3g)

3g was synthesized according to GP2 with **1g** (21 mg, 0.098 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL,



0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 10/1) provided **3g** as a liquid (29 mg, 68%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 3H), 7.15 – 7.09 (m, 1H), 3.09 (ddt, *J* = 9.9, 8.0, 4.9 Hz, 1H), 2.83 – 2.64 (m, 2H), 2.55-2.23 (m, 5H), 2.19 (s, 3H), 2.07 – 1.96 (m, 1H), 1.80 (dd, *J* = 10.2, 6.0 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.48 , 137.97 , 132.13 , 129.05 , 128.64 , 128.16 , 122.72 , 88.83 , 83.43 , 40.87 , 36.19 (t, *J* = 21.0 Hz), 30.07 , 29.10 , 24.67 (t, *J* = 3.2 Hz), 21.14 . **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.02 (tt, *J* = 9.7, 3.3 Hz, 3F), -113.37 – -113.57 (m, 2F), -124.39 – -124.62 (m, 2F), -125.75 – -126.01 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2946, 2361, 1719, 1487, 1356, 1234, 1134 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{17}OF_9Na$ ($[M+Na]^+$): 455.1028, mass found: 455.1044.

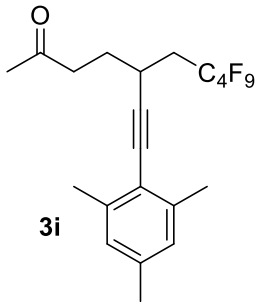
7,7,8,8,9,9,10,10,10-Nonafluoro-5-(*o*-tolylethynyl)decan-2-one (3h)



3h was synthesized according to GP2 with **1h** (21 mg, 0.098 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 10/1) provided **3h** as a liquid (33 mg, 78%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.23 – 7.16 (m, 2H), 7.16 – 7.08 (m, 1H), 3.14 (ddt, *J* = 9.8, 8.4, 4.8 Hz, 1H), 2.77 (td, *J* = 7.6, 6.9, 1.9 Hz, 2H), 2.54-2.23 (m, 5H), 2.19 (s, 3H), 2.11 – 1.98 (m, 1H), 1.87 – 1.76 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.44 , 140.02 , 131.94 , 129.42 , 128.18 , 125.51 , 122.70 , 93.19 , 82.20 , 40.88 , 36.37 (t, *J* = 21.1 Hz), 30.08 , 29.26 , 24.82 (t, *J* = 3.1 Hz), 20.57 . **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.03 (tt, *J* = 9.7, 3.3 Hz, 3F), -113.12 – -113.51 (m, 2F), -124.43 – -124.65 (m, 2F), -125.75 – -126.00 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2954, 1719, 1487, 1356, 1220, 1165, 1133, 1037 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{17}OF_9Na$ ($[M+Na]^+$): 455.1028, mass found: 455.1045.

7,7,8,8,9,9,10,10,10-Nonafluoro-5-(mesitylethynyl)decan-2-one (3i)

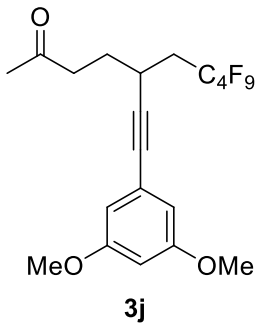
3i was synthesized according to GP2 with **1i** (24 mg, 0.099 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL,



3i

0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 10/1) provided **3i** as a liquid (28 mg, 61%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.86 (s, 2H), 3.18 (dq, *J* = 13.2, 4.6 Hz, 1H), 2.88 – 2.70 (m, 2H), 2.55-2.23 (m, 11H), 2.18 (s, 3H), 2.12 – 1.98 (m, 1H), 1.88 – 1.74 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.45 , 140.05 , 137.57 , 127.58 , 119.64 , 96.95 , 80.97 , 40.93 , 36.60 (t, *J* = 21.1 Hz), 30.04 , 29.49 , 24.99 (t, *J* = 3.2 Hz), 21.22 , 20.87 . **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.03 (tt, *J* = 9.7, 3.4 Hz, 3F), -112.86 – -113.59 (m, 2F), -124.44 – -124.68 (m, 2F), -125.78 – -125.98 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2921, 2362, 2336, 1718, 1375, 1365, 1217, 1131, 1109, 1034, 1014 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{17}OF_9Na$ ($[M+Na]^+$): 483.1341, mass found: 483.1353.

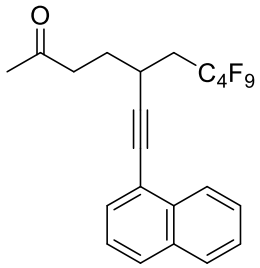
5-((3,5-Dimethoxyphenyl)ethynyl)-7,7,8,8,9,9,10,10,10-nonafluorodecan-2-one (3j)



3j

3j was synthesized according to GP2 with **1j** (26 mg, 0.100 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 6/1) provided **3j** as a liquid (27 mg, 57%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.54 (d, *J* = 2.4 Hz, 2H), 6.43 (t, *J* = 2.3 Hz, 1H), 3.78 (s, 6H), 3.08 (dt, *J* = 7.9, 5.0 Hz, 1H), 2.80 – 2.64 (m, 2H), 2.57 – 2.22 (m, 2H), 2.19 (s, 3H), 2.11 – 1.95 (m, 1H), 1.87 – 1.75 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.47 , 160.55 , 124.22 , 109.50 , 101.53 , 88.86 , 83.26 , 55.39 , 40.87 , 36.13 (t, *J* = 21.2 Hz), 30.11 , 29.03 , 24.67 (t, *J* = 2.9 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.02 (tt, *J* = 9.7, 3.3 Hz, 3F), -113.29 – -113.57 (m, 2F), -124.34 – -124.66 (m, 2F), -125.75 – -125.96 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2945, 1720, 1590, 1454, 1422, 1355, 1233, 1207, 1157, 1134, 1066 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{20}H_{19}O_3F_9Na$ ($[M+Na]^+$): 501.1083, mass found: 501.1098.

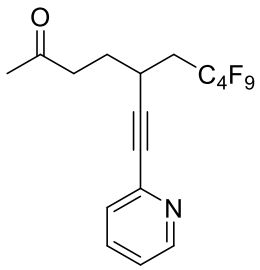
7,7,8,8,9,9,10,10,10-Nonafluoro-5-(naphthalen-1-ylethynyl)decan-2-one (3k)



3k

3k was synthesized according to GP2 with **1k** (25 mg, 0.100 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 10/1) provided **3k** as a liquid (33 mg, 71%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.28 – 8.20 (m, 1H), 7.90 – 7.79 (m, 2H), 7.64 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.61 – 7.48 (m, 2H), 7.42 (dd, *J* = 8.3, 7.1 Hz, 1H), 3.27 (ddd, *J* = 10.1, 5.0, 3.5 Hz, 1H), 2.92 – 2.74 (m, 2H), 2.65 – 2.32 (m, 2H), 2.21 (s, 3H), 2.16 – 2.07 (m, 1H), 1.98 – 1.84 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.44 , 133.33 , 133.18 , 130.47 , 128.66 , 128.31 , 126.77 , 126.38 , 125.86 , 125.15 , 120.56 , 94.17 , 81.45 , 40.95 , 36.37 (t, *J* = 21.1 Hz), 30.11 , 29.27 , 25.01 (t, *J* = 3.0 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.91 – -81.09 (m, 3F), -112.99 – -113.43 (m, 2F), -124.26 – -124.61 (m, 2F), -125.64 – -126.01 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 3063, 1718, 1508, 1397, 1355, 1219, 1165, 1132, 1017 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{22}H_{17}OF_9Na$ ($[M+Na]^+$): 491.1028, mass found: 491.1030.

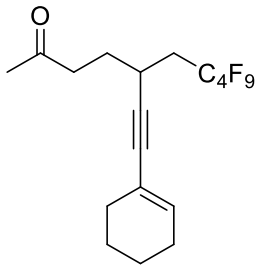
7,7,8,8,9,9,10,10,10-Nonafluoro-5-(pyridin-2-ylethynyl)decan-2-one (3l)



3l

3l was synthesized according to GP2 with **1l** (20 mg, 0.099 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 1/3) provided **3l** as a liquid (25 mg, 60%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.56 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.39 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.22 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 3.13 (ddd, *J* = 10.0, 8.0, 5.0 Hz, 1H), 2.87 – 2.67 (m, 2H), 2.63 – 2.25 (m, 2H), 2.18 (s, 3H), 2.13 – 1.98 (m, 1H), 1.93 – 1.77 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.32 , 149.92 , 143.04 , 136.15 , 127.18 , 122.86 , 89.53 , 82.83 , 40.81 , 35.91 (t, *J* = 21.1 Hz), 30.06 , 28.76 , 24.59 (t, *J* = 3.1 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.03 (tt, *J* = 9.8, 3.3 Hz, 3F), -113.29 – -113.57 (m, 2F), -124.31 – -124.58 (m, 2F), -125.73 – -126.00 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2931, 1716, 1583, 1564, 1466, 1429, 1356, 1217, 1165, 1131, 1016 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{17}H_{14}NOF_9Na$ ($[M+Na]^+$): 442.0824, mass found: 442.0823.

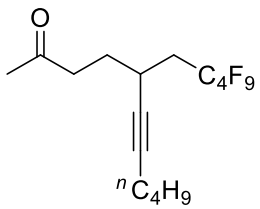
5-(Cyclohexylethynyl)-7,7,8,8,9,9,10,10,10-nonafluorodecan-2-one (3m)



3m

3m was synthesized according to GP2 with **1m** (21 mg, 0.103 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 10/1) provided **3m** as a liquid (19 mg, 44%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.04 (p, *J* = 2.1 Hz, 1H), 2.96 (td, *J* = 10.0, 9.3, 5.0 Hz, 1H), 2.77 – 2.56 (m, 2H), 2.49 – 1.86 (m, 11H), 1.77 – 1.52 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.61 , 134.45 , 120.39 , 86.42 , 85.08 , 40.93 , 36.31 (t, *J* = 21.1 Hz), 30.07 , 29.29 , 29.19 , 25.54 , 24.59 (t, *J* = 3.0 Hz), 22.28 , 21.49 . **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.04 (tt, *J* = 9.7, 3.3 Hz, 3F), -113.33 – -113.66 (m, 2F), -124.40 – -124.64 (m, 2F), -125.75 – -126.00 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2934, 2364, 2335, 1718, 1437, 1355, 1217, 1164, 1131, 1108, 1022 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{19}OF_9Na$ ($[M+Na]^+$): 445.1184, mass found: 445.1188.

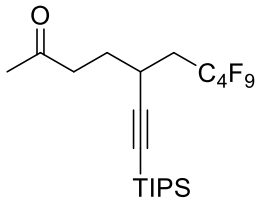
5-(2,2,3,3,4,4,5,5,5-Nonafluoropentyl)undec-6-yn-2-one (3n)



3n

3n was synthesized according to GP2 with **1n** (18 mg, 0.100 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 10/1) provided **3n** as a liquid (16 mg, 40%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.81 (ddd, *J* = 7.1, 4.8, 2.4 Hz, 1H), 2.65 (dt, *J* = 8.2, 6.3 Hz, 2H), 2.38 – 2.21 (m, 1H), 2.20 – 2.11 (m, 5H), 1.97 – 1.83 (m, 1H), 1.72 – 1.32 (m, 6H), 0.90 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.72 , 83.43 , 79.82 , 40.97 , 36.47 (t, *J* = 20.8 Hz), 30.89 , 30.03 , 29.37 , 24.15 (t, *J* = 3.1 Hz), 21.85 , 18.28 , 13.52 . **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.05 (tt, *J* = 9.7, 3.4 Hz, 3F), -113.37 – -113.67 (m, 2F), -124.47 – -124.72 (m, 2F), -125.73 – -126.03 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2960, 1720, 1437, 1356, 1218, 1203, 1165, 1132, 1109 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{17}H_{14}NOF_9Na$ ($[M+Na]^+$): 421.1184, mass found: 421.1195.

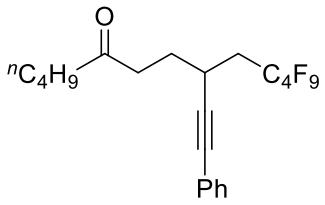
5-(2,2,3,3,4,4,5,5,5-Nonafluoropentyl)undec-6-yn-2-one (3o)



3o

3o was synthesized according to GP2 with **1o** (28 mg, 0.100 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 10/1) provided **3o** as a liquid (41 mg, 82%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.92 (ddd, *J* = 10.3, 5.1, 3.6 Hz, 1H), 2.72 (t, *J* = 7.3 Hz, 2H), 2.47 – 2.07 (m, 5H), 2.03 – 1.90 (m, 1H), 1.72 – 1.60 (m, 1H), 1.08 – 1.03 (m, 21H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.42 , 107.95 , 83.78 , 40.74 , 36.49 (t, *J* = 21.1 Hz), 29.99 , 29.15 , 24.97 (t, *J* = 3.2 Hz), 18.57 , 18.49 , 11.17 . **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.08 (tt, *J* = 9.7, 3.4 Hz, 3F), -112.06 – -114.26 (m, 2F), -124.47 – -124.74 (m, 2F), -125.80 – -126.04 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2944, 2893, 2867, 1721, 1464, 1356, 1234, 1133, 1018 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{17}H_{14}NOF_9Na$ ($[M+Na]^+$): 521.1893, mass found: 521.1888.

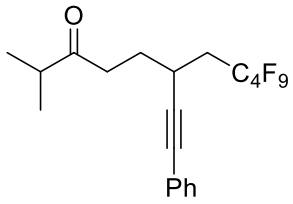
10,10,11,11,12,12,13,13,13-Nonafluoro-8-(phenylethynyl)tridecan-5-one (3p)



3p

3p was synthesized according to GP2 with **1p** (24 mg, 0.099 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 30/1) provided **3p** as a liquid (29 mg, 64%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.30 (dt, *J* = 5.0, 2.0 Hz, 3H), 3.10 (dt, *J* = 8.0, 5.0 Hz, 1H), 2.71 (dd, *J* = 8.0, 6.5 Hz, 2H), 2.53 – 2.22 (m, 4H), 2.12 – 1.95 (m, 1H), 1.88 – 1.72 (m, 1H), 1.63 – 1.52 (m, 2H), 1.38 – 1.27 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 209.97 , 131.59 , 128.26 , 128.15 , 123.00 , 89.36 , 83.28 , 42.78 , 39.87 , 36.23 (t, *J* = 21.0 Hz), 29.12 , 26.00 , 24.74 (t, *J* = 3.1 Hz), 22.34 , 13.79 . **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.93 – -81.11 (m, 3F), -113.22 – -113.54 (m, 2F), -124.29 – -124.63 (m, 2F), -125.68 – -126.01 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2964, 1715, 1599, 1491, 1444, 1413, 1380, 1355, 1220, 1169, 1132, 1070, 1019 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{21}H_{21}OF_9Na$ ($[M+Na]^+$): 483.1341, mass found: 483.1351.

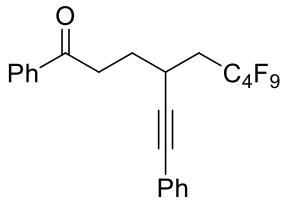
8,8,9,9,10,10,11,11,11-Nonafluoro-2-methyl-6-(phenylethynyl)undecan-3-one (3q)



3q

3q was synthesized according to GP2 with **1q** (23 mg, 0.101 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 30/1) provided **3q** as a liquid (28 mg, 62%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 2H), 7.34 – 7.27 (m, 3H), 3.10 (ddd, *J* = 10.3, 5.1, 3.2 Hz, 1H), 2.76 (td, *J* = 6.8, 6.1, 1.6 Hz, 2H), 2.64 (p, *J* = 6.9 Hz, 1H), 2.56 – 2.18 (m, 2H), 2.03 (ddt, *J* = 13.4, 7.6, 3.8 Hz, 1H), 1.89 – 1.70 (m, 1H), 1.13 (dd, *J* = 7.0, 3.3 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 213.50 , 131.58 , 128.27 , 128.14 , 123.03 , 89.40 , 83.26 , 41.04 , 37.46 , 36.27 (t, *J* = 21.0 Hz), 29.17 , 24.72 (t, *J* = 3.0 Hz), 18.33 , 18.21 . **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.03 (tt, *J* = 9.6, 3.3 Hz, 3F), -113.30 – -113.51 (m, 2F), -124.38 – -124.59 (m, 2F), -125.75 – -125.95 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2975, 1713, 1491, 1355, 1217, 1132, 1019 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{21}H_{21}OF_9Na$ ($[M+Na]^+$): 469.1184, mass found: 469.1189.

6,6,7,7,8,8,9,9,9-Nonafluoro-1-phenyl-4-(phenylethynyl)nonan-1-one (3r)



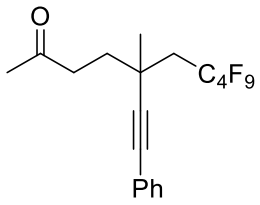
3r

3r was synthesized according to GP2 with **1r** (26 mg, 0.099 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 45/1) provided **3r** as a yellow solid (42 mg, 88%); **MP**: 43 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.05 – 7.96 (m, 2H), 7.62 – 7.53 (m, 1H), 7.52 – 7.43 (m, 2H), 7.42 – 7.34 (m, 2H), 7.32 – 7.26 (m, 3H), 3.35 – 3.26 (m, 2H), 3.26 – 3.16 (m, 1H), 2.65 – 2.30 (m, 2H), 2.29 – 2.16 (m, 1H), 2.08 – 1.91 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 199.03 , 136.83 , 133.16 , 131.60 , 128.64 , 128.25 , 128.15 , 128.04 , 122.97 , 89.43 , 83.44 , 36.31 (t, *J* = 21.1 Hz), 35.95 , 29.70 , 24.92 . **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.01 (tt, *J* = 9.7, 3.3 Hz, 3F), -113.25 – -113.47 (m, 2F), -124.32 – -124.57 (m, 2F), -125.72 – -125.94 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2951, 1680, 1599, 1491, 1451, 1354, 1282, 1229, 1196, 1129, 1102, 1013 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{23}H_{17}OF_9Na$ ($[M+Na]^+$): 503.1028, mass found: 503.1037.

Chiral **3r** was synthesized according to GP2 with chiral **1r** (26 mg, 0.099 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and

2a (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 45/1) provided chiral **3r** as a yellow solid (39 mg, 82%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.05 – 7.97 (m, 2H), 7.62 – 7.54 (m, 1H), 7.52 – 7.43 (m, 2H), 7.43 – 7.34 (m, 2H), 7.33 – 7.26 (m, 3H), 3.35 – 3.16 (m, 3H), 2.66 – 2.16 (m, 3H), 2.08 – 1.94 (m, 1H). The pure product was analyzed by chiral HPLC. Chiral HPLC (Chiralcel OJ-RH column with guard, 20 °C, 1 mL/min, MeCN:H_2O = 65:35); Elution time: t_{major} = 8.734 min and t_{minor} = 10.047 min, enantiomeric excess (7%).

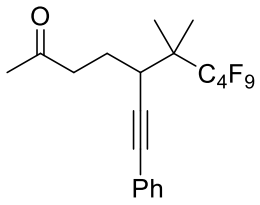
7,7,8,8,9,9,10,10,10-Nonafluoro-5-methyl-5-(phenylethynyl)decan-2-one (3s)



3s

3s was synthesized according to GP2 with **1s** (21 mg, 0.098 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 15/1) provided **3s** as a liquid (31 mg, 73%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.30 (dt, *J* = 5.1, 1.6 Hz, 3H), 2.72 (dd, *J* = 8.7, 7.0 Hz, 2H), 2.51 – 2.23 (m, 2H), 2.20 (s, 3H), 2.10 – 1.86 (m, 2H), 1.48 (d, *J* = 1.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.54 , 131.54 , 128.25 , 128.11 , 123.02 , 92.25 , 83.06 , 40.24 (t, *J* = 20.0 Hz), 39.43 , 35.71 , 32.79 , 30.06 , 26.97 (t, *J* = 2.1 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.06 (td, *J* = 9.7, 4.8 Hz, 3F), -110.35 – -112.84 (m, 2F), -124.41 – -124.69 (m, 2F), -125.54 – -125.77 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2942, 1719, 1491, 1354, 1218, 1131, 1071, 1025 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{17}OF_9Na$ ($[M+Na]^+$): 455.1028, mass found: 455.1046.

7,7,8,8,9,9,10,10,10-Nonafluoro-6,6-dimethyl-5-(phenylethynyl)decan-2-one (3t)

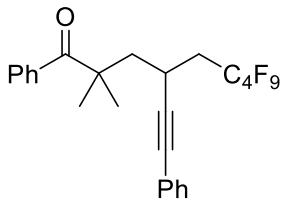


3t

3t was synthesized according to GP2 with **1t** (23 mg, 0.101 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 15/1) provided **3t** as a liquid (19 mg, 42%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.29 (dt, *J* = 5.1, 1.8 Hz, 3H), 2.86 – 2.60 (m, 2H), 2.41 – 2.22 (m, 1H), 2.20 – 1.98 (m, 5H), 1.52 (d, *J* = 2.0 Hz, 3H), 1.48 (s, 3H). **^{13}C**

NMR (75 MHz, $CDCl_3$) δ 207.17 , 131.43 , 128.26 , 127.97 , 123.22 , 95.04 , 81.73 , 48.60 – 47.83 (m), 43.66 , 35.51 (d, *J* = 2.4 Hz), 29.76 , 29.47 (d, *J* = 5.7 Hz), 26.93 – 26.61 (m), 20.97 – 20.60 (m). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.90 (tt, *J* = 9.9, 3.5 Hz, 3F), -108.57 – -112.47 (m, 2F), -119.98 – -123.35 (m, 2F), -124.34 – -127.10 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2984, 1720, 1598, 1491, 1419, 1351, 1233, 1217, 1166, 1016 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{20}H_{19}OF_9Na$ ($[M+Na]^+$): 469.1184, mass found: 469.1192.

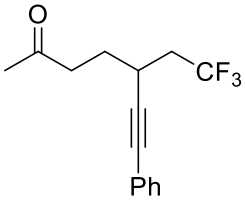
6,6,7,7,8,8,9,9,9-Nonafluoro-2,2-dimethyl-1-phenyl-4-(phenylethynyl)nonan-1-one (3u)



3u

3u was synthesized according to GP2 with **1u** (29 mg, 0.100 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 50/1) provided **3u** as a liquid (23 mg, 57%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H), 7.43 – 7.30 (m, 3H), 7.22 (dd, *J* = 6.1, 2.4 Hz, 5H), 3.23 – 3.10 (m, 1H), 2.57 – 2.23 (m, 3H), 2.00 (dd, *J* = 13.8, 3.7 Hz, 1H), 1.48 (s, 3H), 1.46 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.83 , 138.74 , 131.39 , 130.79 , 128.07 , 128.02 , 127.99 , 123.00 , 90.42 , 83.90 , 47.58 , 45.62 , 37.24 (t, *J* = 20.8 Hz), 27.44 , 25.94 , 22.25 (t, *J* = 2.9 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.01 (tt, *J* = 9.7, 3.3 Hz, 3F), -113.08 – -113.54 (m, 2F), -124.35 – -124.76 (m, 2F), -125.60 – -126.06 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2971, 1674, 1491, 1353, 1217, 1131, 1019 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{25}H_{21}OF_9Na$ ($[M+Na]^+$): 531.1341, mass found: 531.1342.

7-Phenyl-5-(2,2,2-trifluoroethyl)hept-6-yn-2-one (3v)

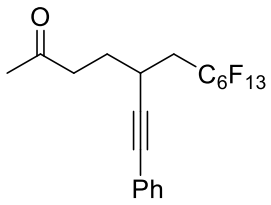


3v

3v was synthesized according to GP2 with **1a** (20 mg, 0.100 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2b** (60 μL, 0.180 mmol, 0.588 g/mL in DME) in 1.25 mL of DME under visible-light at 50 °C for 8 h. Then second part of **2b (**60 μL, 0.180 mmol, 0.588 g/mL in DME**)**was added and the reaction was reacted for another 16 h. Purification by flash column chromatography (pentane/ethyl ether = 10/1) provided **3v** as a liquid (11 mg, 41%); **^{1}H NMR** (300

MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.34 – 7.27 (m, 3H), 3.05 – 2.93 (m, 1H), 2.83 – 2.63 (m, 2H), 2.52 – 2.39 (m, 1H), 2.37 – 2.25 (m, 1H), 2.19 (s, 3H), 2.06 – 1.94 (m, 1H), 1.83 – 1.73 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.51, 131.59, 128.27, 128.16, 126.54 (q, *J* = 117.8 Hz), 122.99, 88.95, 83.42, 40.87, 39.34 (q, *J* = 27.9 Hz), 30.10, 28.51, 26.96 (q, *J* = 3.0 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -64.12. **FTIR (neat)**: $\tilde{\nu}$ = 2929, 1718, 1491, 1381, 1255, 1164, 1140, 1111 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{15}H_{15}OF_3Na$ ($[M+Na]^+$): 291.0966, mass found: 291.0967.

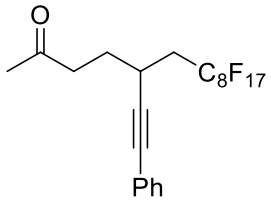
7,7,8,8,9,9,10,10,11,11,12,12,12-Tridecafluoro-5-(phenylethynyl)dodecan-2-one (3w)



3w

3w was synthesized according to GP2 with **1a** (20 mg, 0.100 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2c** (39 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 10/1) provided **3w** as a liquid (32 mg, 62%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.33 – 7.27 (m, 3H), 3.10 (ddt, *J* = 9.9, 8.0, 5.0 Hz, 1H), 2.84 – 2.65 (m, 2H), 2.59 – 2.23 (m, 2H), 2.19 (s, 3H), 2.03 (dtd, *J* = 15.3, 7.3, 4.5 Hz, 1H), 1.81 (dtd, *J* = 10.1, 7.6, 3.9 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.45 , 131.58 , 128.27 , 128.18 , 122.95 , 89.26 , 83.32 , 40.88 , 36.29 (t, *J* = 21.0 Hz), 30.08 , 29.09 , 24.73 (t, *J* = 2.9 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.80 (tt, *J* = 10.0, 5.0 Hz, 3F), -113.09 – -113.30 (m, 2F), -121.58 – -121.93 (m, 2F), -122.66 – -123.00 (m, 2F), -123.42 – -123.69 (m, 2F), -125.97 – -126.23 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2954, 1719, 1491, 1444, 1360, 1318, 1235, 1190, 1164, 1144, 1122, 1049, 1027 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{20}H_{15}OF_{13}Na$ ($[M+Na]^+$): 541.0808, mass found: 541.0819.

7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-Heptadecafluoro-5-(phenylethynyl)tetradecan-2-one (3x)

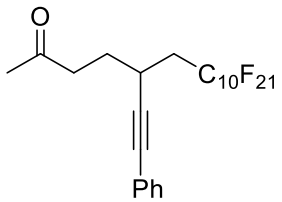


3x

3x was synthesized according to GP2 with **1a** (20 mg, 0.100 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2d** (48 μL, 0.182 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by

flash column chromatography (pentane/ethyl ether = 10/1) provided **3x** as a yellow solid (34 mg, 55%); **MP**: 39 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 2H), 7.30 (dt, *J* = 3.8, 2.7 Hz, 3H), 3.09 (ddd, *J* = 9.9, 8.0, 4.9 Hz, 1H), 2.84 – 2.64 (m, 2H), 2.53 – 2.23 (m, 2H), 2.19 (s, 3H), 2.11 – 1.97 (m, 1H), 1.88 – 1.75 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.45 , 131.59 , 128.27 , 128.18 , 122.96 , 89.27 , 83.32 , 40.89 , 36.30 (t, *J* = 21.0 Hz), 30.08 , 29.09 , 24.73 (t, *J* = 3.1 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.79 (t, *J* = 9.8 Hz, 3F), -113.18 (t, *J* = 14.5 Hz, 2F), -121.37 – -121.68 (m, 2F), -121.70 – -122.04 (m, 4F), -122.45 – -122.90 (m, 2F), -123.30 – -123.72 (m, 2F), -125.90 – -126.26 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2944, 1718, 1600, 191, 1443, 1370, 1329, 1236, 1200, 1145, 1134, 1113, 1027 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{22}H_{15}OF_{17}Na$ ($[M+Na]^+$): 641.0744, mass found: 641.0740.

7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Henicosafluoro-5-(phenylethynyl)hexadecan-2-one (3y)

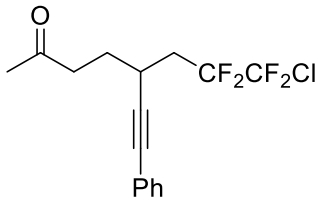


3y

3y was synthesized according to GP2 with **1a** (20 mg, 0.100 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2e** (116 mg, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 10/1) provided **3y** as a white solid (34 mg, 47%); **MP**: 69 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 2H), 7.34 – 7.27 (m, 3H), 3.10 (ddt, *J* = 9.9, 8.0, 4.9 Hz, 1H), 2.86 – 2.64 (m, 2H), 2.60 – 2.23 (m, 2H), 2.19 (s, 3H), 2.11 – 1.96 (m, 1H), 1.90 – 1.72 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.46 , 131.59 , 128.28 , 128.18 , 122.96 , 89.27 , 83.32 , 40.89 , 36.31 (t, *J* = 21.0 Hz), 30.09 , 29.10 , 24.74 (t, *J* = 3.0 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.71 – -80.84 (m, 3F), -113.08 – -113.30 (m, 2F), -121.31 – -122.07 (m, 10F), -122.68 (brs, 2F), -123.51 (brs, 2F), -125.92 – -126.24 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2962, 1718, 1491, 1444, 1372, 1211, 1150, 1110, 1053 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{24}H_{15}OF_{21}Na$ ($[M+Na]^+$): 741.0680, mass found: 741.0680.

8-Chloro-7,7,8,8-tetrafluoro-5-(phenylethynyl)octan-2-one (3z)

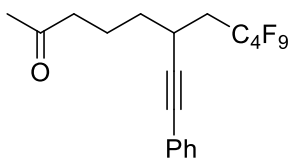
3z was synthesized according to GP2 with **1a** (20 mg, 0.100 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2f** (47 mg, 0.179 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column



3z

chromatography (pentane/ethyl ether = 10/1) provided **3z** as a liquid (27 mg, 81%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.34 – 7.27 (m, 3H), 3.08 (ddt, *J* = 10.0, 8.0, 5.0 Hz, 1H), 2.85 – 2.63 (m, 2H), 2.60 – 2.23 (m, 2H), 2.19 (s, 3H), 2.11 – 1.96 (m, 1H), 1.88 – 1.76 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.51 , 131.58 , 128.26 , 128.14 , 123.00 , 89.39 , 83.28 , 40.91 , 36.02 (t, *J* = 21.4 Hz), 30.09 , 29.03 , 25.08 (t, *J* = 2.8 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -71.45 (t, *J* = 2.3 Hz, 2F), -113.02 – -113.09 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2958, 1717, 1599, 1419, 1443, 1374, 1252, 1212, 1148, 1094, 1050, 1026 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{16}H_{15}O^{35}ClF_4Na$ ($[M+Na]^+$): 357.0640, mass found: 357.0650.

8,8,9,9,10,10,11,11,11-Nonafluoro-6-(phenylethynyl)undecan-2-one (3va)



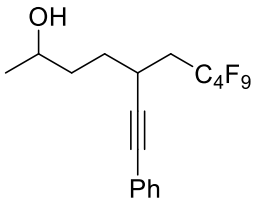
3va

3va was synthesized according to GP2 with **1v** (21 mg, 0.098 mmol), LiHMDS (0.12 mL, 0.120 mmol, 1.0 M in THF solution), LiOH (1 mg, 0.042 mmol), DABCO (17 mg, 0.152 mmol), and **2a** (31 μL, 0.180 mmol) in 1.25 mL of DME under visible-light at 50 °C for 18 h. Purification by flash column chromatography (pentane/ethyl ether = 10/1) provided **3va** as a liquid (28 mg, 66%); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 2H), 7.29 (ddd, *J* = 3.4, 2.5, 1.5 Hz, 3H), 3.06 (tt, *J* = 8.3, 5.3 Hz, 1H), 2.57 – 2.21 (m, 4H), 2.16 (s, 3H), 1.96 – 1.86 (m, 1H), 1.86 – 1.72 (m, 1H), 1.71 – 1.55 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 208.11 , 131.60 , 128.23 , 128.03 , 123.15 , 89.79 , 82.88 , 43.01 , 35.96 (t, *J* = 21.0 Hz), 34.69 , 29.87 , 25.15 (t, *J* = 3.2 Hz), 21.15 . **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.03 (tt, *J* = 9.7, 3.3 Hz, 3F), -113.34 – -113.61 (m, 2F), -124.36 – -124.60 (m, 2F), -125.73 – -125.95 (m, 2F). **FTIR (neat)**: $\tilde{\nu}$ = 2942, 1718, 1599, 1491, 1444, 1356, 1222, 1167, 1133 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{19}H_{17}OF_9Na$ ($[M+Na]^+$): 455.1028, mass found: 455.1030.

4. Follow-up chemistry

7,7,8,8,9,9,10,10,10-nonafluoro-5-(phenylethynyl)decan-2-ol (4)

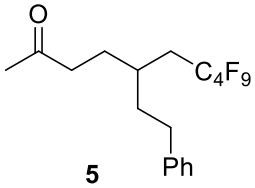
To a flame-dried Schlenk tube equipped with a magnetic stir bar $LiAlH_4$ (0.050 mmol, 1 M in THF, 0.050 mL), THF (1 mL) and **3a** (21 mg, 0.050 mmol) were added sequentially under Ar atmosphere. The mixture was allowed to stir at 80 °C for 3 h. After that, the reaction was quenched with 5 mL of H_2O at 0 °C. Then 5 mL of saturated potassium sodium tartrate solution was added into this mixture.



4, d.r. = 1:1

The mixture was extracted with 5 mL of ethyl ether three times. The organic phase was combined, washed with brine and dried over Na_2SO_4. The solvent was then removed and the residue was purified by flash column chromatography (pentane/ethyl acetate = 10/1) to provide **4** as a liquid (16 mg, 76%, d.r. = 1:1); **^{1}H NMR** (600 MHz, C_6D_6) δ 7.46 – 7.40 (m, 2H), 7.00 – 6.94 (m, 3H), 3.47 – 3.41 (m, 1H), 2.92 – 2.84 (m, 1H), 2.26 – 2.15 (m, 1H), 1.99 – 1.90 (m, 1H), 1.56 – 1.46 (m, 2H), 1.38 – 1.30 (m, 2H), 0.93 (d, *J* = 6.2 Hz, 1.46H), & 0.93 (d, *J* = 6.1 Hz, 1.49H), 0.65 (s, 1H). **^{13}C NMR** (75 MHz, C_6D_6) δ 131.89, 128.54, 128.19, 123.84, 90.61 & 90.48, 83.46 & 83.40, 67.45 & 66.94, 36.81 & 36.50, 36.21 , 36.72 – 35.92 (m), 32.09 & 31.76, 25.67 (t, *J* = 3.3 Hz) & 25.34 (t, *J* = 2.8 Hz), 23.86 & 23.77. **^{19}F NMR** (282 MHz, C_6D_6) δ -81.06 – -81.21 (m), -112.01 – -114.47 (m), -124.15 – -124.41 (m), -125.72 – -125.92 (m). **FTIR (neat)**: $\tilde{\nu}$ = 3349, 2969, 2928, 1355, 1217, 1131, 1070, 1016 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{17}OF_9Na$ ([M+Na]$^+$): 443.1028, mass found: 443.1002.

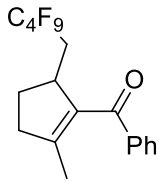
7,7,8,8,9,9,10,10,10-Nonafluoro-5-phenethyldecan-2-one (5)



5

To a flame-dried Schlenk tube equipped with a magnetic stir bar Palladium 5% on activated carbon (5 mg, 0.0023 mmol), **3a** (21 mg, 0.050 mmol), and MeOH (1 mL) were added sequentially under H_2 atmosphere. The mixture was allowed to stir at room temperature with a H_2 balloon for 23 h. After that, the solvent was then removed and the residue was purified by flash column chromatography (pentane/ethyl ether = 20/1) to provide **5** as a liquid (17 mg, 80%); **^{1}H NMR** (600 MHz, $CDCl_3$) δ7.26 – 7.17 (m, 2H), 7.16 – 7.06 (m, 3H), 2.61 – 2.50 (m, 2H), 2.37 (t, *J* = 7.7 Hz, 2H), 2.08 (s, 3H), 2.05 – 1.79 (m, 3H), 1.74 – 1.59 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.55, 128.47, 128.26, 126.01, 40.44, 36.09, 33.85 (t, *J* = 21.0 Hz), 32.54, 30.56, 29.92, 27.80. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -81.05 (tt, *J* = 9.7, 3.3 Hz), -112.94 – -113.11 (m), -124.33 – -124.51 (m), -125.72 – -125.91 (m). **FTIR (neat)**: $\tilde{\nu}$ = 2923, 1719, 1497, 1455, 1356, 1217, 1131, 1046, 1022 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{19}OF_9Na$ ([M+Na]$^+$): 445.1184, mass found: 45.1188.

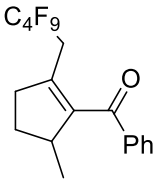
(2-Methyl-5-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)cyclopent-1-en-1-yl)(phenyl)methanone (6)



6

To a flame-dried Schlenk tube equipped with a magnetic stir bar **3a** (21 mg, 0.050 mmol), MeOH (1 mL) and TfOH (0.2 μL, 0.002 mmol) were added sequentially under Ar atmosphere. The mixture was allowed to stir at 80 °C for 5 h. After that, the solvent was removed and the residue was purified by flash column chromatography (pentane/ethyl acetate = 80/1) provided **6** as a liquid (16 mg, 76%);[3] **^{1}H NMR** (600 MHz, C_6D_6) δ 7.71 – 7.65 (m, 2H), 7.13 – 7.03 (m, 3H), 3.68 – 3.51 (m, 1H), 2.93 – 2.66 (m, 1H), 2.08 – 1.75 (m, 4H), 1.51 – 1.39 (m, 1H), 1.23 (s, 3H). **^{13}C NMR** (75 MHz, C_6D_6) δ 195.25, 149.77, 139.64, 137.59, 132.55, 129.04, 128.66, 41.66, 38.74, 34.27 (t, J = 20.8 Hz), 29.61, 16.69. **^{19}F NMR** (282 MHz, C_6D_6) δ -80.88 – -81.24 (m), -110.49 – -114.70 (m), -124.08 – -124.43 (m), -125.55 – -125.84 (m). **FTIR (neat)**: $\tilde{\nu}$ = 2935, 1640, 1349, 1216, 1131, 1101, 1017 cm^{-1}. **HRMS (ESI)**: Exact mass calculated for $C_{18}H_{15}OF_9Na$ ([M+Na]$^+$): 441.0871, mass found: 441.0847.

(5-Methyl-2-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)cyclopent-1-en-1-yl)(phenyl)methanone (6)



6

To a flame-dried Schlenk tube equipped with a magnetic stir bar $AuCl_3$ (0.6 mg, 0.002 mmol), $AgSbF_6$ (2.0 mg, 0.006 mmol), **3a** (42 mg, 0.100 mmol), and toluene (1 mL) were added sequentially under Ar atmosphere. The mixture was allowed to stir at 100 °C for 18 h. After that, 5 mL of H_2O was added to the mixture and then the aqueous phase was extracted with 5 mL of ethyl acetate three times. The combined organic phase was washed with brine and dried over Na_2SO_4. The solvent was then removed and the residue was purified by flash column chromatography (pentane/ethyl acetate = 350/1) provided **6** as a liquid (25 mg, 60%);[4] **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 2H), 7.60 – 7.52 (m, 1H), 7.50 – 7.42 (m, 2H), 3.70 – 3.54 (m, 1H), 2.70 – 2.44 (m, 3H), 2.40 – 2.30 (m, 1H), 2.03 – 1.86 (m, 1H), 1.85 – 1.73 (m, 1H), 1.62 (d, 7H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 196.50, 150.82, 139.00, 137.49, 132.84, 128.87, 128.61, 41.38, 39.06, 34.04 (t, J = 21.0 Hz), 29.62, 16.98. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -80.98 – -81.24 (m), -111.01 – -115.27 (m), -124.37 – -124.58 (m), -125.79 – -126.05 (m).

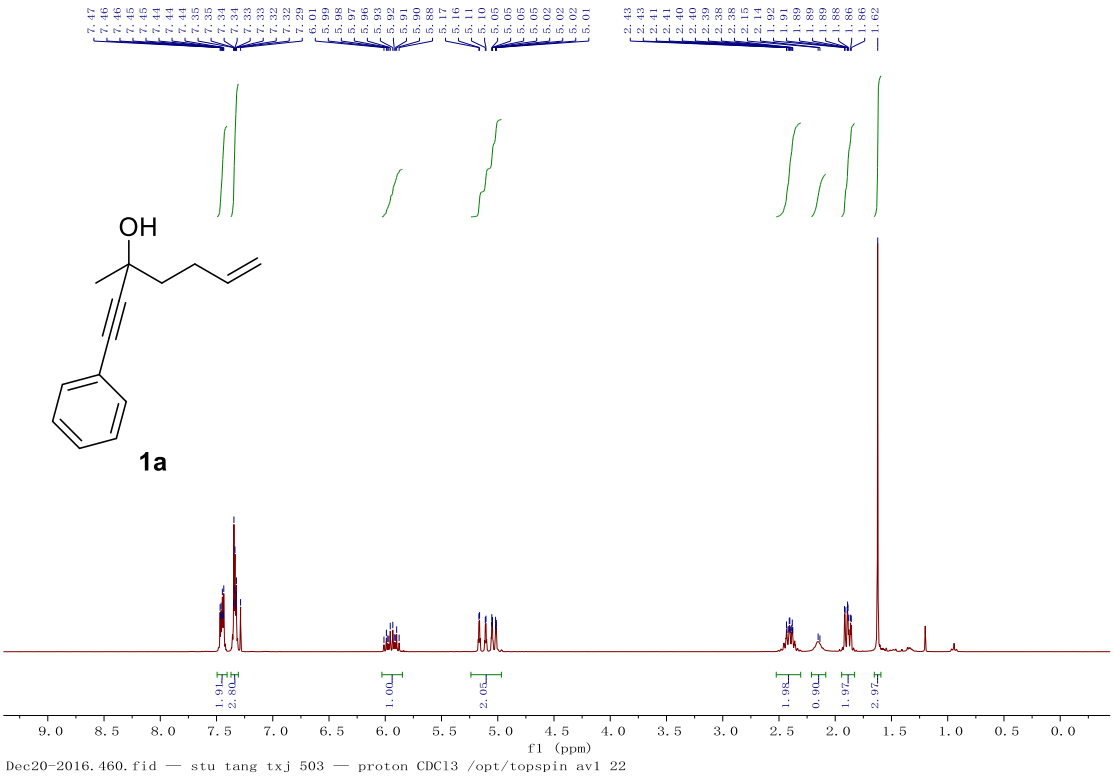
5. References:

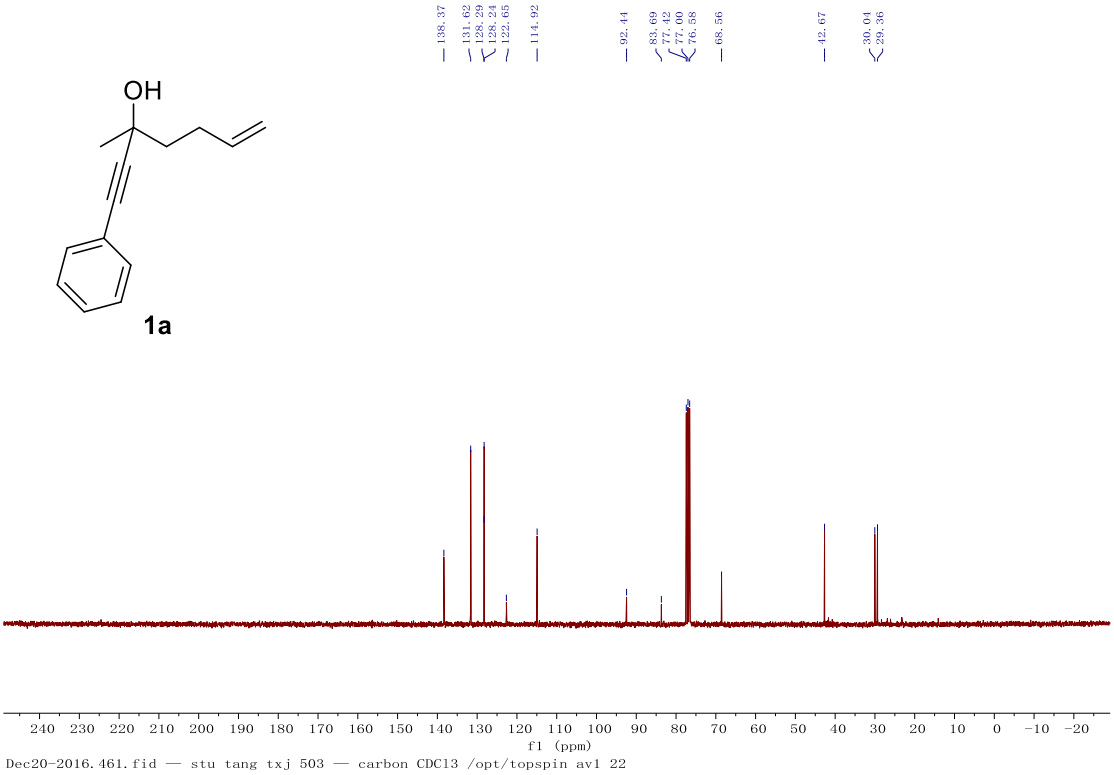
(1) G. A. Phillips, C. Palmer, A. C. Stevens, M. L. Piotrowski, D. S. R. Dekruyf, B. L. Pagenkopf, *Tetrahedron Letter* **2015**, *56*, 6052-6055.

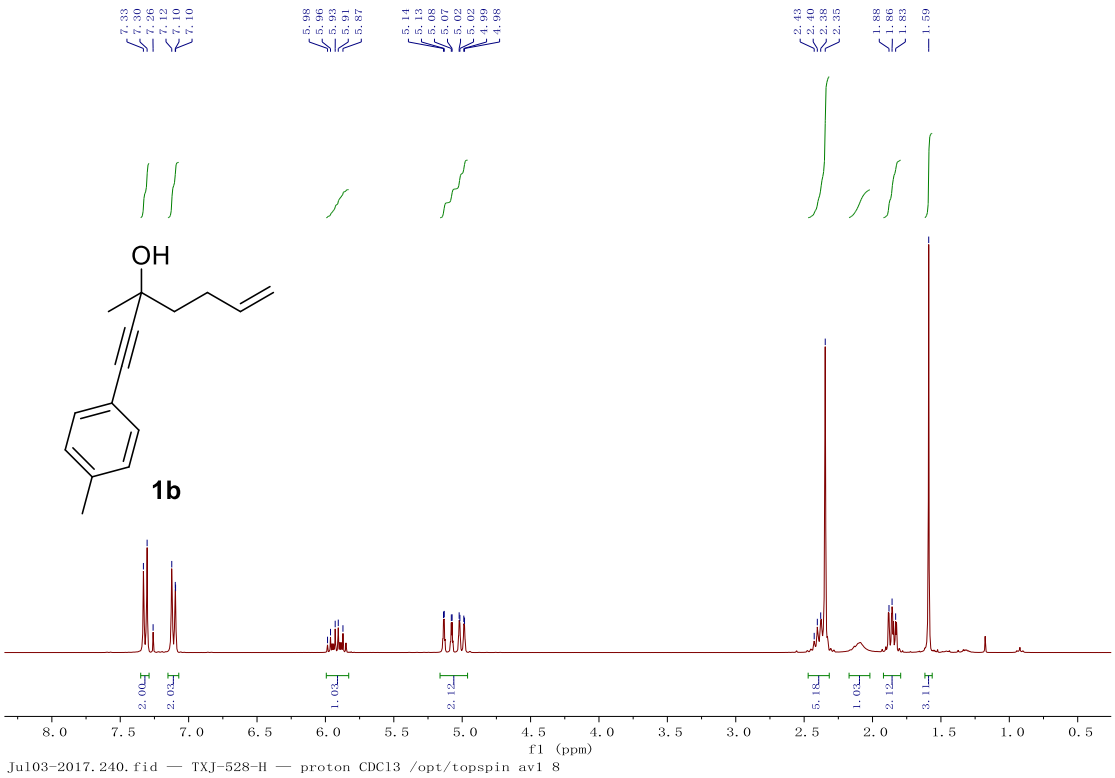
(2) P. G. Cozzi, S. Alesi, *Chem. Commun.* **2004**, 2448-2449.

(3) T. Jin, F. Yang, C. Liu, Y. Yamamoto, *Chem. Commun*. **2009**, 3533-3535.

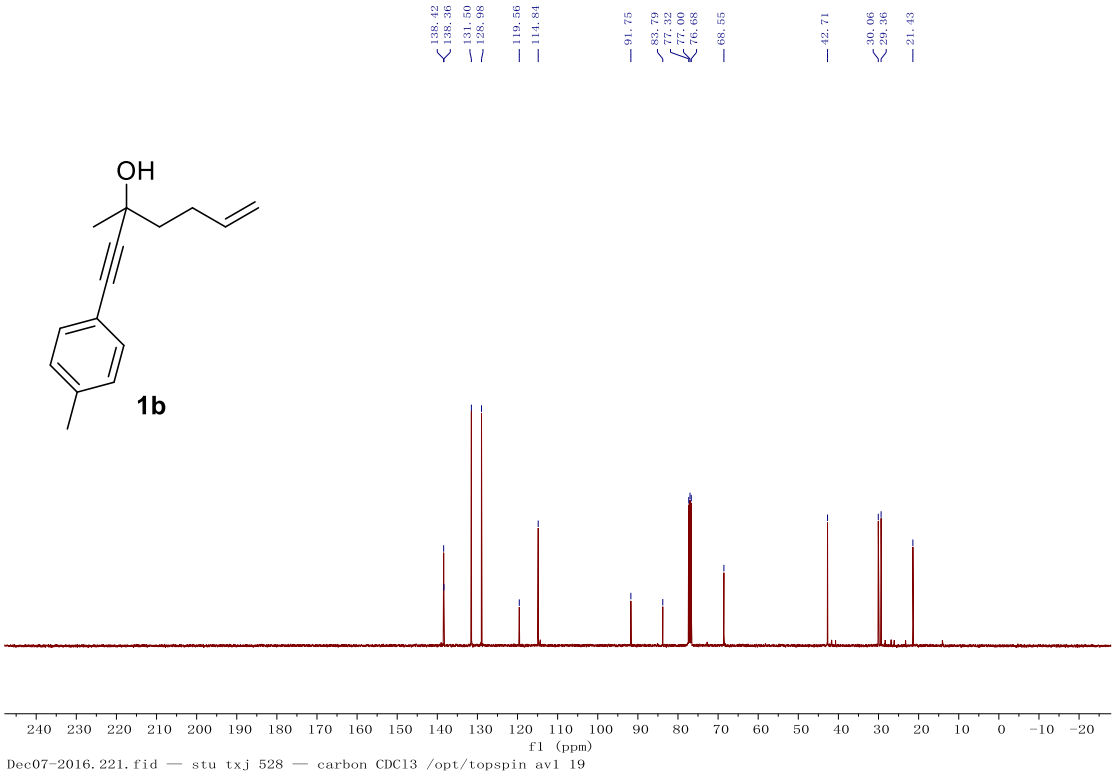
(4) T. Jin, Y. Yamamoto, *Org. Lett.* **2007**, *9*, 5259-5262.







Jul03-2017.240.fid — TXJ-528-H — proton CDCl3 /opt/topspin av1 8



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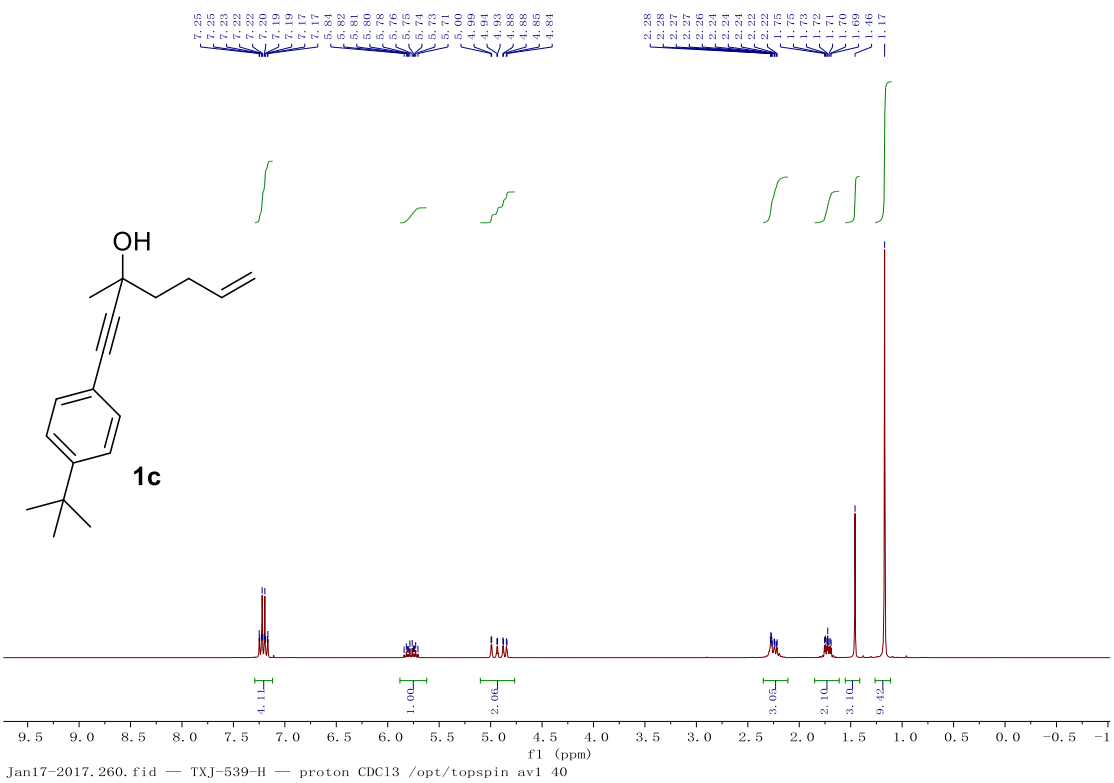
OH
1c
f1 (ppm)
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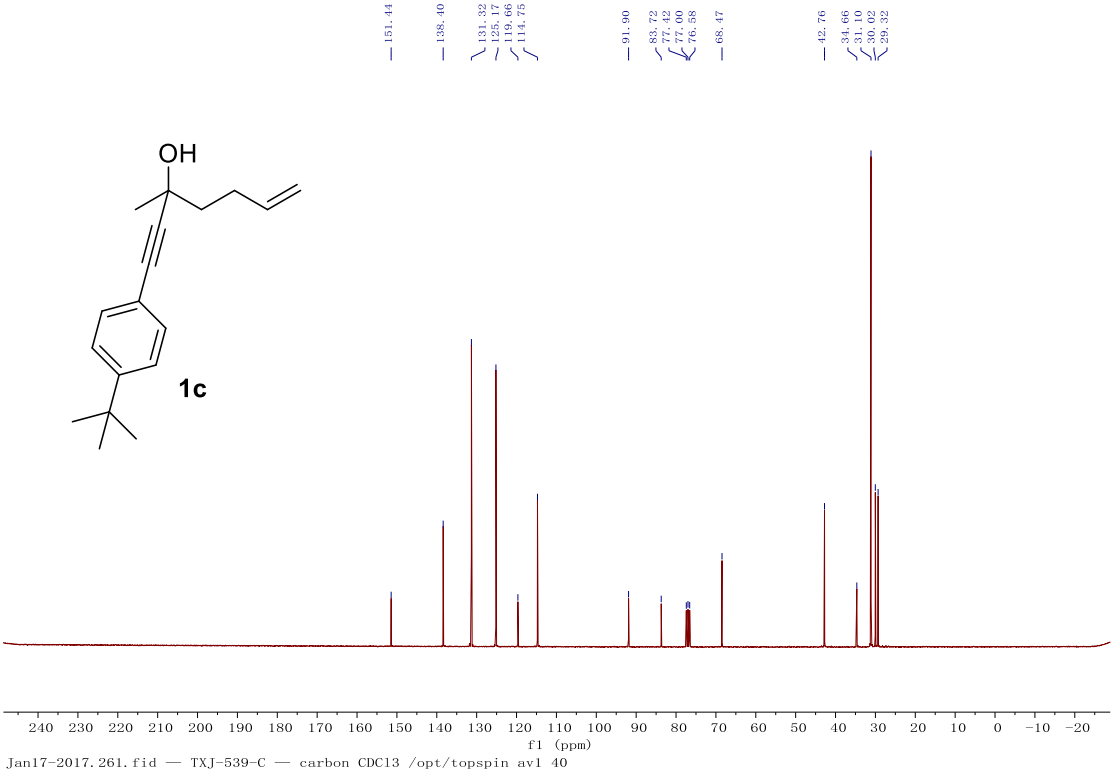
OH
1c
f1 (ppm)
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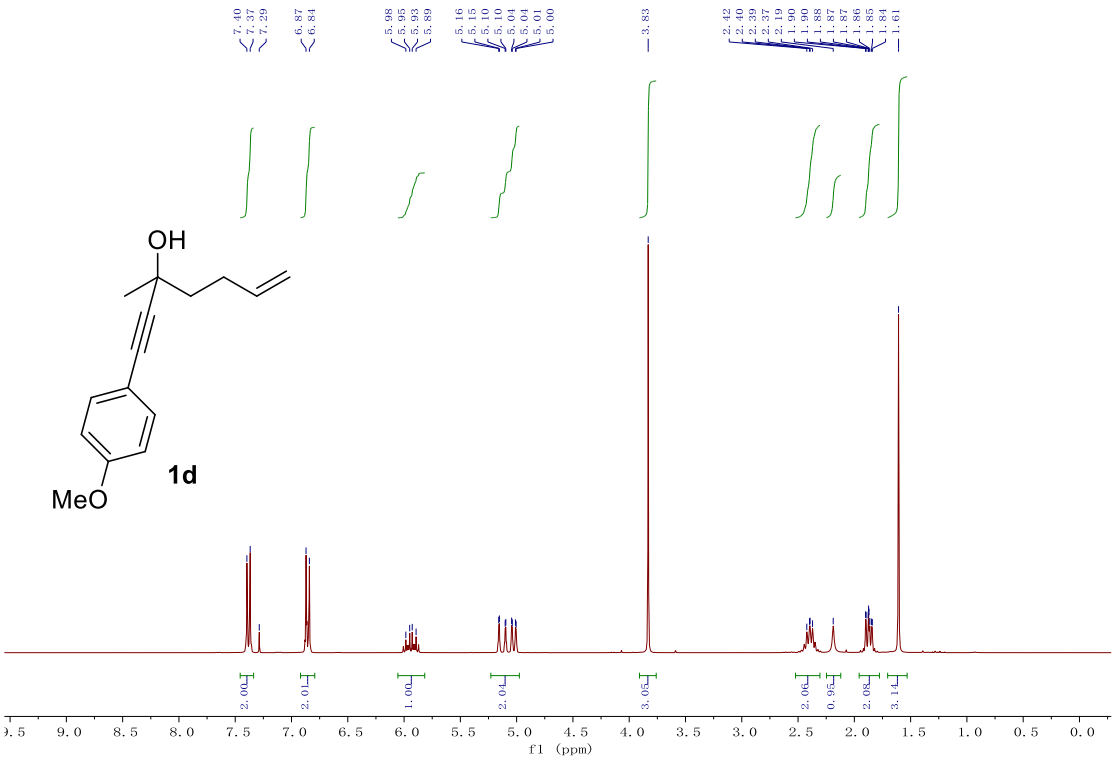

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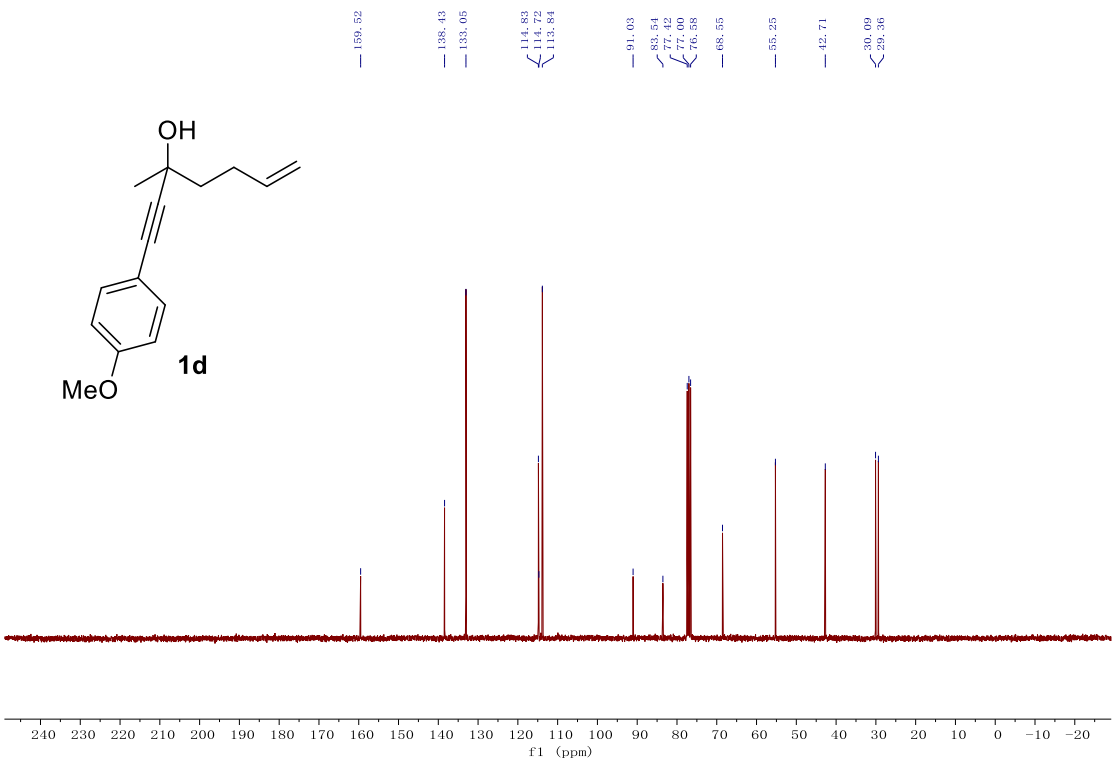

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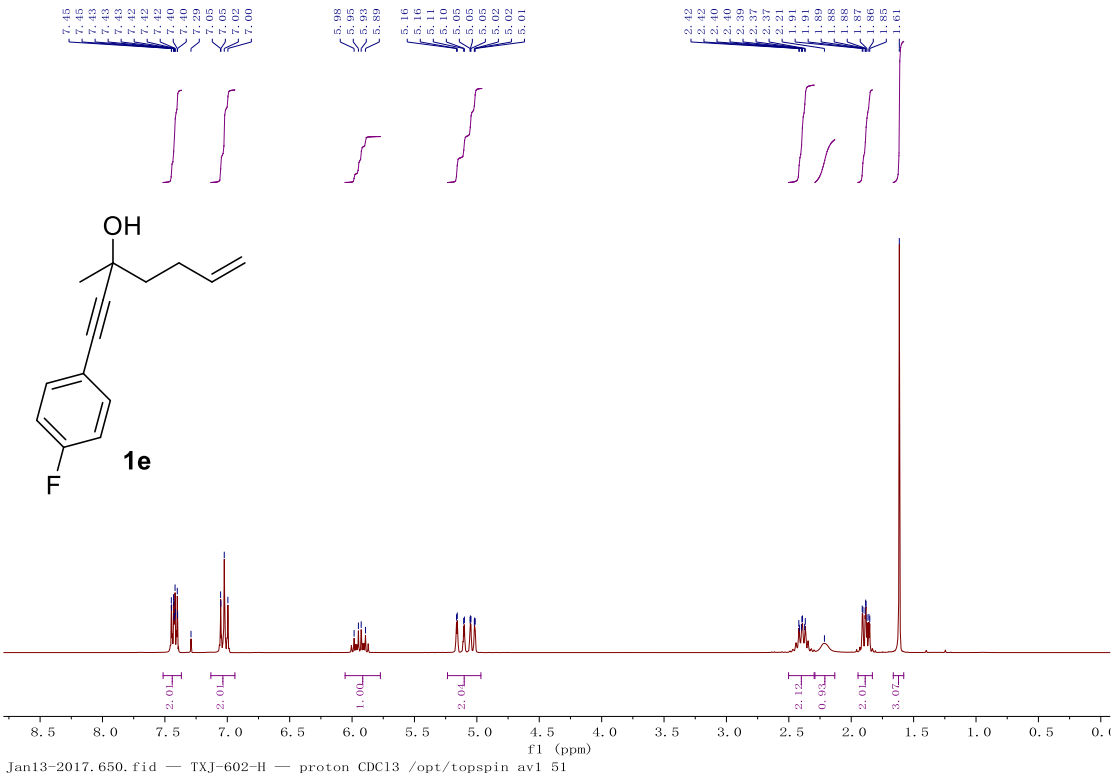
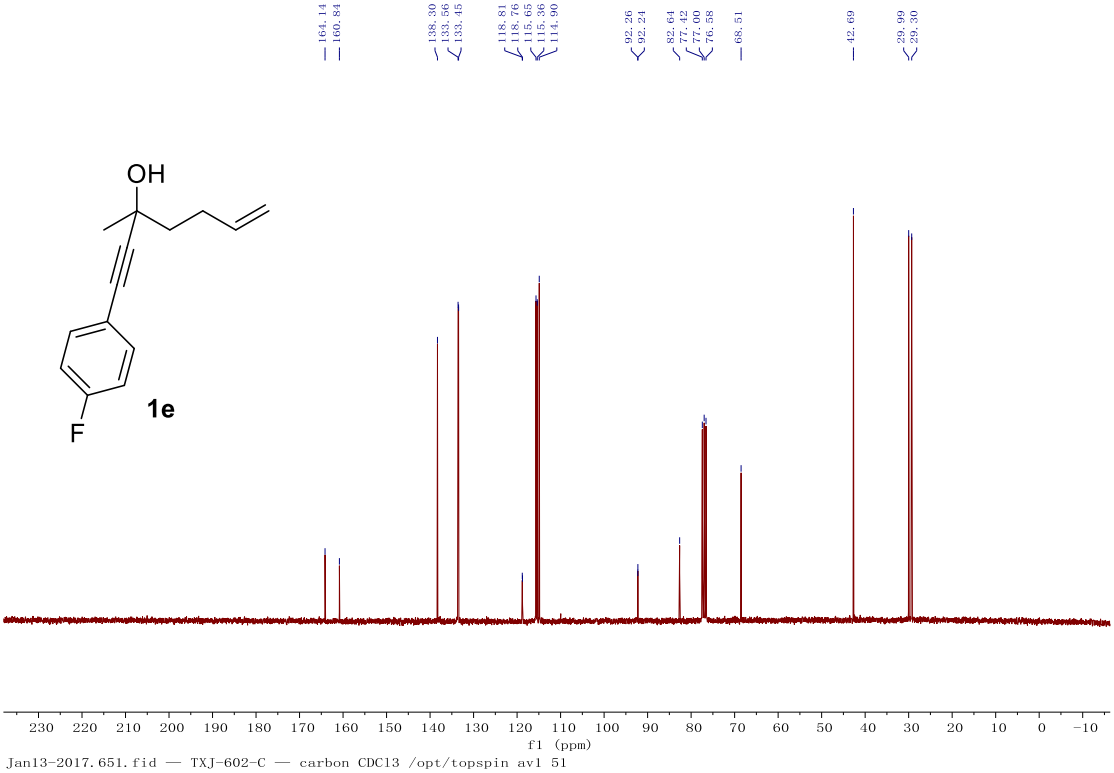
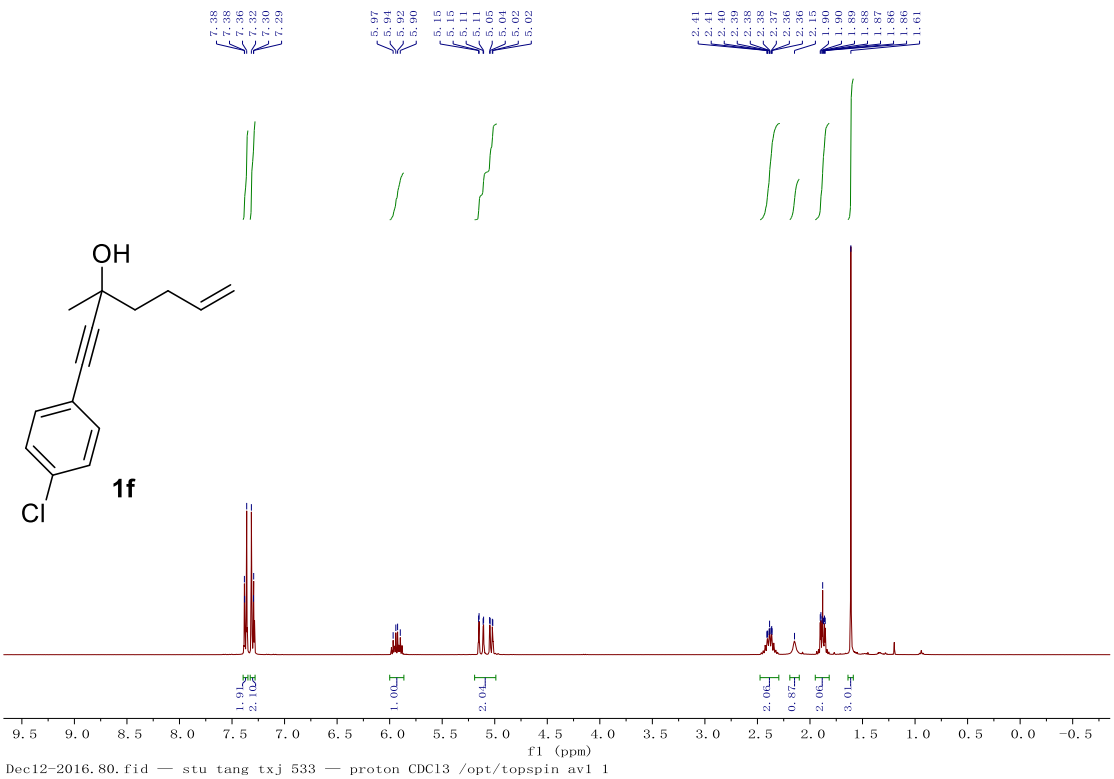
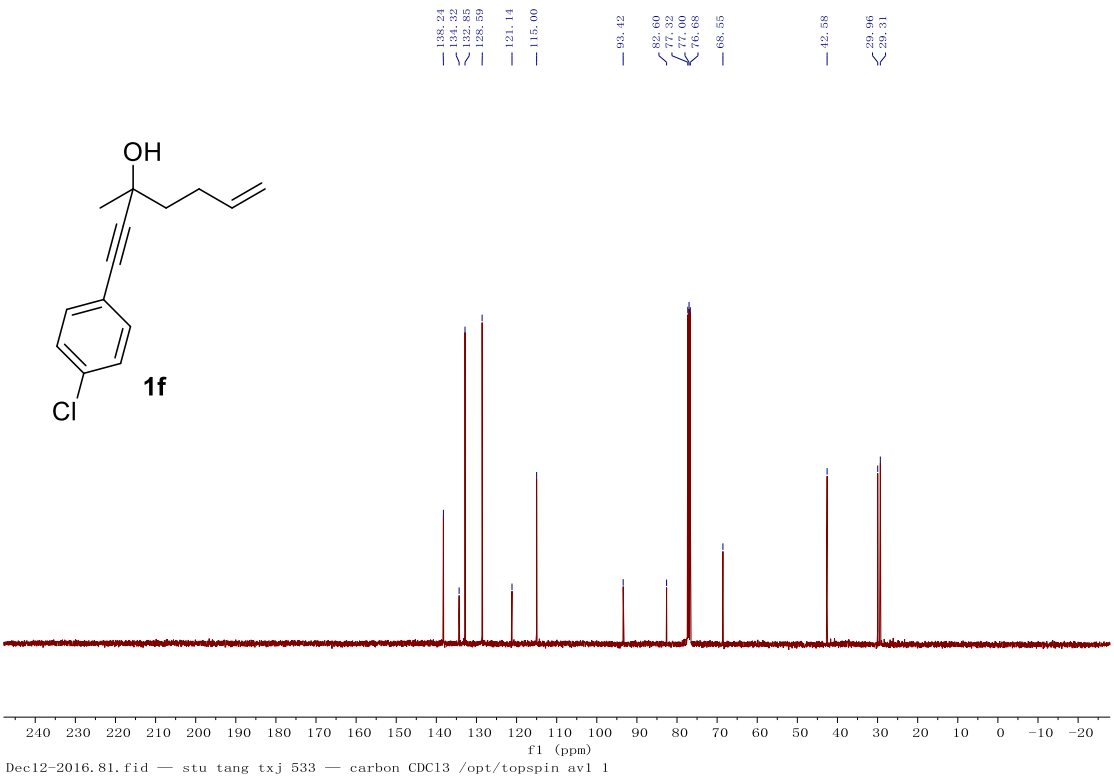


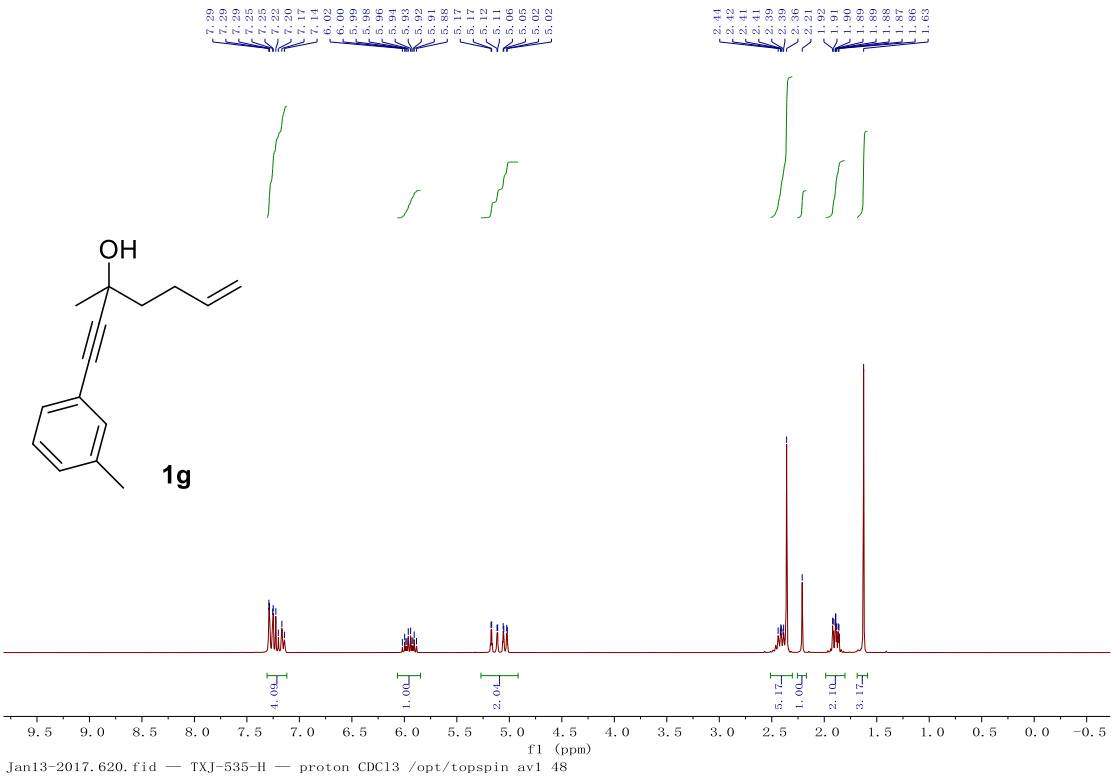
Jan13-2017.650.fid — TXJ-602-H — proton CDCl3 /opt/topspin av1 51

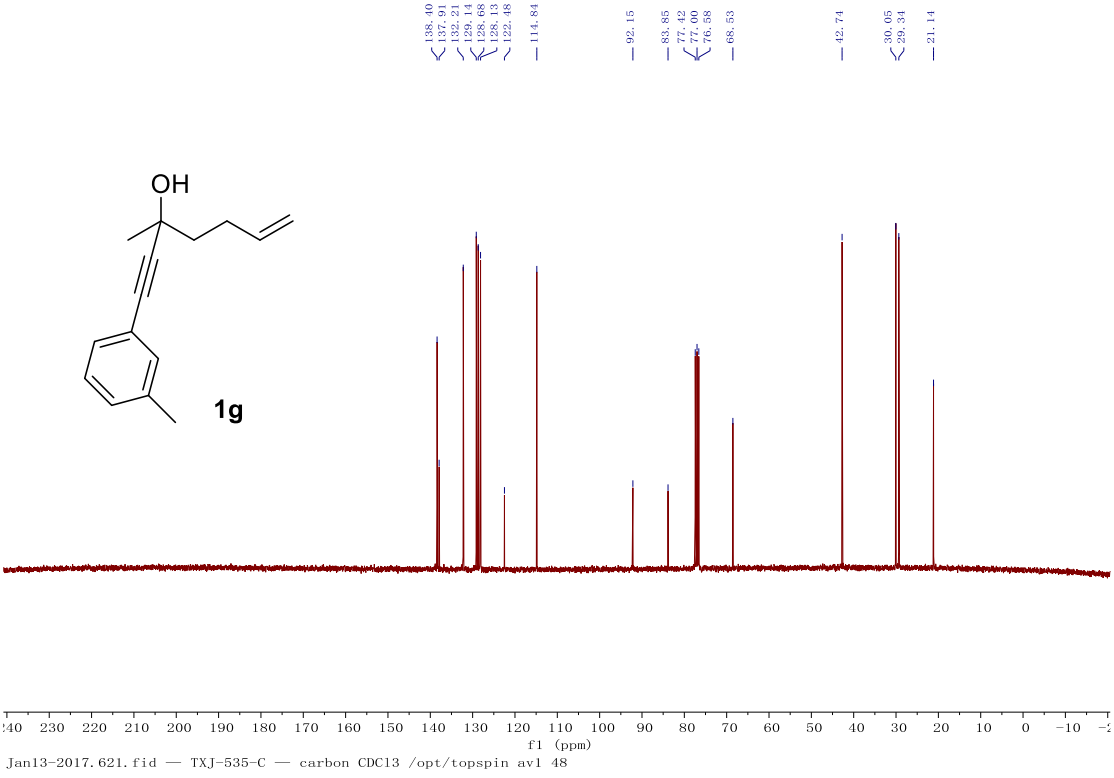


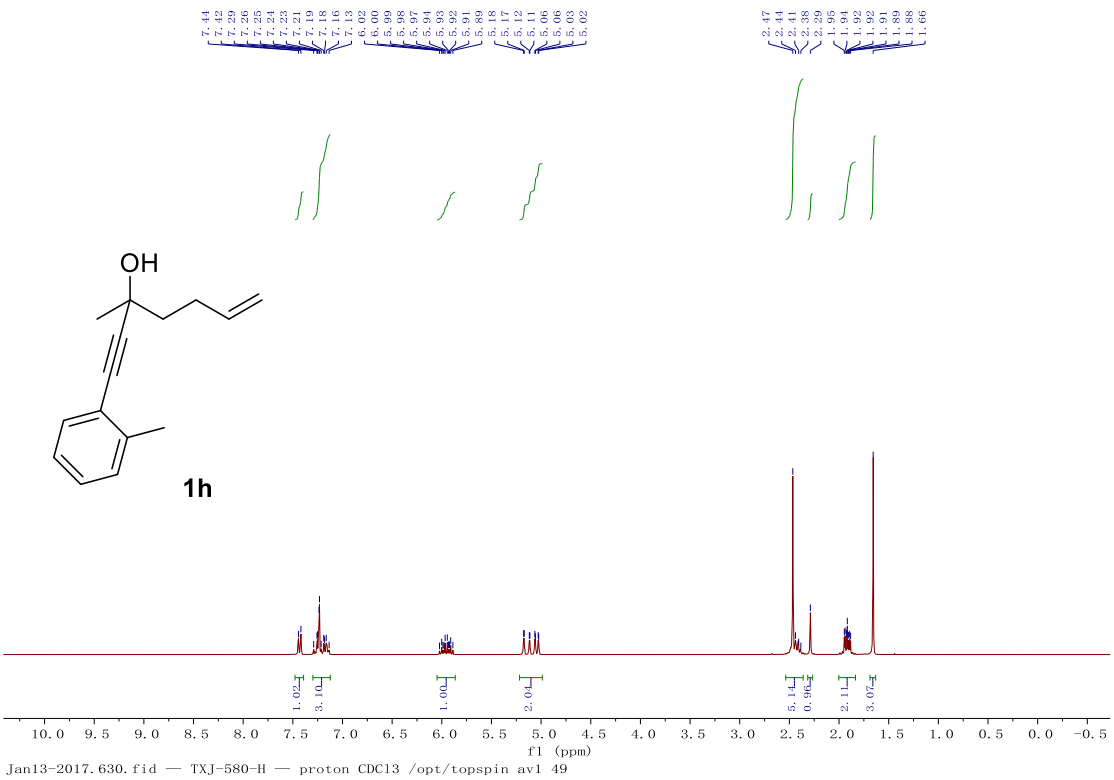
Jan13-2017.651.fid — TXJ-602-C — carbon CDCl3 /opt/topspin av1 51

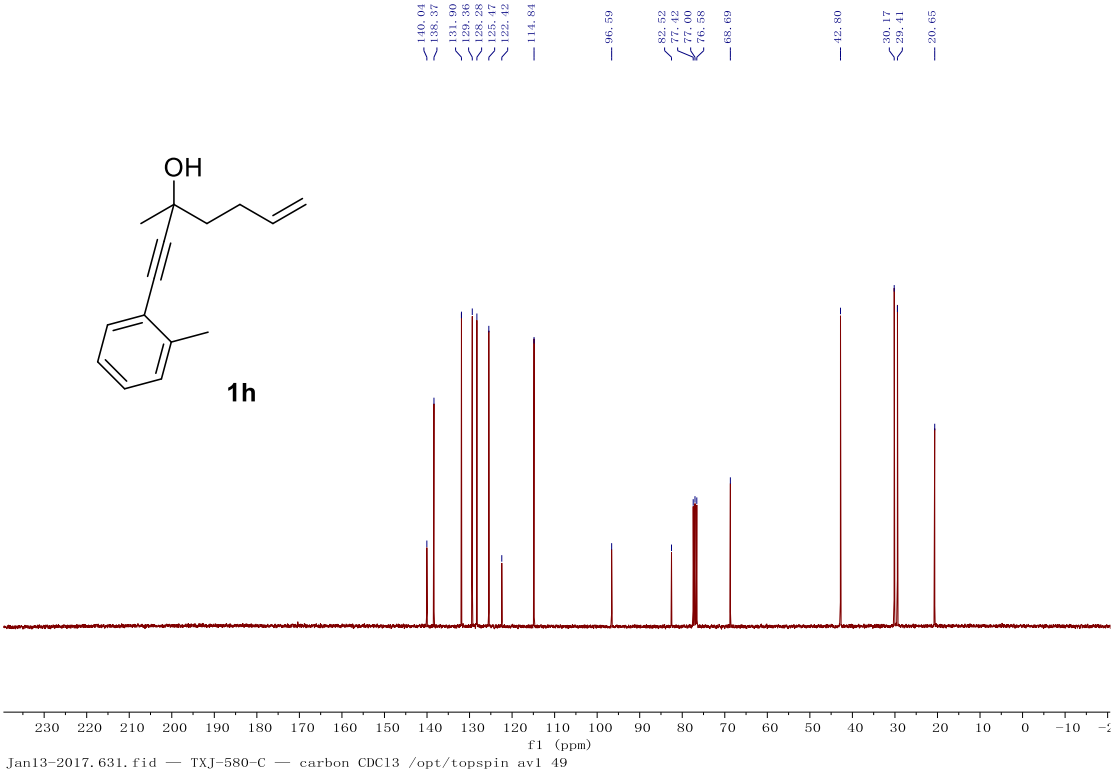

7.38
7.38
7.36
7.32
7.30
7.29
5.97
5.94
5.92
5.90
5.15
5.15
5.11
5.11
5.05
5.04
5.02
5.02
2.41
2.41
2.40
2.39
2.38
2.38
2.37
2.36
2.36
2.15
1.90
1.89
1.88
1.87
1.86
1.86
1.61
OH
1f
Cl
1.91
2.10
1.00
2.04
2.06
0.87
2.06
3.01
f1 (ppm)
Dec12-2016.80.fid — stu tang txj 533 — proton CDCl3 /opt/topspin av1 1

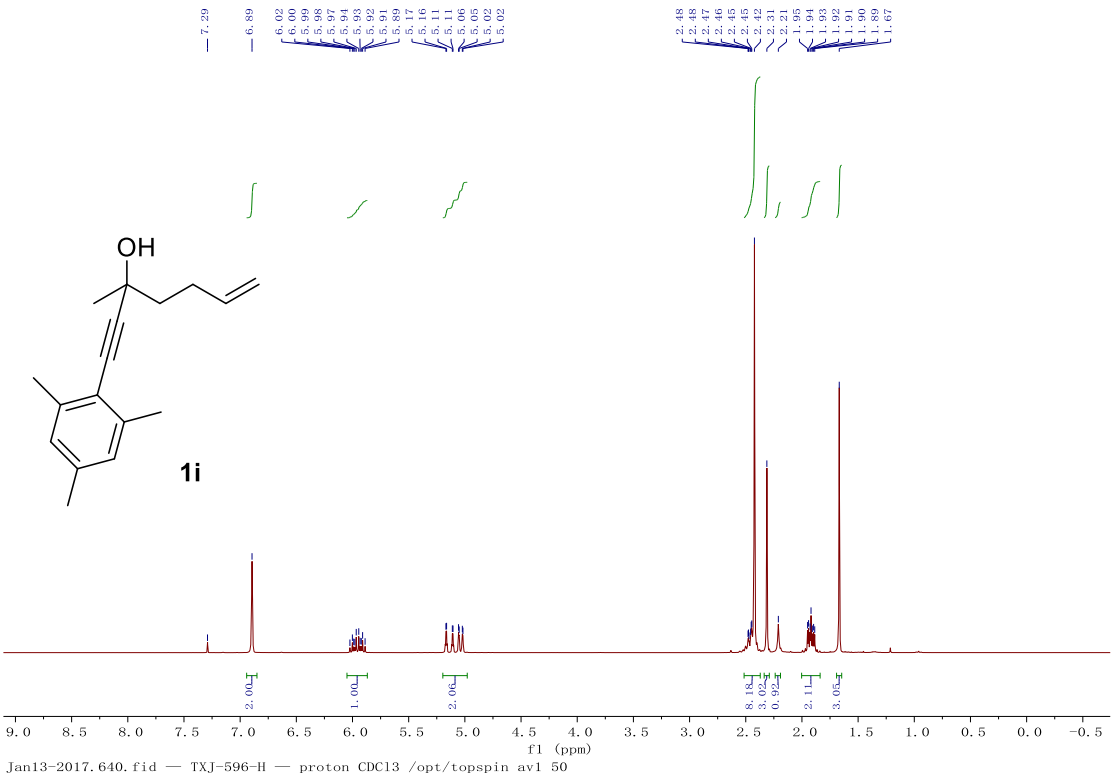

138.24
134.32
132.85
128.59
121.14
115.00
93.42
82.60
77.32
77.00
76.68
68.55
42.58
29.96
29.31
OH
1f
Cl
f1 (ppm)
Dec12-2016.81.fid — stu tang txj 533 — carbon CDCl3 /opt/topspin av1 1

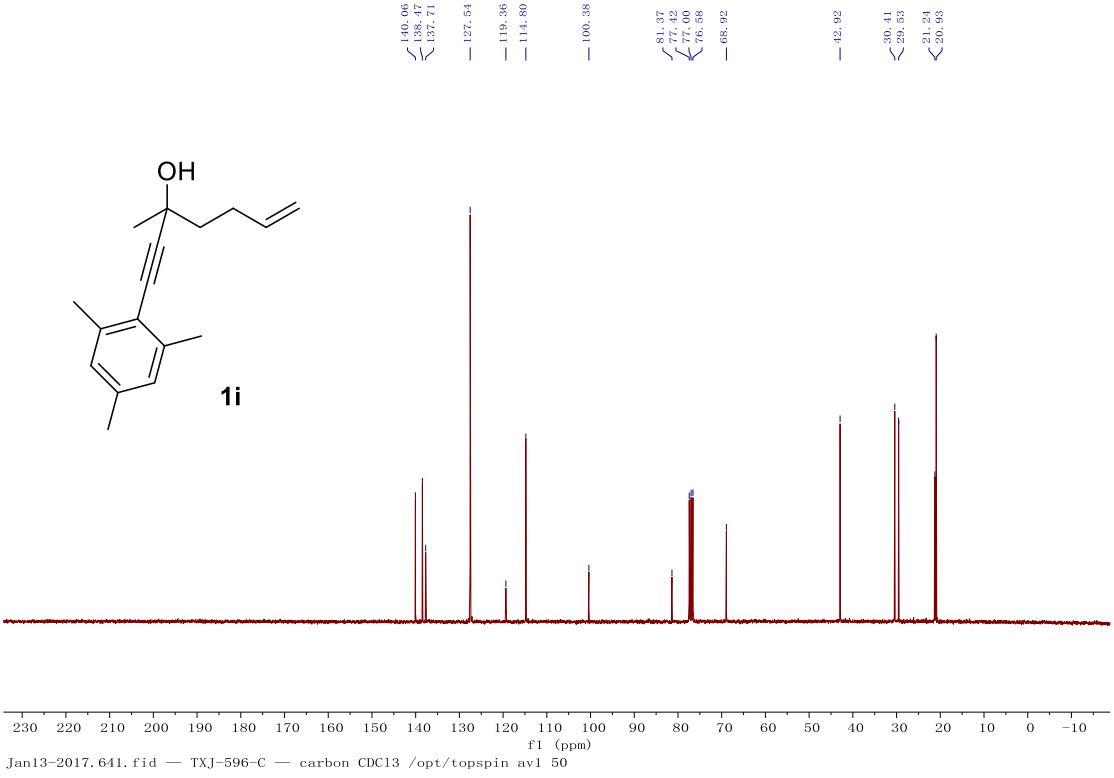

OH
1g
f1 (ppm)
Jan13-2017.620.fid — TXJ-535-H — proton CDCl3 /opt/topspin av1 48

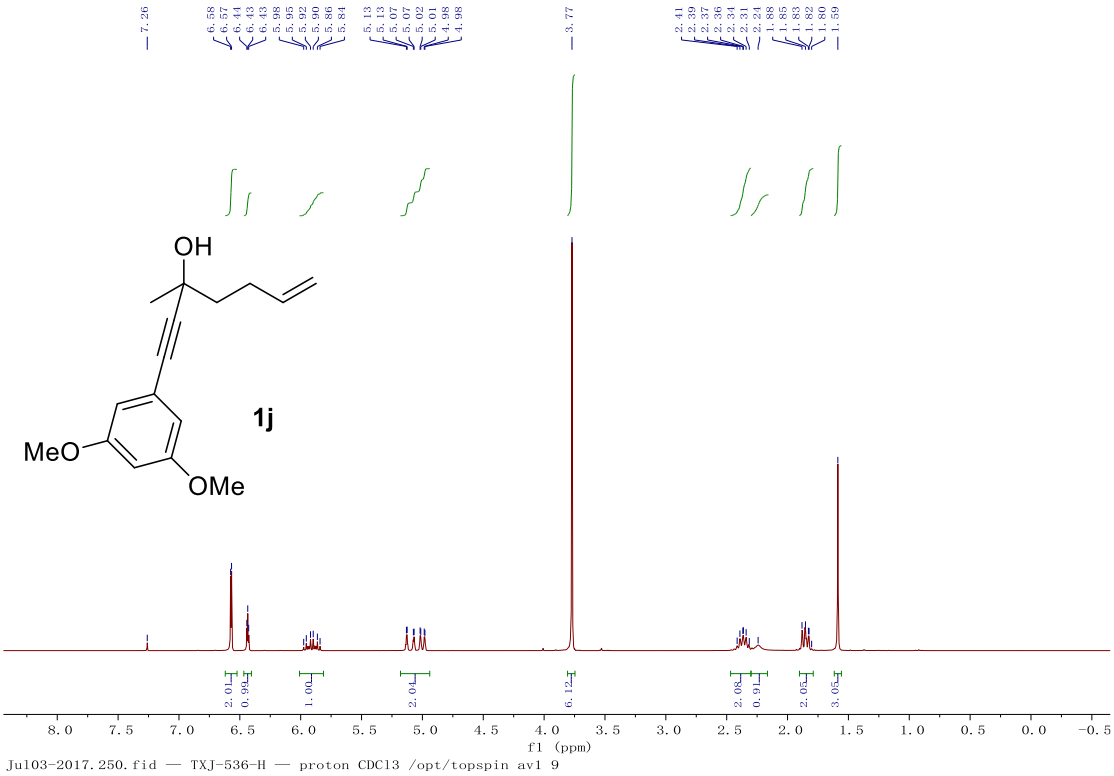

OH
1g
f1 (ppm)
Jan13-2017.621.fid — TXJ-535-C — carbon CDCl3 /opt/topspin av1 48


OH
1h
7.44 7.42 7.29 7.26 7.25 7.24 7.23 7.21 7.19 7.18 7.15 7.13 6.02 6.00 5.99 5.98 5.97 5.94 5.93 5.92 5.91 5.89 5.18 5.17 5.12 5.11 5.06 5.03 5.02
2.47 2.44 2.41 2.38 2.29 1.95 1.94 1.92 1.92 1.91 1.89 1.88 1.66
1.02 3.10 1.00 2.04 5.14 0.96 2.11 3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
Jan13-2017.630.fid — TXJ-580-H — proton CDCl3 /opt/topspin av1 49

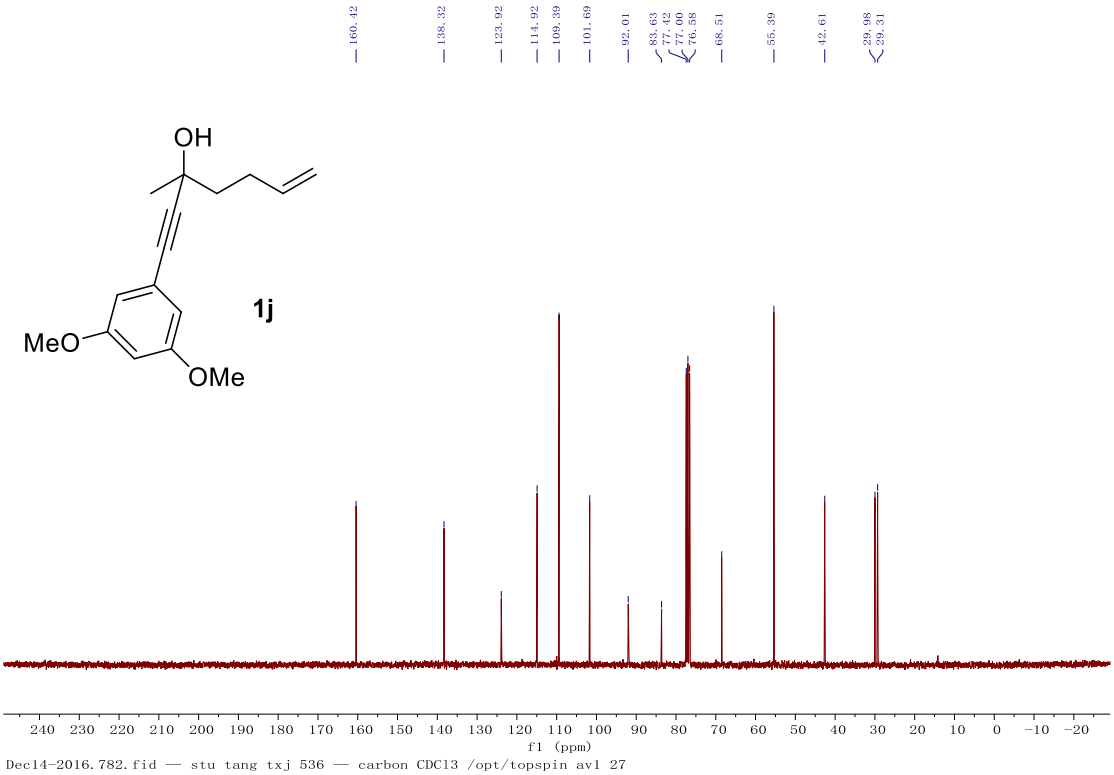

OH
1h
140.04 138.37 131.90 129.36 128.28 125.47 122.42 114.84 96.59 82.52 77.42 77.00 76.58 68.69 42.80 30.17 29.41 20.65
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
Jan13-2017.631.fid — TXJ-580-C — carbon CDCl3 /opt/topspin av1 49


OH
1i
7.29
6.89
6.02
6.00
5.99
5.98
5.97
5.94
5.93
5.92
5.91
5.89
5.17
5.16
5.11
5.11
5.06
5.05
5.02
5.02
2.48
2.48
2.47
2.46
2.45
2.45
2.42
2.31
2.21
1.95
1.94
1.93
1.92
1.91
1.90
1.89
1.67
2.00
1.00
2.06
8.18
3.02
0.92
2.11
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
Jan13-2017.640.fid — TXJ-596-H — proton CDCl3 /opt/topspin av1 50

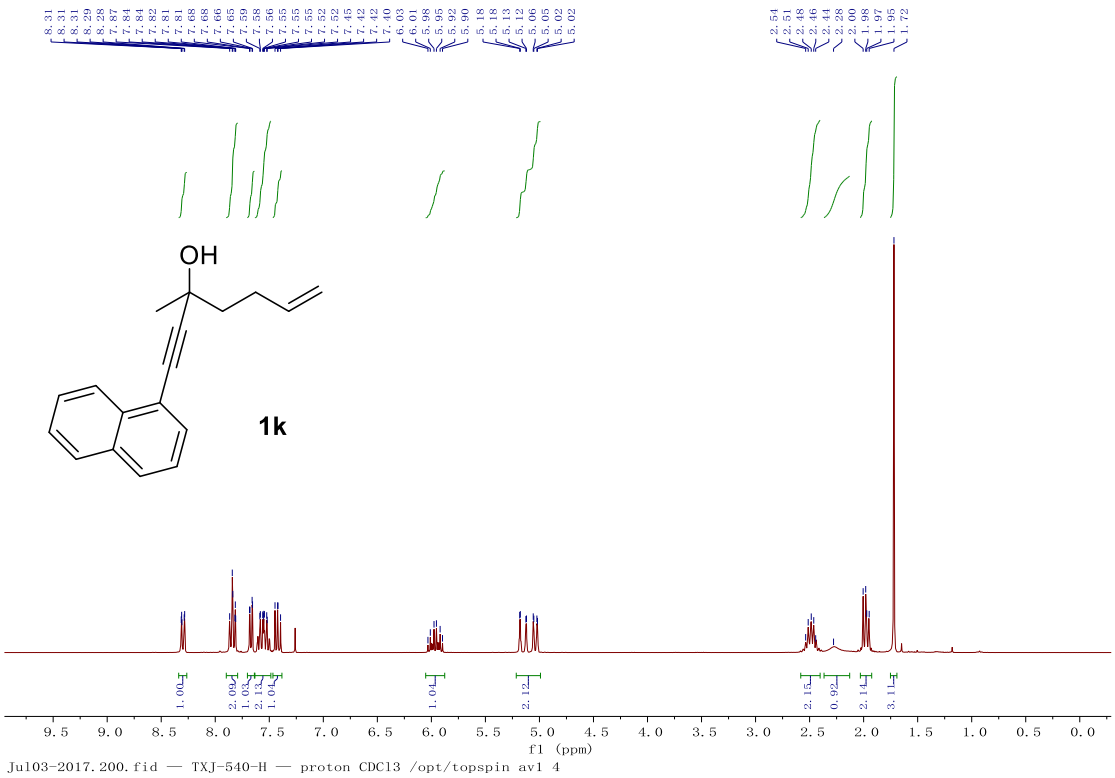

140.06
138.47
137.71
127.54
119.36
114.80
100.38
81.37
77.42
77.00
76.58
68.92
42.92
30.41
29.53
21.24
20.93
OH
1i
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
Jan13-2017.641.fid — TXJ-596-C — carbon CDCl3 /opt/topspin av1 50



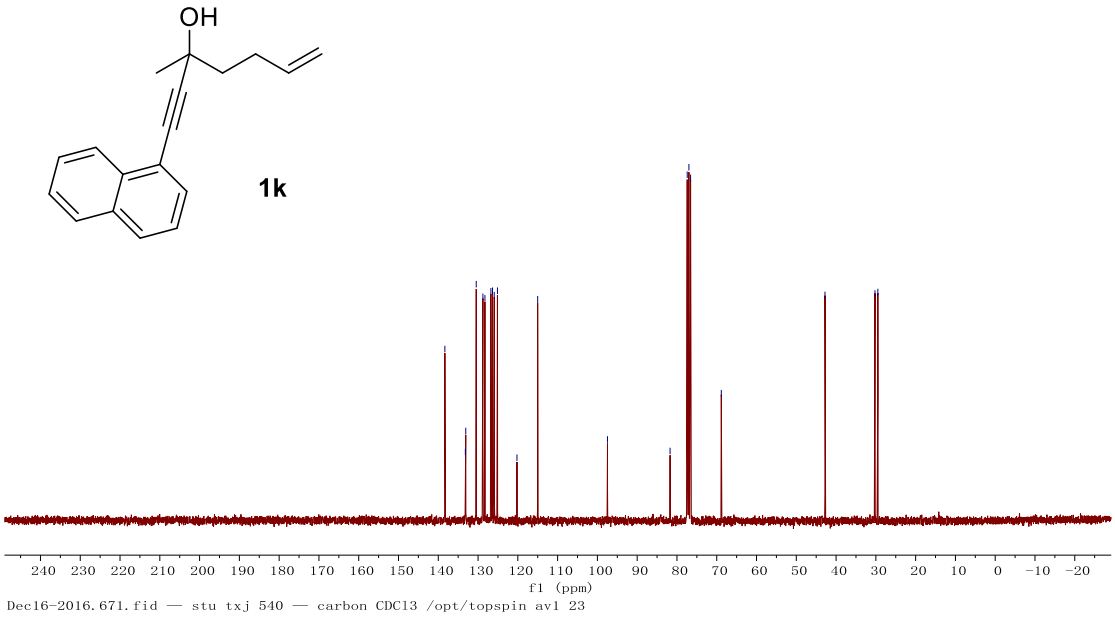
Jul03-2017.250.fid — TXJ-536-H — proton CDCl3 /opt/topspin av1 9



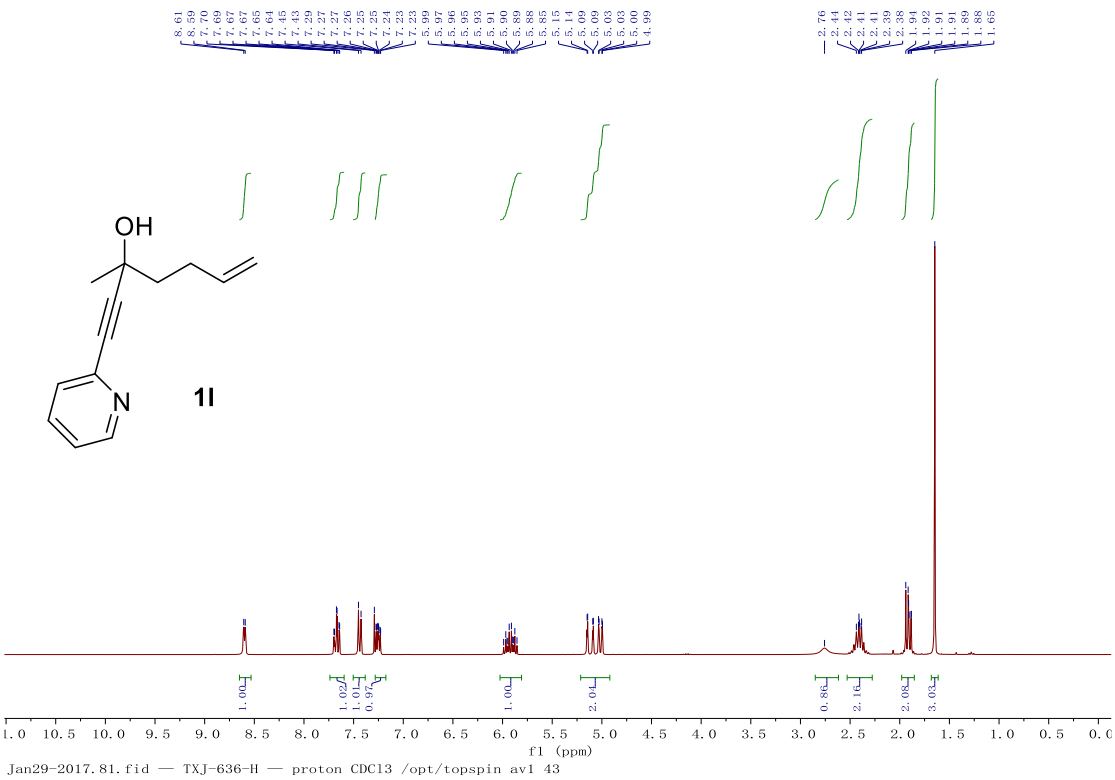
Dec14-2016.782.fid — stu tang txj 536 — carbon CDCl3 /opt/topspin av1 27

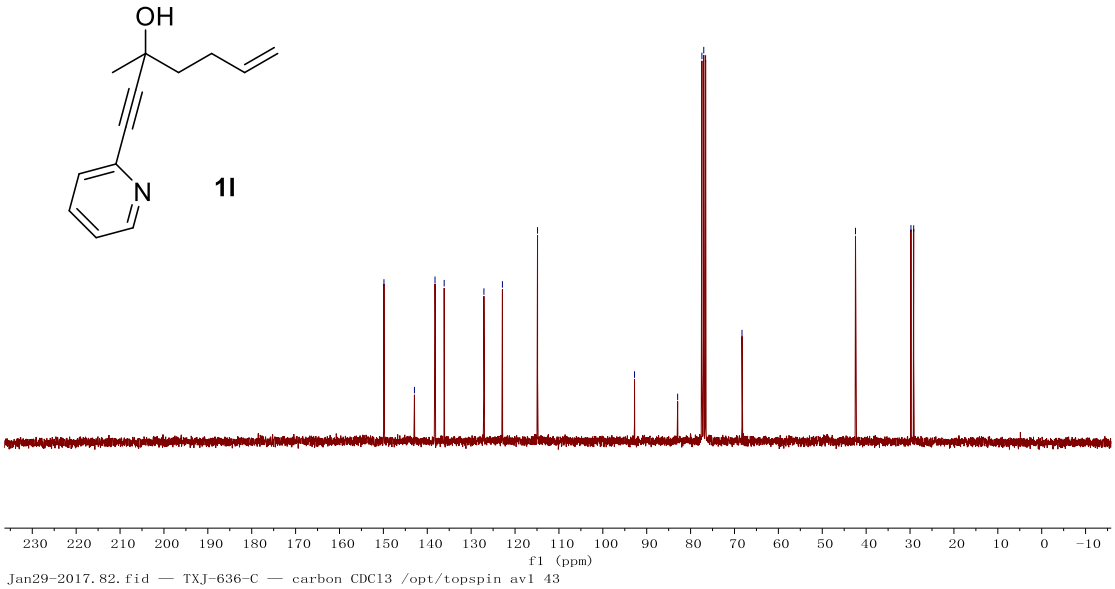


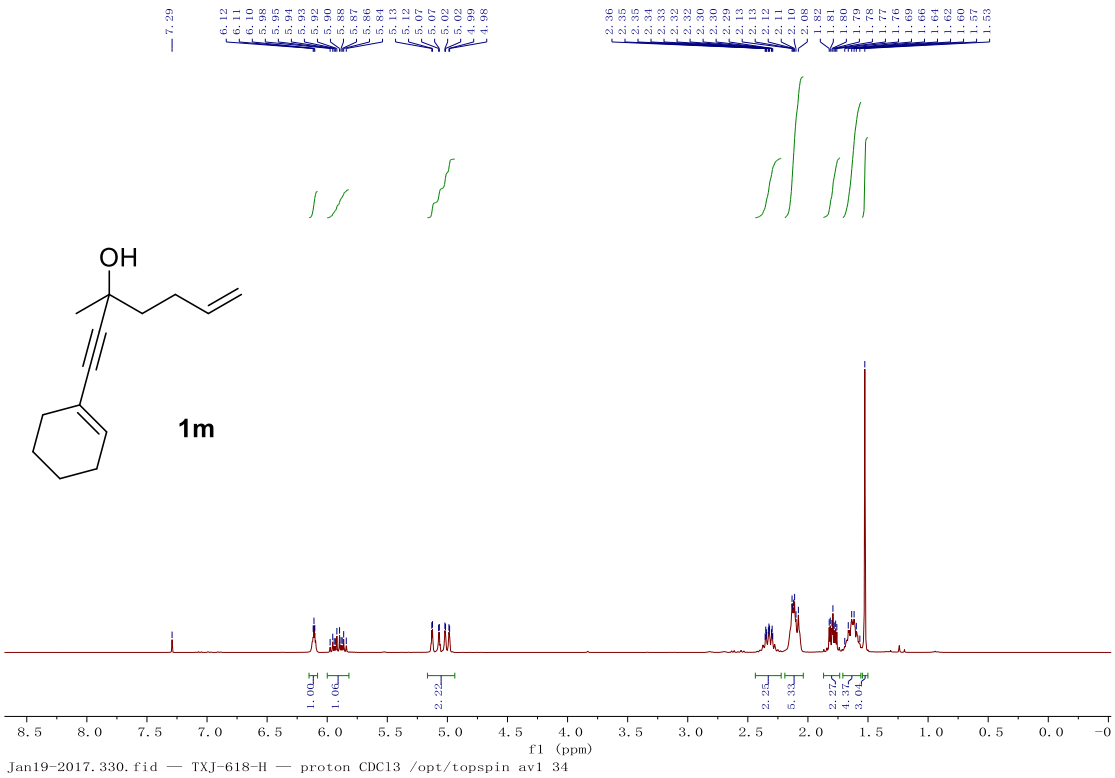
Jul03-2017.200.fid — TXJ-540-H — proton CDCl3 /opt/topspin av1 4

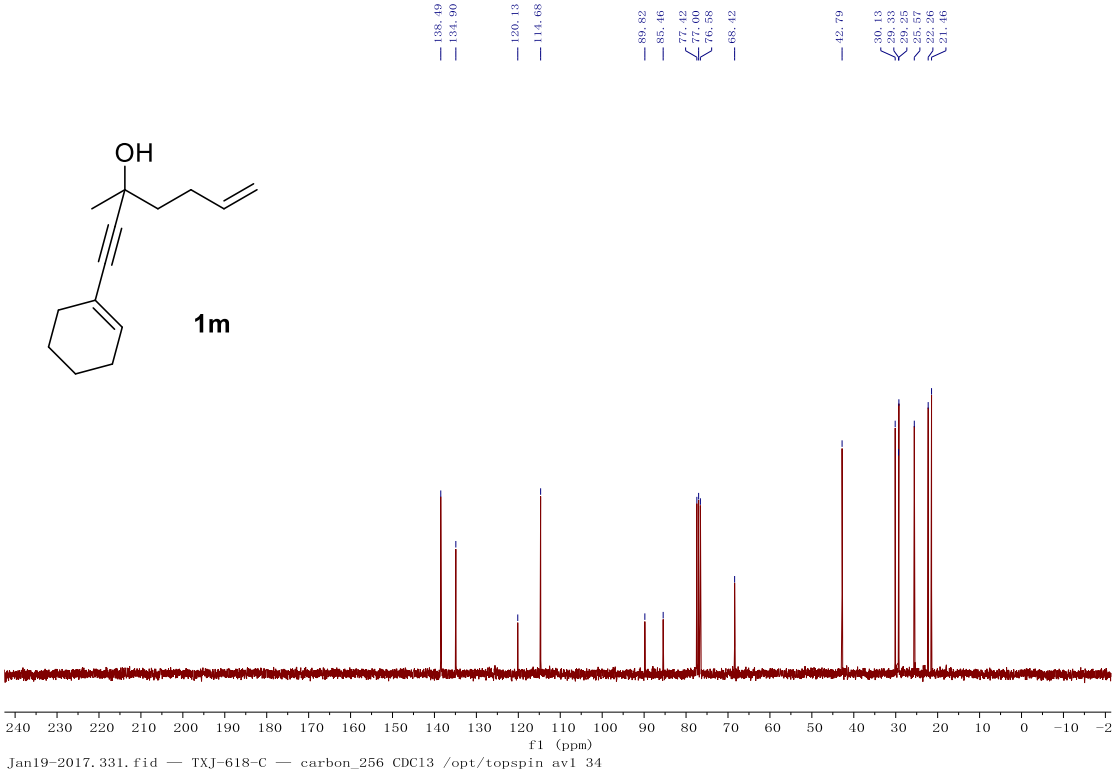


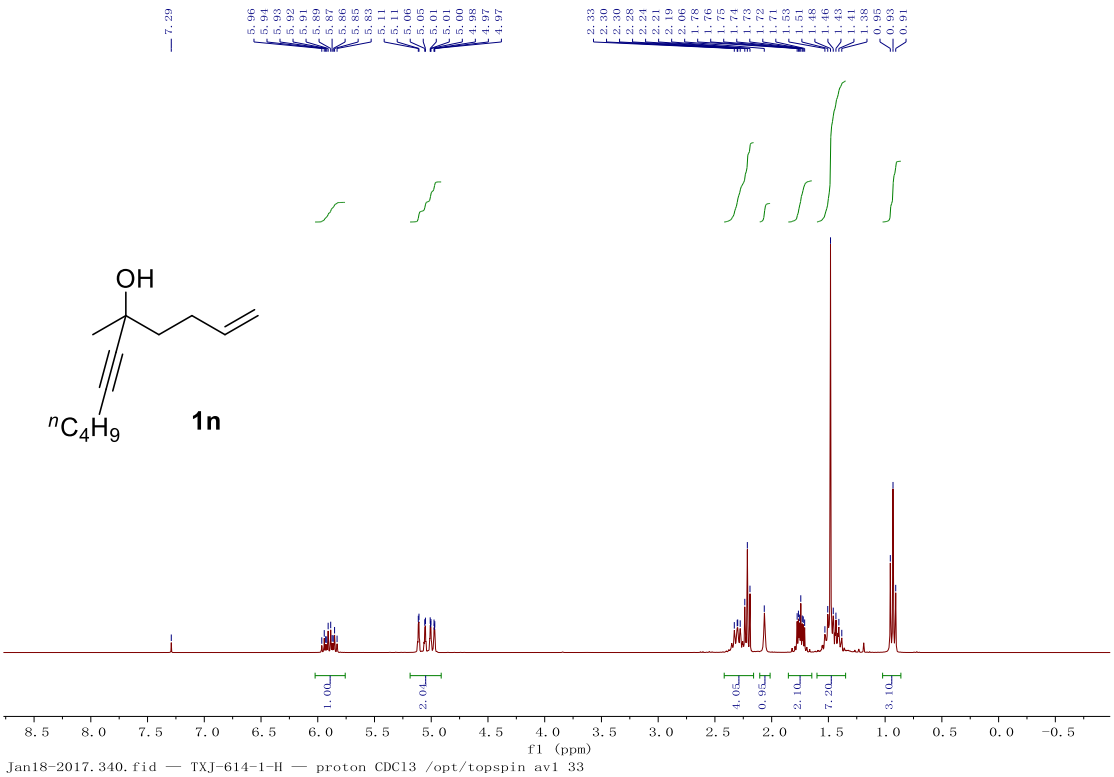
Dec16-2016.671.fid — stu txj 540 — carbon CDCl3 /opt/topspin av1 23

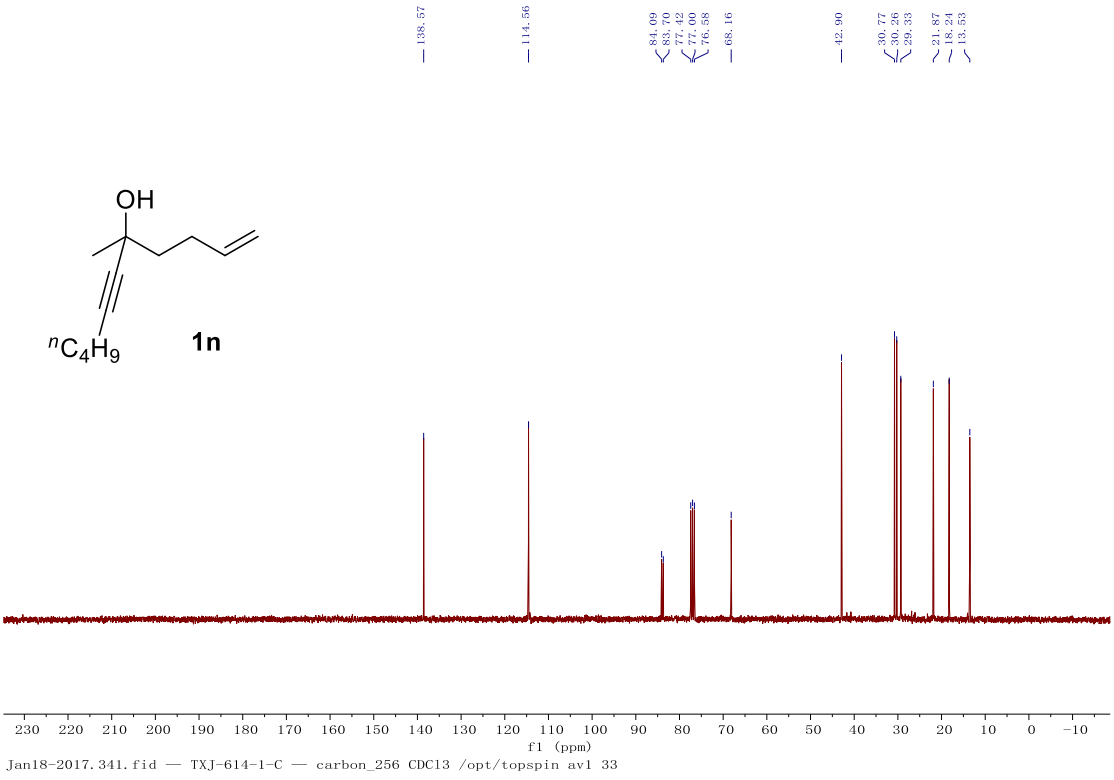

OH
N
1l
f1 (ppm)
Jan29-2017.81.fid — TXJ-636-H — proton CDCl3 /opt/topspin av1 43

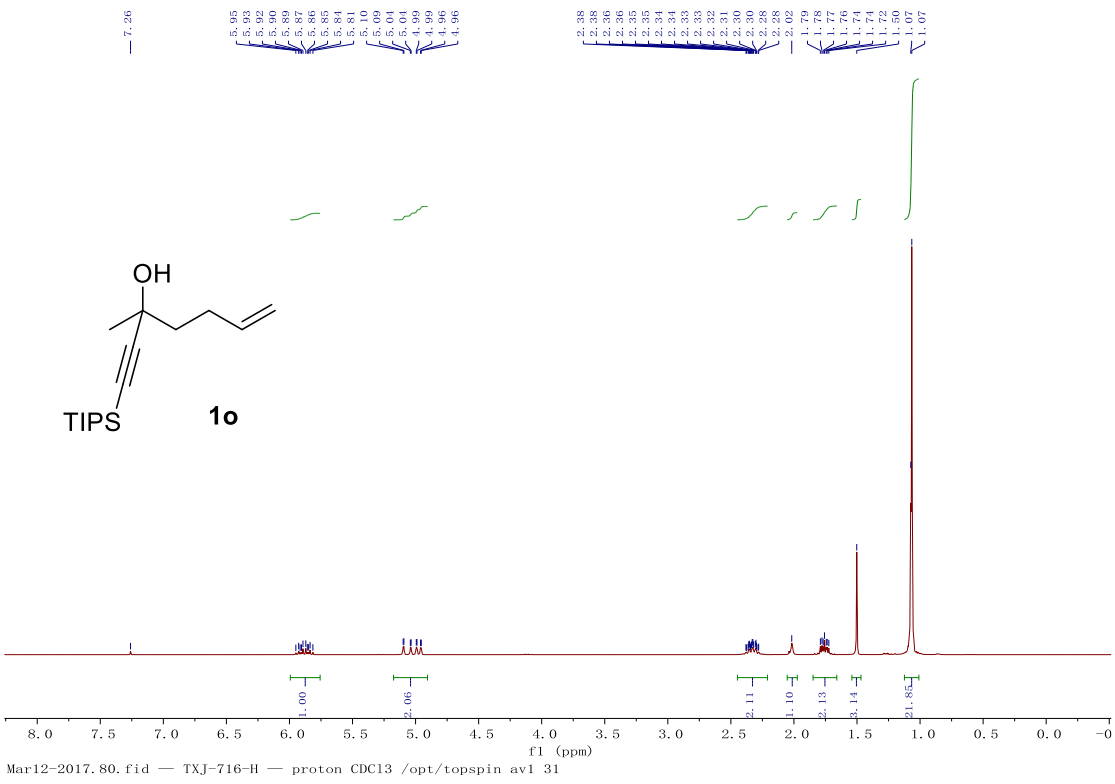

OH
N
1l
f1 (ppm)
Jan29-2017.82.fid — TXJ-636-C — carbon CDCl3 /opt/topspin av1 43

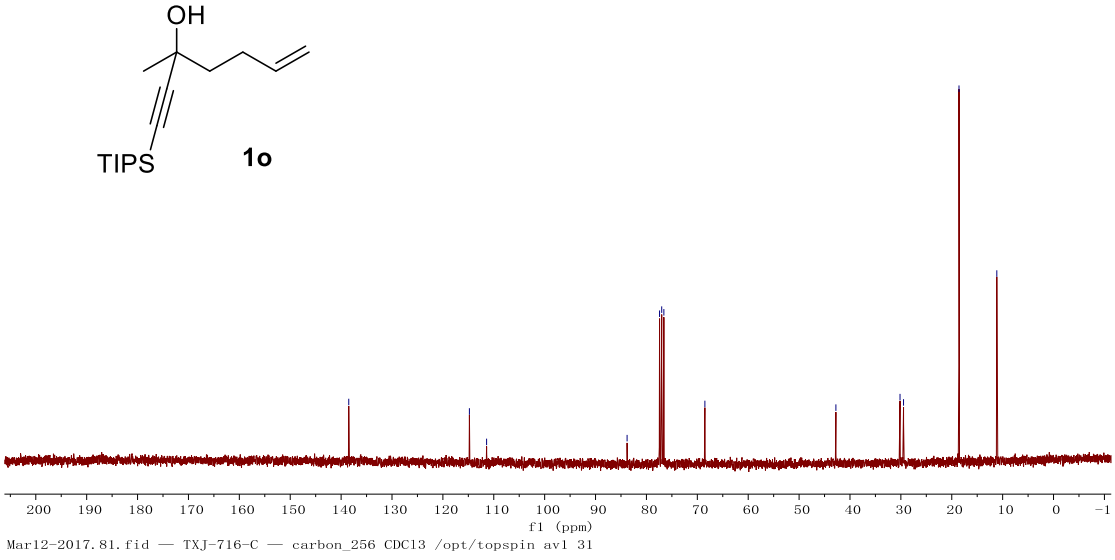

OH
1m
f1 (ppm)
Jan19-2017.330.fid — TXJ-618-H — proton CDCl3 /opt/topspin av1 34

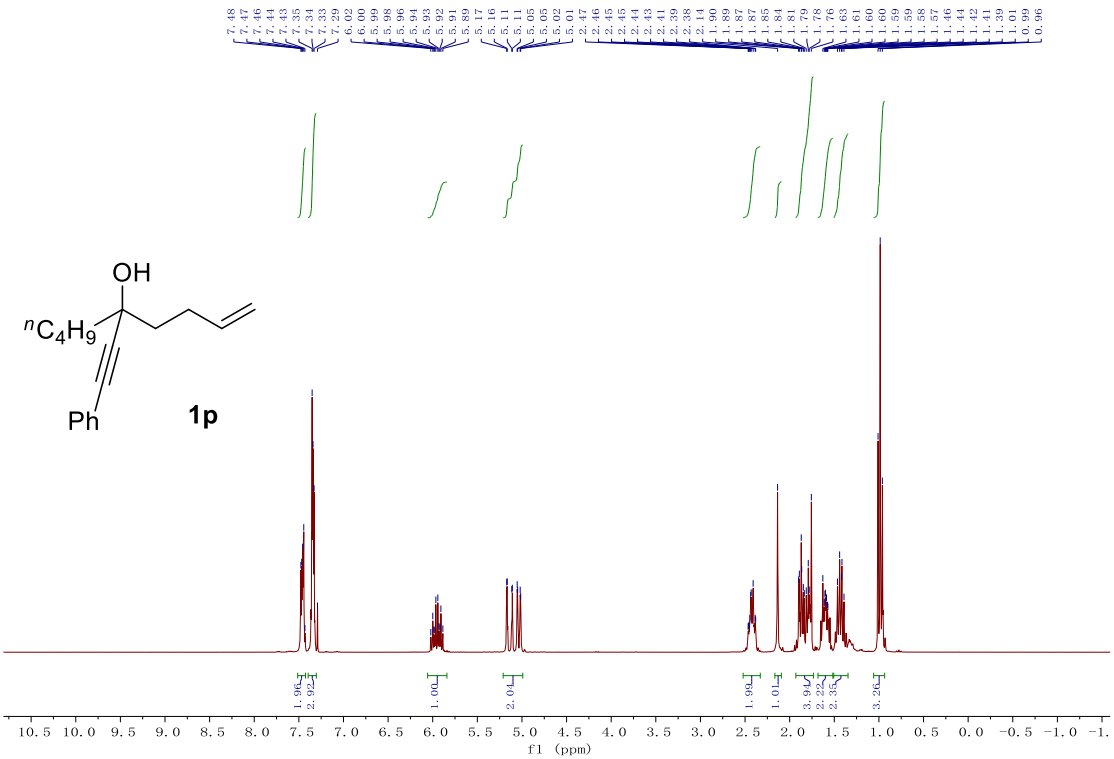

OH
1m
f1 (ppm)
Jan19-2017.331.fid — TXJ-618-C — carbon_256 CDCl3 /opt/topspin av1 34

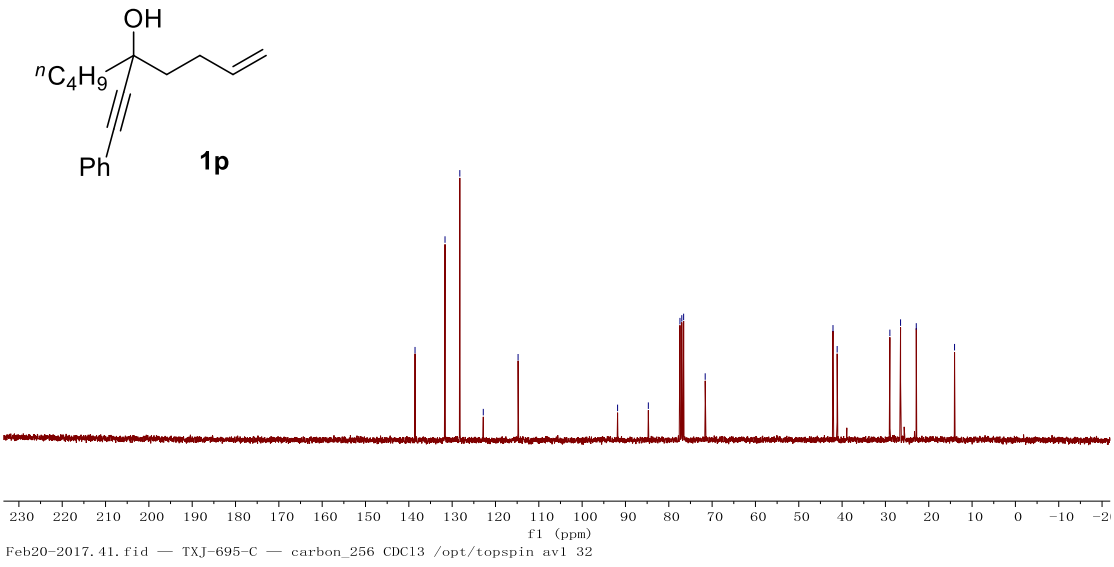

7.29
5.96
5.94
5.93
5.92
5.91
5.89
5.87
5.86
5.85
5.83
5.11
5.06
5.05
5.01
5.00
4.98
4.97
4.97
2.33
2.30
2.30
2.28
2.24
2.21
2.19
2.06
1.78
1.76
1.75
1.74
1.73
1.72
1.71
1.53
1.51
1.48
1.43
1.41
1.38
0.95
0.93
0.91
OH
$^{n}C_4H_9$
1n
1.00
2.04
4.05
0.95
2.10
7.20
3.10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
Jan18-2017.340.fid — TXJ-614-1-H — proton CDCl3 /opt/topspin av1 33

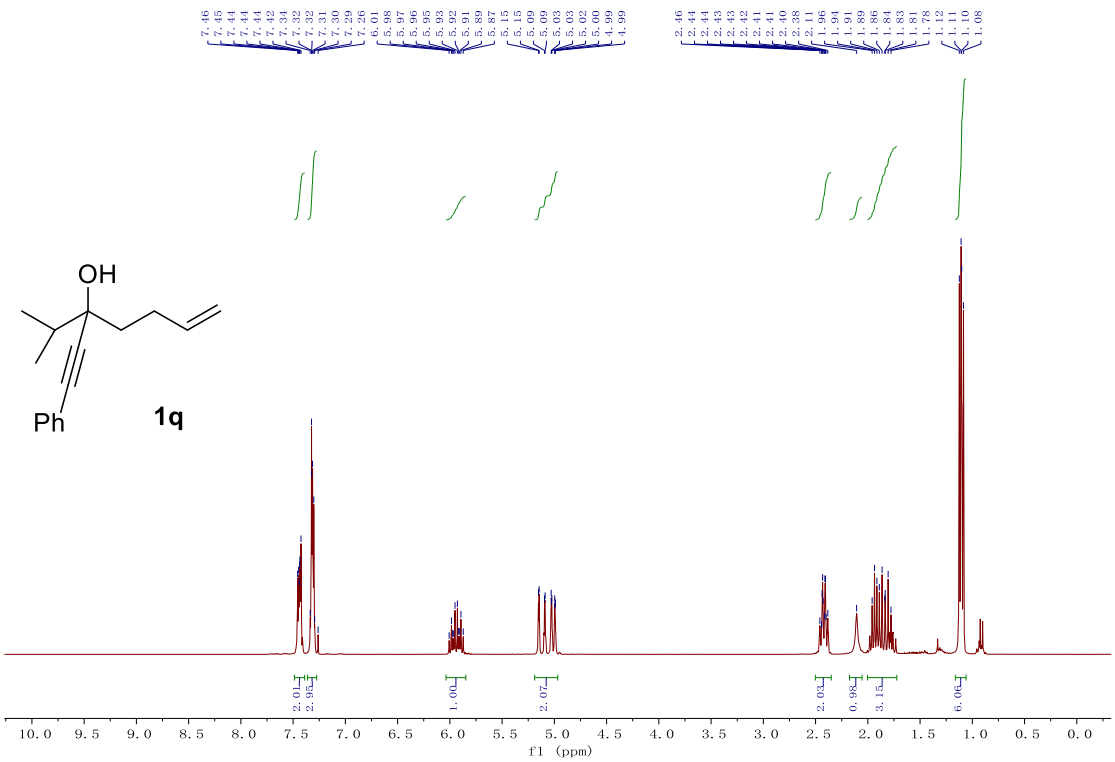

138.57
114.56
84.09
83.70
77.42
77.00
76.58
68.16
42.90
30.77
30.26
29.33
21.87
18.24
13.53
OH
$^{n}C_4H_9$
1n
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
Jan18-2017.341.fid — TXJ-614-1-C — carbon_256 CDCl3 /opt/topspin av1 33

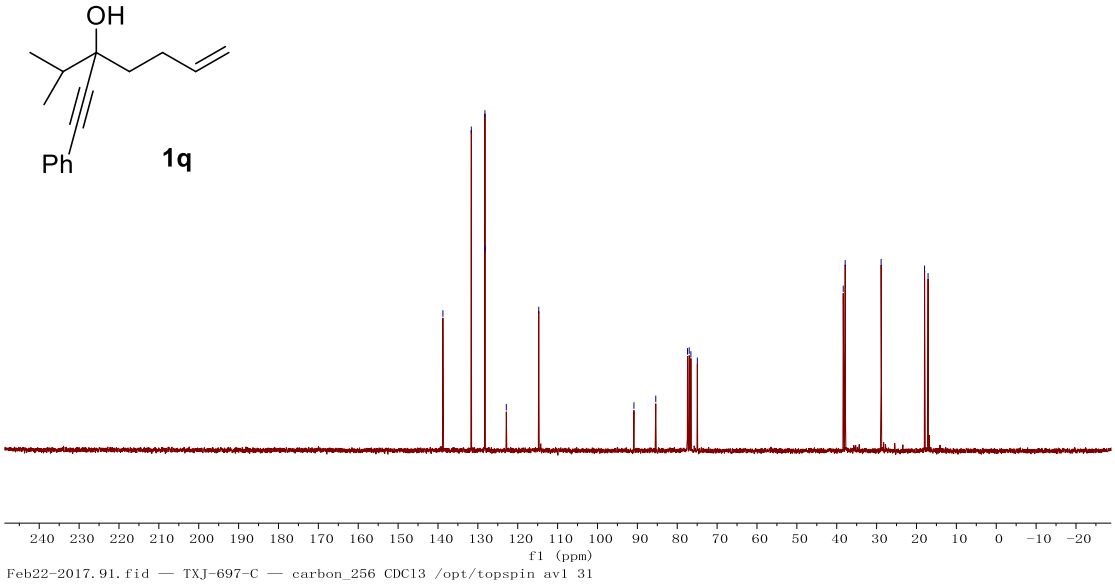

OH
TIPS
1o
f1 (ppm)
Mar12-2017.80.fid — TXJ-716-H — proton CDCl3 /opt/topspin av1 31

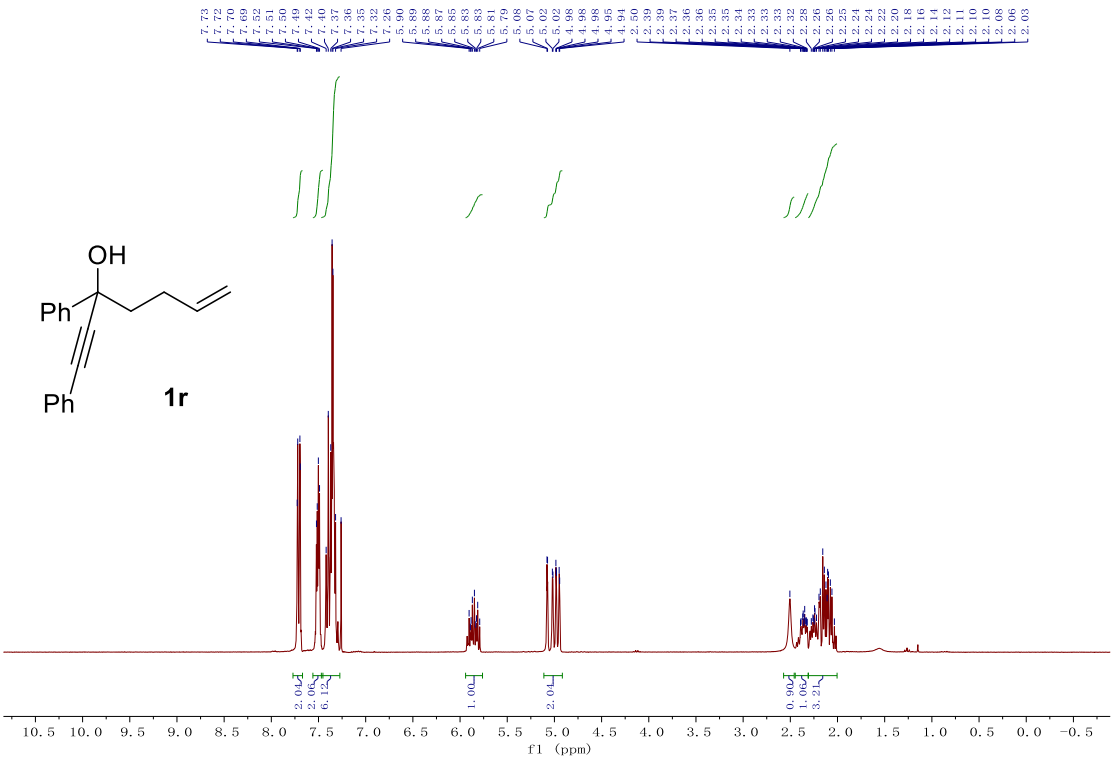

OH
TIPS
1o
f1 (ppm)
Mar12-2017.81.fid — TXJ-716-C — carbon_256 CDCl3 /opt/topspin av1 31

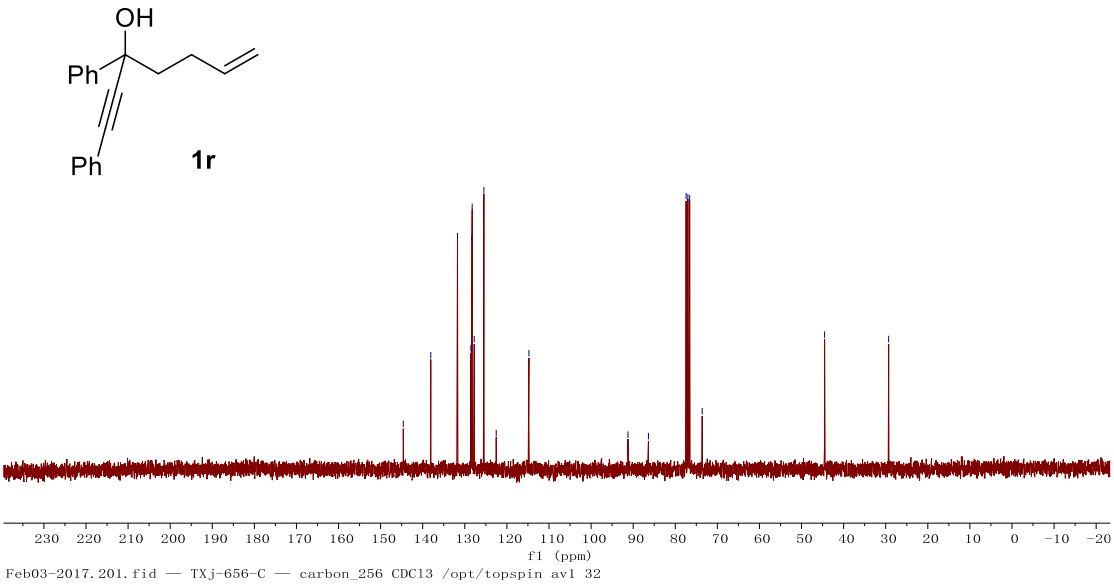

OH
$^{n}C_4H_9$
Ph
1p
f1 (ppm)
Feb20-2017.40.fid — TXJ-695-H — proton CDCl3 /opt/topspin av1 32

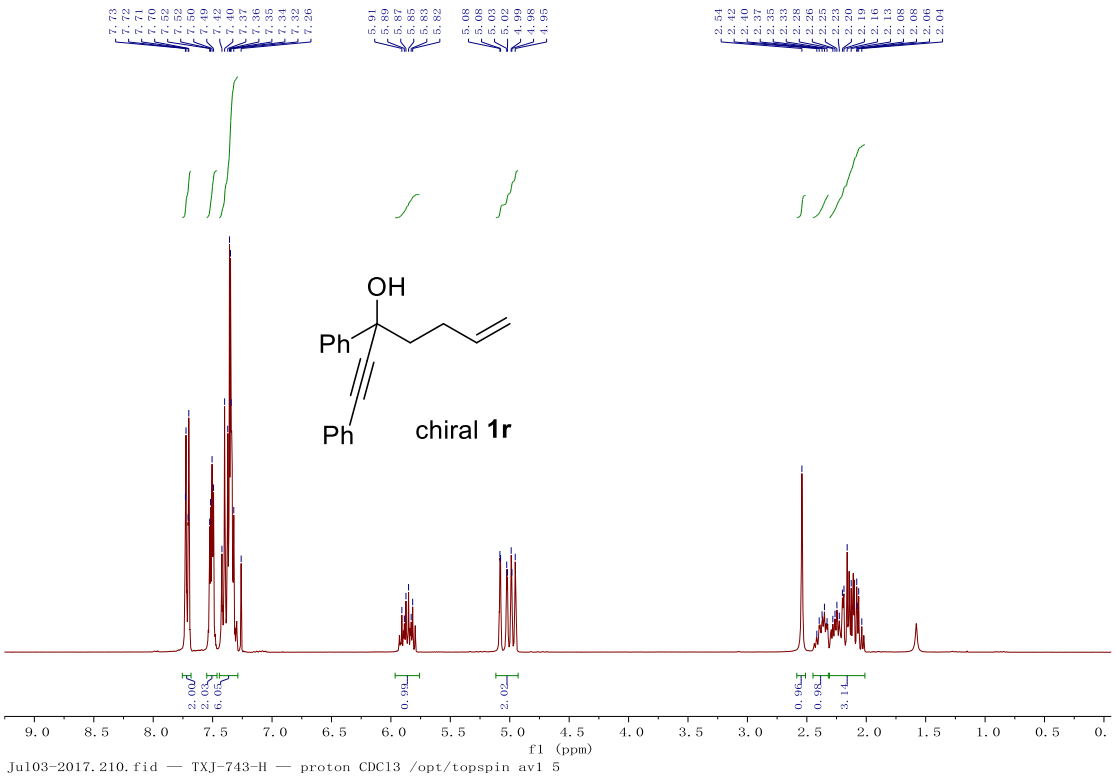

OH
$^{n}C_4H_9$
Ph
1p
f1 (ppm)
Feb20-2017.41.fid — TXJ-695-C — carbon_256 CDCl3 /opt/topspin av1 32


OH
Ph
1q
f1 (ppm)
Feb22-2017.90.fid — TXJ-697-H — proton CDCl3 /opt/topspin av1 31

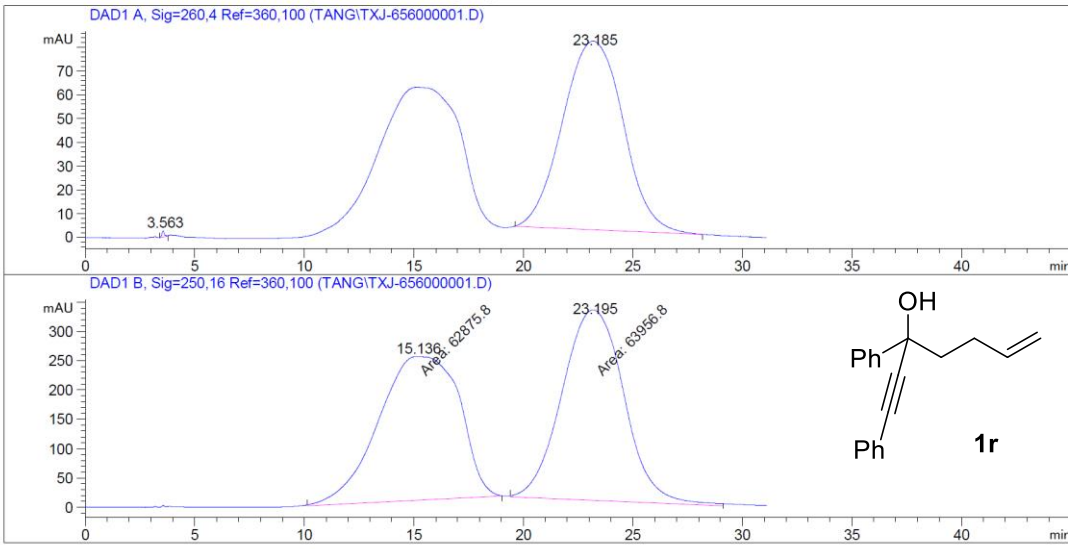

OH
Ph
1q
f1 (ppm)
Feb22-2017.91.fid — TXJ-697-C — carbon_256 CDCl3 /opt/topspin av1 31


OH
Ph
Ph
1r
f1 (ppm)
Feb03-2017.200.fid — TXj-656-H — proton CDCl3 /opt/topspin av1 32


OH
Ph
Ph
1r
f1 (ppm)
Feb03-2017.201.fid — TXj-656-C — carbon_256 CDCl3 /opt/topspin av1 32


7.73
7.72
7.71
7.70
7.52
7.52
7.50
7.49
7.42
7.40
7.37
7.36
7.35
7.34
7.32
7.26
5.91
5.89
5.87
5.85
5.83
5.82
5.08
5.08
5.03
5.02
4.99
4.98
4.95
2.54
2.42
2.40
2.37
2.35
2.33
2.28
2.26
2.25
2.23
2.20
2.19
2.16
2.13
2.08
2.08
2.06
2.04
OH
Ph
Ph
chiral 1r
2.00
2.03
6.05
0.99
2.02
0.96
0.98
3.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)
Jul03-2017.210.fid — TXJ-743-H — proton CDCl3 /opt/topspin av1 5

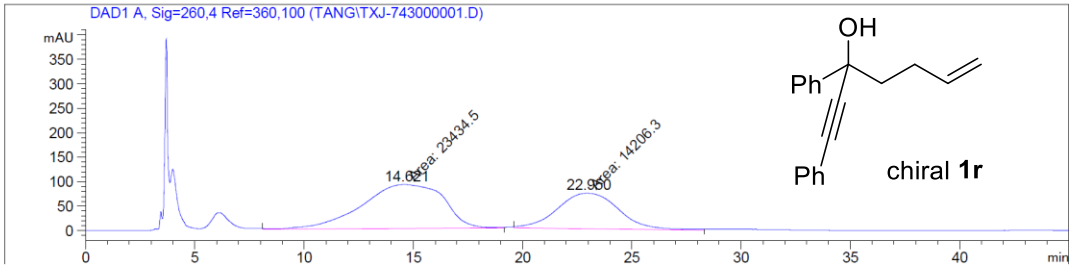
```
Data File C:\CHEM32\1\DATA\TANG\TXJ-656000001.D
Sample Name: TXJ-656

    ======================================================================
    Acq. Operator   : kischkewitz
    Acq. Instrument : Instrument 1                    Location : Vial 1
    Injection Date  : 11.05.2017 10:09:11
                                                    Inj Volume : 15.0 µl
    Acq. Method     : C:\CHEM32\1\METHODS\AK STUDER\STANDARD METHODS\M20_S.M
    Last changed    : 04.04.2017 13:39:48 by prekel
    Analysis Method : C:\CHEM32\1\METHODS\AK STUDER\STANDARD METHODS\M1_S.M
    Last changed    : 11.05.2017 10:55:10 by kischkewitz
                      (modified after loading)
    Method Info     : standard method M1_S, solvent system 90:10, time 60 min, flow 1 mL/min, 25
                      °C, 15 microL injection vol.

    Sample Info     : OD-H

    ======================================================================

    Instrument Conditions   :    At Start           At Stop
    Column Temp. (left)     :      25.0              25.0   °C
    Column Temp. (right)    :      25.0              25.0   °C
    Pressure                :     132.9             134.6   bar
    Flow                    :     1.000             1.000 ml/min

    Detector Lamp Burn Times: Current On-Time  Accumulated On-Time
    DAD 1, UV Lamp          :       0.27           3733.6   h
    DAD 1, Visible Lamp     :      OFF              567.1   h

    Solvent Description     :
    PMP1 , Solvent A        : Cyclohexan
    PMP1 , Solvent B        : Cyclohexan:Isoprop 90:10
```




```
Signal 2: DAD1 B, Sig=250,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.136 MM    4.2695 6.28758e4   245.44820  49.5738
   2  23.195 MM    3.2754 6.39568e4   325.44220  50.4262

Totals :                 1.26833e5   570.89040
```

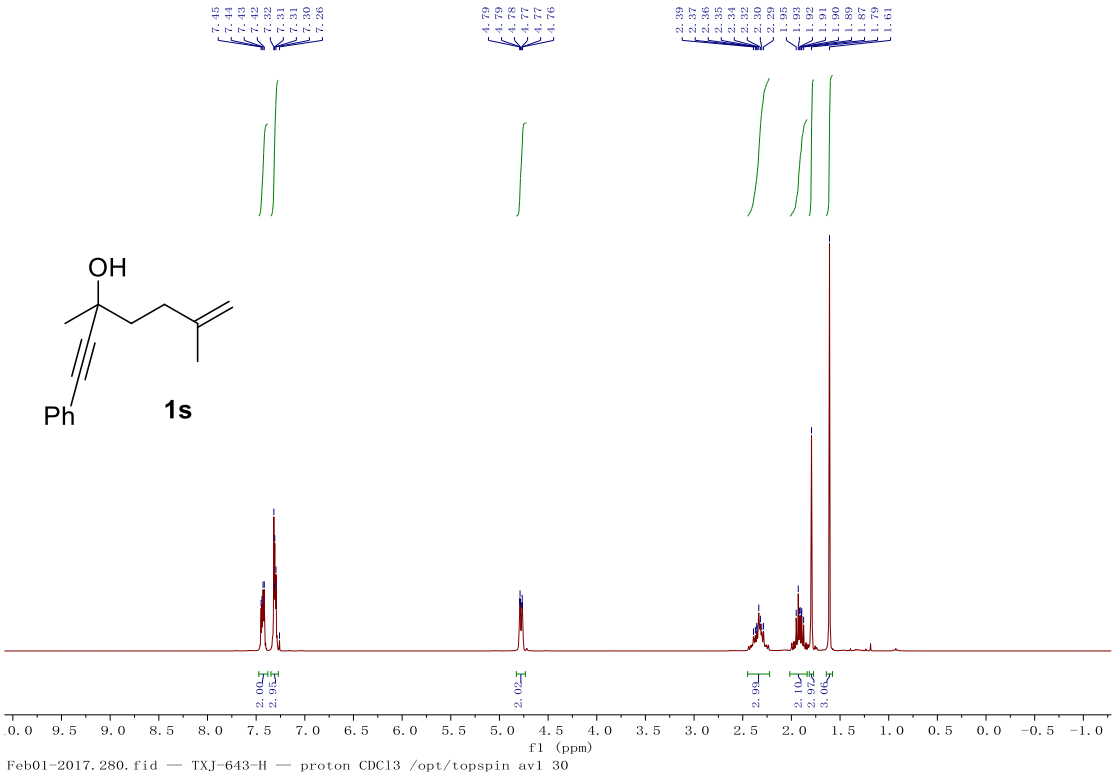
Data File C:\CHEM32\1\DATA\TANG\TXJ-743000001.D
Sample Name: TXJ-743

```
==========================================================================
Acq. Operator   : kischkewitz
Acq. Instrument : Instrument 1                    Location : Vial 2
Injection Date  : 11.05.2017 10:56:21
                                                  Inj Volume : 15.0 µl
Acq. Method     : C:\CHEM32\1\METHODS\AK STUDER\STANDARD METHODS\M20_S.M
Last changed    : 11.05.2017 10:40:42 by kischkewitz
Analysis Method : C:\CHEM32\1\METHODS\AK STUDER\STANDARD METHODS\M1_S.M
Last changed    : 11.05.2017 12:56:08 by kischkewitz
                  (modified after loading)
Method Info     : standard method M1_S, solvent system 90:10, time 60 min, flow 1 mL/min, 25
                  °C, 15 microL injection vol.

Sample Info     : OD-H
```

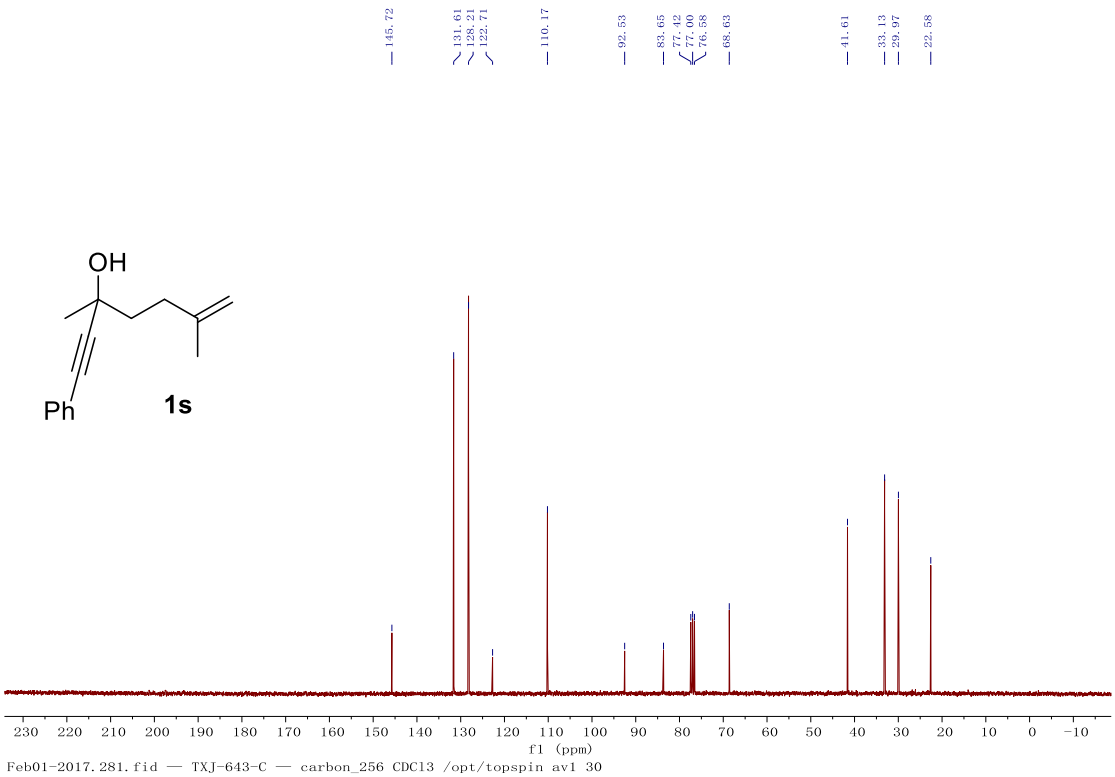


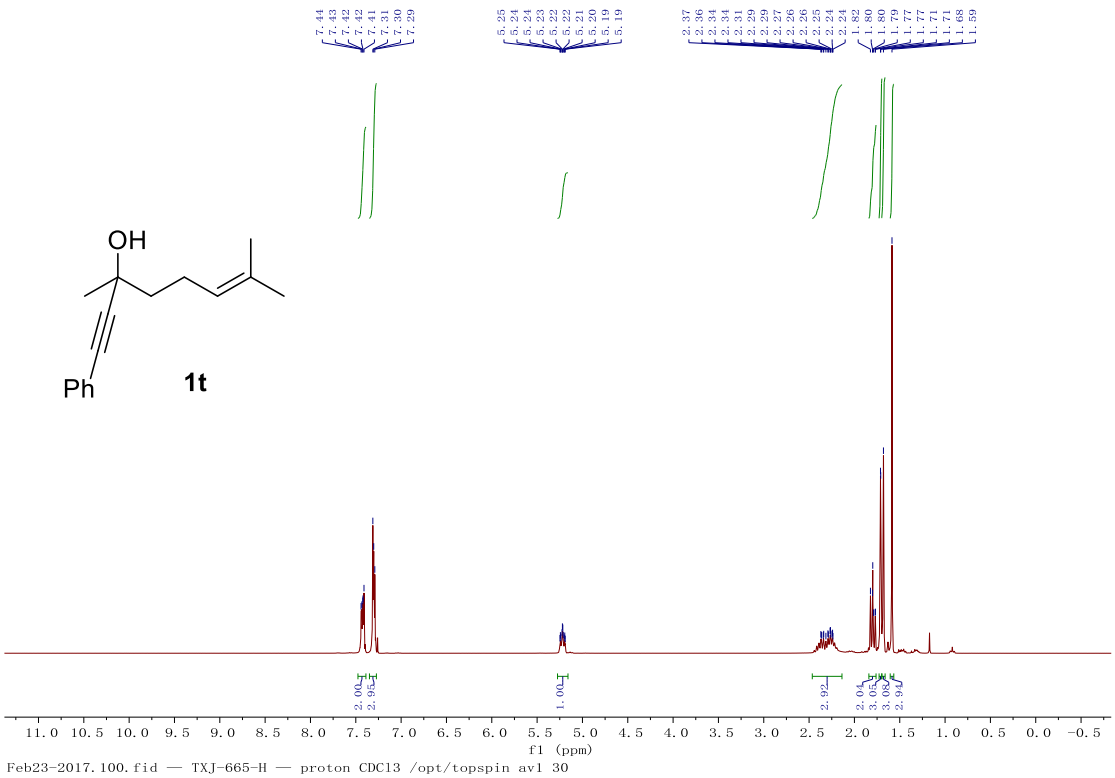
Signal 1: DAD1 A, Sig=260,4 Ref=360,100

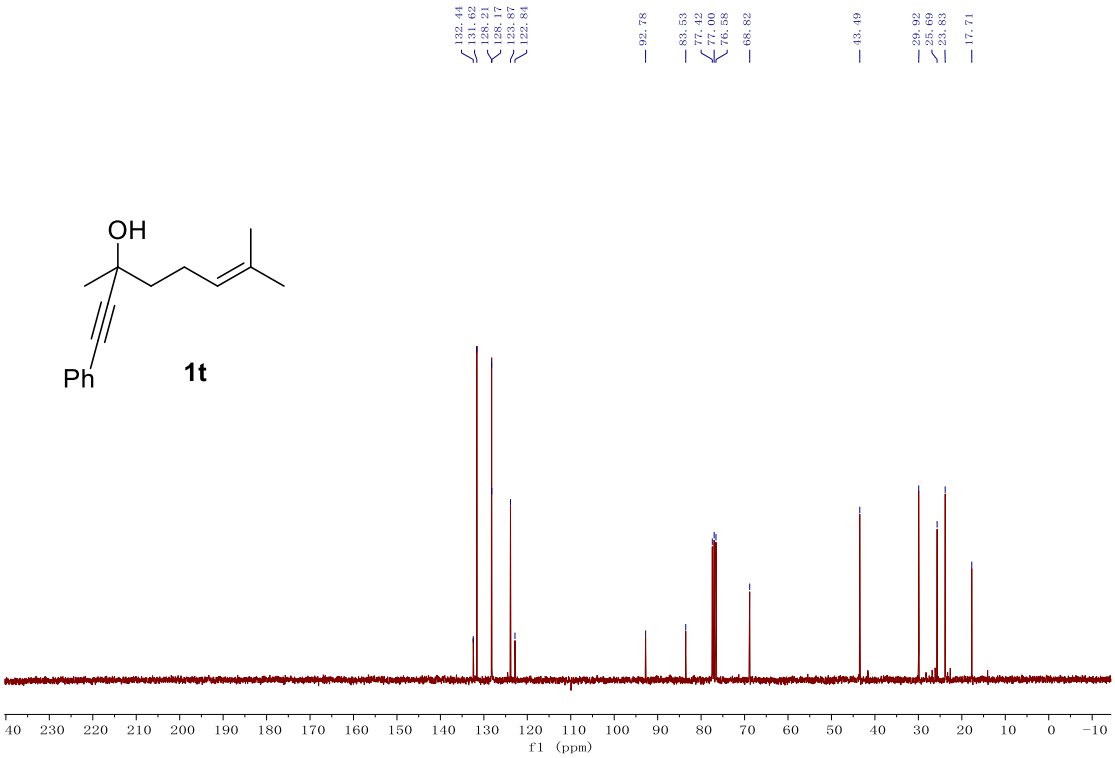
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.621	MM	4.3488	2.34345e4	89.81277	62.2583
2	22.950	MM	3.2419	1.42063e4	73.03435	37.7417
Totals :				3.76407e4	162.84712	

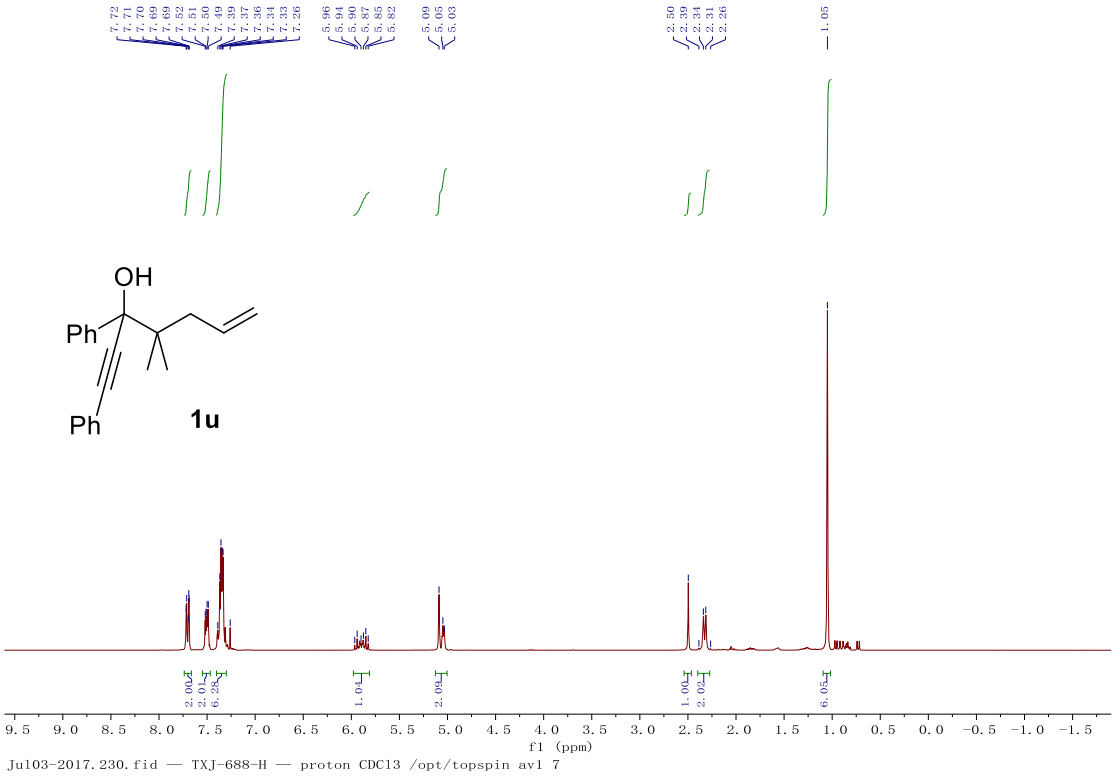


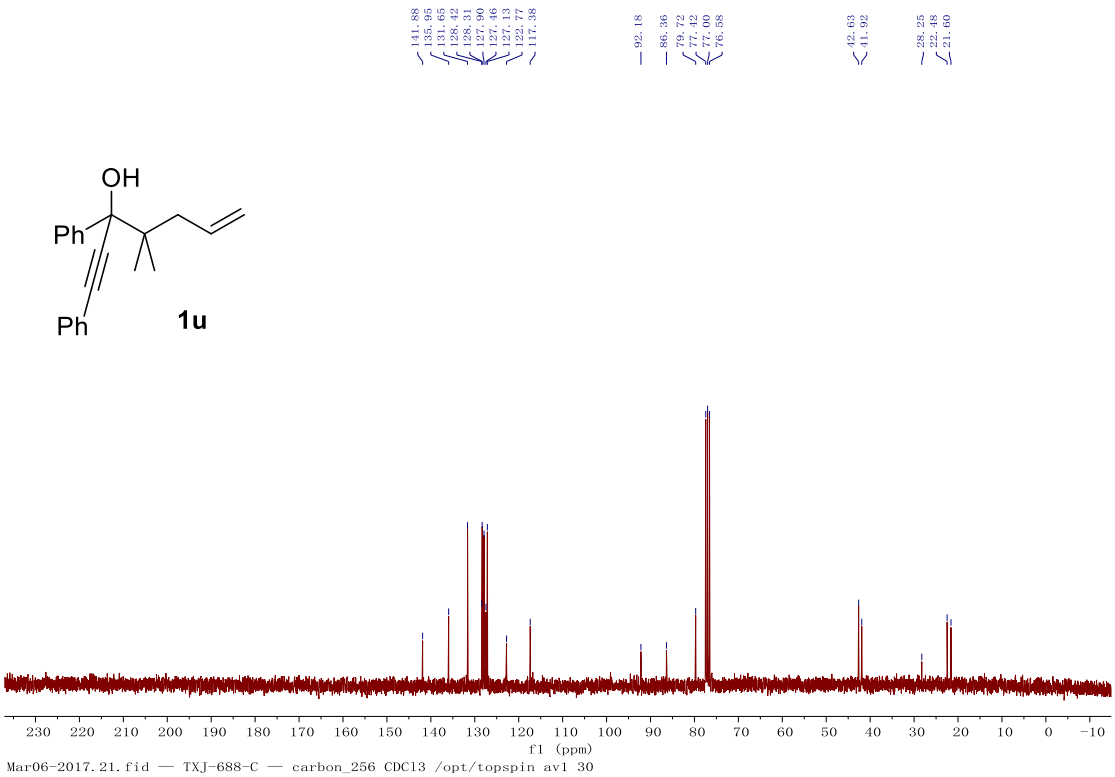
Feb01-2017.280.fid — TXJ-643-H — proton CDCl3 /opt/topspin avl 30

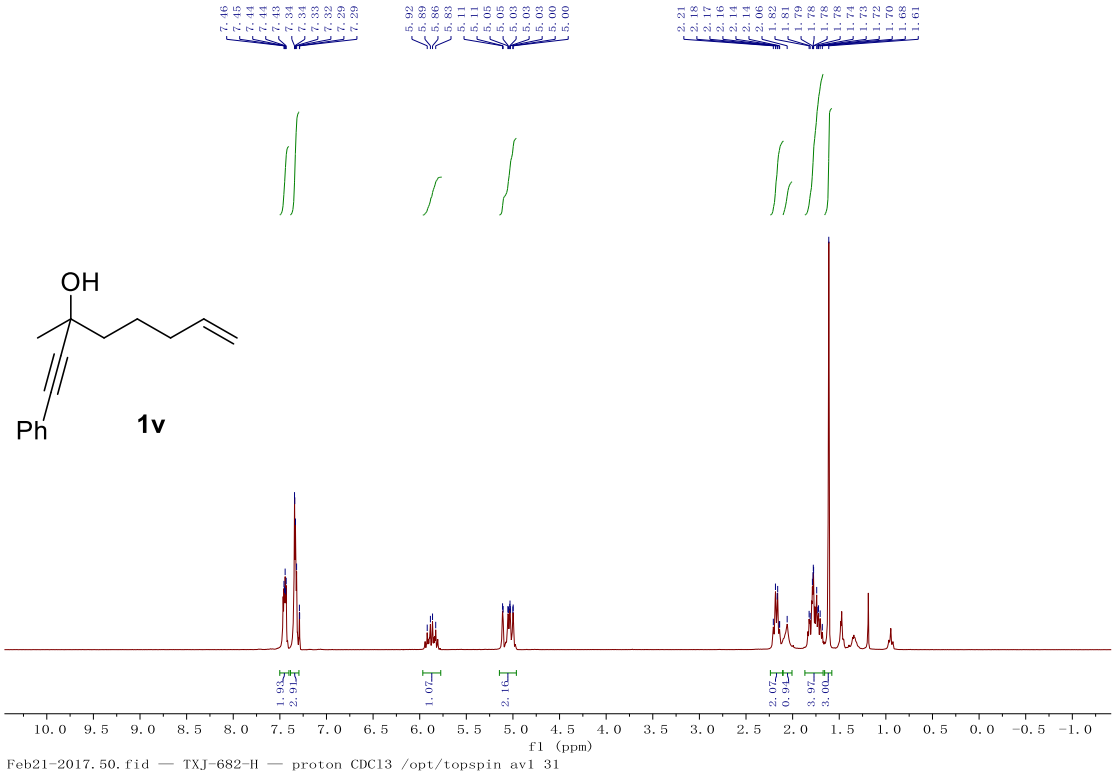

145.72
131.61
128.21
122.71
110.17
92.53
83.65
77.42
77.00
76.58
68.63
41.61
33.13
29.97
22.58
OH
Ph
1s
f1 (ppm)
Feb01-2017.281.fid — TXJ-643-C — carbon_256 CDCl3 /opt/topspin av1 30

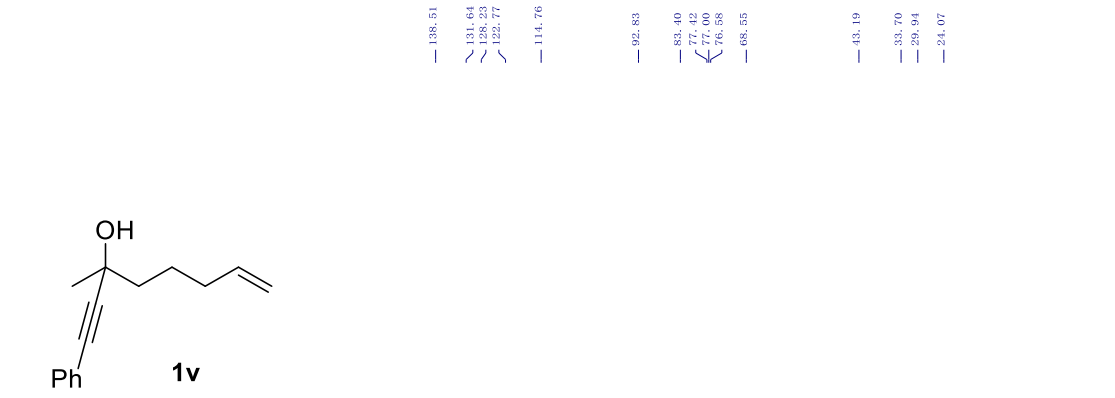

OH
Ph
1t
f1 (ppm)
Feb23-2017.100.fid — TXJ-665-H — proton CDCl3 /opt/topspin av1 30

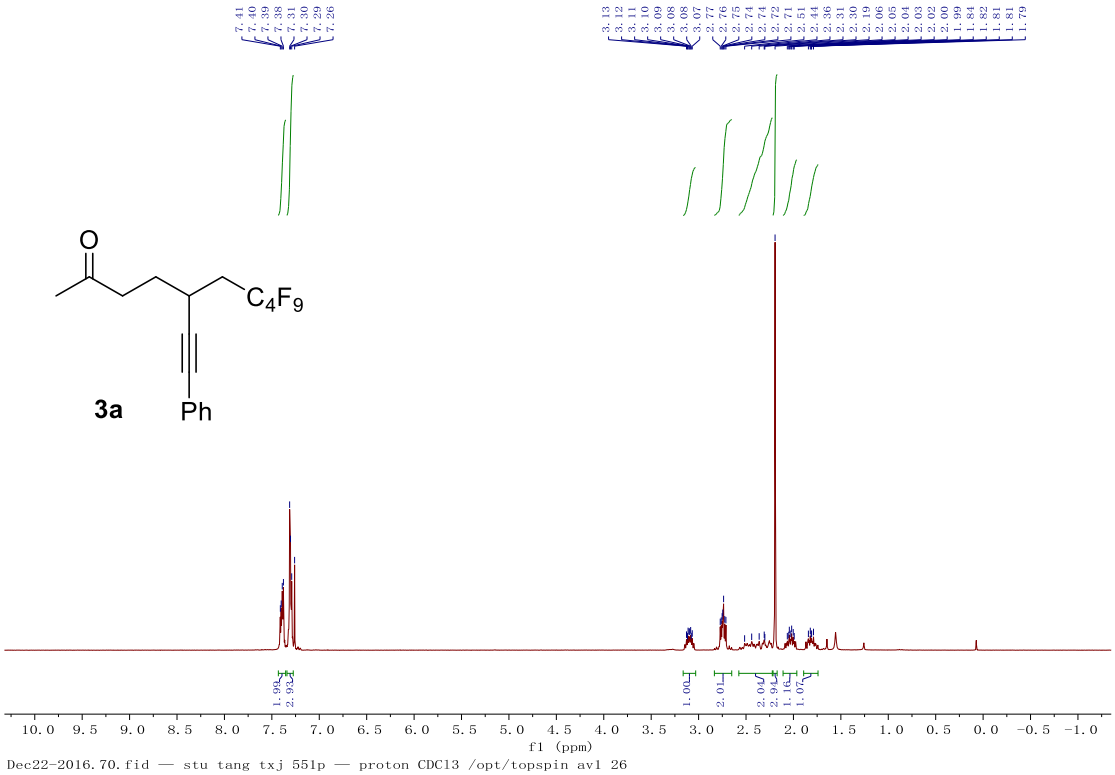

132.44
131.62
128.21
128.17
123.87
122.84
92.78
83.53
77.42
77.00
76.58
68.82
43.49
29.92
25.69
23.83
17.71
OH
Ph
1t
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
Feb23-2017.101.fid — TXJ-665-C — carbon_256 CDCl3 /opt/topspin av1 30

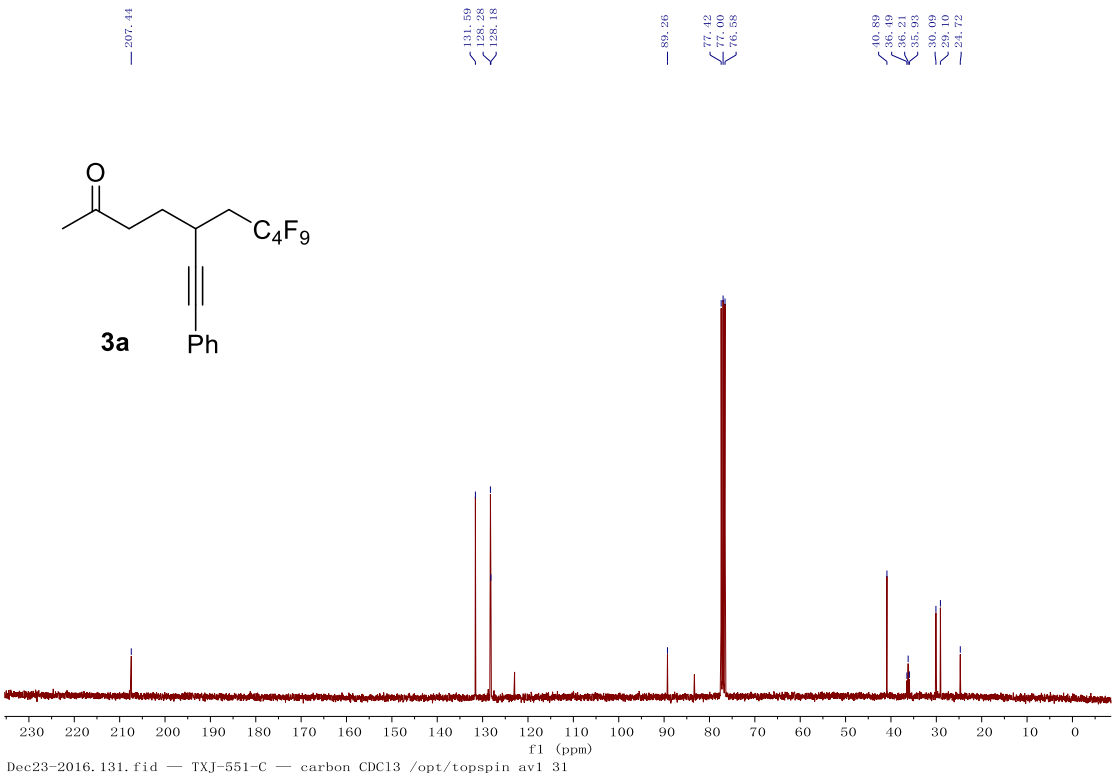

7.72
7.71
7.70
7.69
7.69
7.52
7.51
7.50
7.49
7.39
7.37
7.36
7.34
7.33
7.26
5.96
5.94
5.90
5.87
5.85
5.82
5.09
5.05
5.03
2.50
2.39
2.34
2.31
2.26
1.05
OH
Ph
Ph
1u
2.00
2.01
6.28
1.04
2.09
1.00
2.02
6.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5
f1 (ppm)
Jul03-2017.230.fid — TXJ-688-H — proton CDCl3 /opt/topspin av1 7

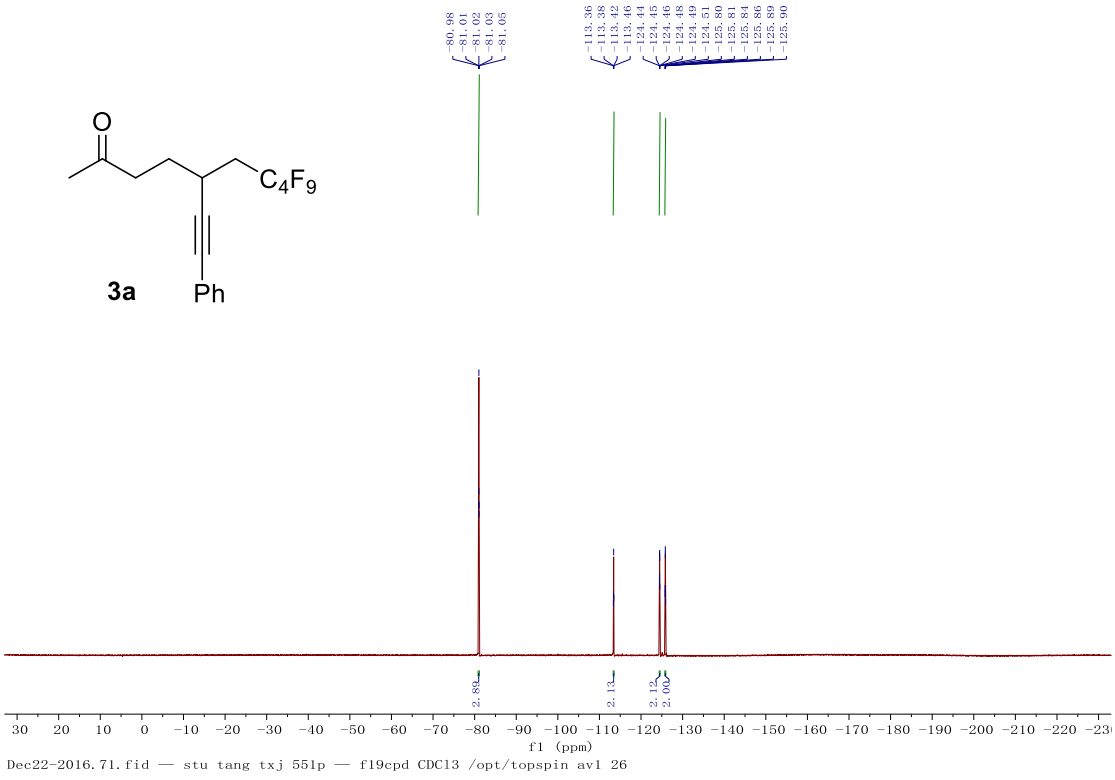

141.88
135.95
131.65
128.42
128.31
127.90
127.46
127.13
122.77
117.38
92.18
86.36
79.72
77.42
77.00
76.58
42.63
41.92
28.25
22.48
21.60
OH
Ph
Ph
1u
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
Mar06-2017.21.fid — TXJ-688-C — carbon_256 CDCl3 /opt/topspin av1 30

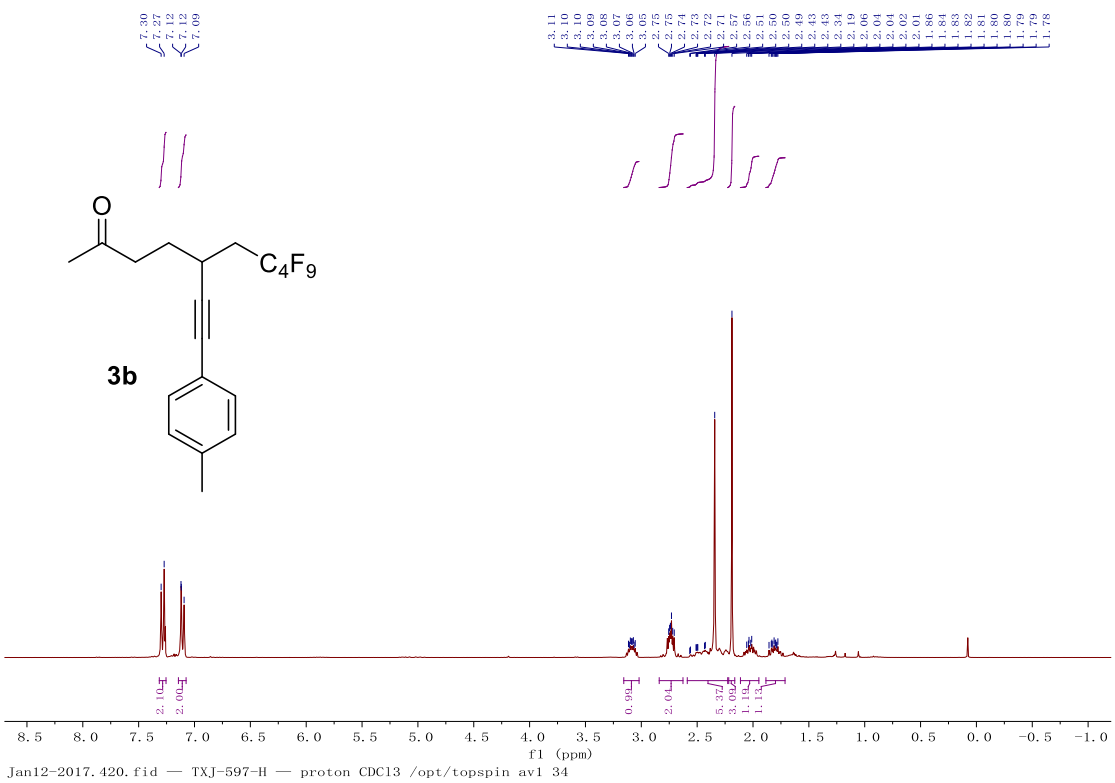

7.46
7.45
7.44
7.44
7.43
7.34
7.34
7.33
7.32
7.29
7.29
7.29
5.92
5.89
5.86
5.83
5.11
5.11
5.05
5.05
5.03
5.03
5.03
5.00
5.00
2.21
2.18
2.17
2.16
2.14
2.14
2.06
1.82
1.81
1.79
1.78
1.78
1.78
1.74
1.73
1.72
1.70
1.68
1.61
OH
Ph
1v
1.93
2.91
1.07
2.16
2.07
0.94
3.97
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)
Feb21-2017.50.fid — TXJ-682-H — proton CDCl3 /opt/topspin av1 31

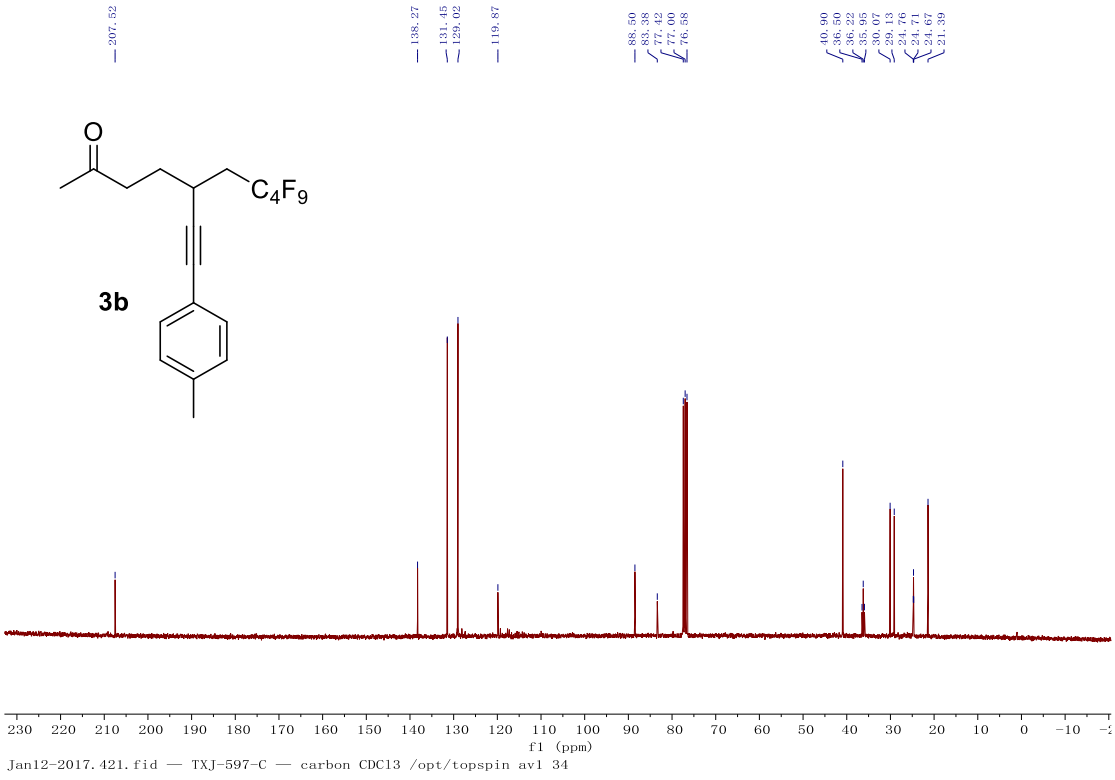

138.51
131.64
128.23
122.77
114.76
92.83
83.40
77.42
77.00
76.58
68.55
43.19
33.70
29.94
24.07
OH
Ph
1v
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
Feb21-2017.51.fid — TXJ-682-C — carbon_256 CDCl3 /opt/topspin av1 31

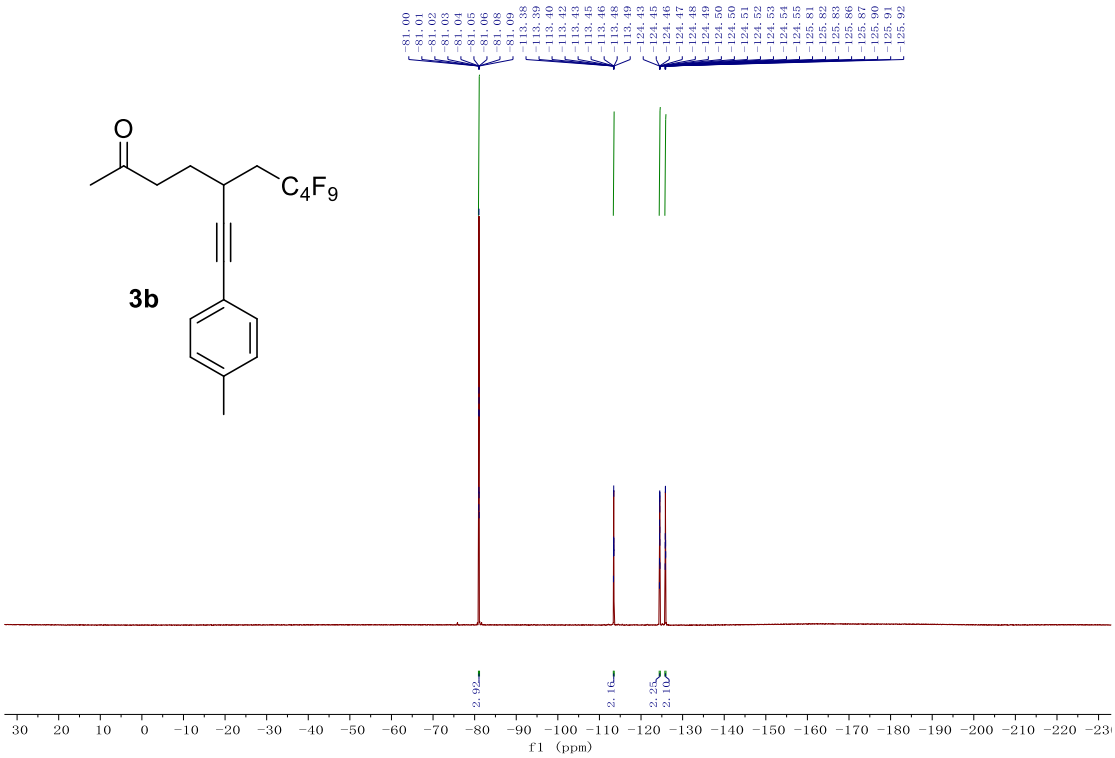

7.41
7.40
7.39
7.38
7.31
7.30
7.29
7.26
3.13
3.12
3.11
3.10
3.09
3.08
3.07
2.77
2.76
2.75
2.74
2.74
2.72
2.71
2.51
2.44
2.36
2.31
2.30
2.19
2.06
2.05
2.04
2.03
2.02
2.00
1.99
1.84
1.82
1.81
1.81
1.79
O
C4F9
Ph
3a
1.99
2.92
1.00
2.01
2.04
2.04
1.06
1.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)
Dec22-2016.70.fid — stu tang txj 551p — proton CDCl3 /opt/topspin av1 26

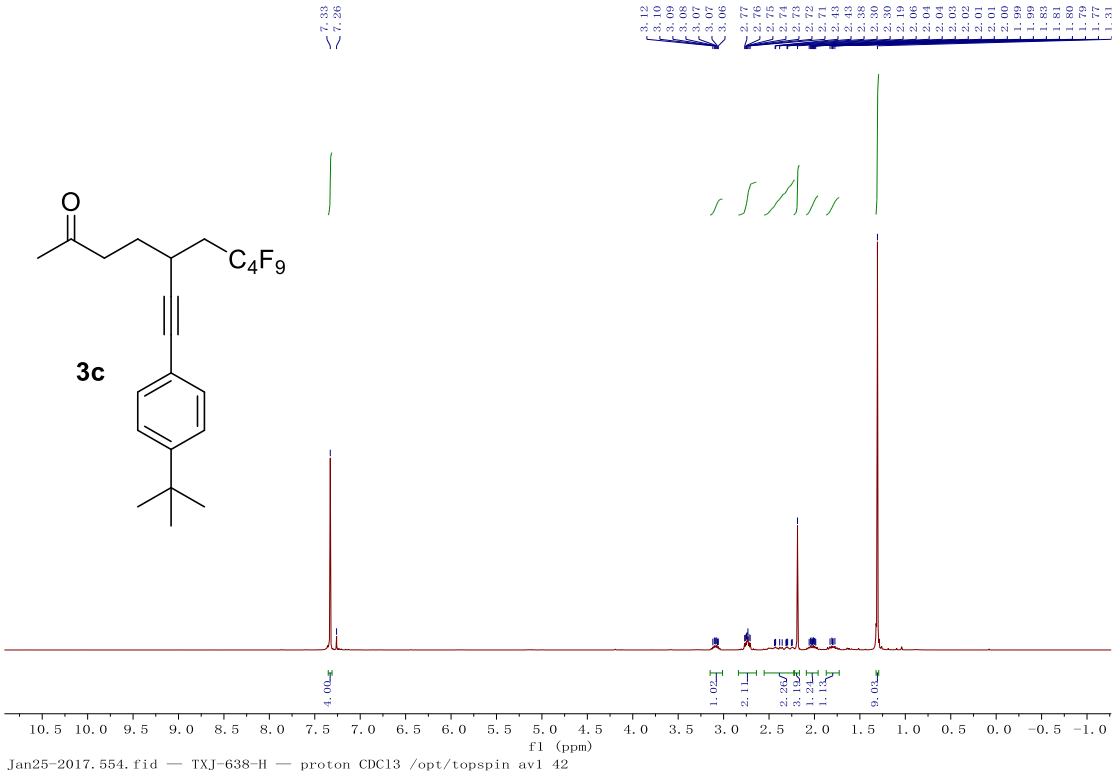

207.44
131.59
128.28
128.18
89.26
77.42
77.00
76.58
40.89
36.49
36.21
35.93
30.09
29.10
24.72
O
C4F9
3a
Ph
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Dec23-2016.131.fid — TXJ-551-C — carbon CDCl3 /opt/topspin av1 31

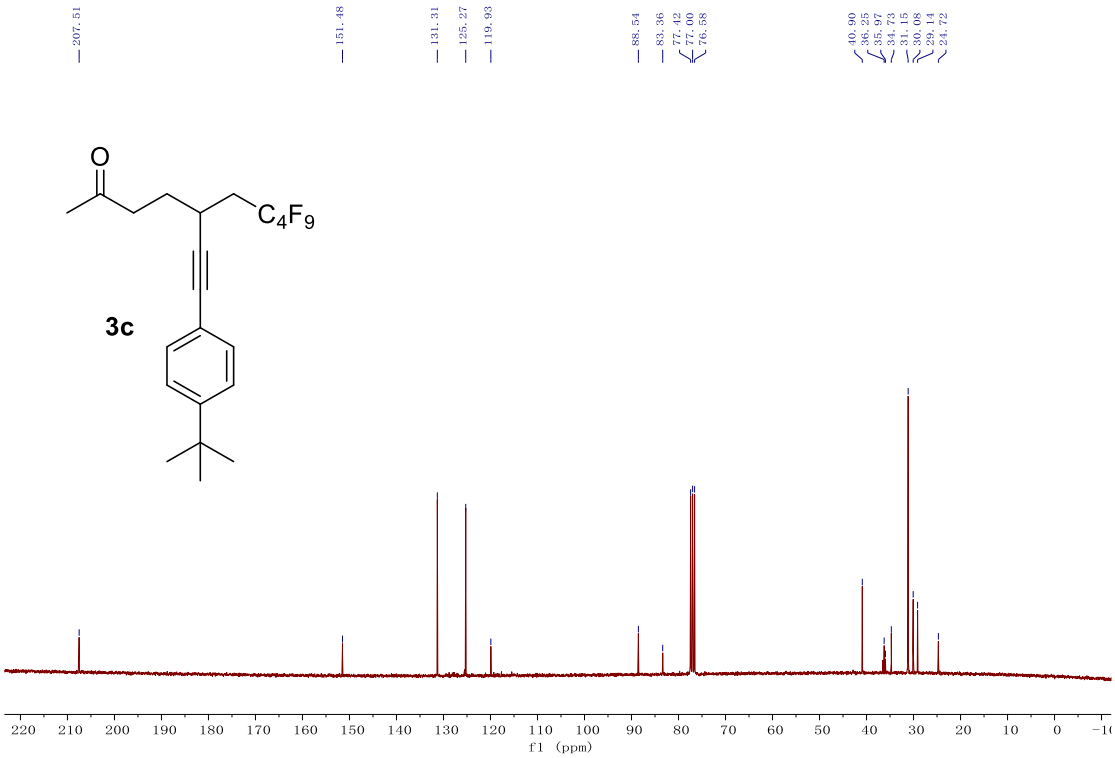

-80.98
-81.01
-81.02
-81.03
-81.05
-113.36
-113.38
-113.42
-113.46
-124.44
-124.45
-124.46
-124.48
-124.49
-124.51
-125.80
-125.81
-125.84
-125.86
-125.89
-125.90
O
C4F9
3a
Ph
2.89
2.13
2.12
2.02
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -23
f1 (ppm)
Dec22-2016.71.fid — stu tang txj 551p — f19cpd CDCl3 /opt/topspin av1 26

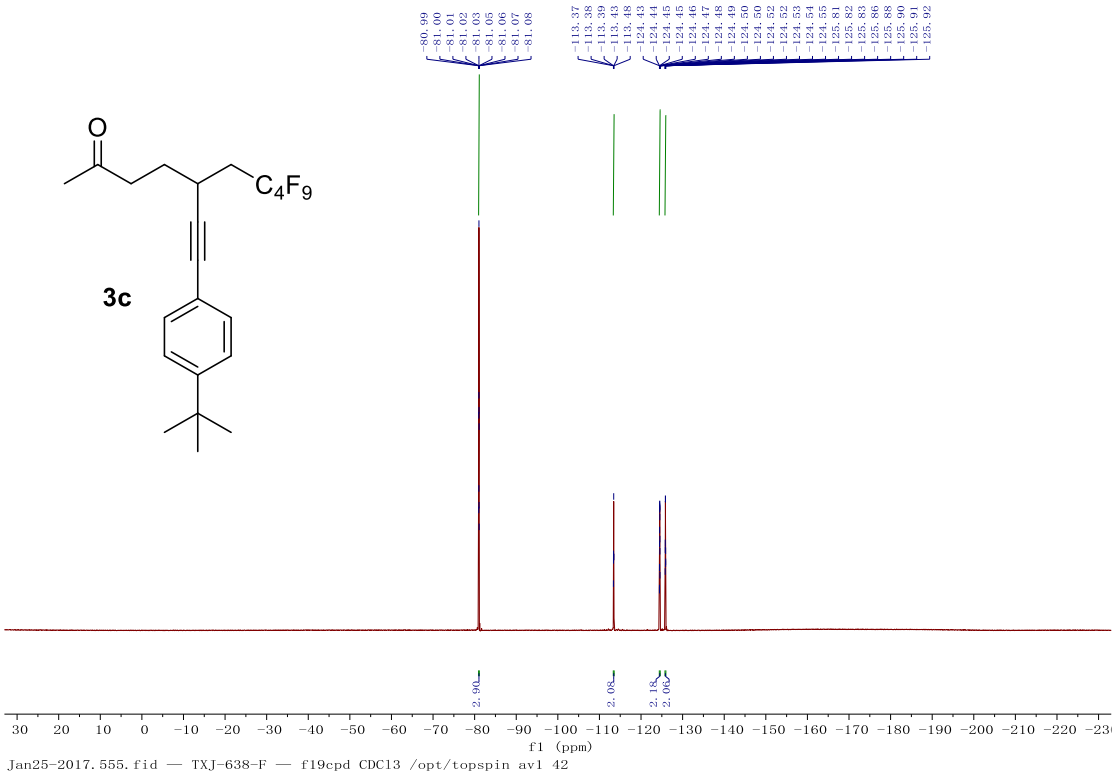

7.30
7.27
7.12
7.12
7.09
3.11
3.10
3.09
3.08
3.07
3.06
3.05
2.75
2.74
2.73
2.72
2.71
2.57
2.56
2.51
2.50
2.50
2.49
2.43
2.43
2.34
2.19
2.06
2.04
2.04
2.02
2.01
1.86
1.84
1.83
1.82
1.81
1.80
1.79
1.79
1.78
O
C_4F_9
3b
2.10
2.00
0.94
2.04
5.37
3.09
1.14
1.13
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
Jan12-2017.420.fid — TXJ-597-H — proton CDCl3 /opt/topspin av1 34

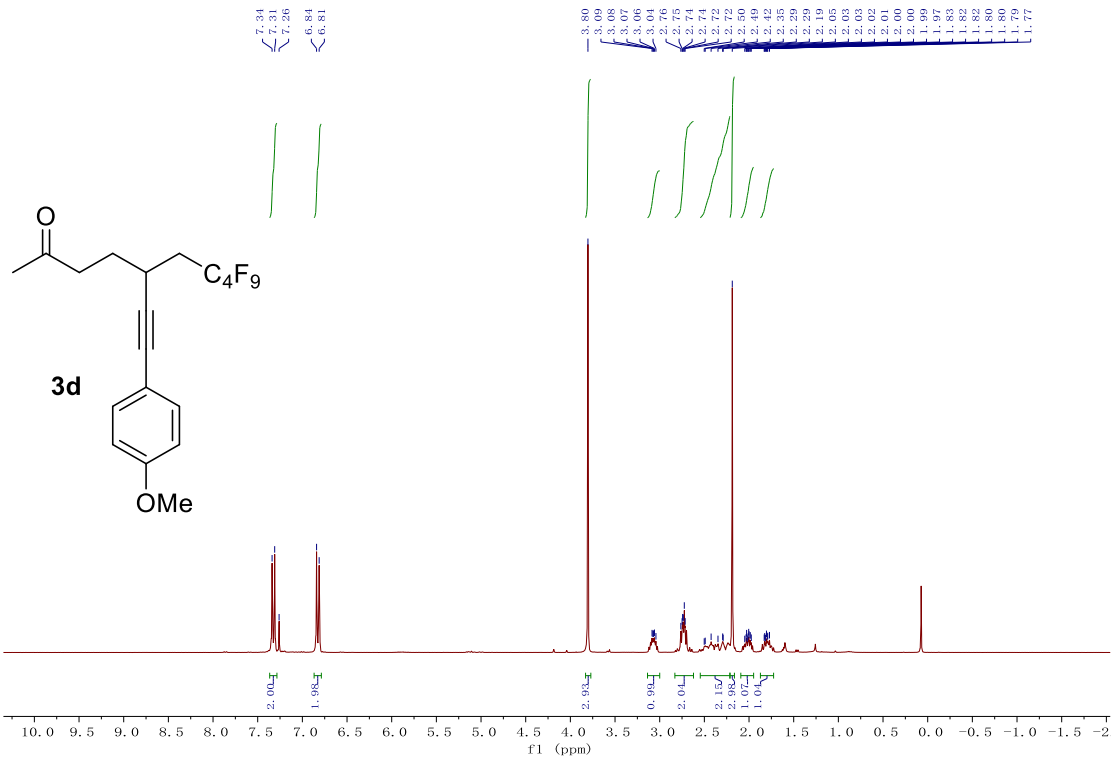

207.52
138.27
131.45
129.02
119.87
88.50
83.38
77.42
77.00
76.58
40.90
36.50
36.22
35.95
30.07
29.13
24.76
24.71
24.67
24.39
O
C_4F_9
3b
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
Jan12-2017.421.fid — TXJ-597-C — carbon CDCl3 /opt/topspin av1 34

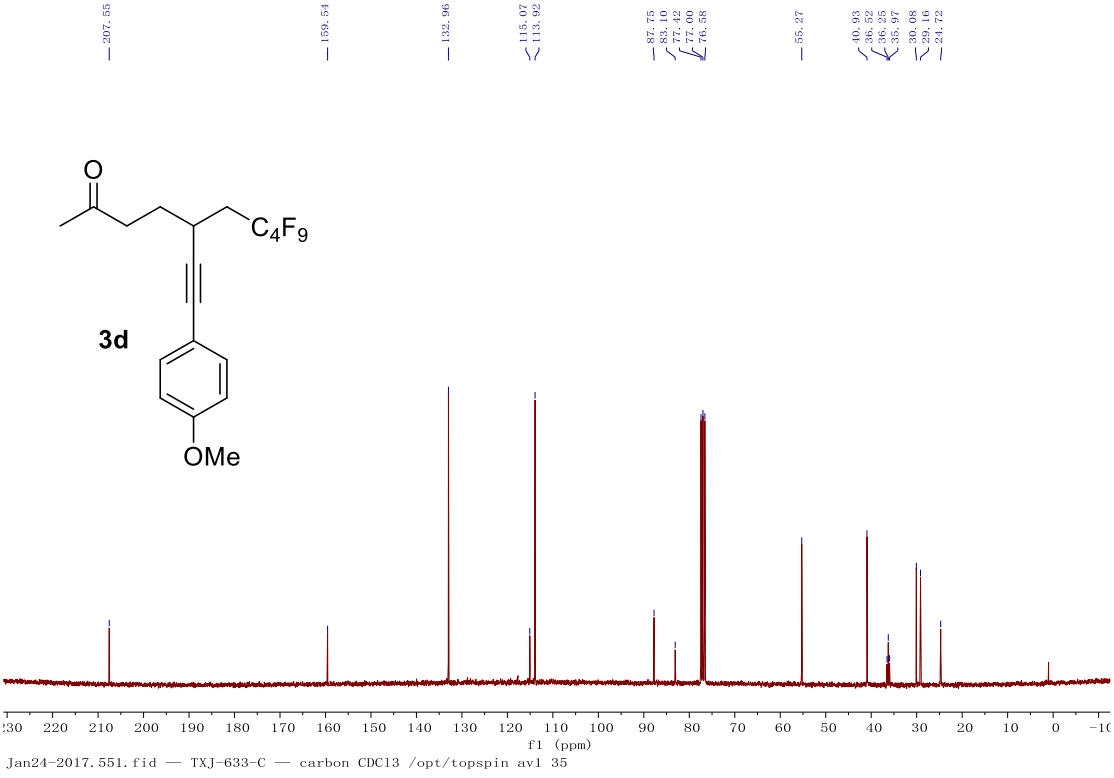

O
C_4F_9
3b
f1 (ppm)
Jan12-2017.425.fid — TXJ-597-F — f19cpd CDCl3 /opt/topspin av1 34

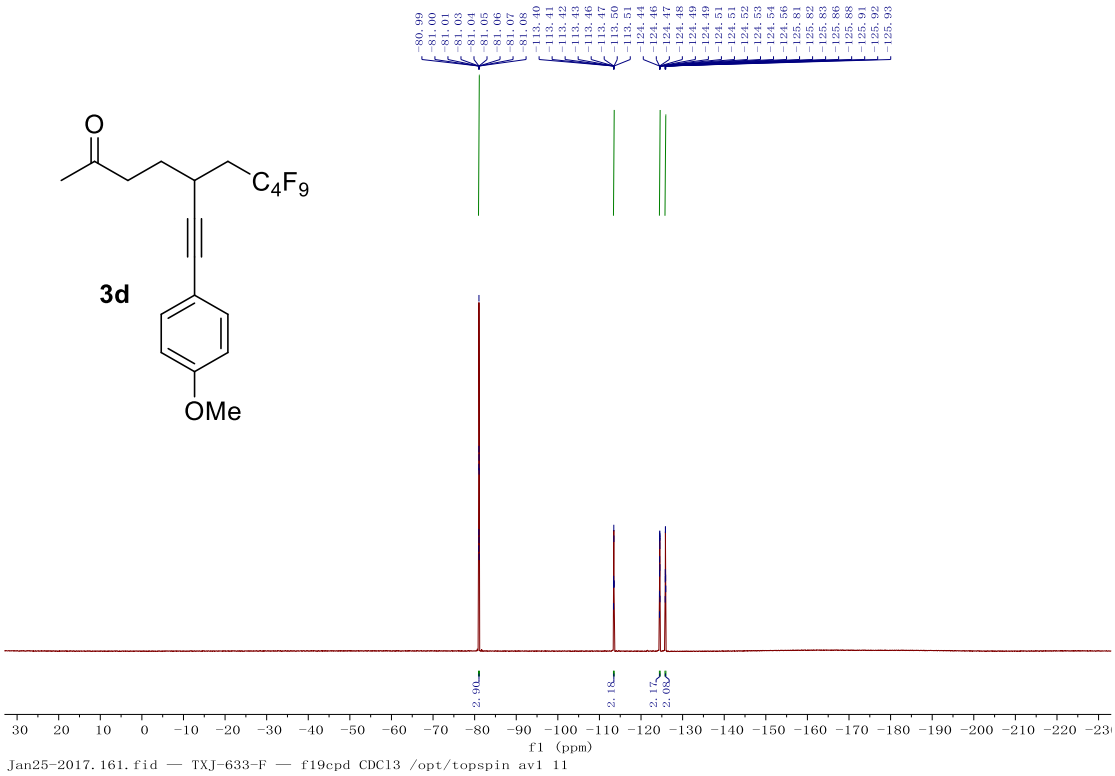

O
C_4F_9
3c
f1 (ppm)
Jan25-2017.554.fid — TXJ-638-H — proton CDCl3 /opt/topspin av1 42

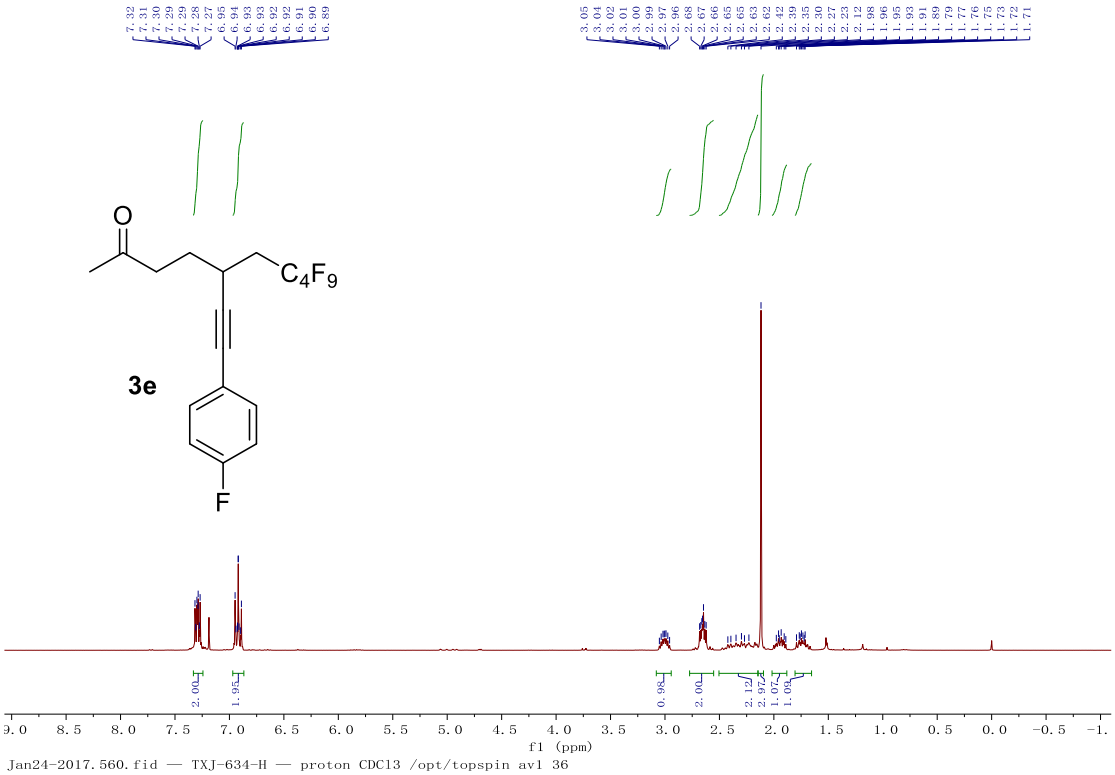

207.51
151.48
131.31
125.27
119.93
88.54
83.36
77.42
77.00
76.58
40.90
36.25
35.97
34.73
31.15
30.08
29.14
24.72
O
C4F9
3c
f1 (ppm)
Jan25-2017.551.fid — TXJ-638-C — carbon CDCl3 /opt/topspin av1 42

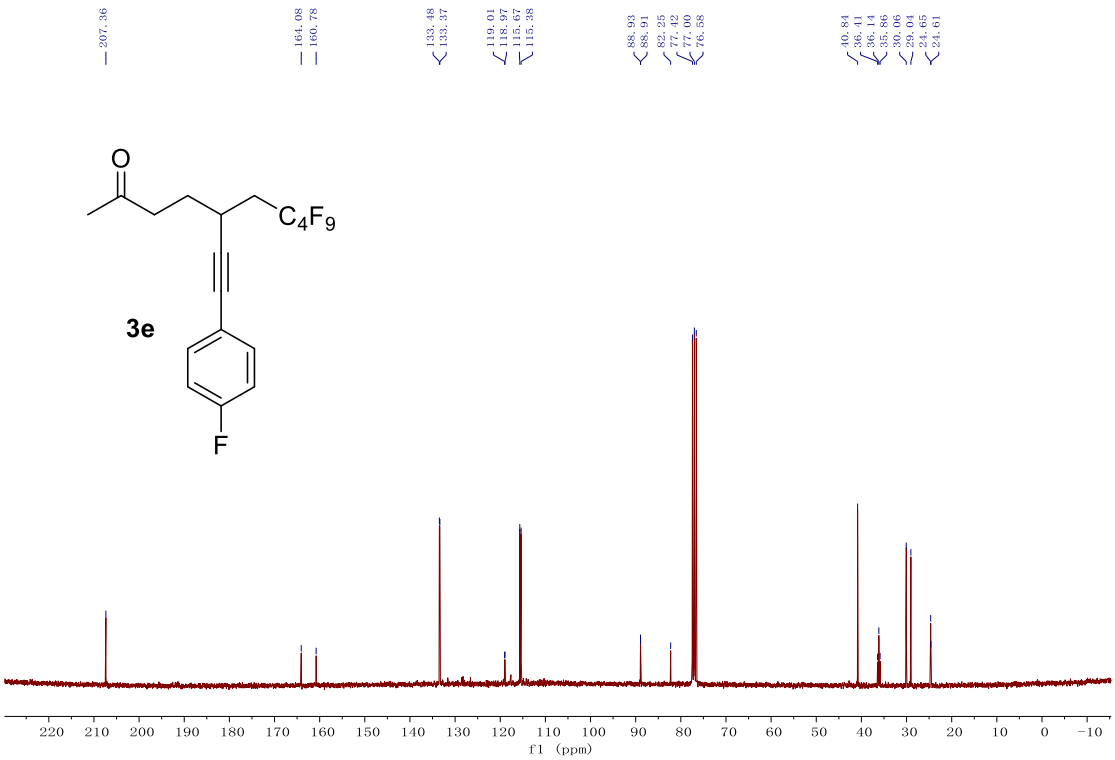

-80.99
-81.00
-81.01
-81.02
-81.03
-81.05
-81.06
-81.07
-81.08
-113.37
-113.38
-113.39
-113.43
-113.48
-124.43
-124.44
-124.45
-124.46
-124.47
-124.48
-124.49
-124.50
-124.50
-124.52
-124.53
-124.54
-124.55
-125.81
-125.82
-125.83
-125.86
-125.88
-125.90
-125.91
-125.92
O
C4F9
3c
2.90
2.08
2.18
2.06
f1 (ppm)
Jan25-2017.555.fid — TXJ-638-F — f19cpd CDCl3 /opt/topspin av1 42

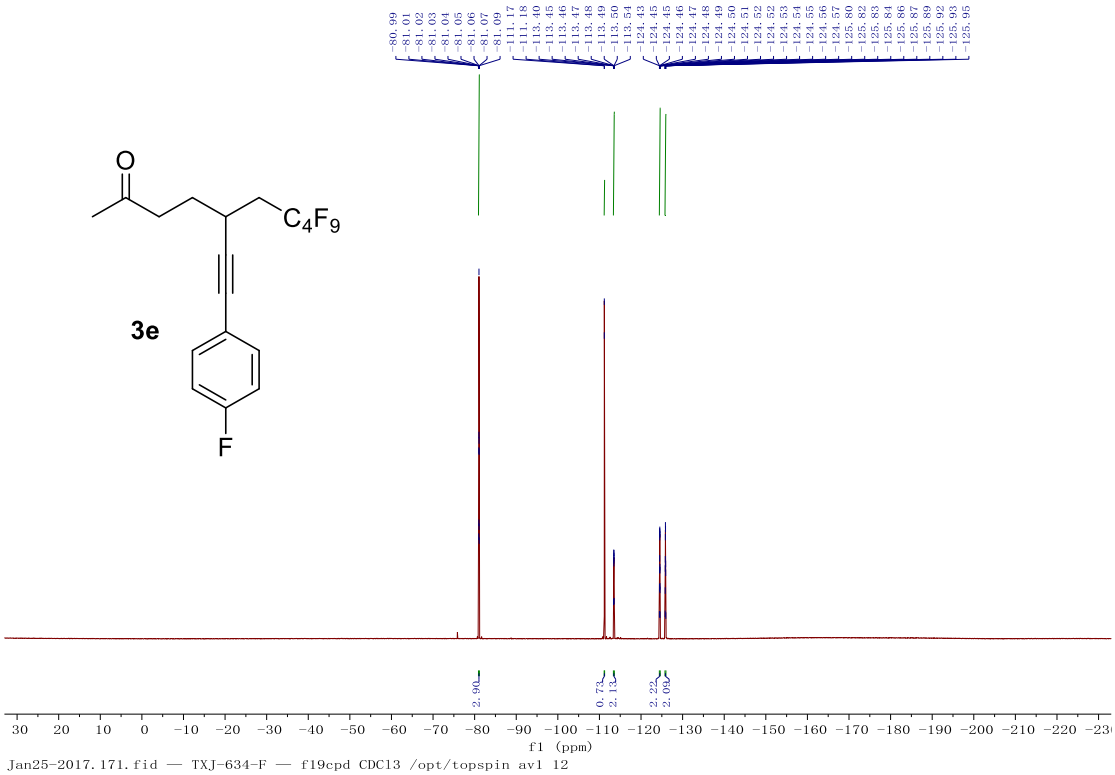

7.34
7.31
7.26
6.84
6.81
3.80
3.09
3.08
3.07
3.06
3.04
2.76
2.75
2.74
2.74
2.72
2.72
2.50
2.49
2.42
2.35
2.29
2.29
2.19
2.05
2.03
2.02
2.01
2.00
2.00
1.99
1.97
1.83
1.82
1.80
1.80
1.79
1.77
O
C4F9
3d
OMe
2.00
1.98
2.93
0.99
2.04
2.15
2.99
1.07
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2
f1 (ppm)
Jan25-2017.160.fid — TXJ-633-H — proton CDCl3 /opt/topspin av1 11

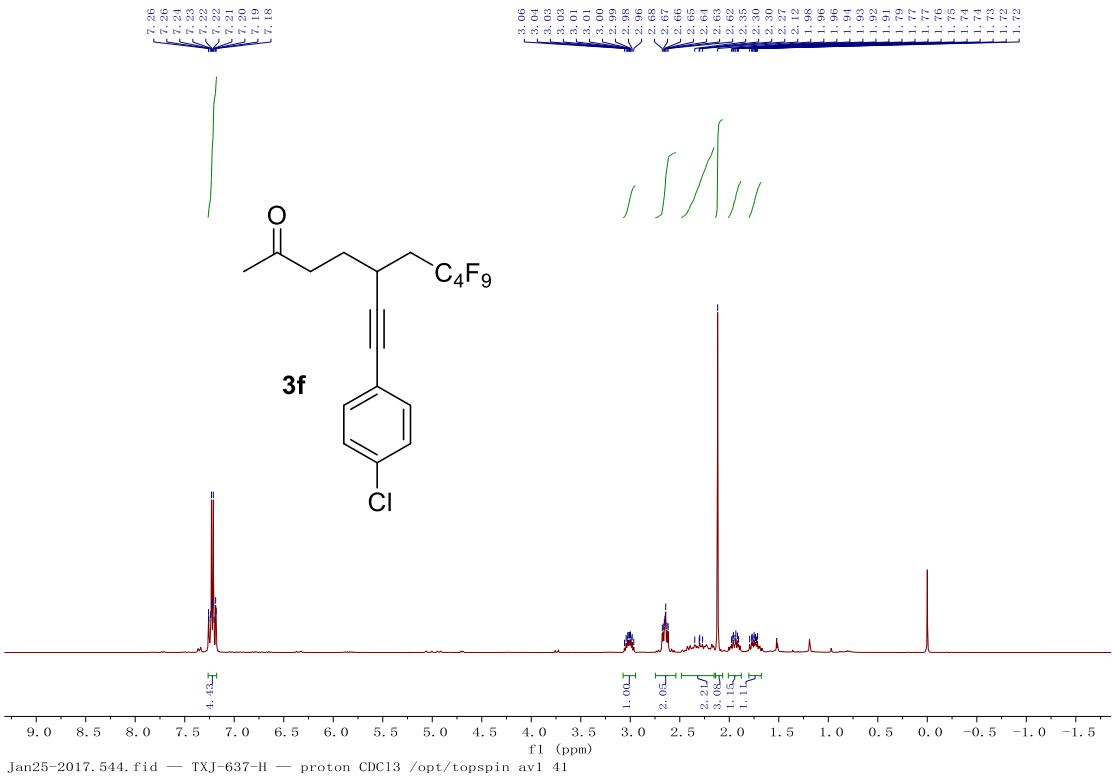

207.55
159.54
132.96
115.07
113.92
87.75
83.10
77.42
77.00
76.58
55.27
40.93
36.52
36.25
35.97
30.08
29.16
24.72
O
C4F9
3d
OMe
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
Jan24-2017.551.fid — TXJ-633-C — carbon CDCl3 /opt/topspin av1 35

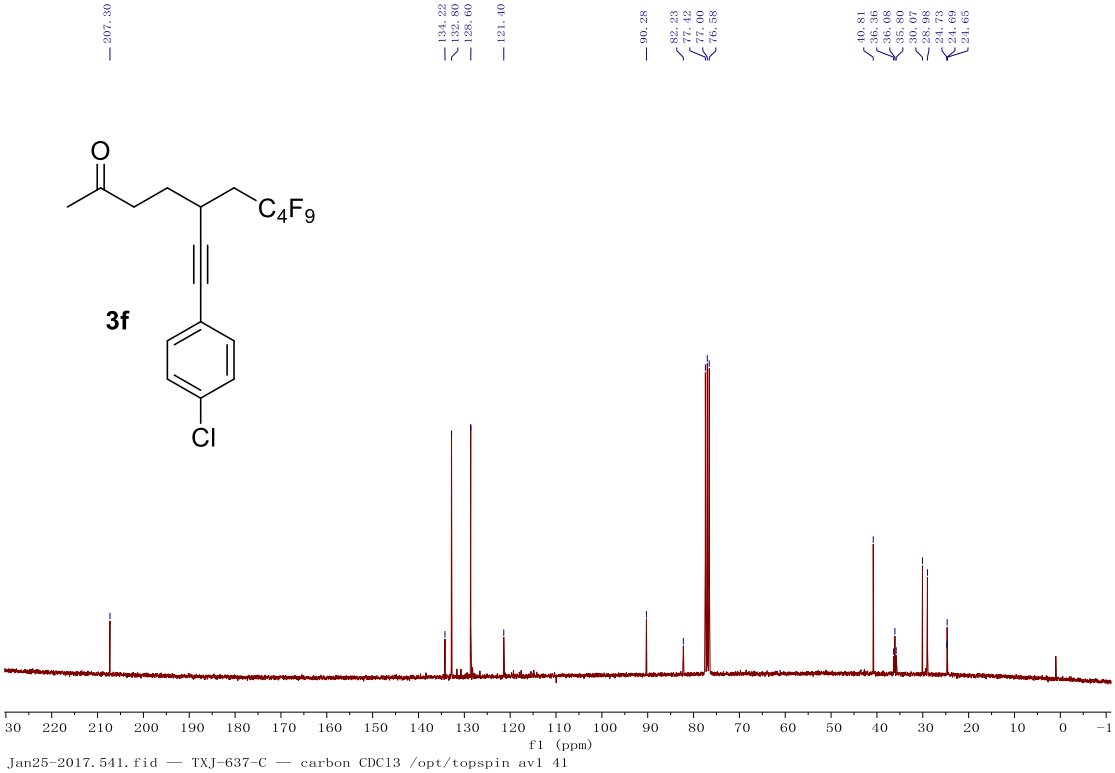

O
C4F9
3d
OMe
f1 (ppm)
Jan25-2017.161.fid — TXJ-633-F — f19cpd CDCl3 /opt/topspin av1 11

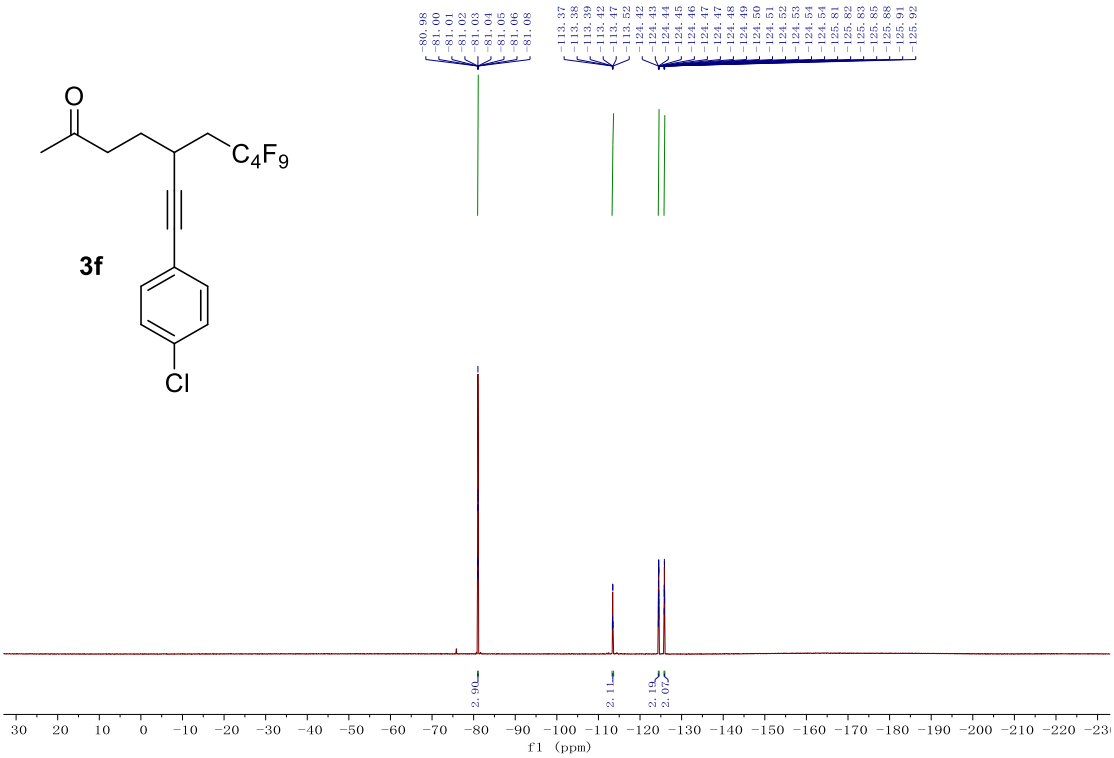

O
C4F9
3e
F
f1 (ppm)
Jan24-2017.560.fid — TXJ-634-H — proton CDCl3 /opt/topspin av1 36

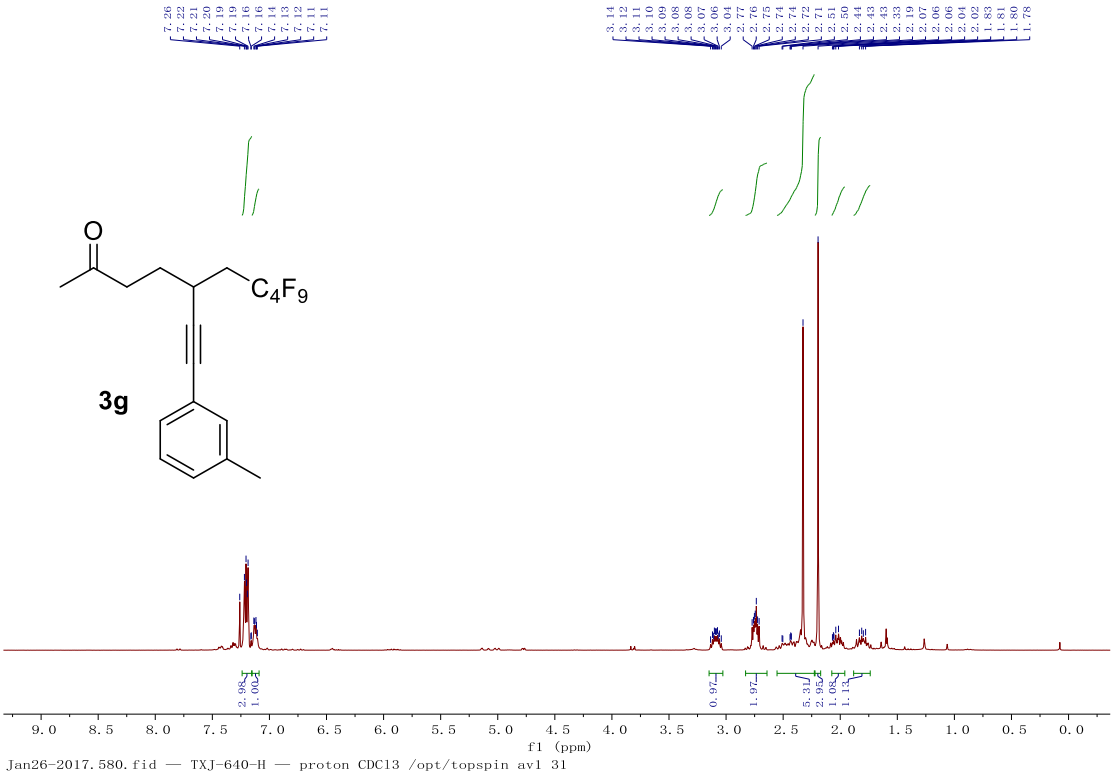

207.36
164.08
160.78
133.48
133.37
119.01
118.97
115.67
115.38
88.93
88.91
82.25
77.42
77.00
76.58
40.84
36.41
36.14
35.86
30.06
29.04
24.65
24.61
O
C4F9
3e
F
f1 (ppm)
Jan24-2017.561.fid — TXJ-634-C — carbon CDCl3 /opt/topspin av1 36

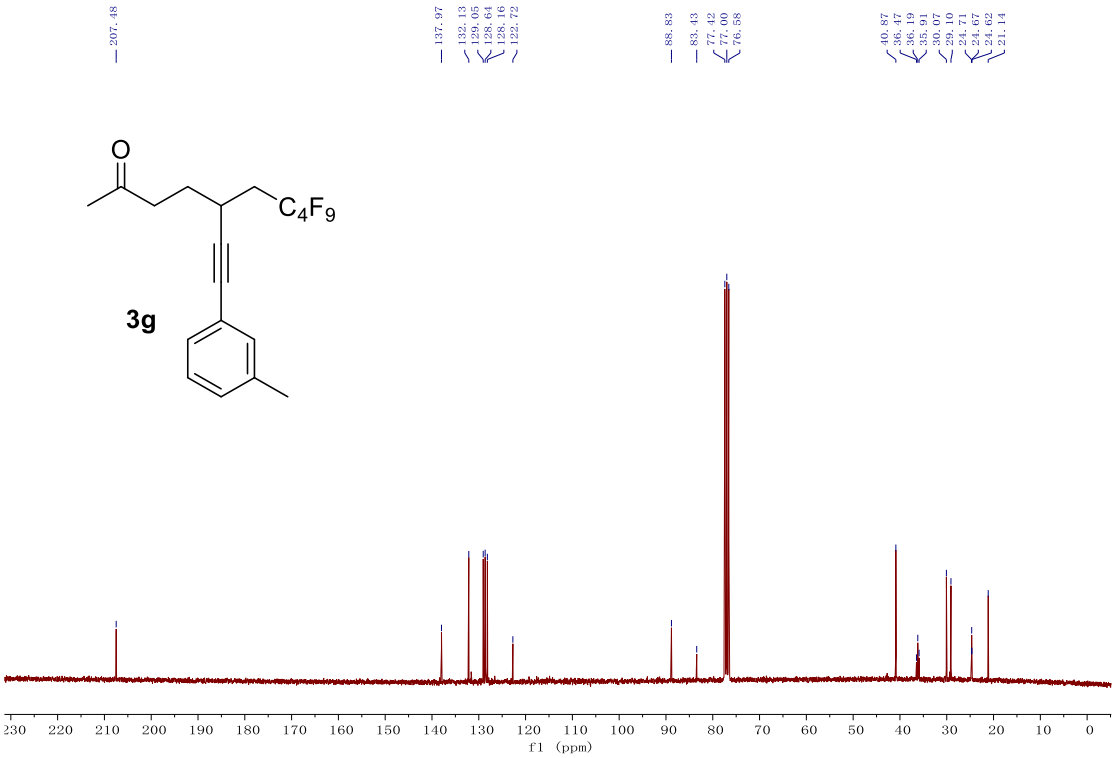

O
C4F9
3e
F
2.90
0.73
2.13
2.22
2.02
f1 (ppm)
Jan25-2017.171.fid — TXJ-634-F — f19cpd CDCl3 /opt/topspin av1 12

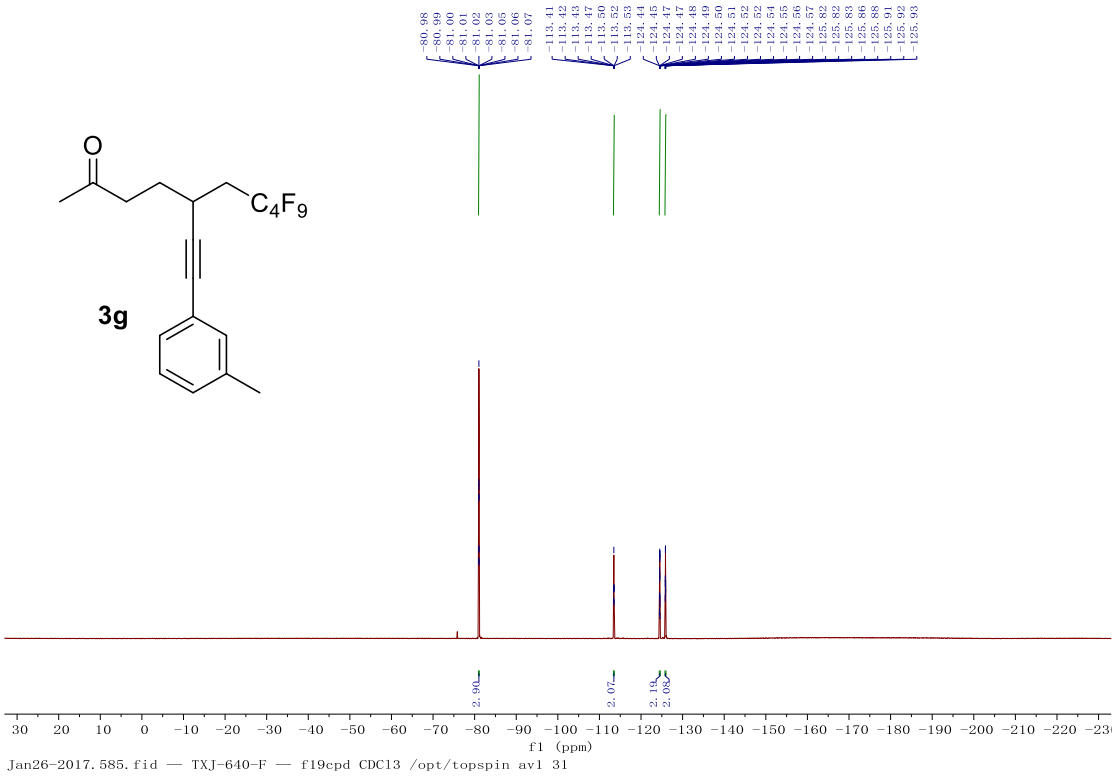

O
C4F9
3f
Cl
f1 (ppm)
Jan25-2017.544.fid — TXJ-637-H — proton CDCl3 /opt/topspin av1 41

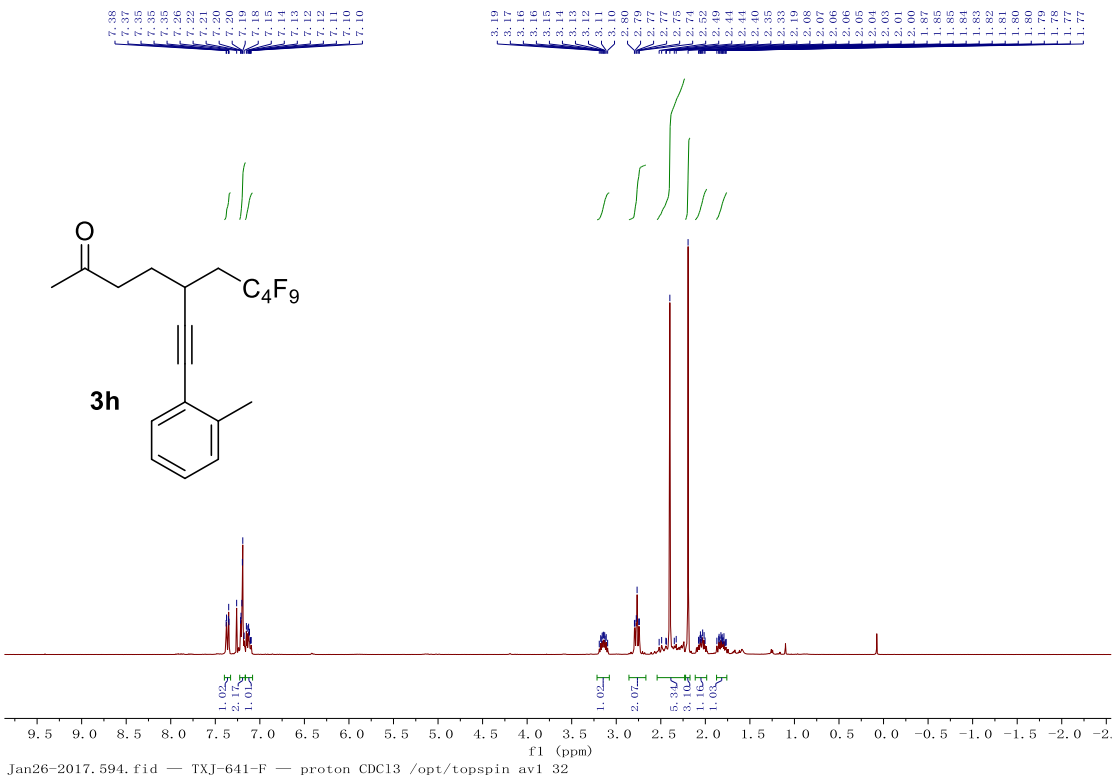

O
C4F9
3f
Cl
f1 (ppm)
Jan25-2017.541.fid — TXJ-637-C — carbon CDCl3 /opt/topspin av1 41

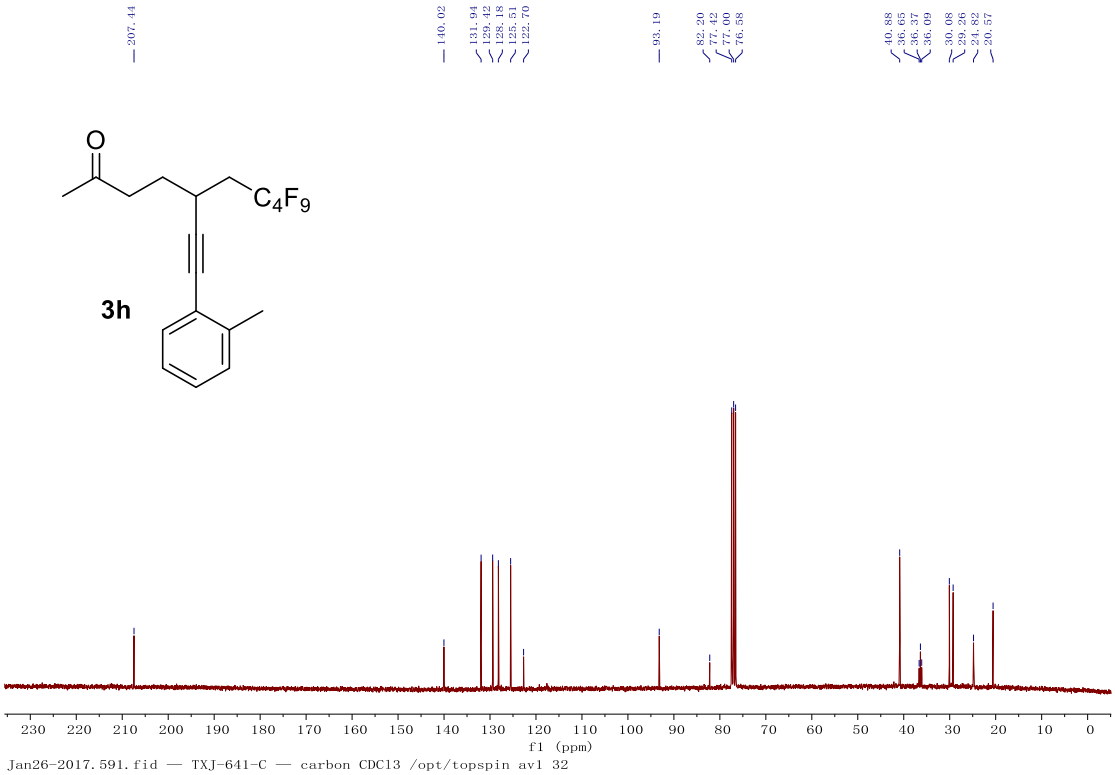

O
C4F9
3f
Cl
f1 (ppm)
Jan25-2017.545.fid — TXJ-637-F — f19cpd CDCl3 /opt/topspin av1 41

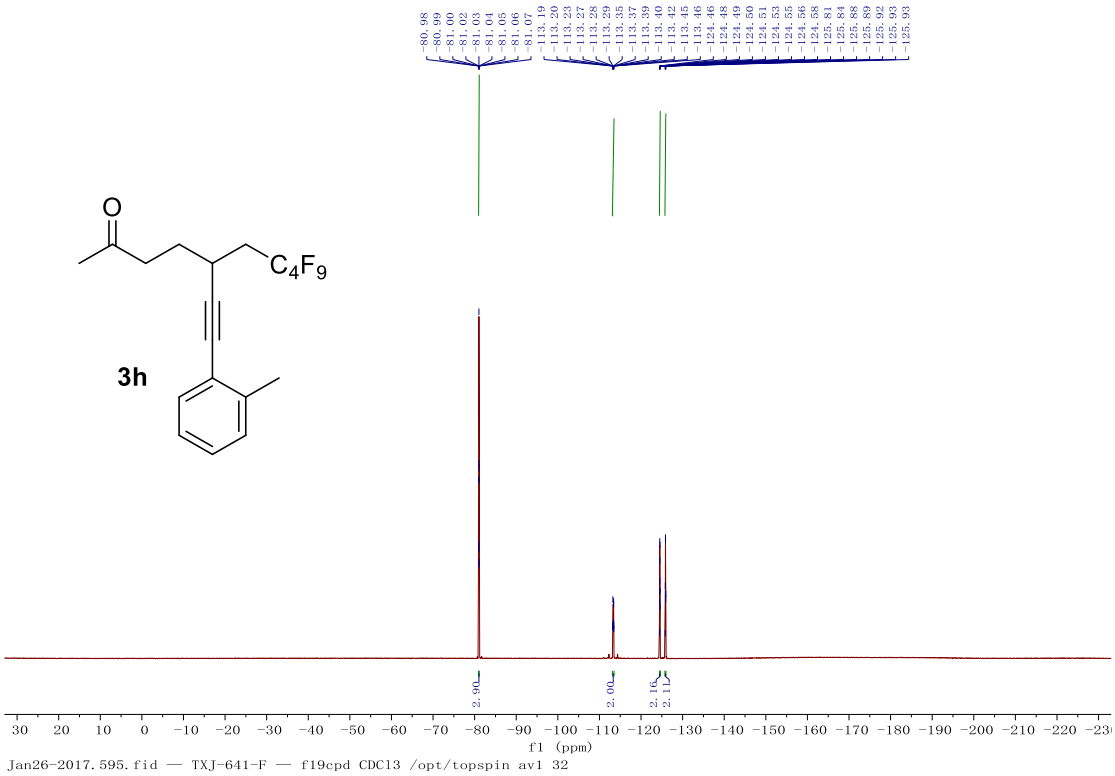

O
C4F9
3g
f1 (ppm)
Jan26-2017.580.fid — TXJ-640-H — proton CDCl3 /opt/topspin av1 31

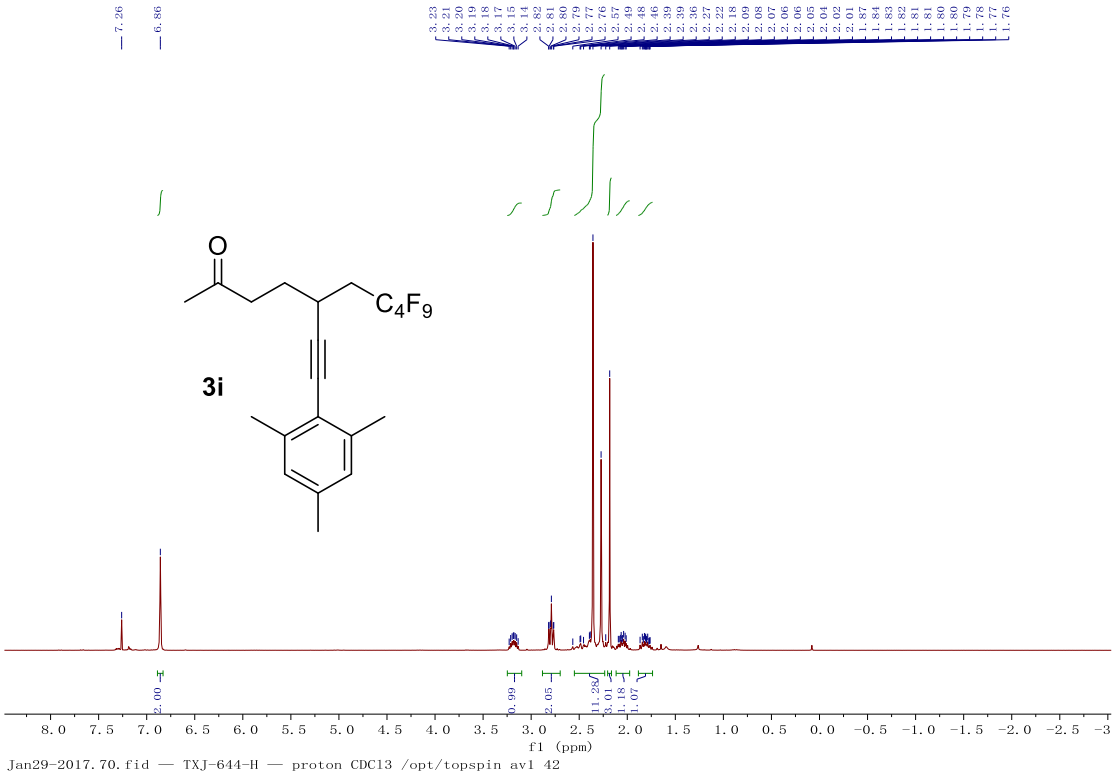

207.48
137.97
132.13
129.05
128.64
128.16
122.72
88.83
83.43
77.42
77.00
76.58
40.97
36.47
36.19
35.91
30.07
29.10
24.71
24.67
24.62
21.14
O
C4F9
3g
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Jan26-2017.581.fid — TXJ-640-C — carbon CDCl3 /opt/topspin av1 31

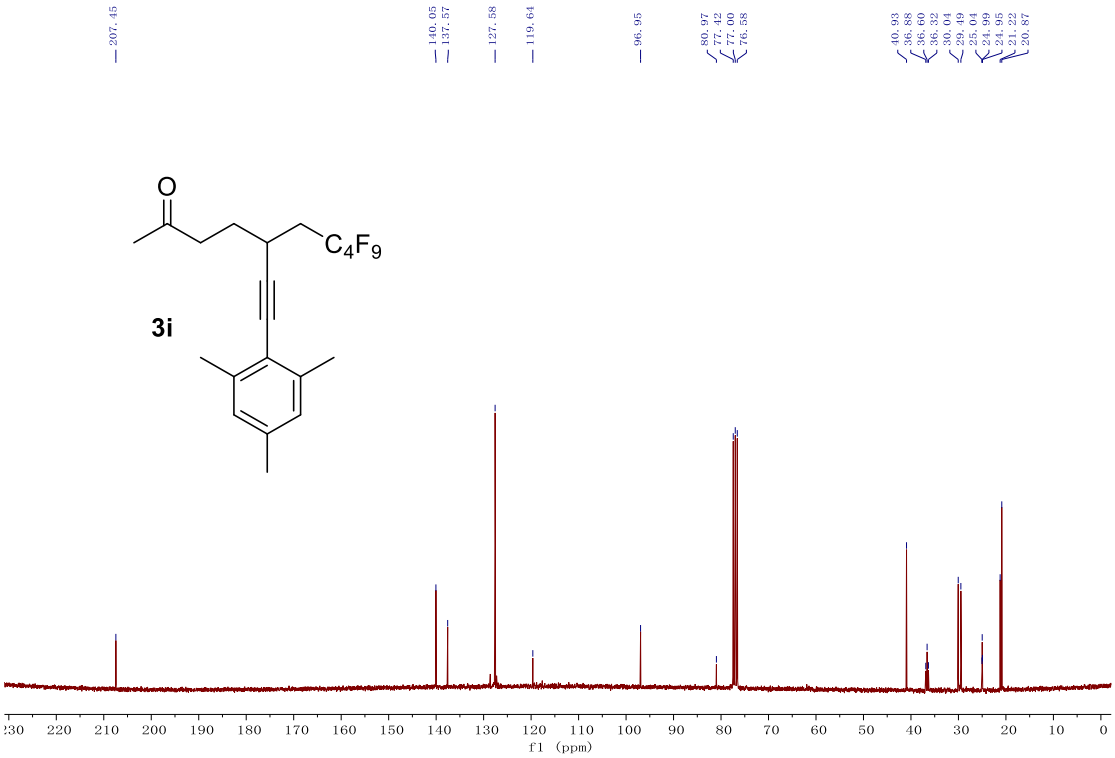

-80.98
-80.99
-81.00
-81.01
-81.02
-81.03
-81.05
-81.06
-81.07
-113.41
-113.42
-113.43
-113.47
-113.50
-113.52
-113.53
-124.44
-124.45
-124.47
-124.47
-124.48
-124.49
-124.50
-124.51
-124.52
-124.52
-124.54
-124.55
-124.56
-124.57
-125.82
-125.82
-125.83
-125.86
-125.88
-125.91
-125.92
-125.93
O
C4F9
3g
2.90
2.07
2.19
2.08
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -23
f1 (ppm)
Jan26-2017.585.fid — TXJ-640-F — f19cpd CDCl3 /opt/topspin av1 31


O
C_4F_9
3h
f1 (ppm)
Jan26-2017.594.fid — TXJ-641-F — proton CDCl3 /opt/topspin av1 32

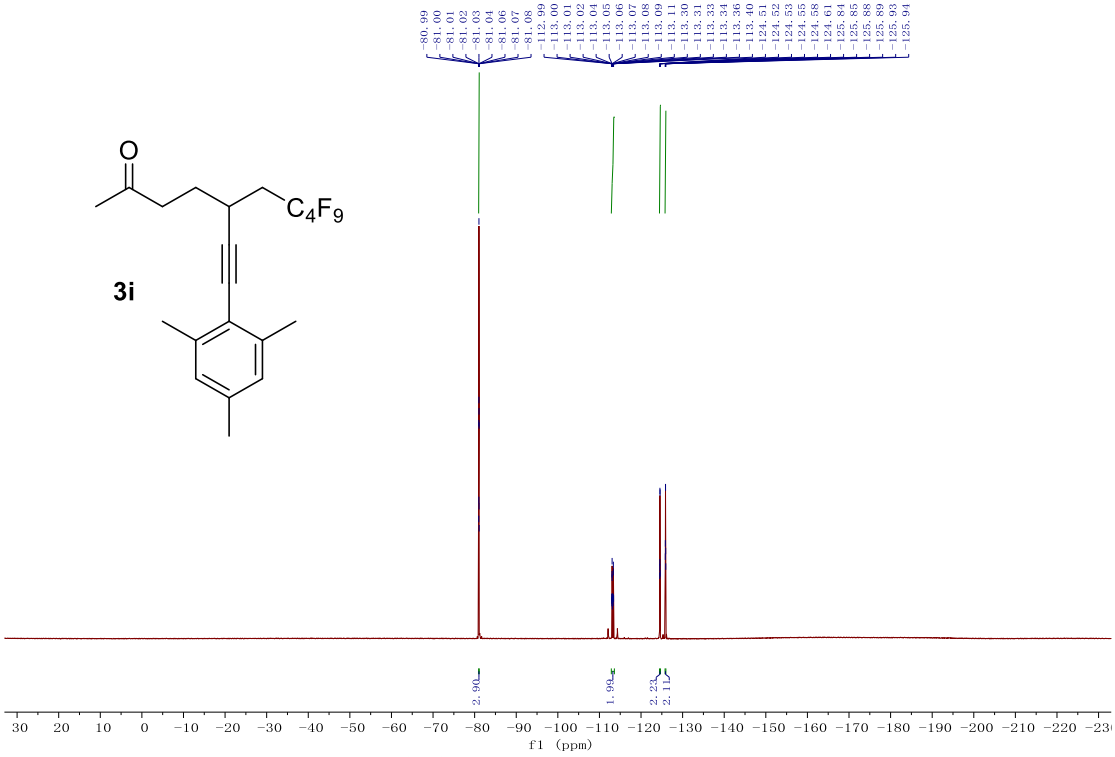

O
C_4F_9
3h
f1 (ppm)
Jan26-2017.591.fid — TXJ-641-C — carbon CDCl3 /opt/topspin av1 32


O
C_4F_9
3h
f1 (ppm)
Jan26-2017.595.fid — TXJ-641-F — f19cpd CDCl3 /opt/topspin av1 32

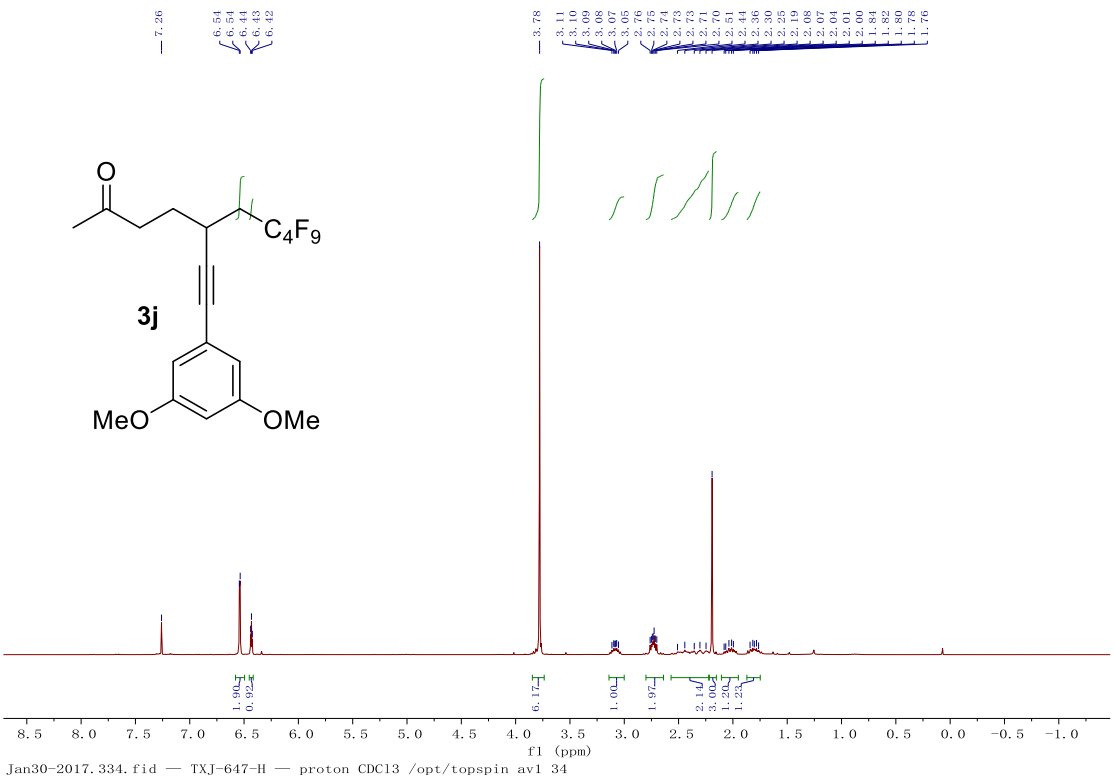

O
C_4F_9
3i
f1 (ppm)
Jan29-2017.70.fid — TXJ-644-H — proton CDCl3 /opt/topspin av1 42

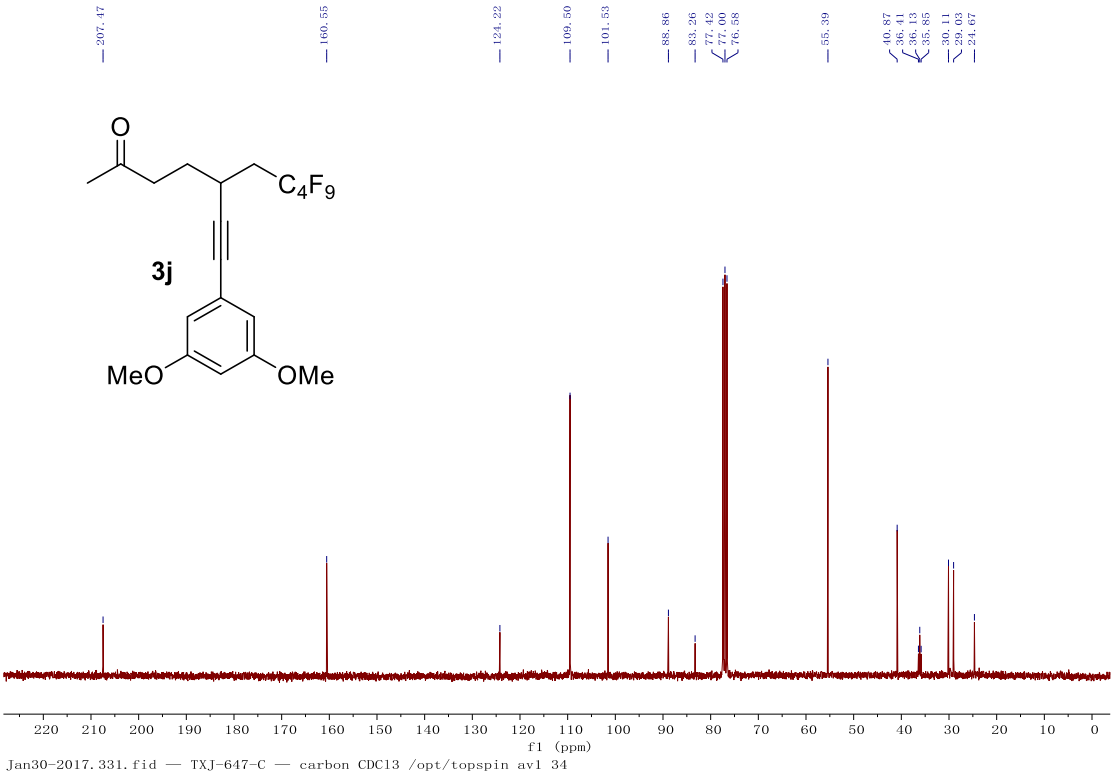


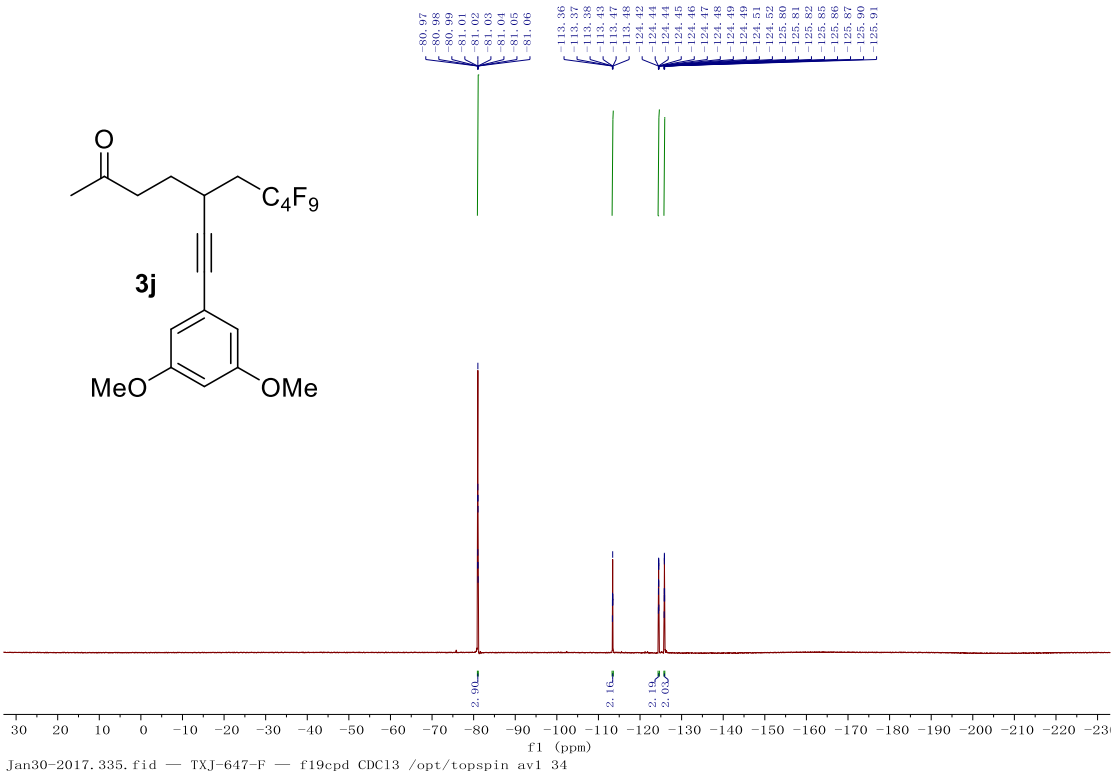
Jan29-2017.71.fid — TXJ-644-C — carbon CDCl3 /opt/topspin av1 42

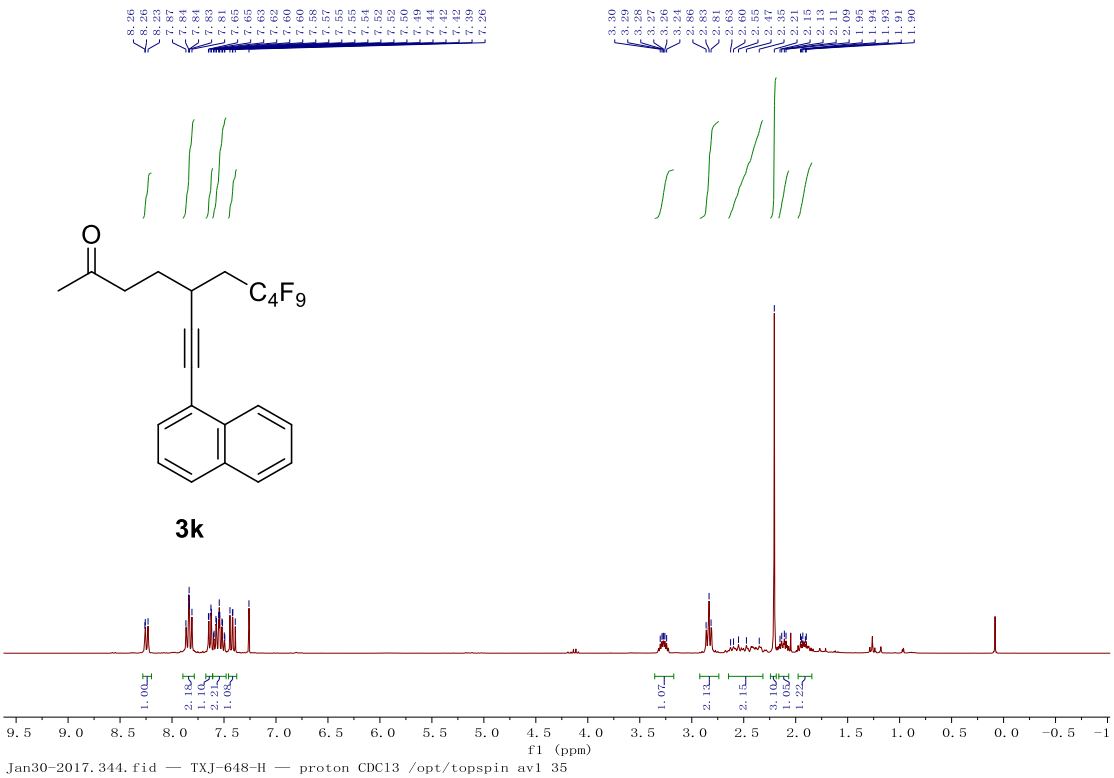


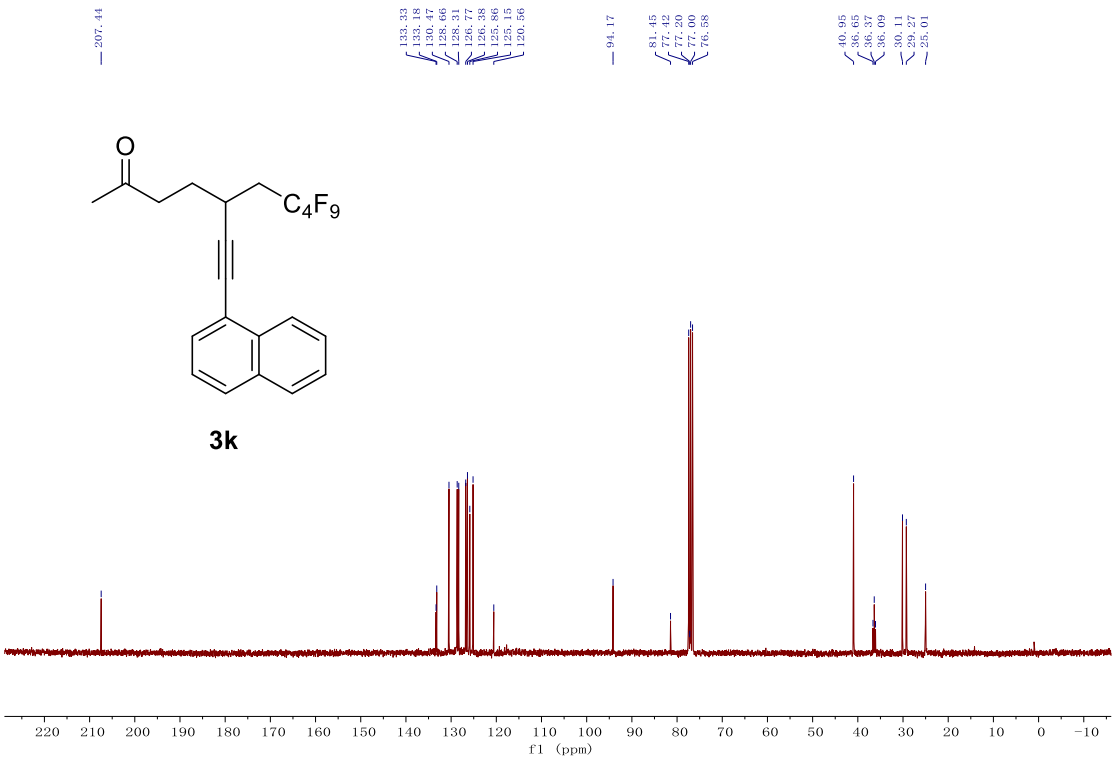
Jan29-2017.75.fid — TXJ-644-F — f19cpd CDCl3 /opt/topspin av1 42


7.26
6.54
6.54
6.44
6.43
6.42
3.78
3.11
3.10
3.09
3.08
3.07
3.05
2.76
2.75
2.74
2.73
2.73
2.71
2.70
2.51
2.44
2.36
2.30
2.25
2.19
2.08
2.07
2.04
2.01
2.00
1.84
1.82
1.80
1.78
1.76
O
C4F9
3j
MeO
OMe
1.90
0.92
6.17
1.00
1.97
2.14
3.00
1.20
1.23
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
Jan30-2017.334.fid — TXJ-647-H — proton CDCl3 /opt/topspin av1 34

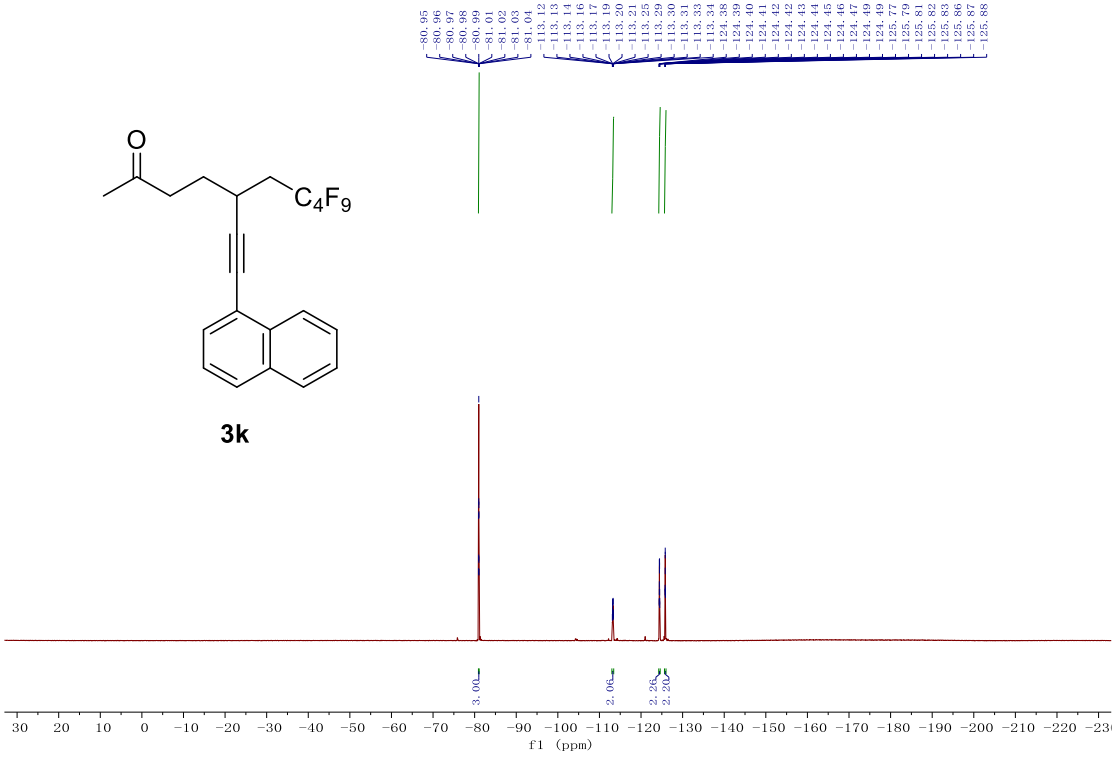

207.47
160.55
124.22
109.50
101.53
88.86
83.26
77.42
77.00
76.58
55.39
40.87
36.41
36.13
35.85
30.11
29.03
24.67
O
C4F9
3j
MeO
OMe
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Jan30-2017.331.fid — TXJ-647-C — carbon CDCl3 /opt/topspin av1 34


O
C_4F_9
3j
MeO
OMe
f1 (ppm)
Jan30-2017.335.fid — TXJ-647-F — f19cpd CDCl3 /opt/topspin av1 34

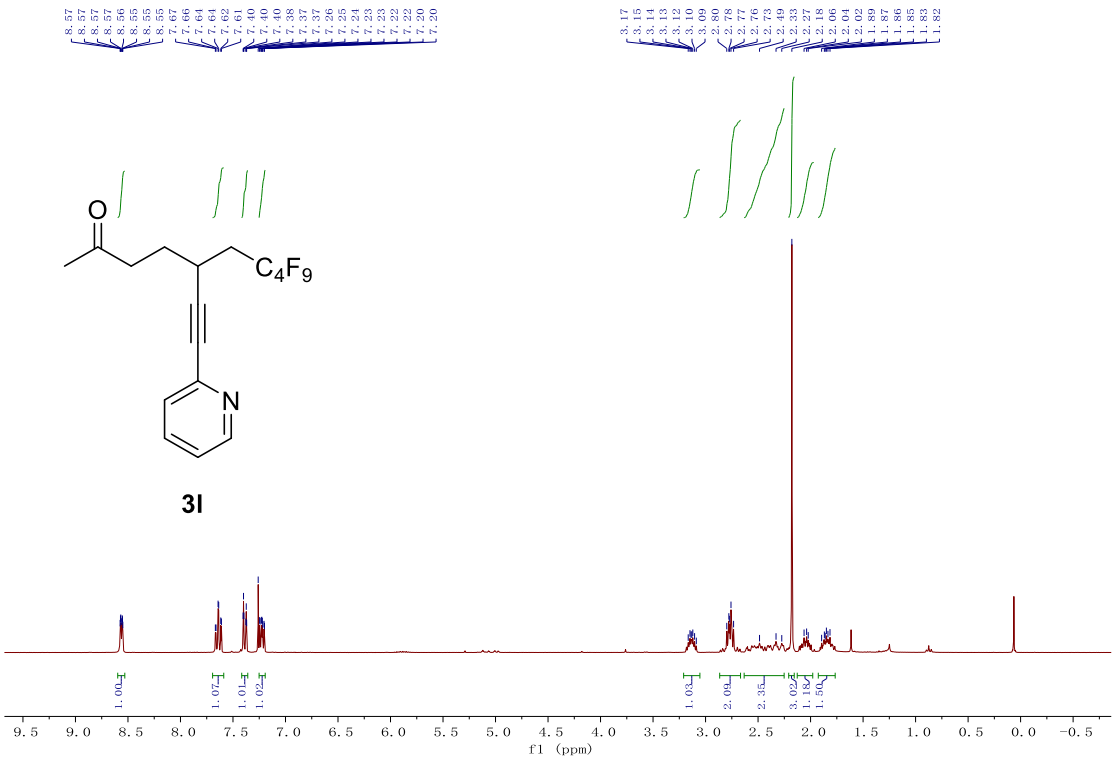

O
C_4F_9
3k
f1 (ppm)
Jan30-2017.344.fid — TXJ-648-H — proton CDCl3 /opt/topspin av1 35



Jan30-2017.341.fid — TXJ-648-C — carbon CDCl3 /opt/topspin av1 35

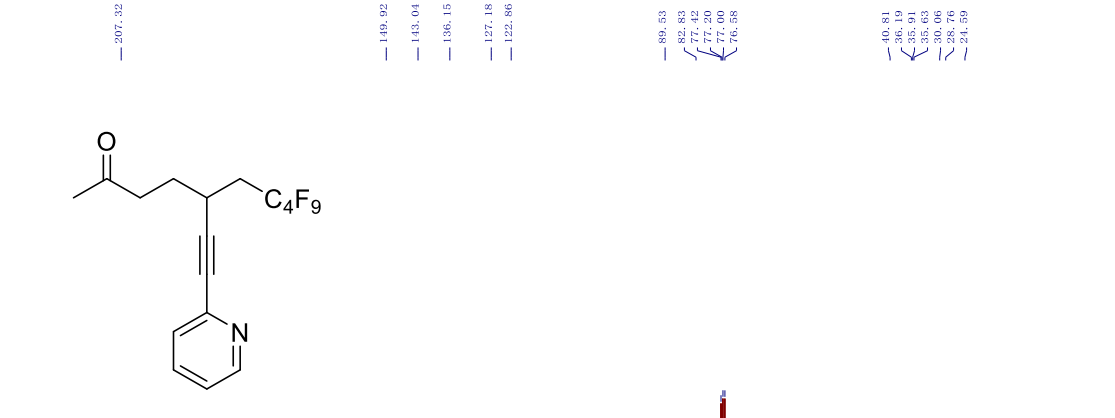


Jan30-2017.345.fid — TXJ-648-F — f19cpd CDCl3 /opt/topspin av1 35


O
C4F9
N

3l

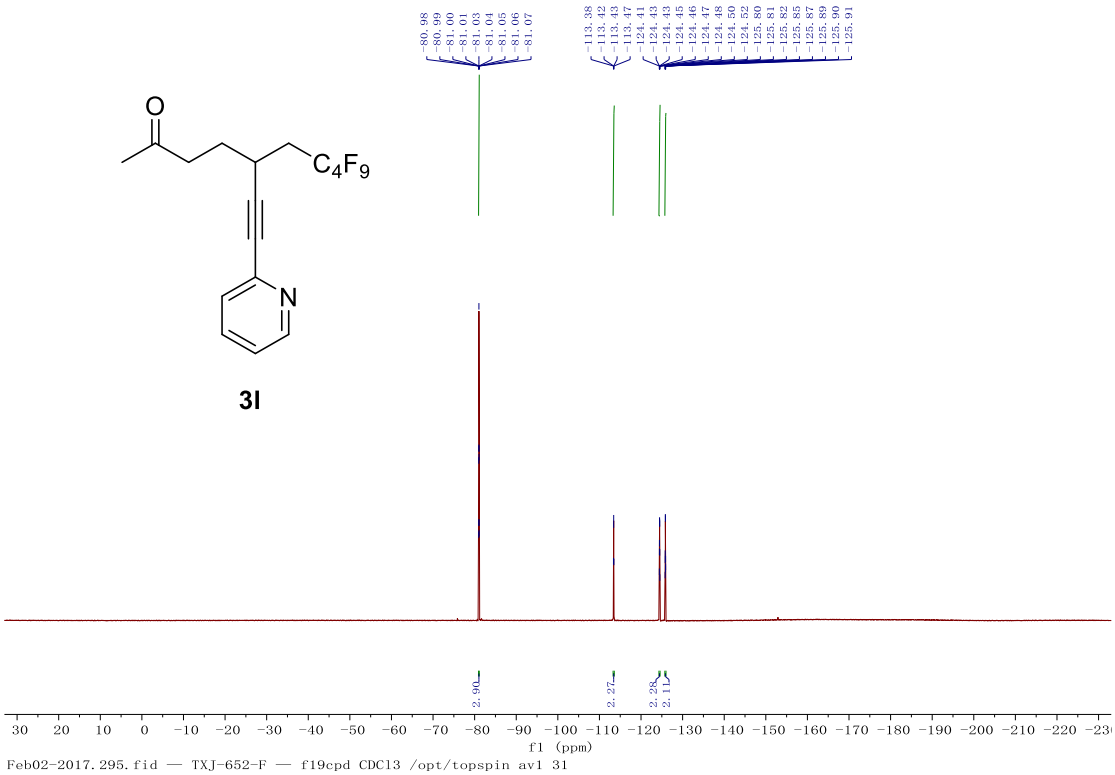
f1 (ppm)
Feb02-2017.294.fid — TXJ-652-H — proton CDCl3 /opt/topspin av1 31

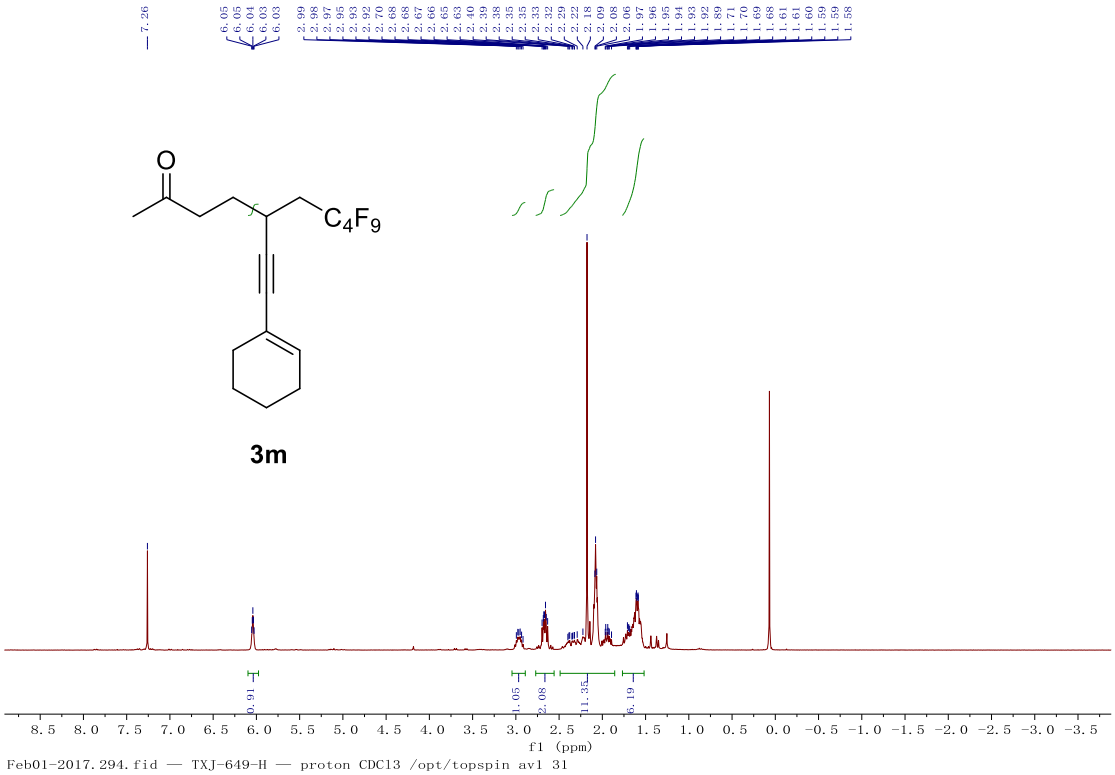


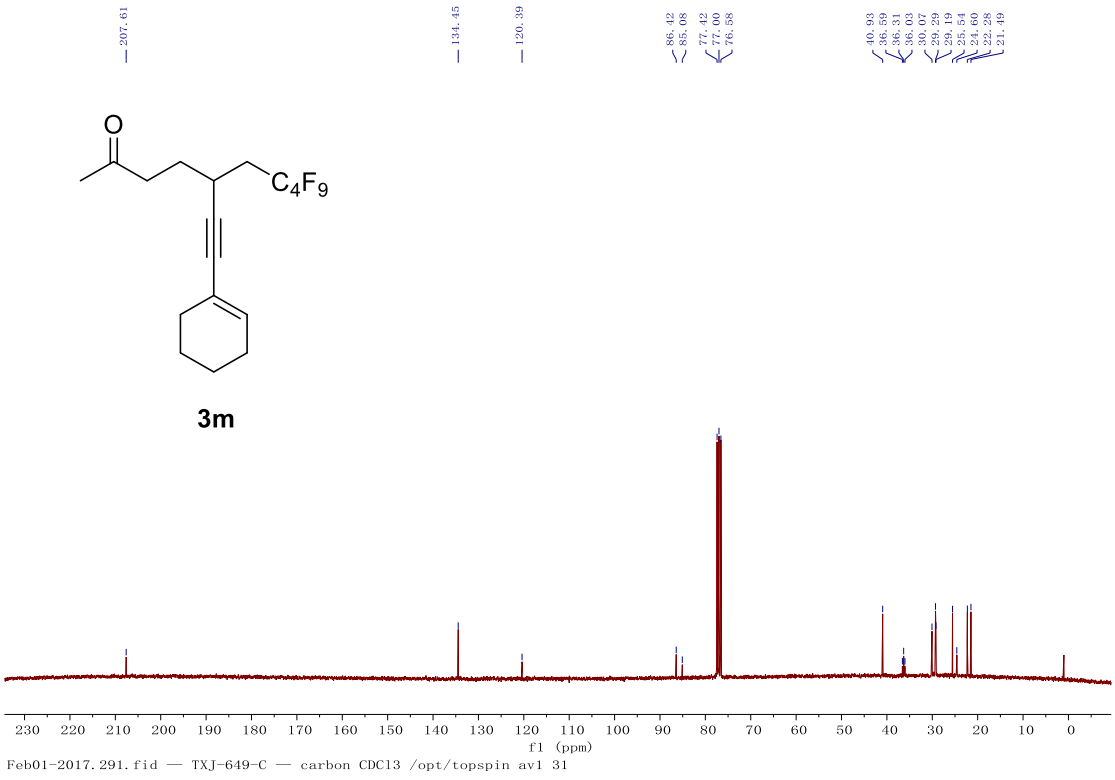
O
C4F9
N

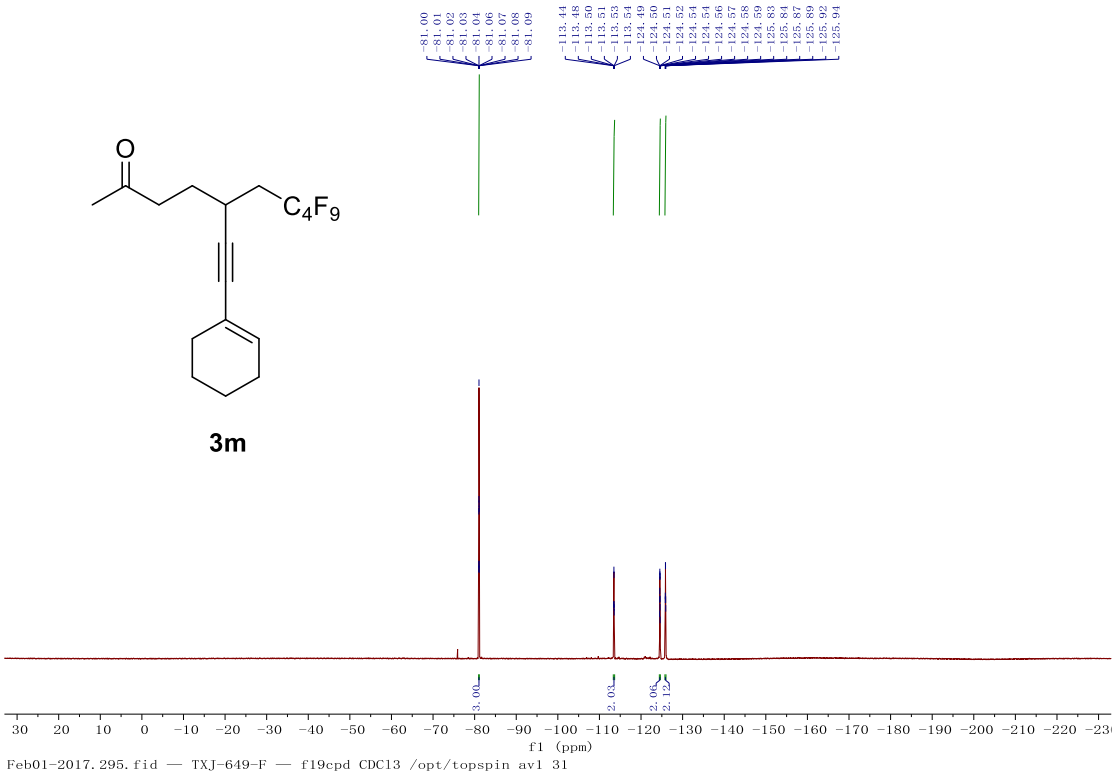
3l

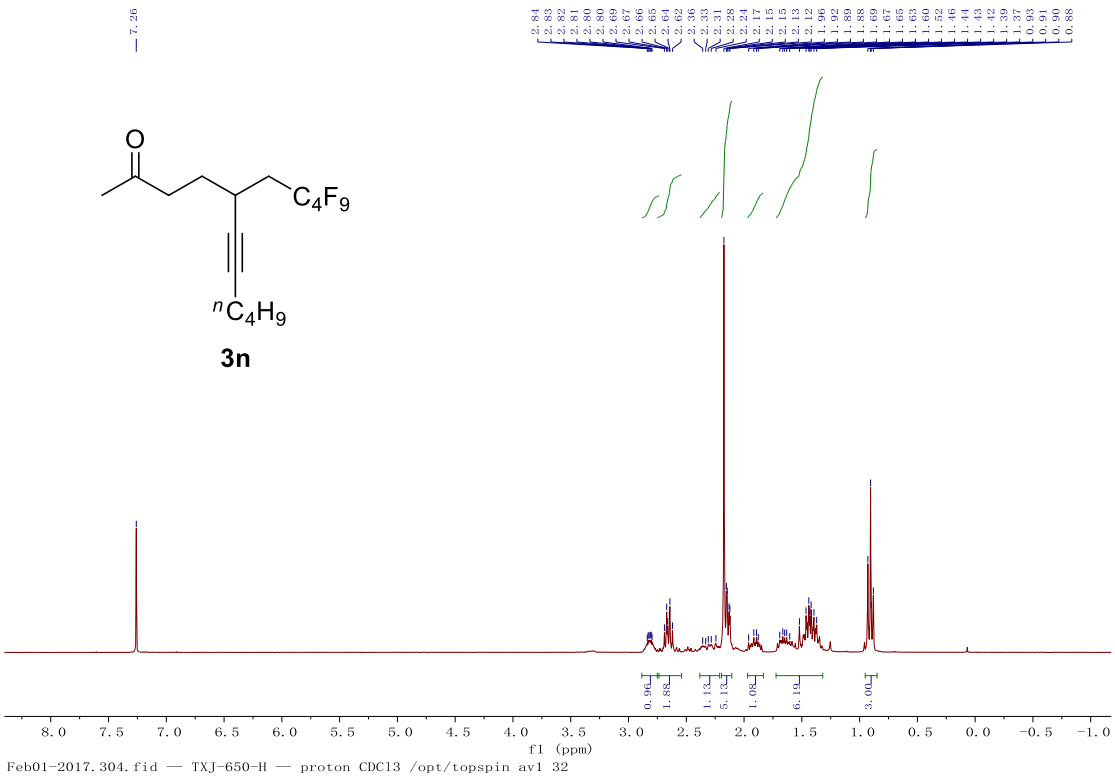
f1 (ppm)
Feb02-2017.291.fid — TXJ-652-C — carbon CDCl3 /opt/topspin av1 31


O
C_4F_9
N
3l
f1 (ppm)
Feb02-2017.295.fid — TXJ-652-F — f19cpd CDCl3 /opt/topspin av1 31


O
C_4F_9
3m
f1 (ppm)
Feb01-2017.294.fid — TXJ-649-H — proton CDCl3 /opt/topspin av1 31

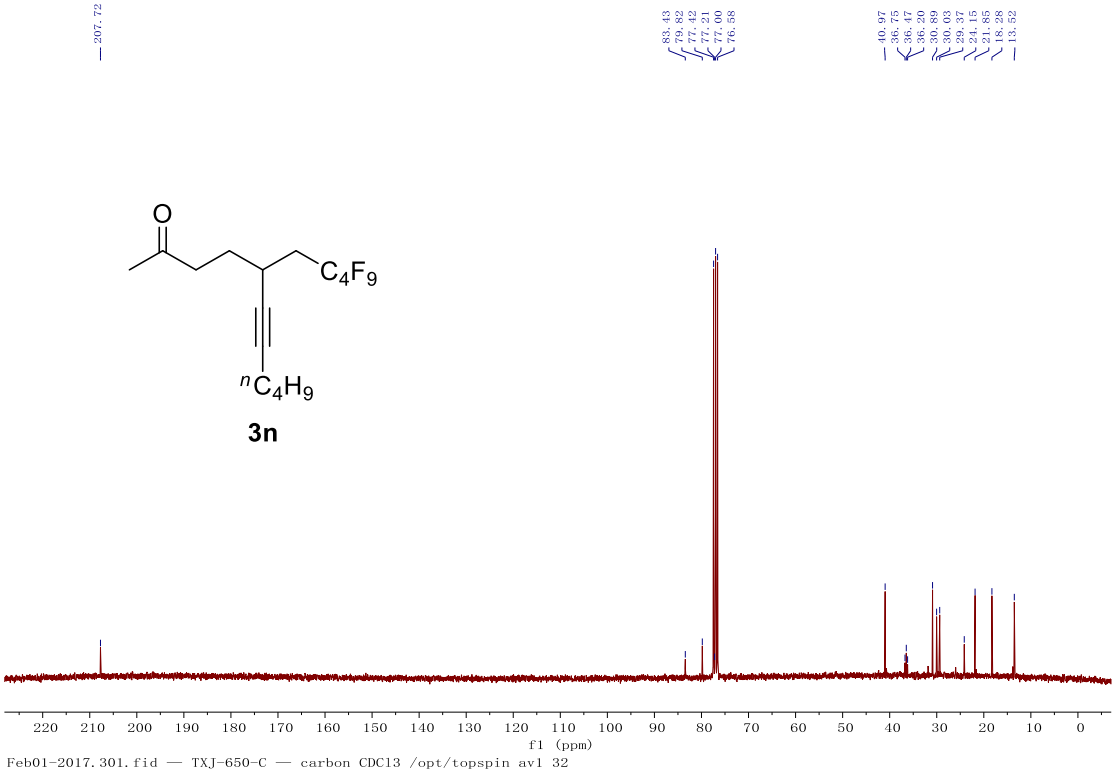

207.61
134.45
120.39
86.42
85.08
77.42
77.00
76.58
40.93
36.59
36.31
36.03
30.07
29.29
29.19
25.54
24.60
22.28
21.49
O
C4F9
3m
f1 (ppm)
Feb01-2017.291.fid — TXJ-649-C — carbon CDCl3 /opt/topspin av1 31


O
C4F9
3m
3.00
2.03
2.06
2.12
f1 (ppm)
Feb01-2017.295.fid — TXJ-649-F — f19cpd CDCl3 /opt/topspin av1 31



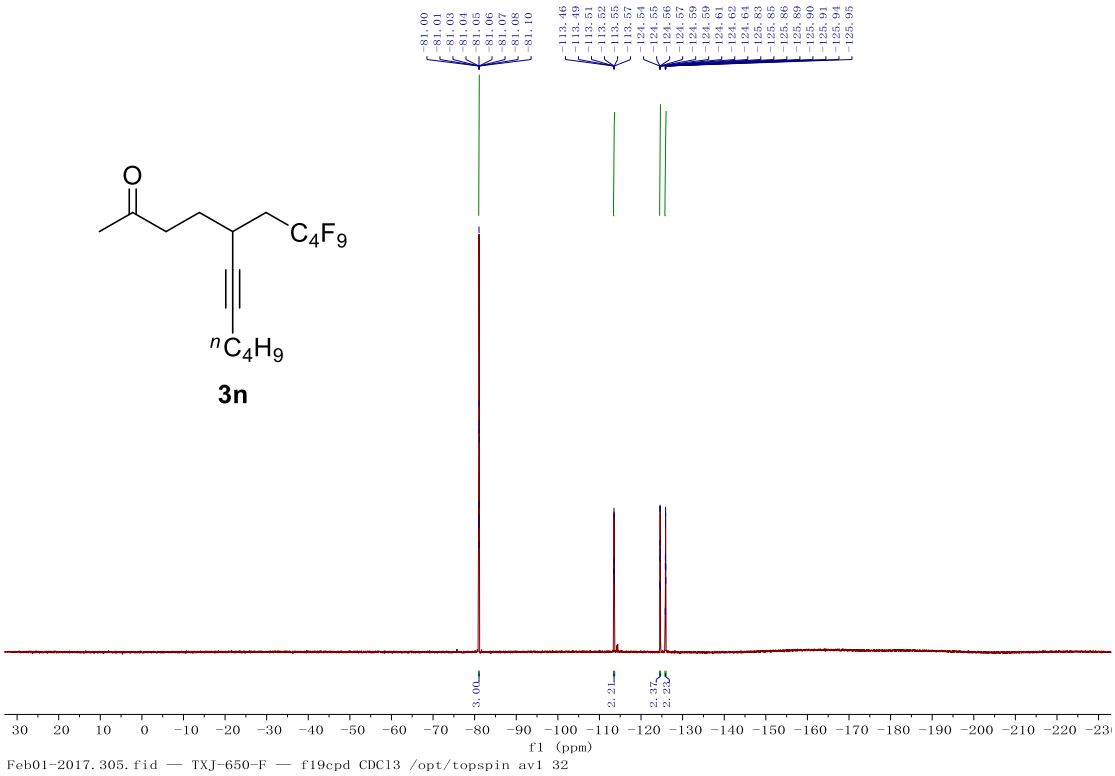
3n

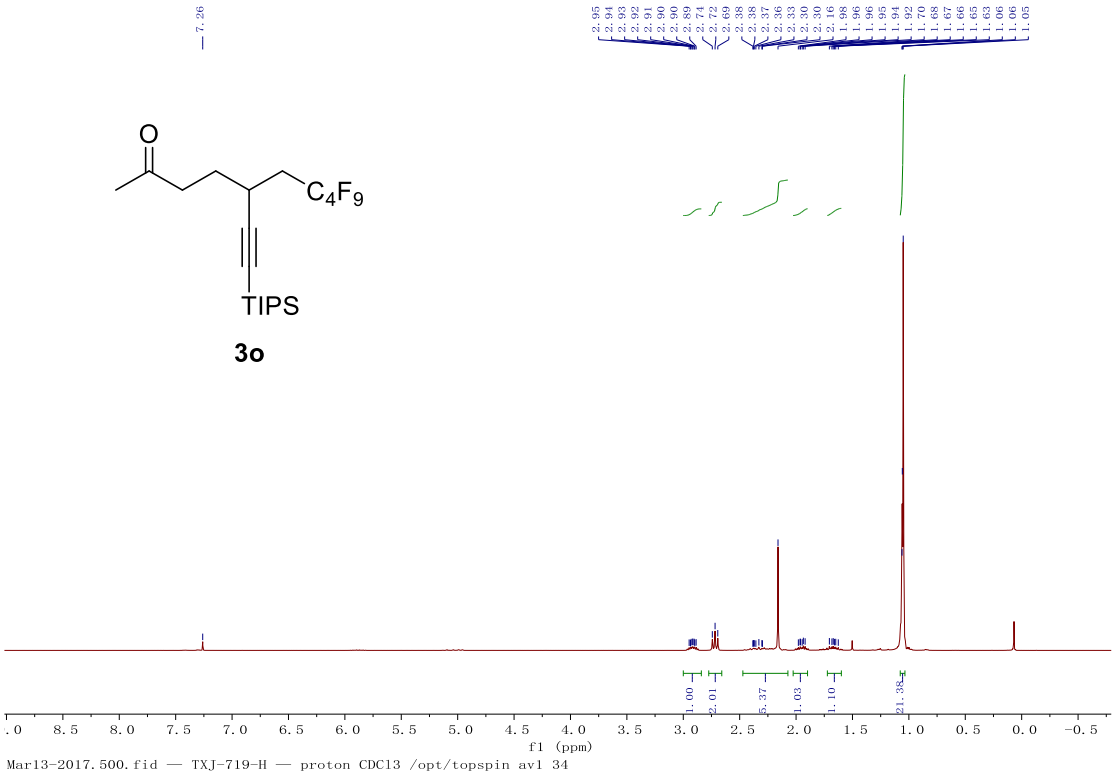
Feb01-2017.304.fid — TXJ-650-H — proton CDCl3 /opt/topspin av1 32

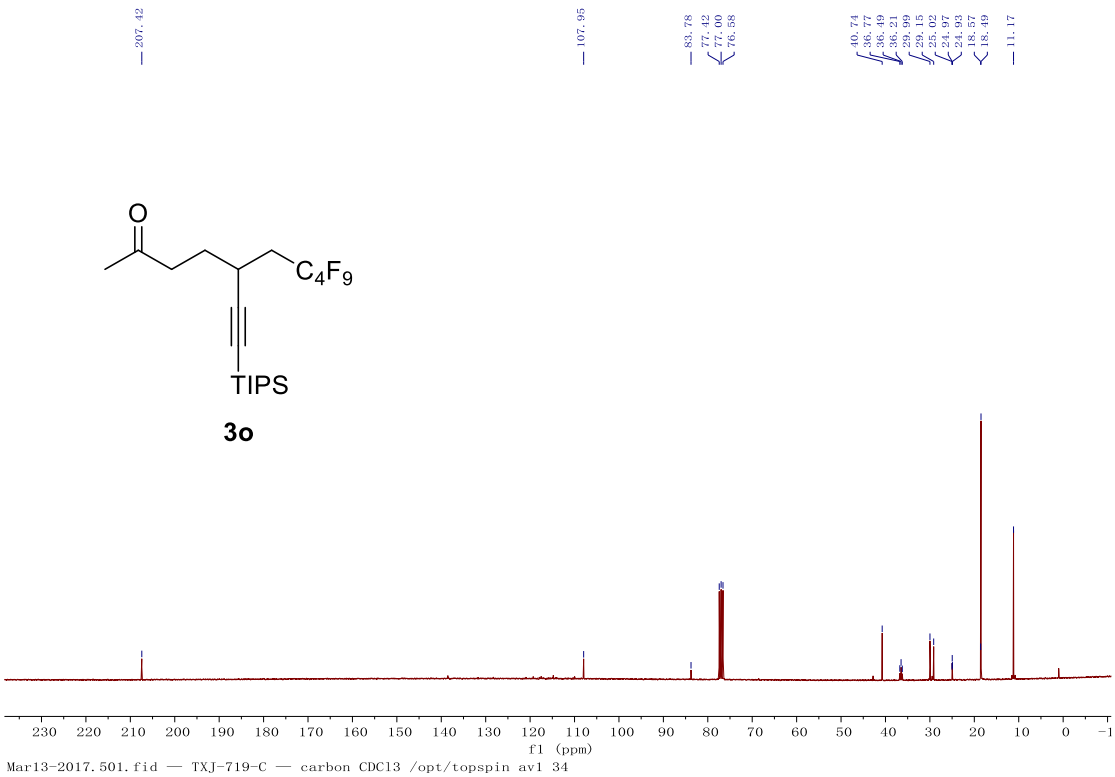


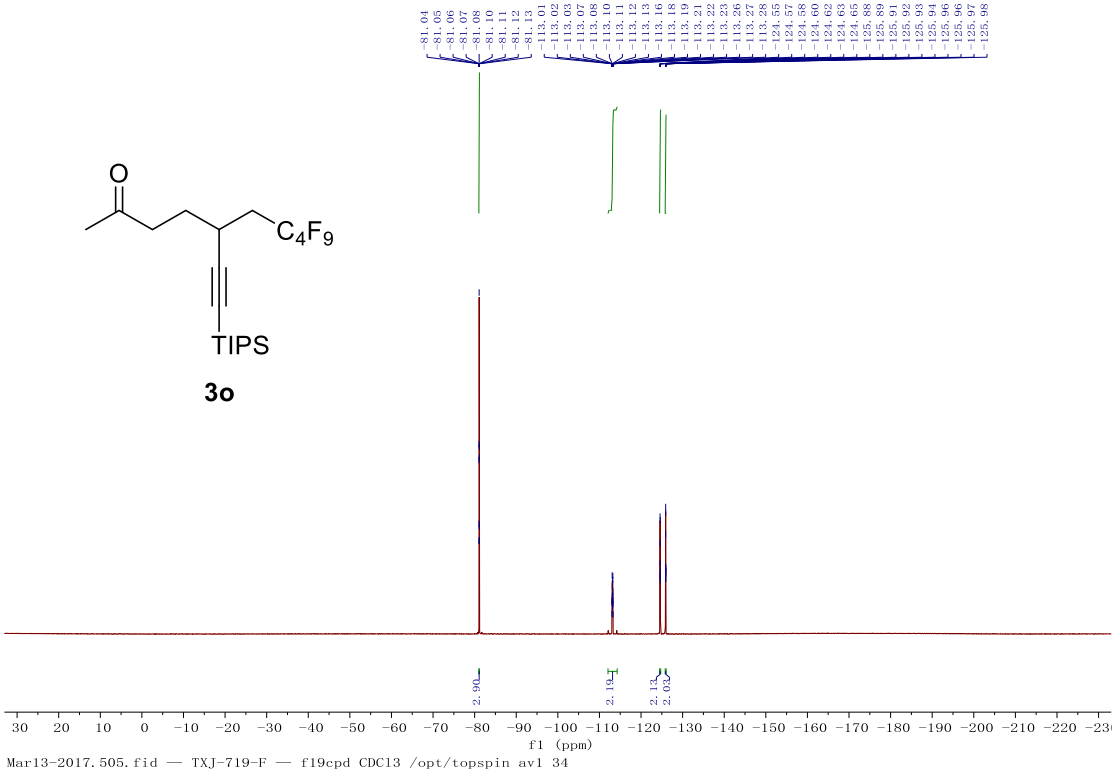
3n

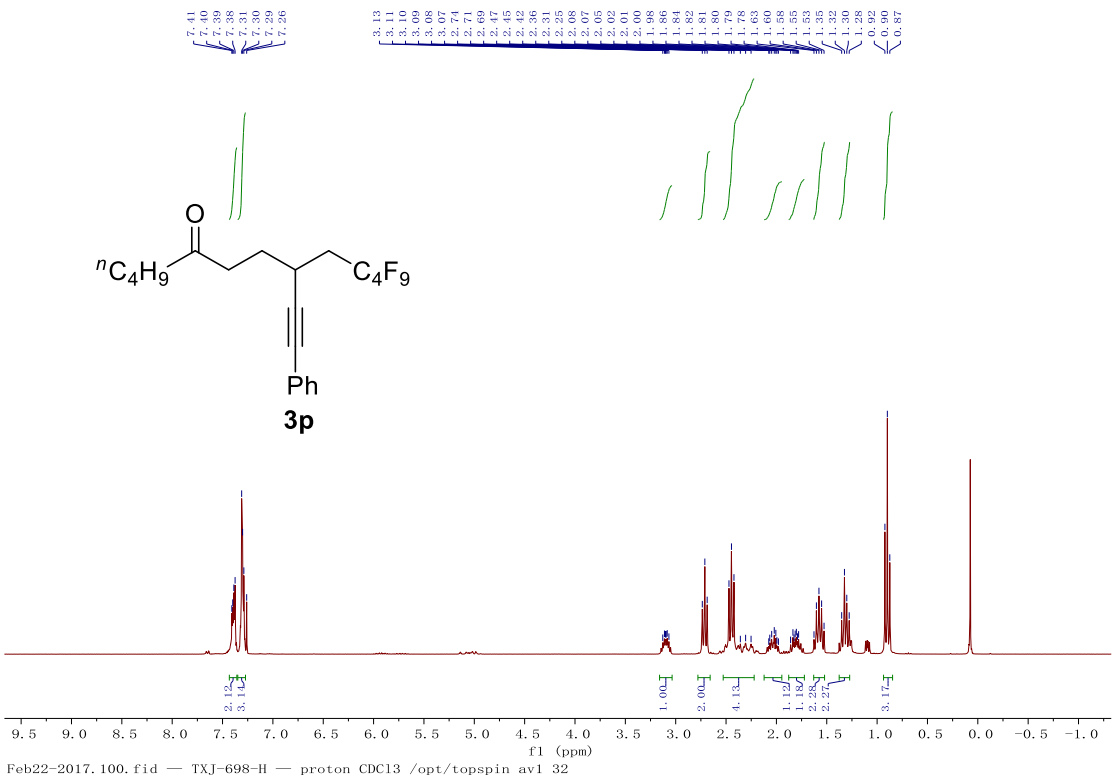
Feb01-2017.301.fid — TXJ-650-C — carbon CDCl3 /opt/topspin av1 32

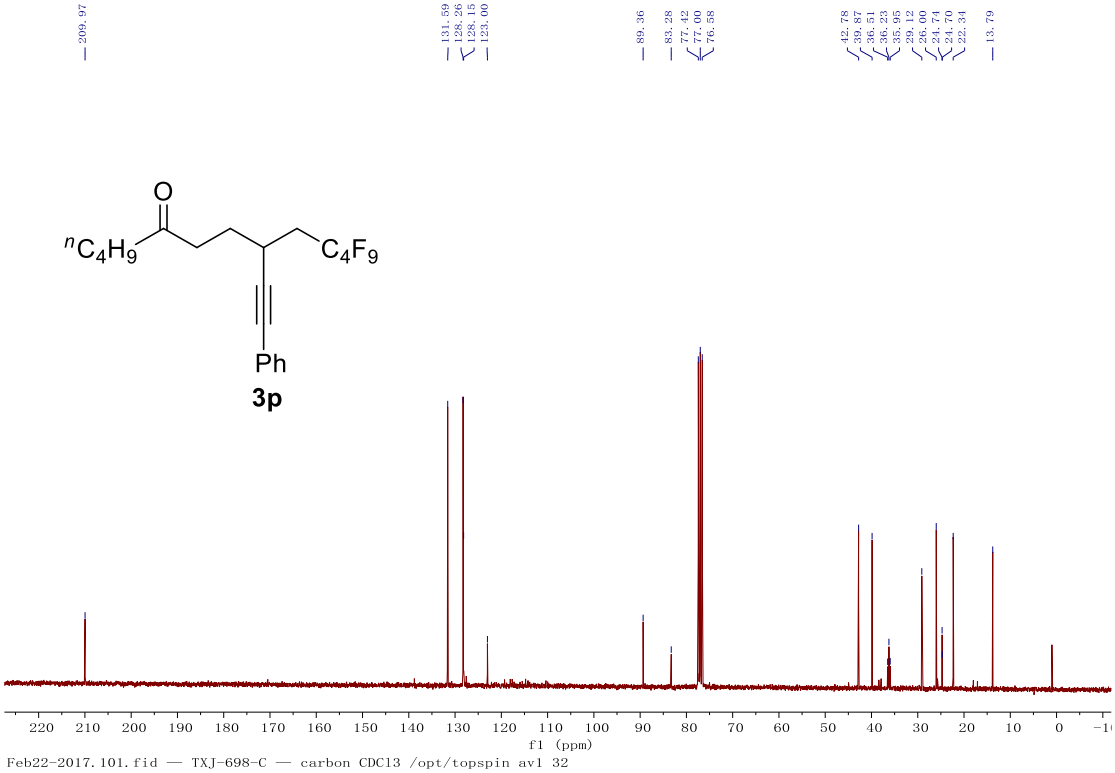

O
C_4F_9
$^nC_4H_9$
3n
f1 (ppm)
Feb01-2017.305.fid — TXJ-650-F — f19cpd CDCl3 /opt/topspin av1 32

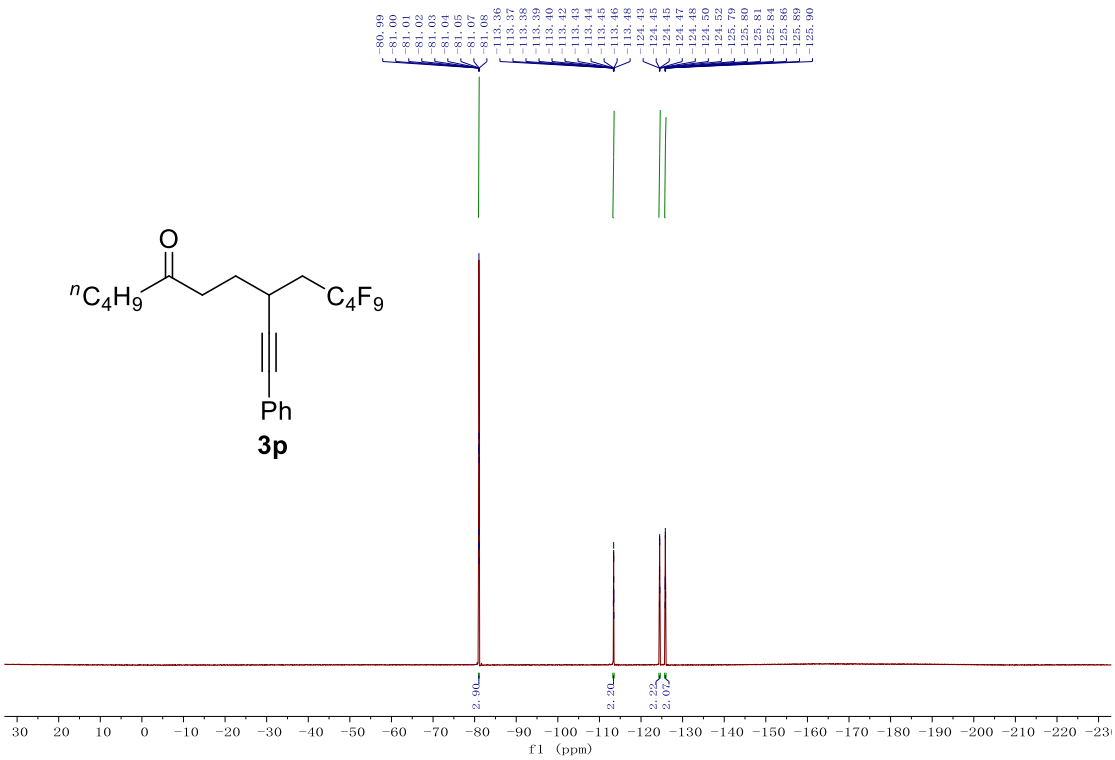

O
C_4F_9
TIPS
3o
f1 (ppm)
Mar13-2017.500.fid — TXJ-719-H — proton CDCl3 /opt/topspin av1 34

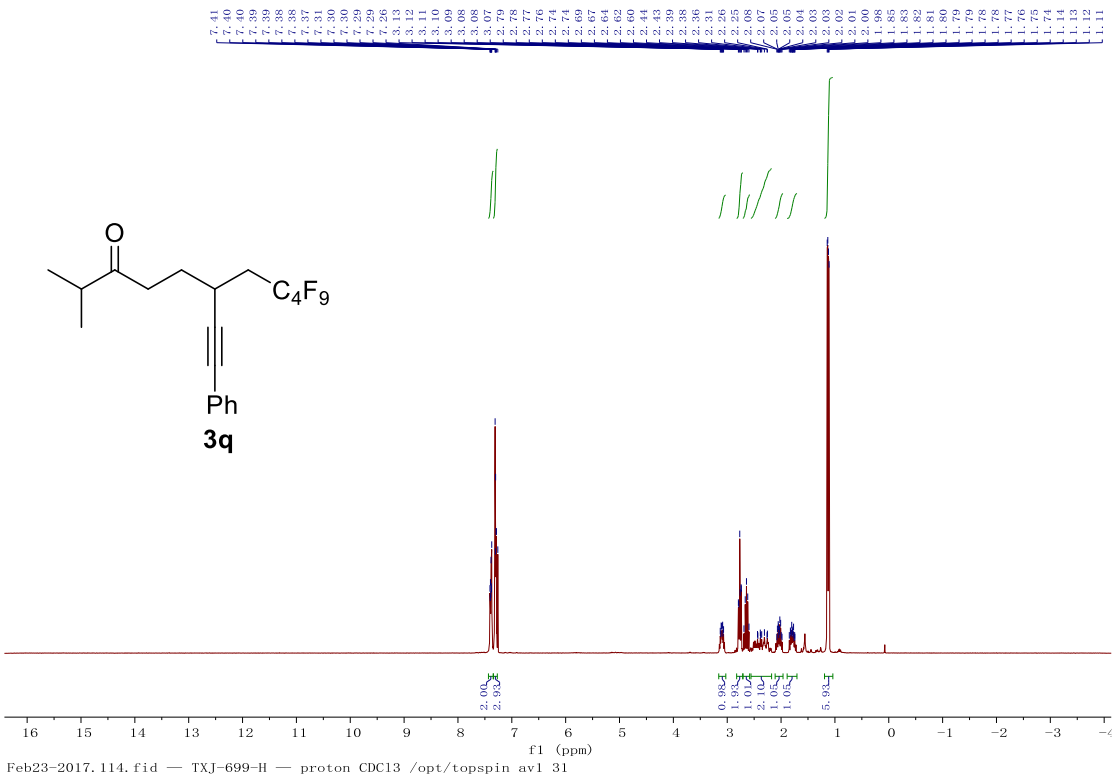

207.42
107.95
83.78
77.42
77.00
76.58
40.74
36.77
36.49
36.21
29.99
29.15
25.02
24.97
24.93
18.57
18.49
11.17
O
C4F9
TIPS
3o
f1 (ppm)
Mar13-2017.501.fid — TXJ-719-C — carbon CDCl3 /opt/topspin av1 34

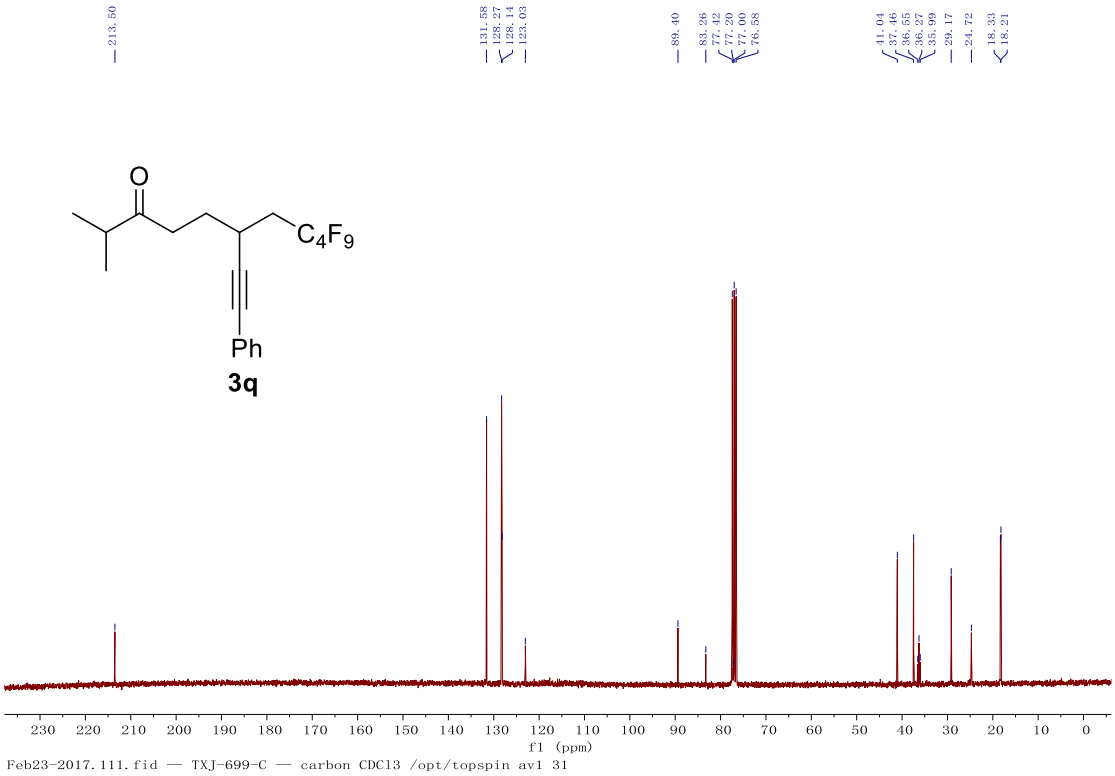

O
C4F9
TIPS
3o
2.90
2.19
2.13
2.02
f1 (ppm)
Mar13-2017.505.fid — TXJ-719-F — f19cpd CDCl3 /opt/topspin av1 34

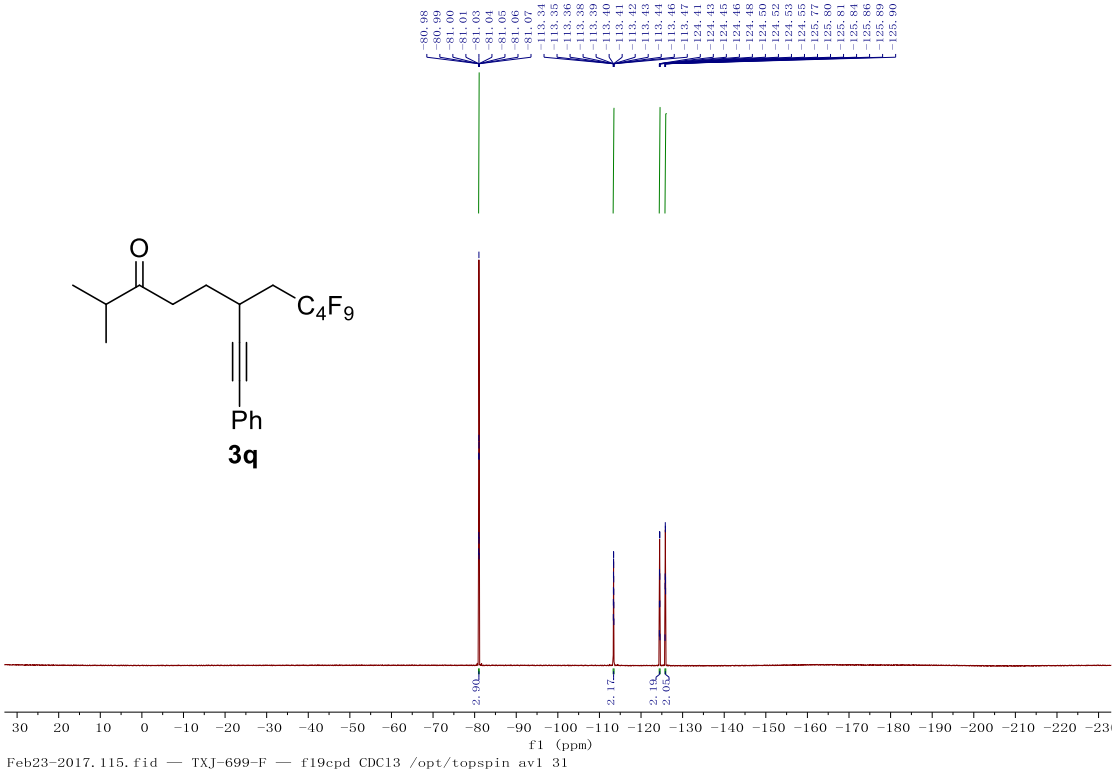

7.41
7.40
7.39
7.38
7.31
7.30
7.29
7.26
3.13
3.11
3.10
3.09
3.08
3.07
2.74
2.71
2.69
2.47
2.45
2.42
2.36
2.31
2.25
2.08
2.07
2.05
2.02
2.01
2.00
1.98
1.86
1.84
1.82
1.81
1.80
1.79
1.78
1.63
1.60
1.58
1.55
1.53
1.35
1.32
1.30
1.28
0.92
0.90
0.87
O
nC4H9
C4F9
Ph
3p
2.12
3.14
1.00
2.00
4.13
1.12
1.18
2.28
2.27
3.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
Feb22-2017.100.fid — TXJ-698-H — proton CDCl3 /opt/topspin av1 32

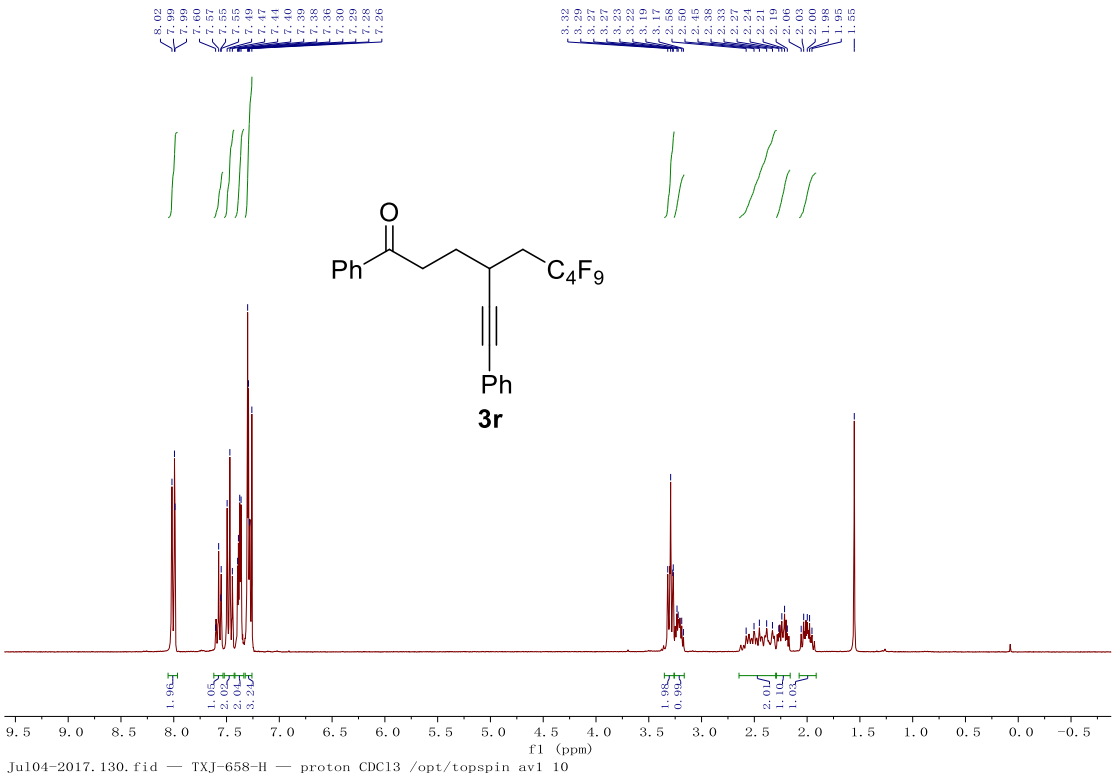

209.97
131.59
128.26
128.15
123.00
89.36
83.28
77.42
77.00
76.58
42.78
39.87
36.51
36.23
35.95
29.12
26.00
24.74
24.70
22.34
13.79
O
nC4H9
C4F9
Ph
3p
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Feb22-2017.101.fid — TXJ-698-C — carbon CDCl3 /opt/topspin av1 32

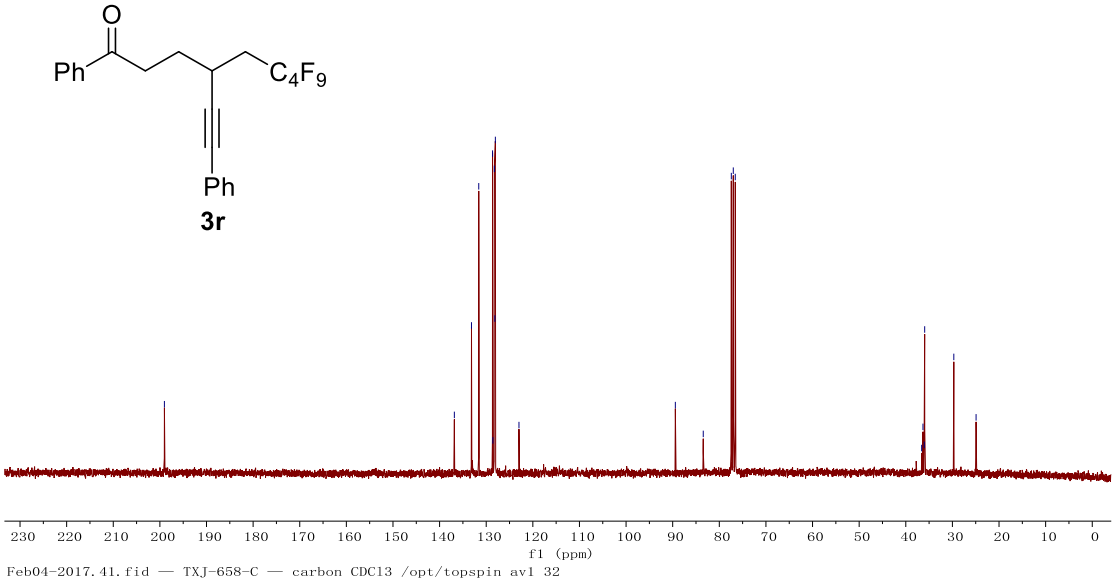

O
$^{n}C_4H_9$
C_4F_9
Ph
3p
f1 (ppm)
Feb22-2017.105.fid — TXJ-698-F — f19cpd CDCl3 /opt/topspin av1 32

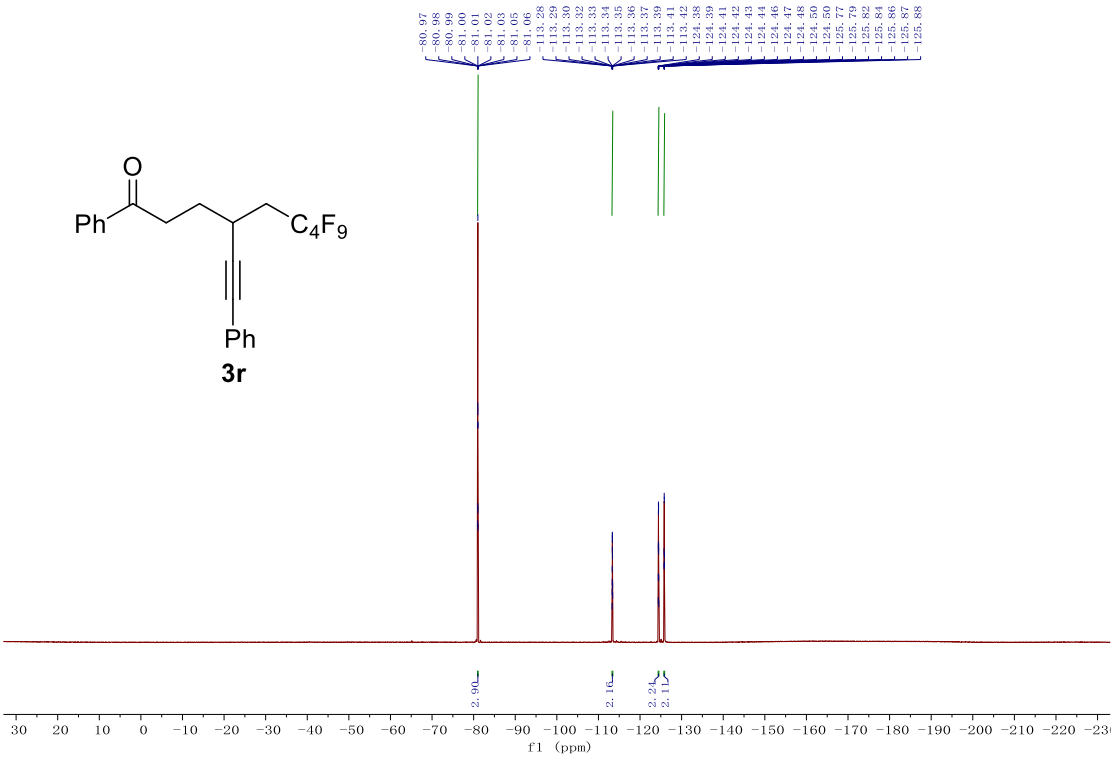

O
C_4F_9
Ph
3q
f1 (ppm)
Feb23-2017.114.fid — TXJ-699-H — proton CDCl3 /opt/topspin av1 31

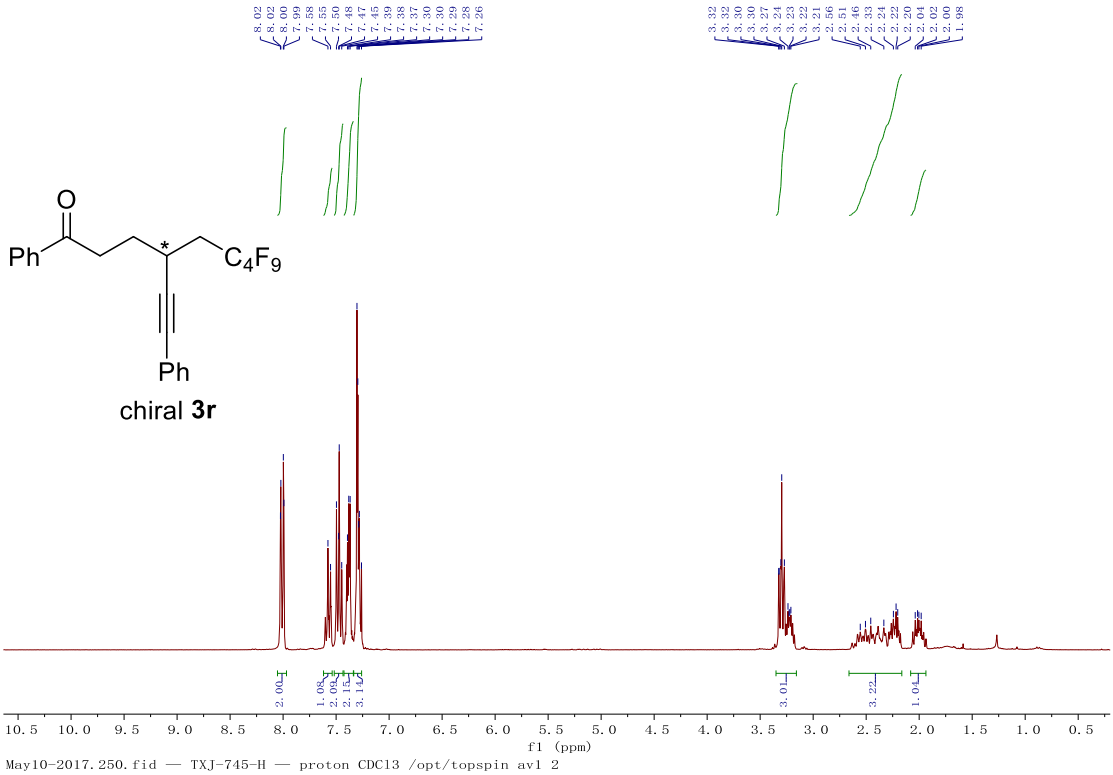

213.50
131.58
128.27
128.14
123.03
89.40
83.26
77.42
77.00
76.58
41.04
37.46
36.55
36.27
35.99
29.17
24.72
18.33
18.21
O
C4F9
Ph
3q
f1 (ppm)
Feb23-2017.111.fid — TXJ-699-C — carbon CDCl3 /opt/topspin av1 31


O
C4F9
Ph
3q
2.90
2.17
2.19
2.05
f1 (ppm)
Feb23-2017.115.fid — TXJ-699-F — f19cpd CDCl3 /opt/topspin av1 31


O
Ph
C4F9
Ph
3r
f1 (ppm)
Jul04-2017.130.fid — TXJ-658-H — proton CDCl3 /opt/topspin av1 10

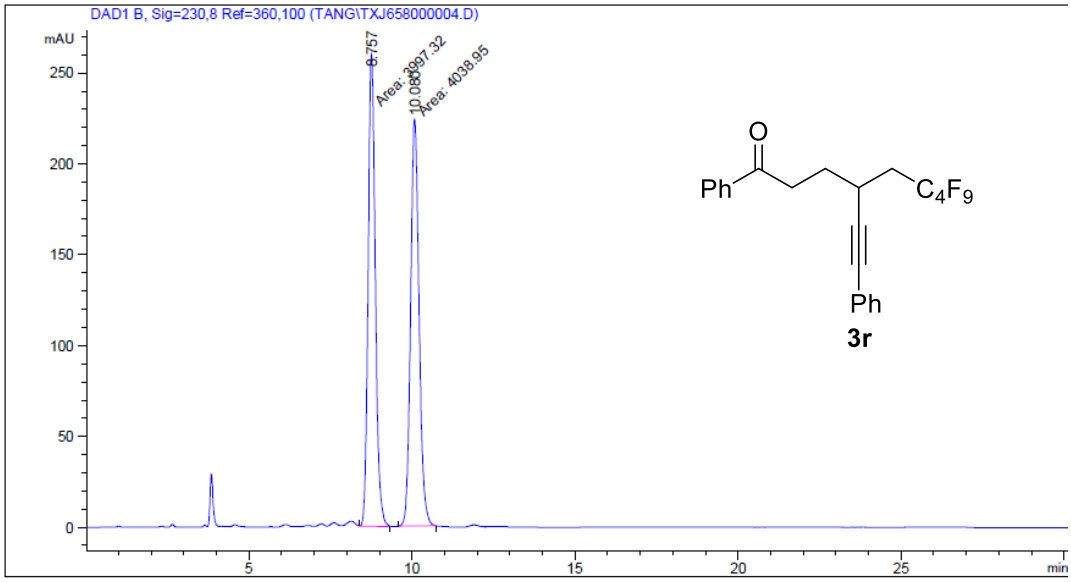

O
Ph
C4F9
Ph
3r
f1 (ppm)
Feb04-2017.41.fid — TXJ-658-C — carbon CDCl3 /opt/topspin av1 32


O
Ph
C4F9
Ph
3r
f1 (ppm)
Feb04-2017.45.fid — TXJ-658-F — f19cpd CDCl3 /opt/topspin av1 32


O
Ph
*
C4F9
Ph
chiral 3r
f1 (ppm)
May10-2017.250.fid — TXJ-745-H — proton CDCl3 /opt/topspin av1 2

Data File C:\CHEM32\1\DATA\TANG\TXJ658000004.D
Sample Name: TXJ658

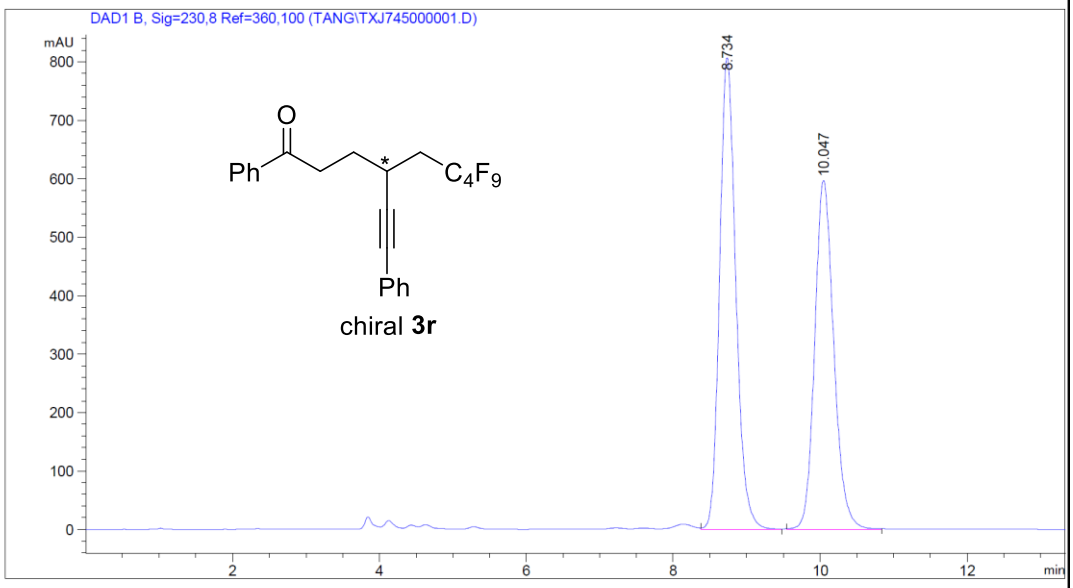
```
==========================================================================
Acq. Operator    :  prekel
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11.04.2017 15:31:48
                                                  Inj Volume : 5.0 µl
Acq. Method     : C:\CHEM32\1\METHODS\RP CHIRAL\RP CHIRAL_65-35.M
Last changed    : 11.04.2017 15:31:35 by  prekel
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\RP NEUTRAL 1ML\RP_65-35_1.M
Last changed    : 24.06.2016 10:35:17 by prekel
Method Info     : Standard Method RP_65:35_1
                  Flow: 1mL/min; 20°C; Injection 5µL; time: 50min
                  Solvent System:MeCN/H2O=65/35
                  isocratic

Sample Info     : OJ-RH
                  ACN/H2O
```




```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Data File C:\CHEM32\1\DATA\TANG\TXJ745000001.D
Sample Name: TXJ745

```
==========================================================================
Acq. Operator   :  prekel
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 11.04.2017 16:05:49
                                                  Inj Volume : 5.0 µl
Acq. Method     : C:\CHEM32\1\METHODS\RP CHIRAL\RP CHIRAL_65-35.M
Last changed    : 11.04.2017 16:03:39 by  prekel
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\RP NEUTRAL 1ML\RP_65-35_1.M
Last changed    : 24.06.2016 10:35:17 by prekel
Method Info     : Standard Method RP_65:35_1
                  Flow: 1mL/min; 20°C; Injection 5µL; time: 50min
                  Solvent System:MeCN/H2O=65/35
                  isocratic

Sample Info     : OJ-RH
                  ACN/H2O
```



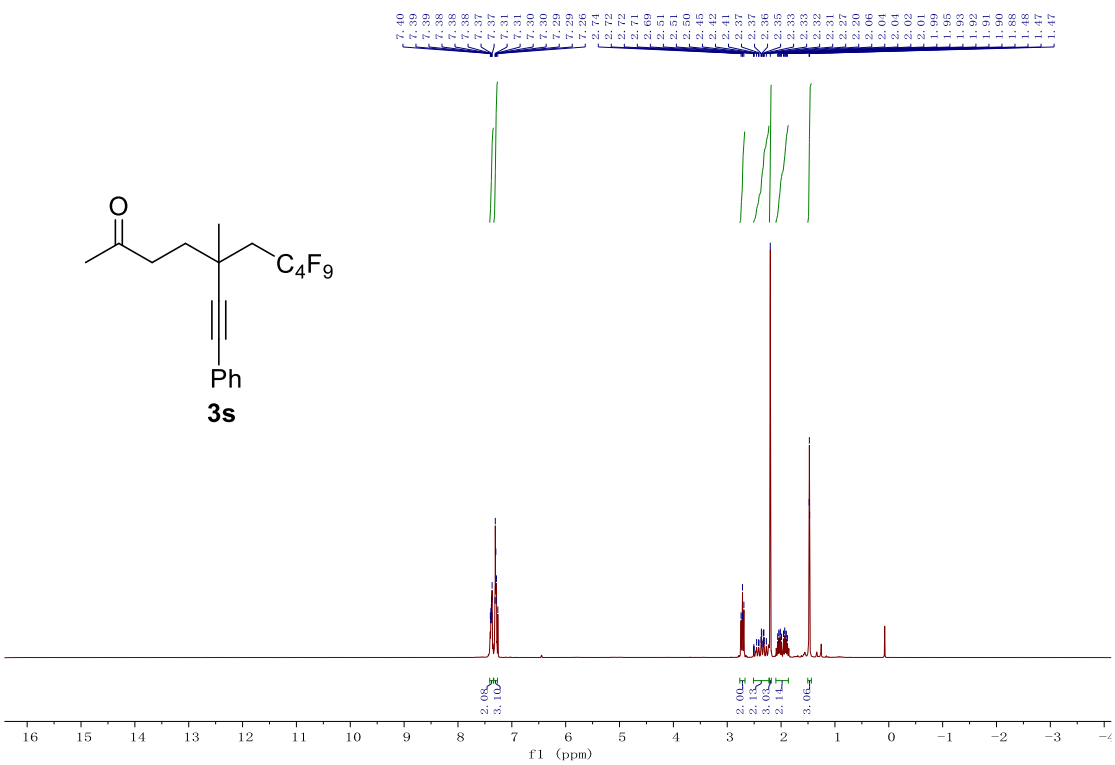

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs
```

Data File C:\CHEM32\1\DATA\TANG\TXJ745000001.D
Sample Name: TXJ745

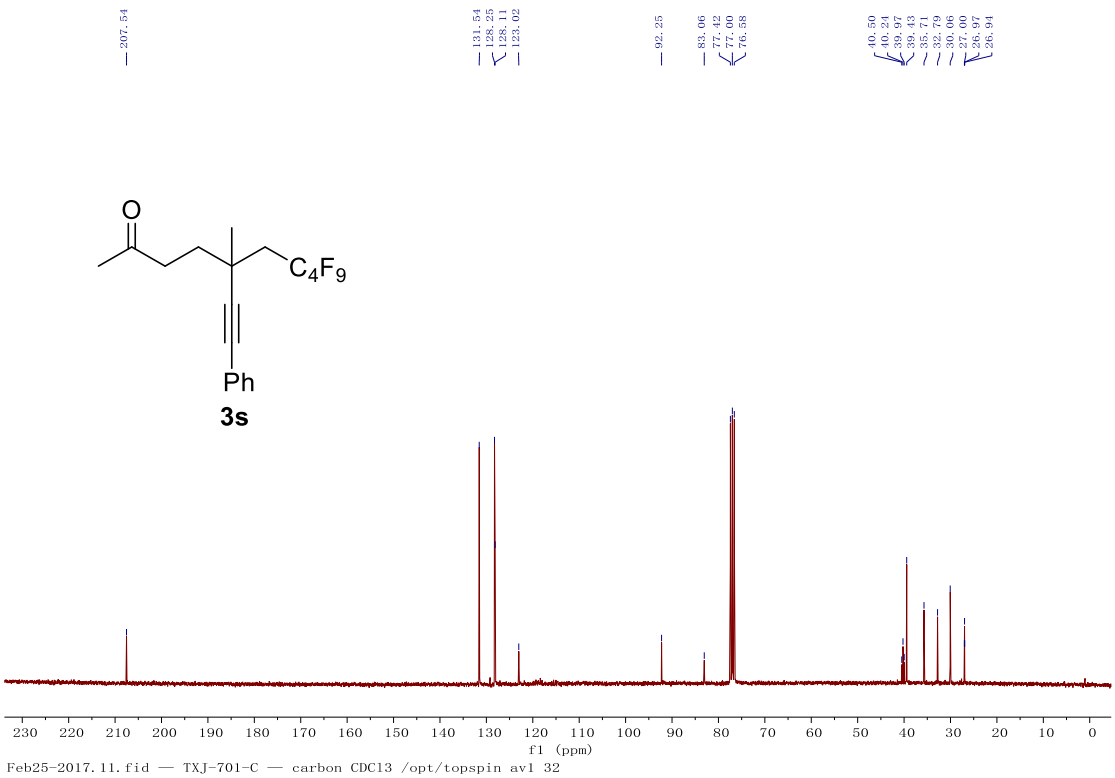
Signal 1: DAD1 B, Sig=230,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.734	VB	0.2367	1.23521e4	806.58051	53.4568
2	10.047	BB	0.2783	1.07546e4	596.59650	46.5432
Totals :				2.31067e4	1403.17700	

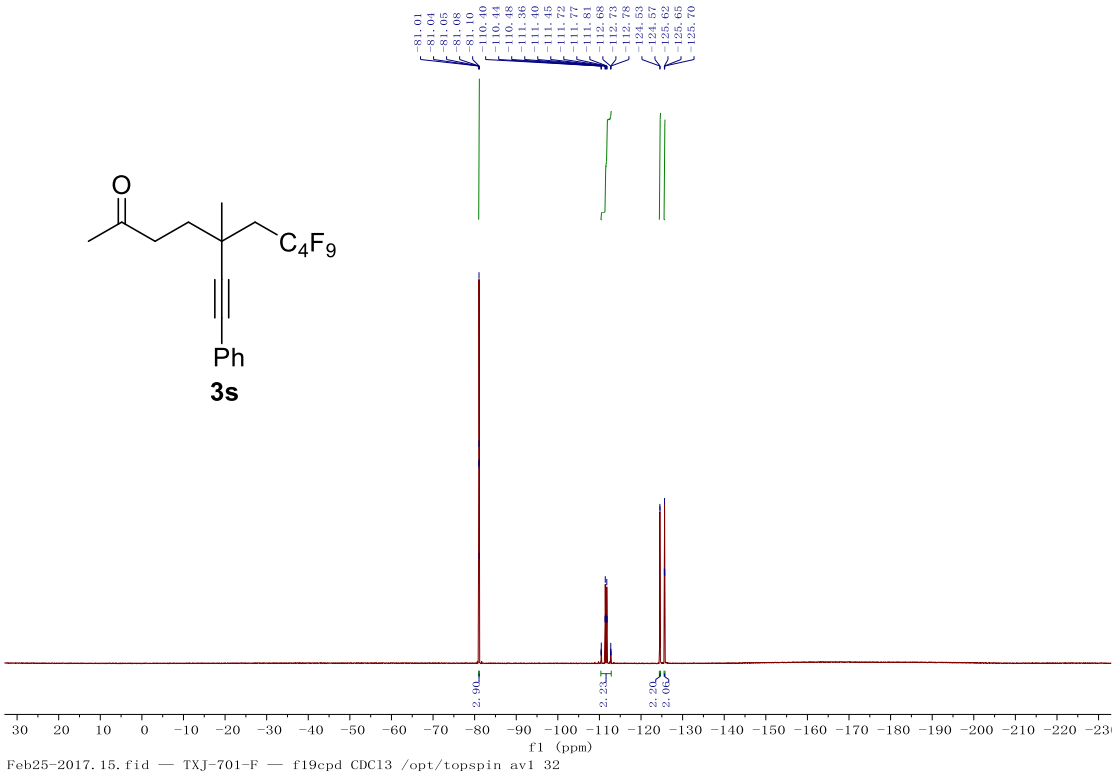
```
==========================================================================
                        *** End of Report ***
```

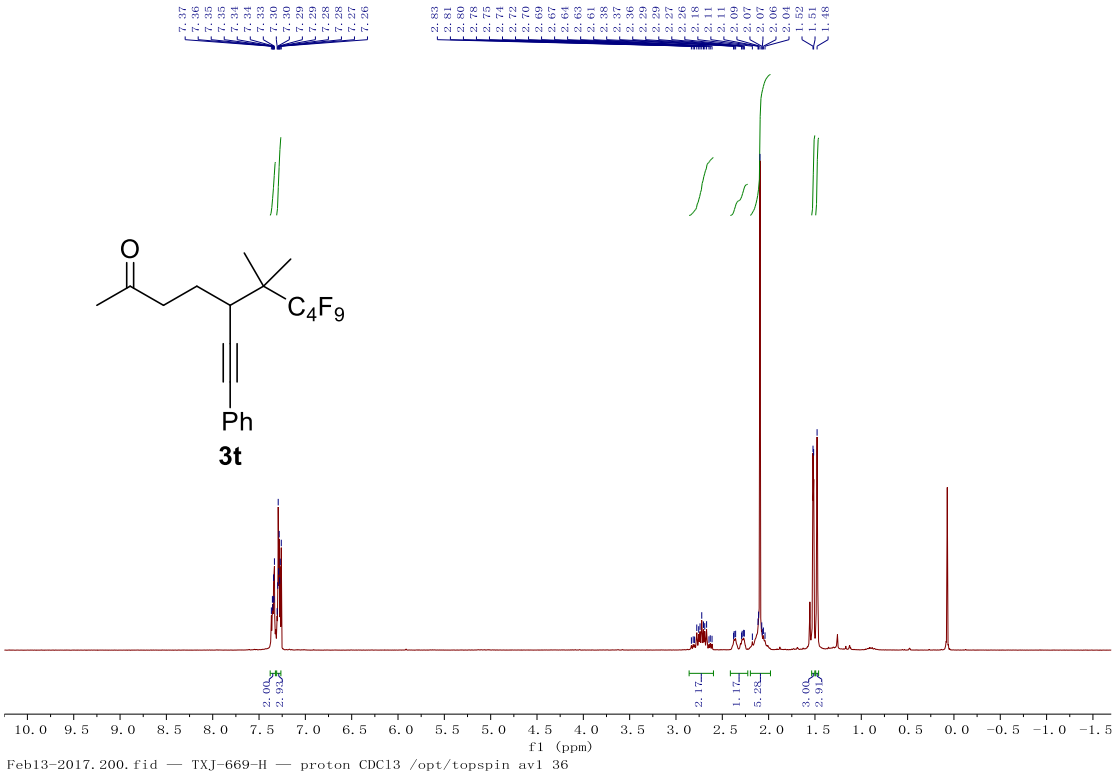


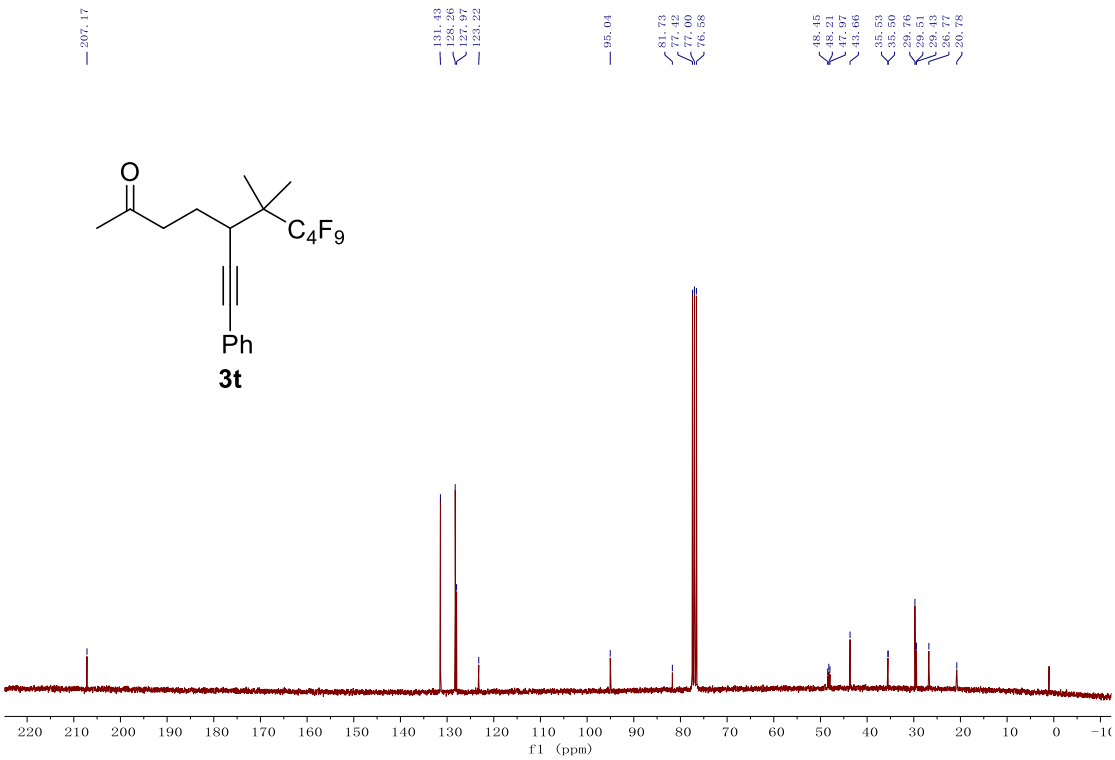
Feb25-2017.14.fid — TXJ-701-H — proton CDCl3 /opt/topspin av1 32

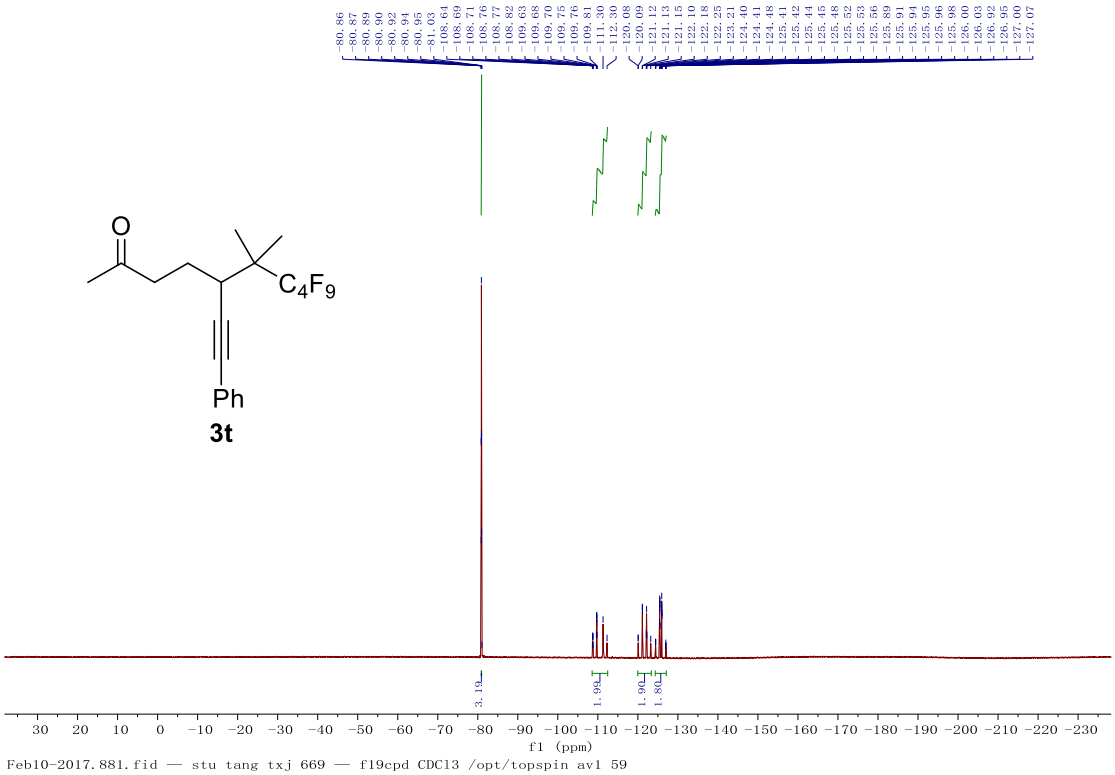


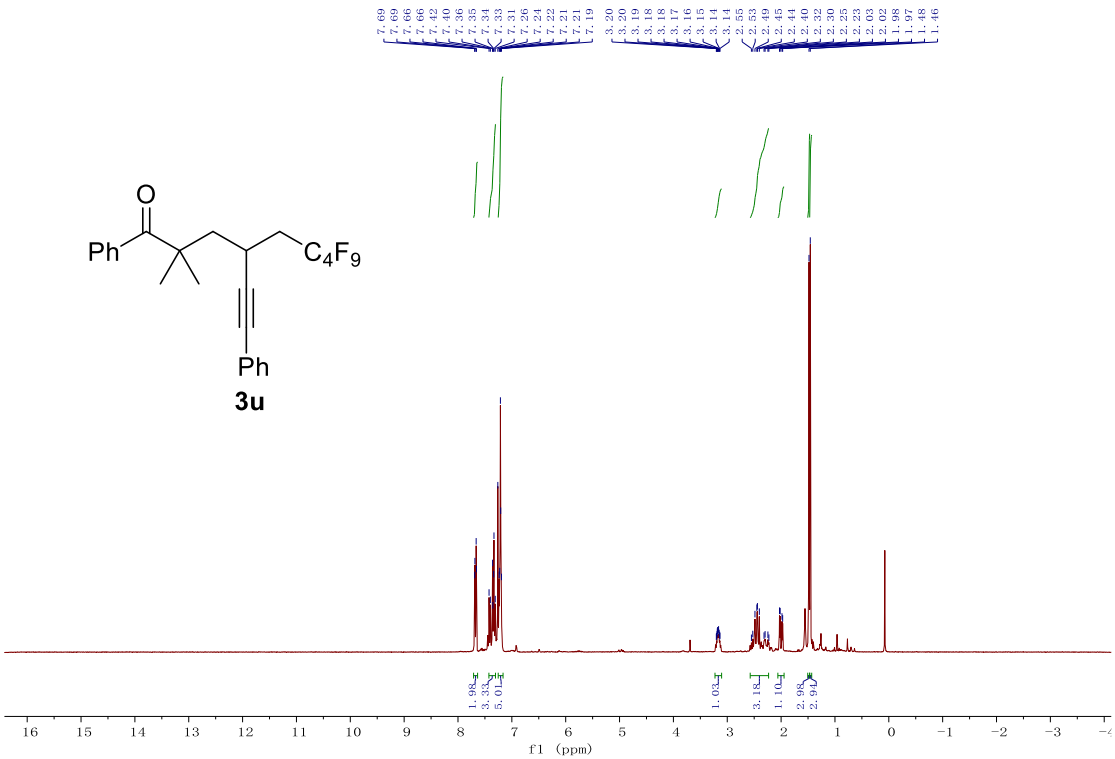
Feb25-2017.11.fid — TXJ-701-C — carbon CDCl3 /opt/topspin av1 32

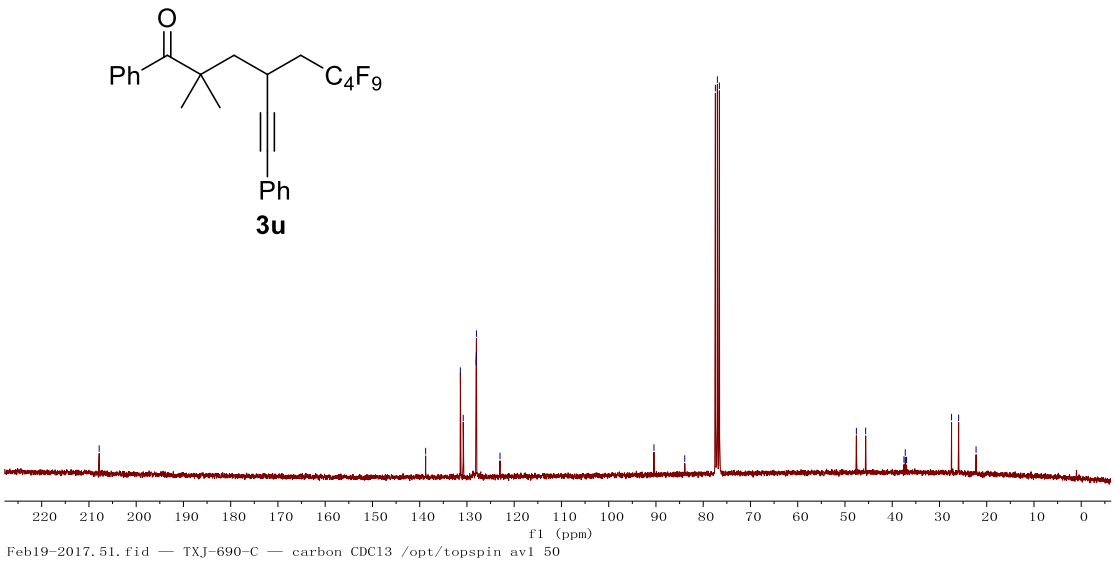

O
C4F9
Ph
3s
f1 (ppm)
Feb25-2017.15.fid — TXJ-701-F — f19cpd CDCl3 /opt/topspin av1 32


O
C4F9
Ph
3t
f1 (ppm)
Feb13-2017.200.fid — TXJ-669-H — proton CDCl3 /opt/topspin av1 36

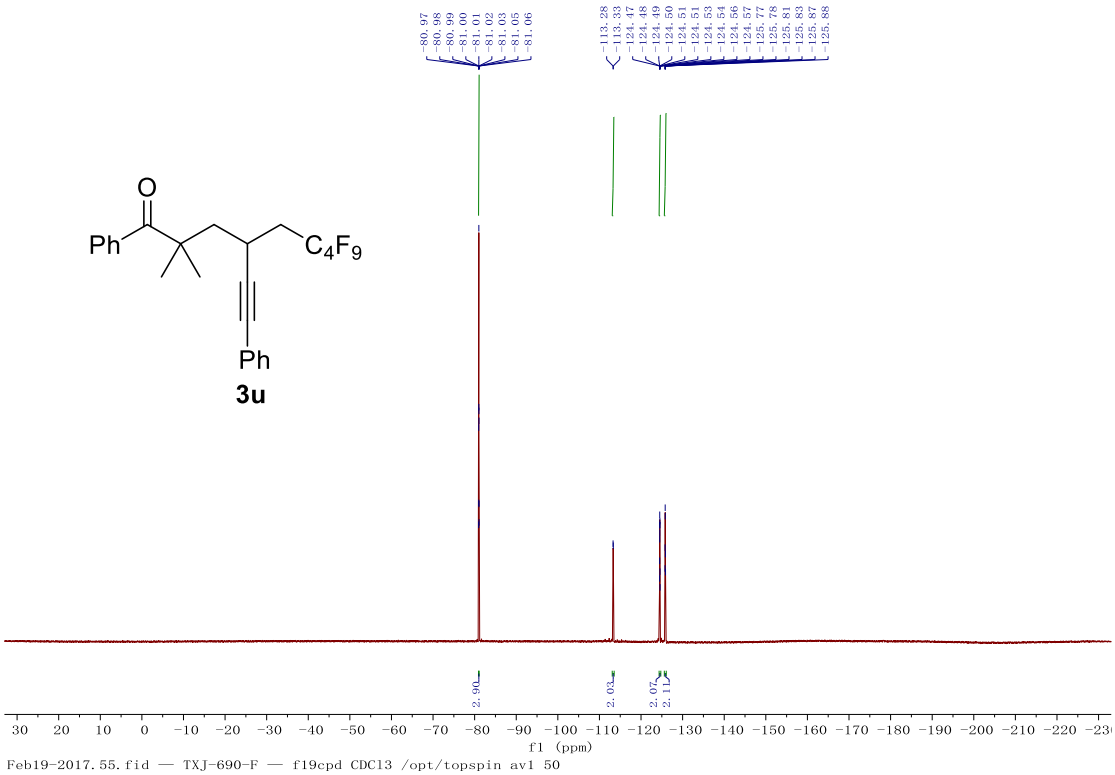

207.17
131.43
128.96
127.97
123.22
95.04
81.73
77.42
77.00
76.58
48.45
48.21
47.97
43.66
35.53
35.50
29.76
29.51
29.43
26.77
20.78
O
C4F9
Ph
3t
f1 (ppm)
Feb13-2017.201.fid — TXJ-669-C — carbon CDCl3 /opt/topspin av1 36

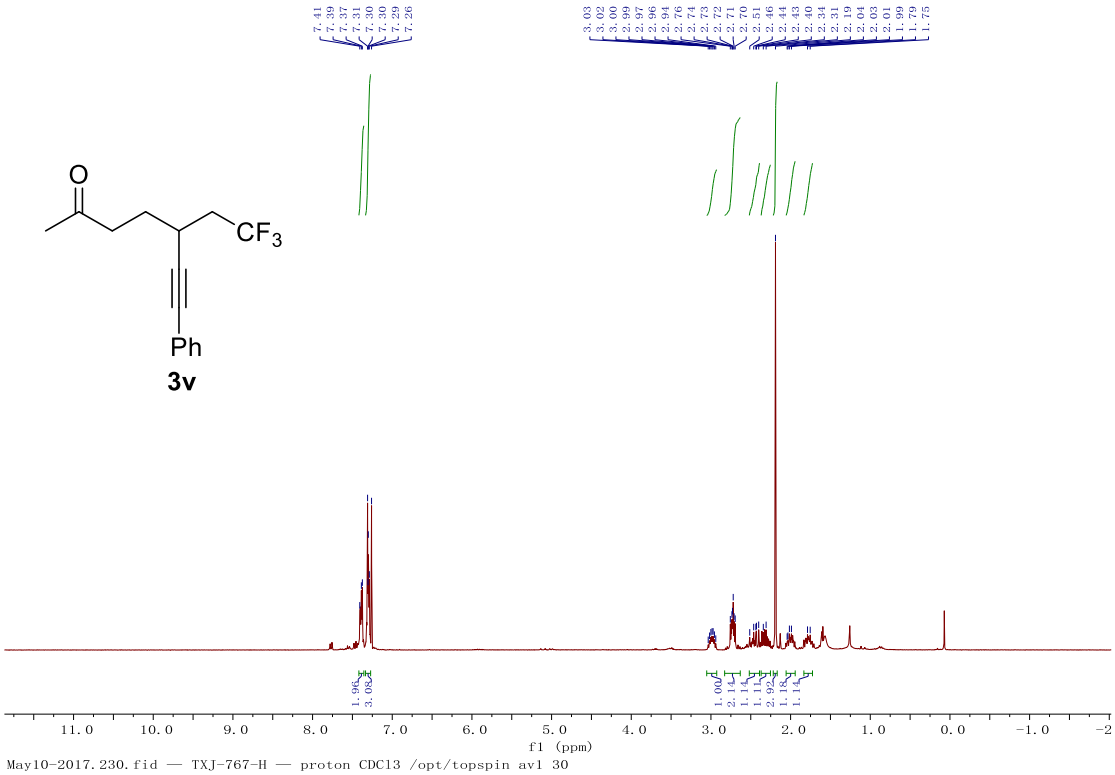

O
C4F9
Ph
3t
3.19
1.99
1.90
1.80
f1 (ppm)
Feb10-2017.881.fid — stu tang txj 669 — f19cpd CDCl3 /opt/topspin av1 59

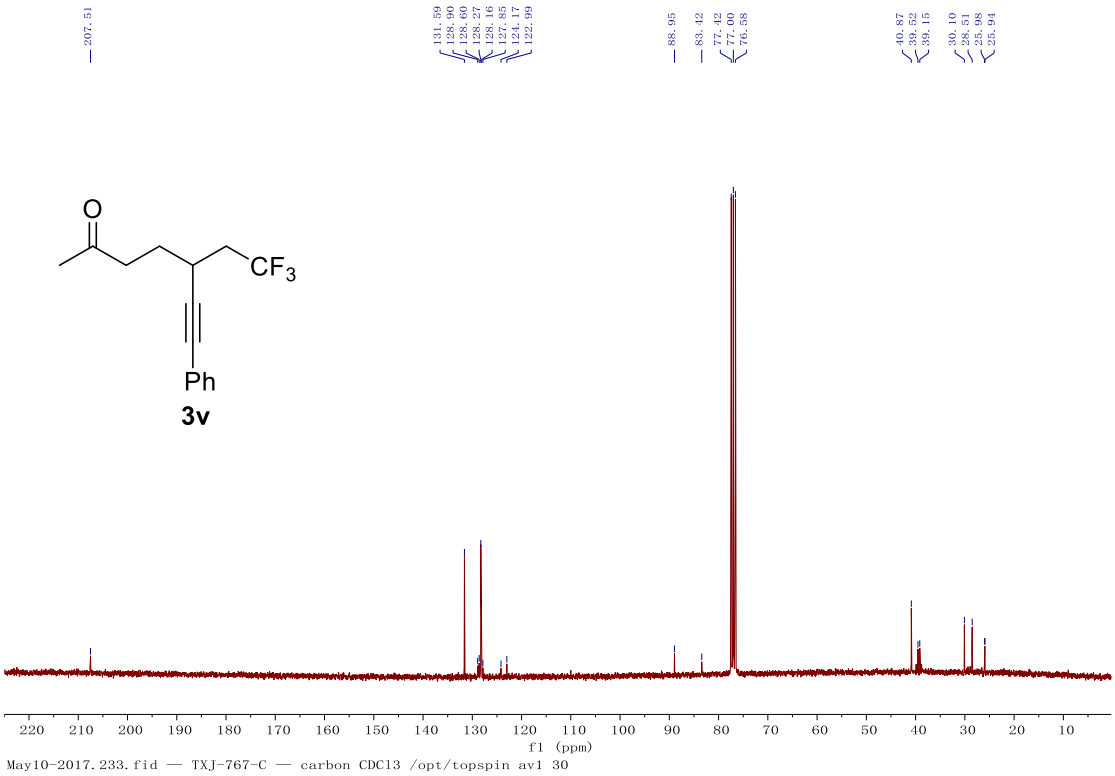

O
Ph
C_4F_9
Ph
3u
7.69 7.69 7.66 7.66 7.42 7.40 7.36 7.35 7.34 7.33 7.31 7.26 7.24 7.22 7.21 7.21 7.19
3.20 3.20 3.19 3.18 3.18 3.17 3.16 3.15 3.14 3.14 2.55 2.53 2.49 2.45 2.44 2.40 2.32 2.30 2.25 2.23 2.03 2.02 1.98 1.97 1.48 1.46
1.98 3.33 5.01 1.03 3.18 1.10 2.98 2.94
f1 (ppm)
Feb19-2017.50.fid — TXJ-690-H — proton CDCl3 /opt/topspin av1 50

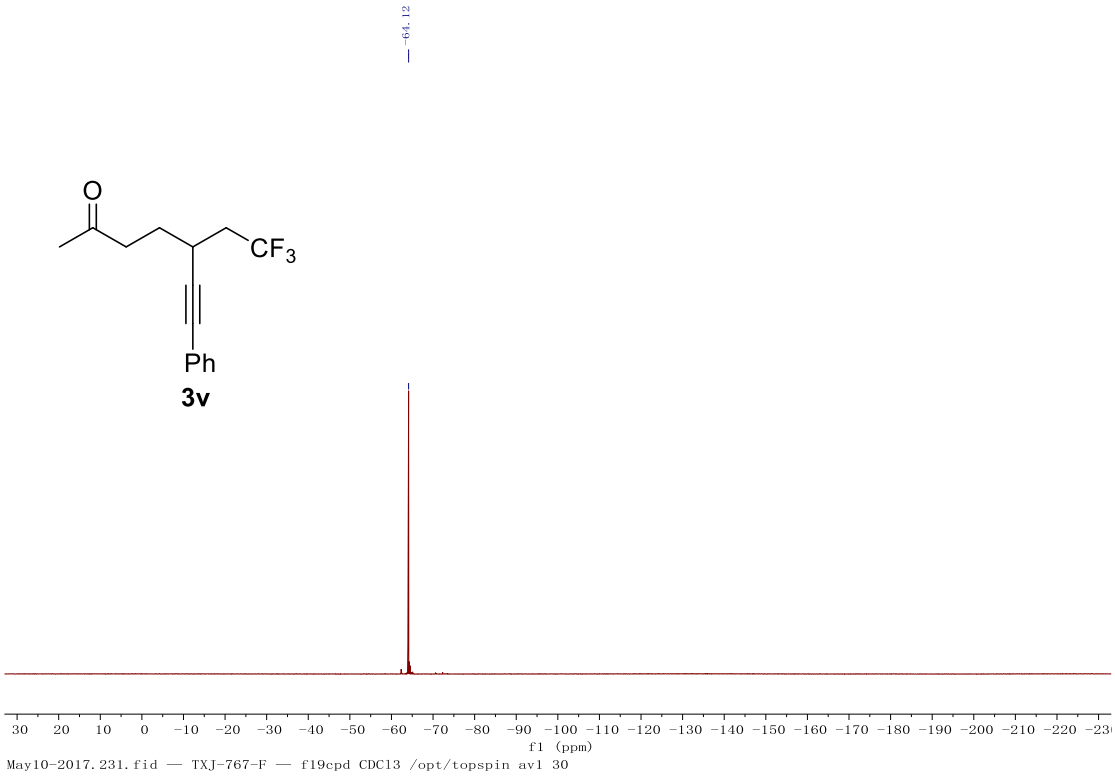

207.83
138.74
131.39 130.79 128.07 128.02 127.99 123.00
90.42
83.90
77.42 77.00 76.58
47.58 45.62 37.52 37.24 36.97 27.44 25.94 22.25
f1 (ppm)
Feb19-2017.51.fid — TXJ-690-C — carbon CDCl3 /opt/topspin av1 50

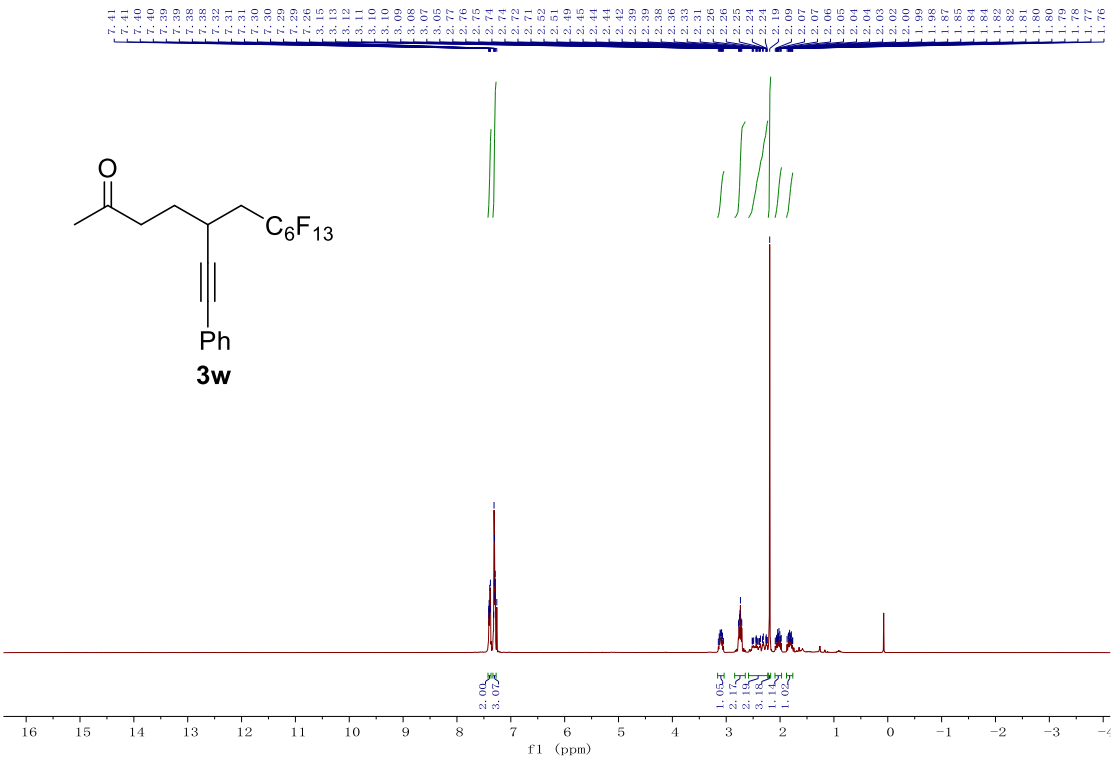
O
Ph
C_4F_9
Ph
3u

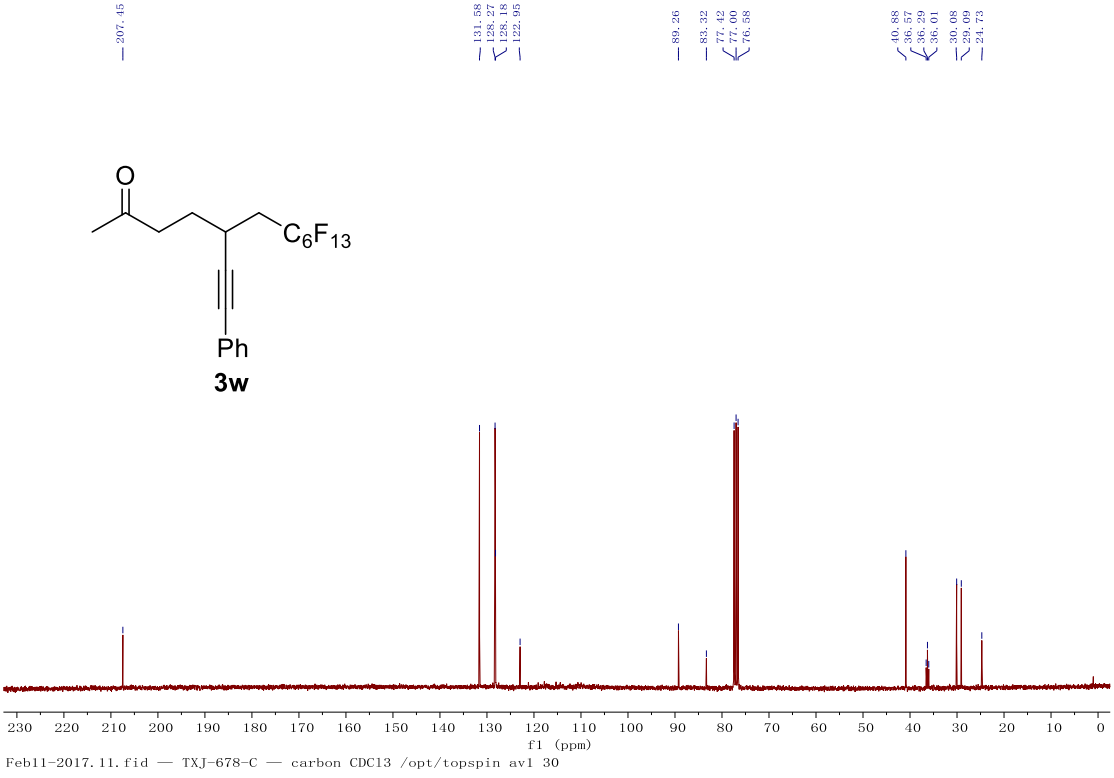

O
Ph
C_4F_9
Ph
3u
f1 (ppm)
Feb19-2017.55.fid — TXJ-690-F — f19cpd CDCl3 /opt/topspin av1 50

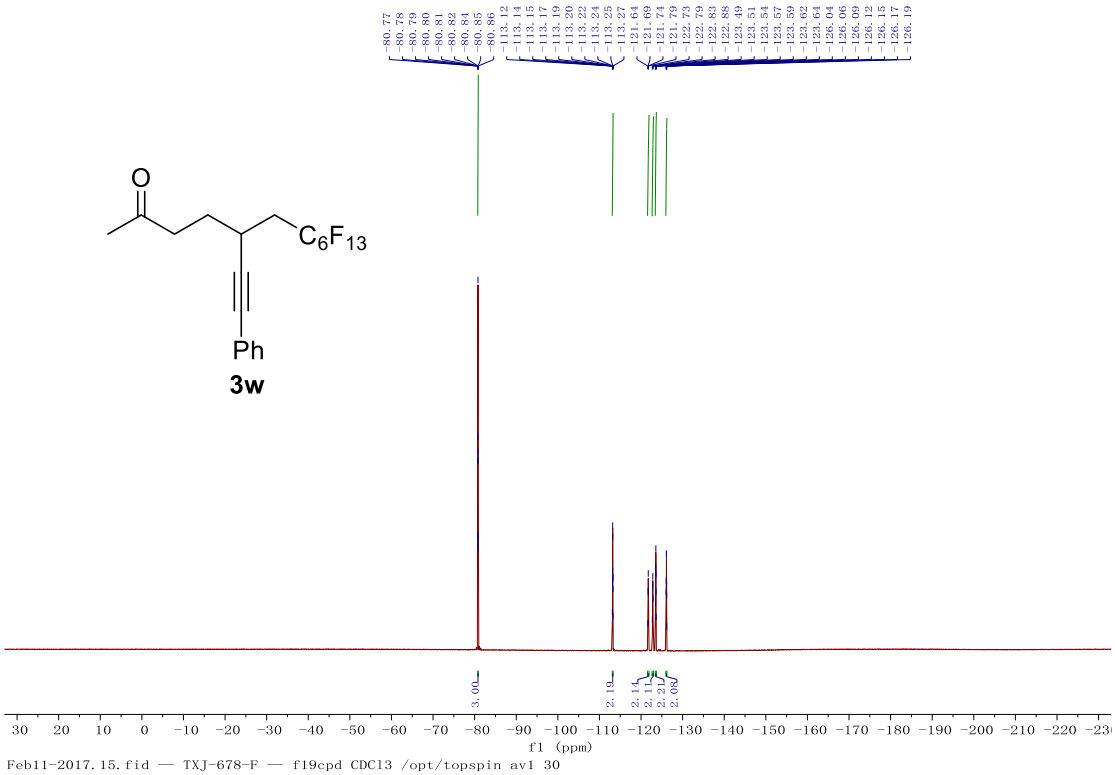

O
CF_3
Ph
3v
f1 (ppm)
May10-2017.230.fid — TXJ-767-H — proton CDCl3 /opt/topspin av1 30


207.51
131.59
128.90
128.60
128.27
128.16
127.85
124.17
122.99
88.95
83.42
77.42
77.00
76.58
40.87
39.52
39.15
30.10
28.51
25.98
25.94
O
CF3
Ph
3v
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)
May10-2017.233.fid — TXJ-767-C — carbon CDCl3 /opt/topspin av1 30

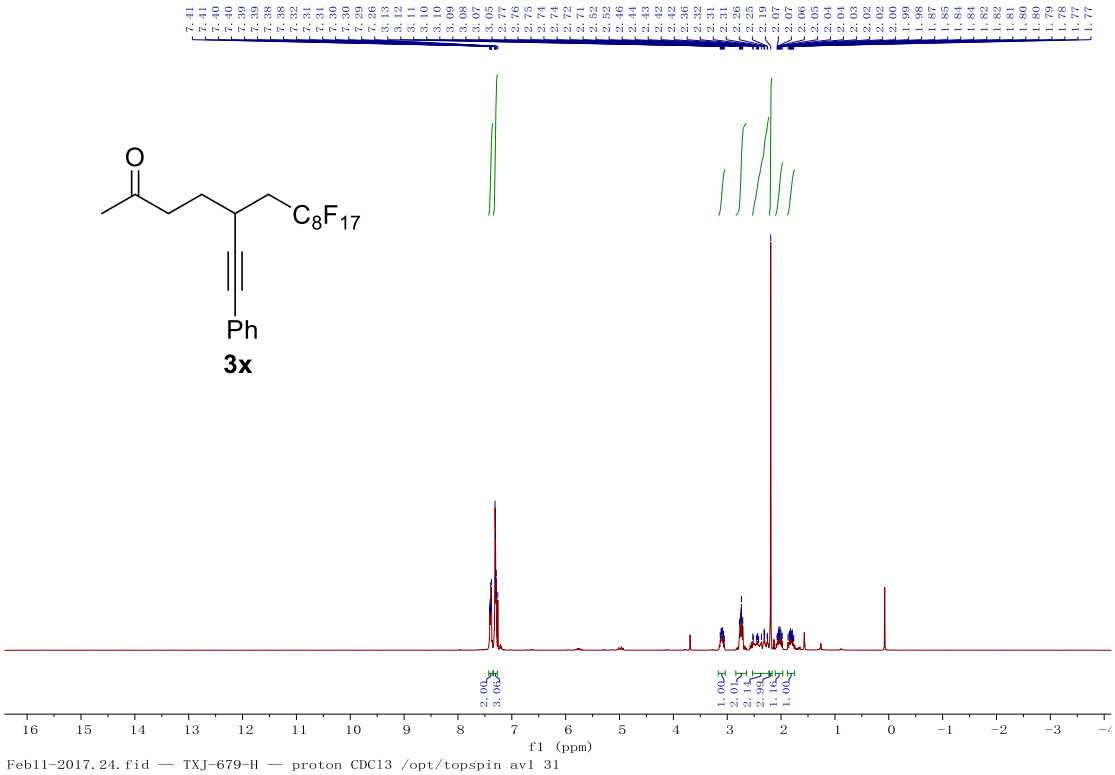

-64.12
O
CF3
Ph
3v
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -23
f1 (ppm)
May10-2017.231.fid — TXJ-767-F — f19cpd CDCl3 /opt/topspin av1 30


O
C6F13
Ph
3w
f1 (ppm)
Feb11-2017.14.fid — TXJ-678-H — proton CDCl3 /opt/topspin av1 30

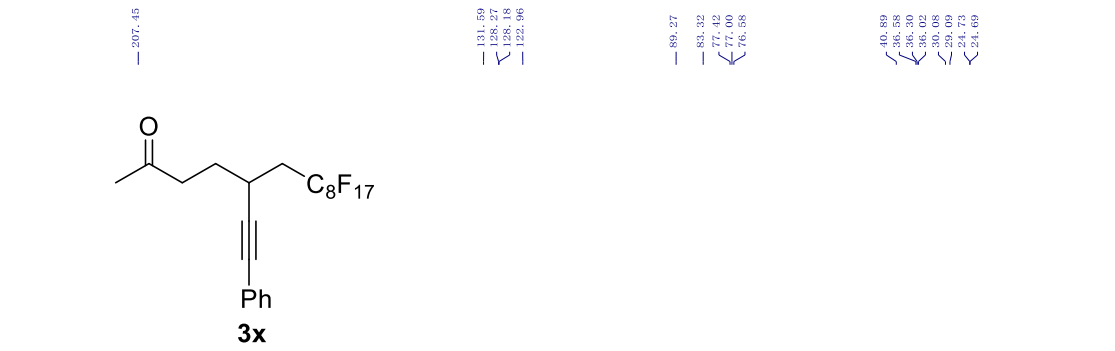

O
C6F13
Ph
3w
f1 (ppm)
Feb11-2017.11.fid — TXJ-678-C — carbon CDCl3 /opt/topspin av1 30

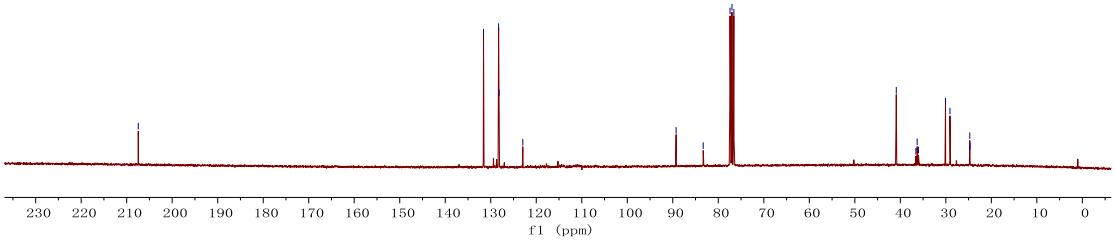


Feb11-2017.15.fid — TXJ-678-F — f19cpd CDCl3 /opt/topspin av1 30

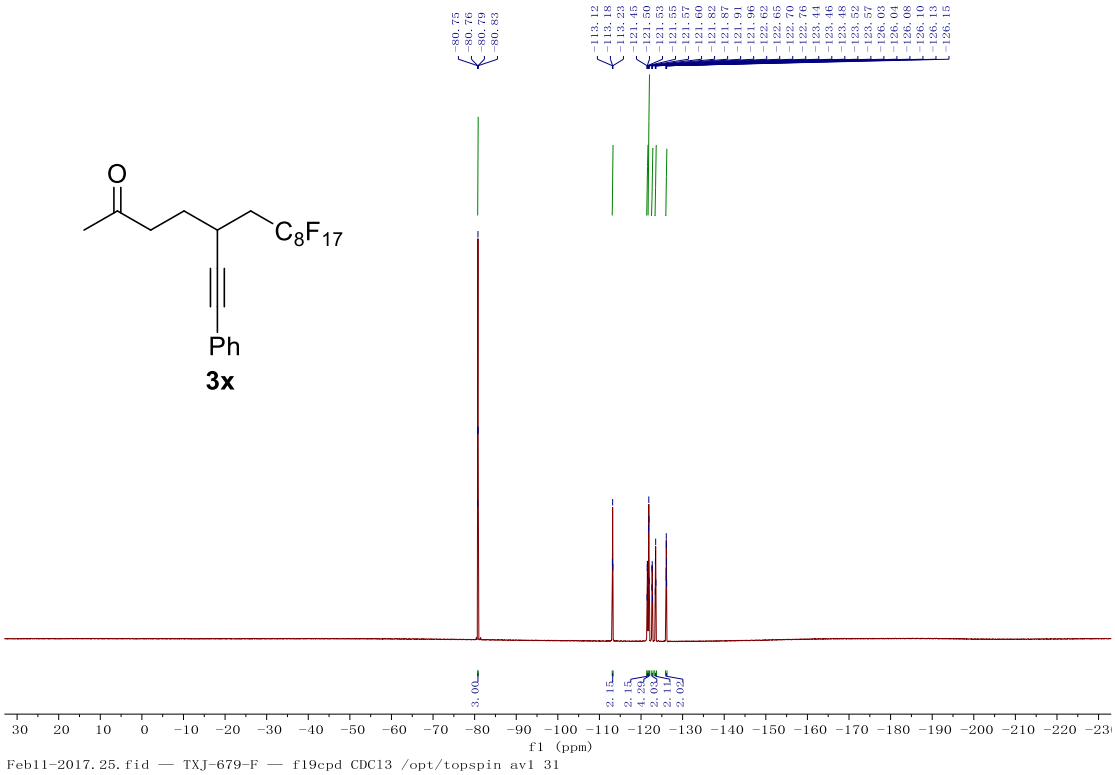


Feb11-2017.24.fid — TXJ-679-H — proton CDCl3 /opt/topspin av1 31

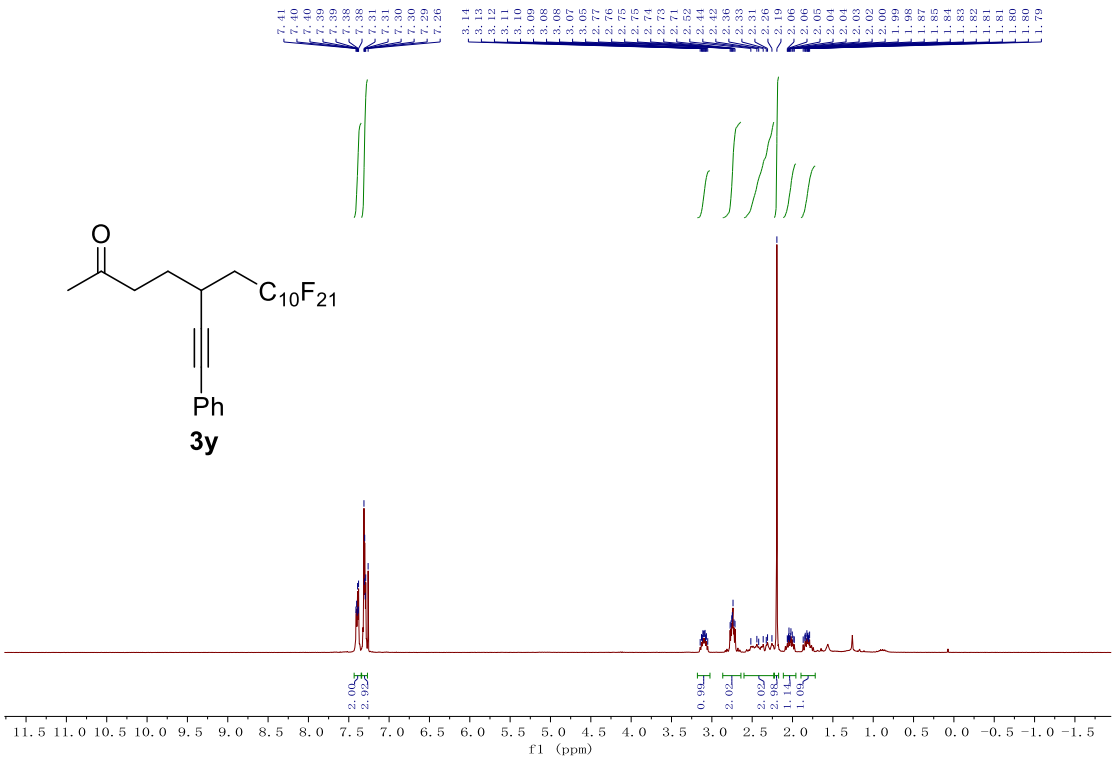




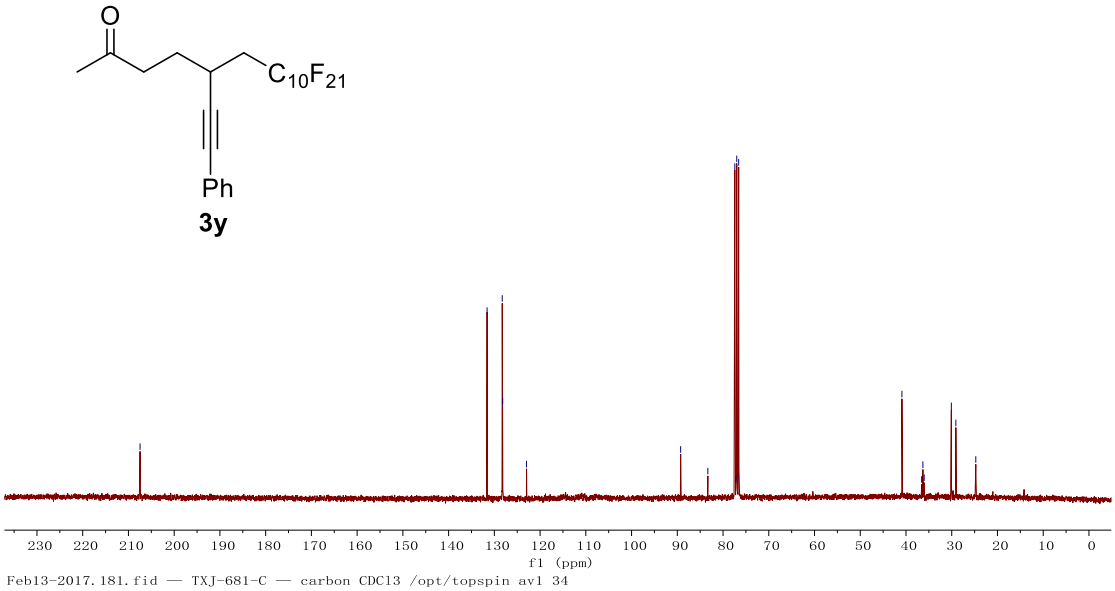
Feb13-2017.191.fid — TXJ-679-C — carbon CDCl3 /opt/topspin av1 35



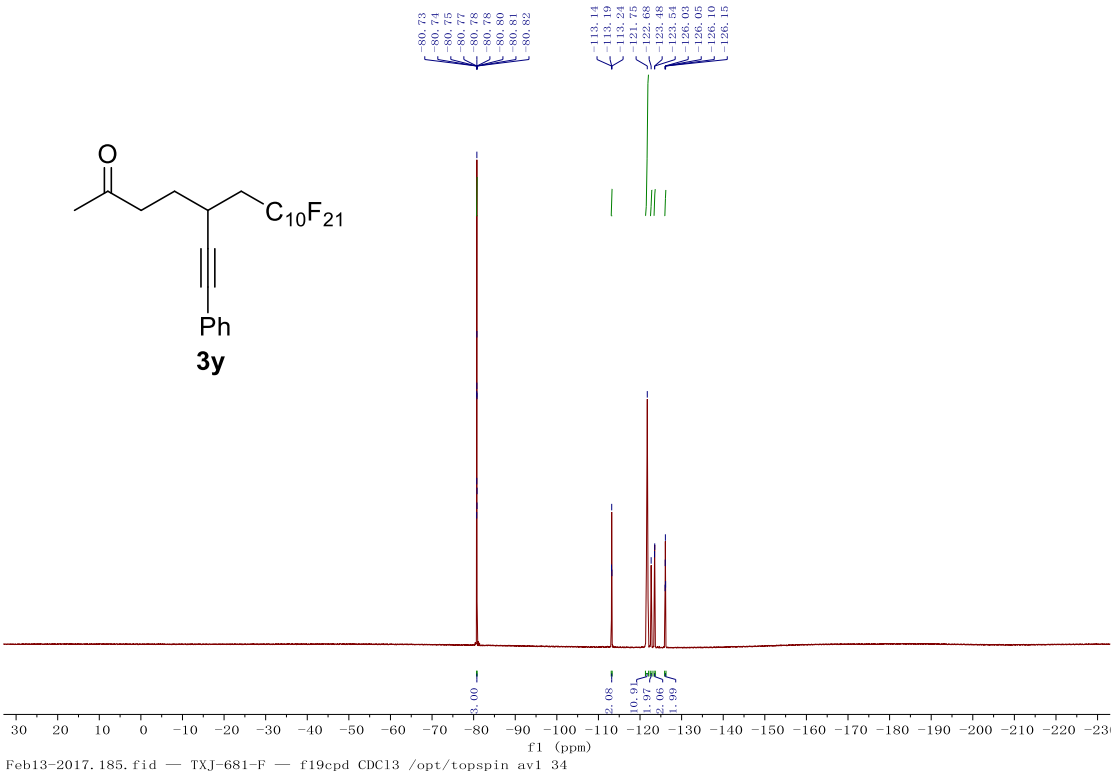
Feb11-2017.25.fid — TXJ-679-F — f19cpd CDCl3 /opt/topspin av1 31

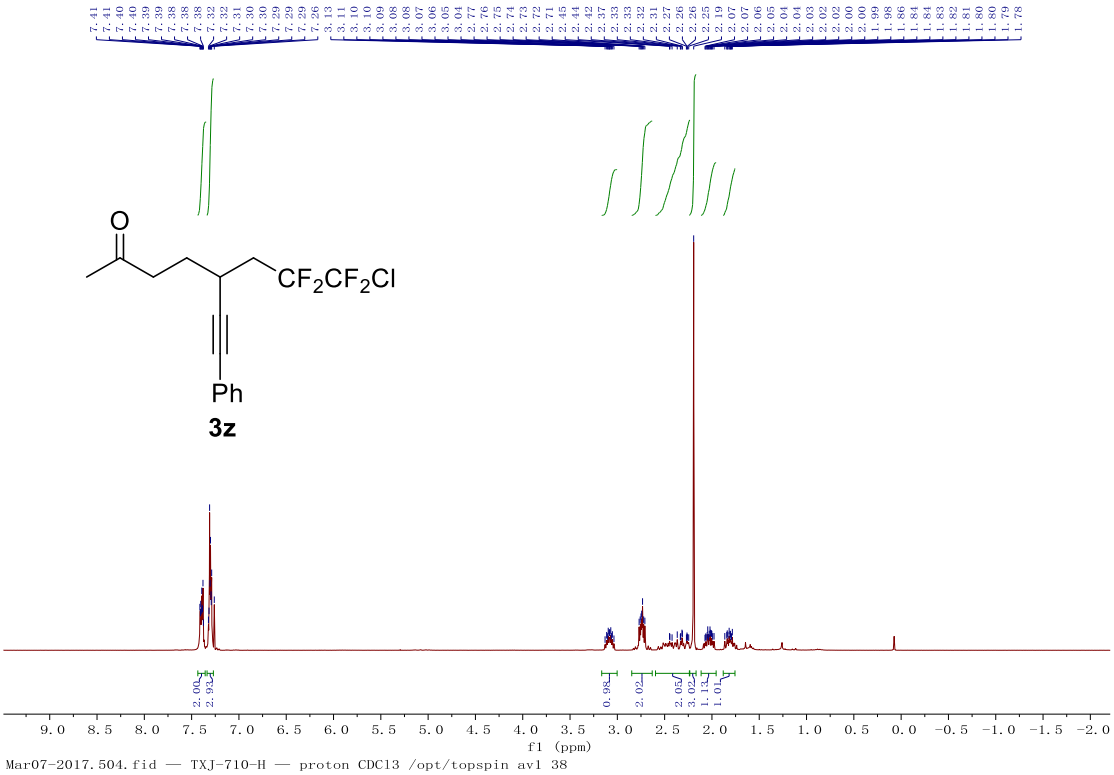


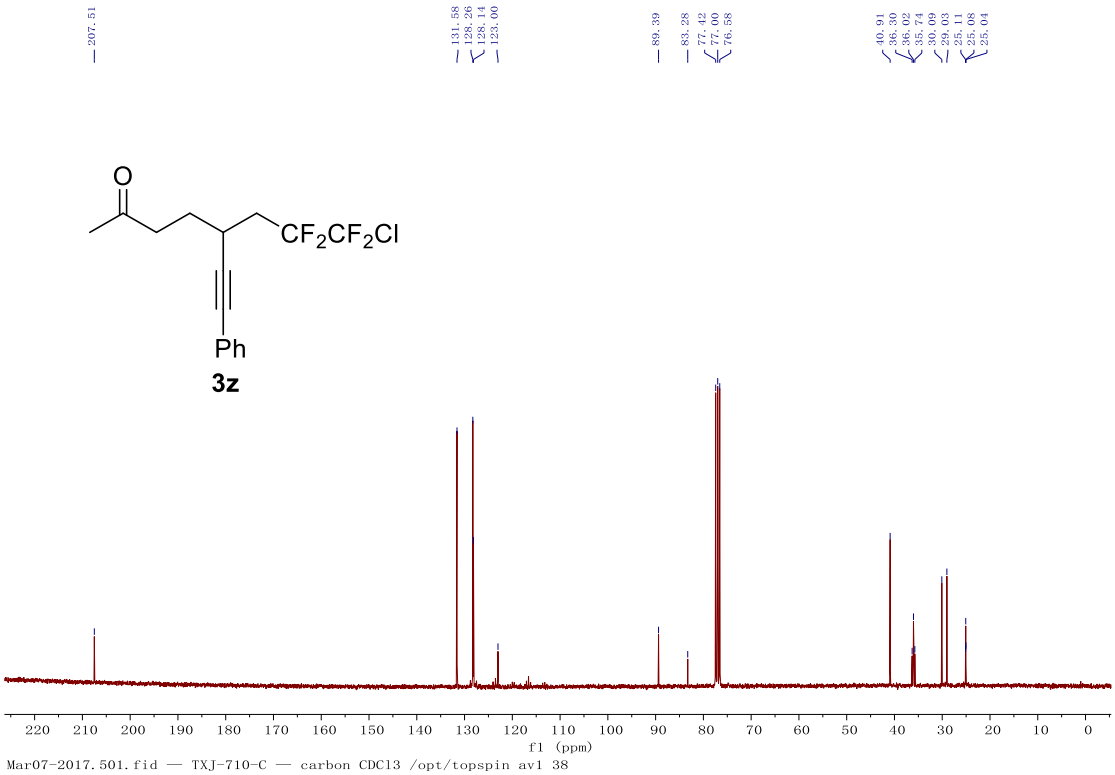
Feb14-2017.520.fid — TXJ-682-H — proton CDCl3 /opt/topspin av1 31

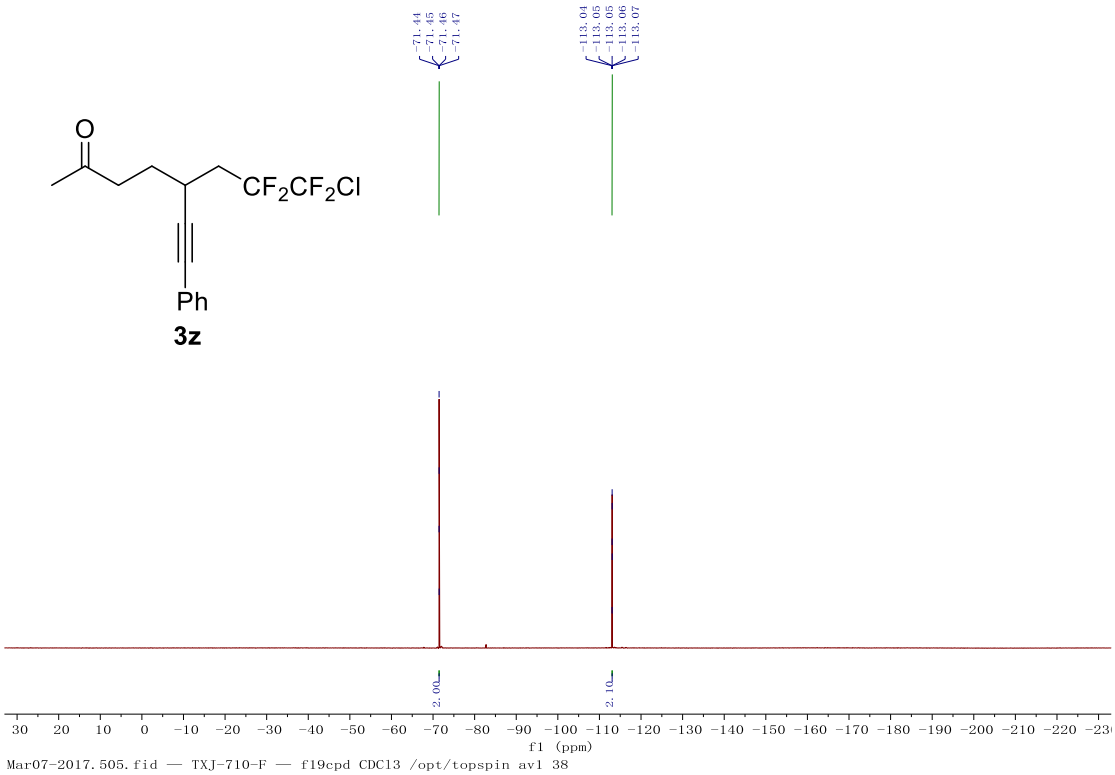


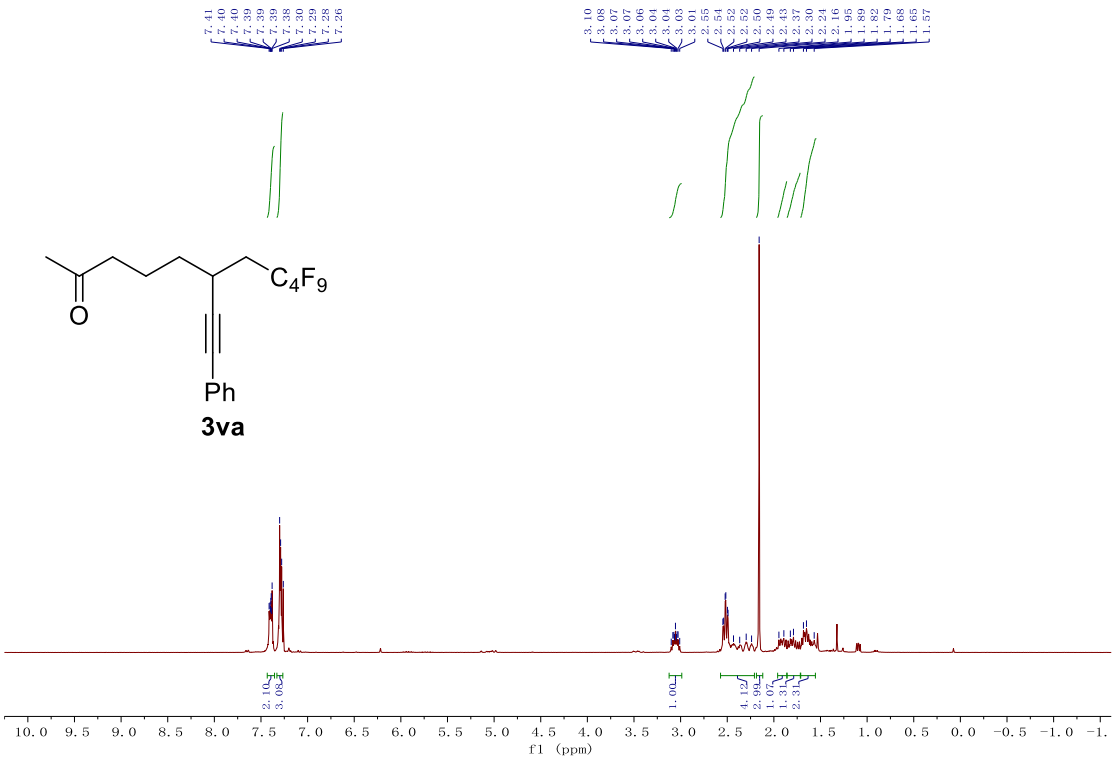
Feb13-2017.181.fid — TXJ-681-C — carbon CDCl3 /opt/topspin av1 34

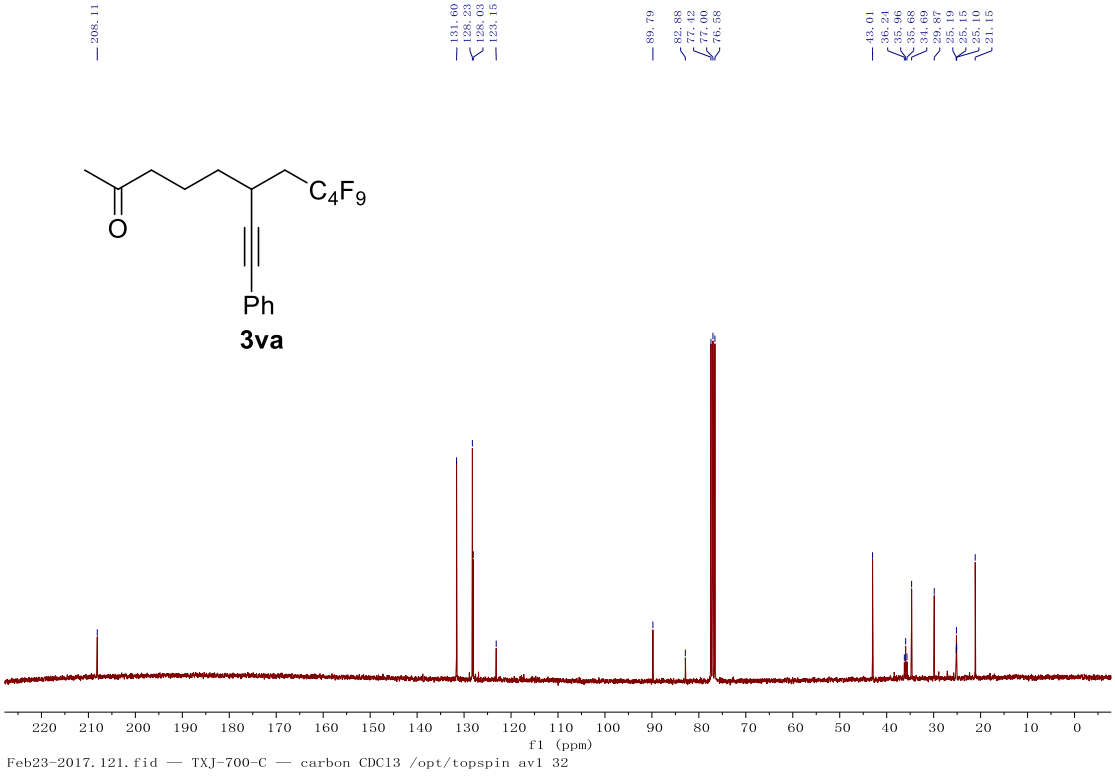

O
$C_{10}F_{21}$
Ph
3y
f1 (ppm)
Feb13-2017.185.fid — TXJ-681-F — f19cpd CDCl3 /opt/topspin av1 34

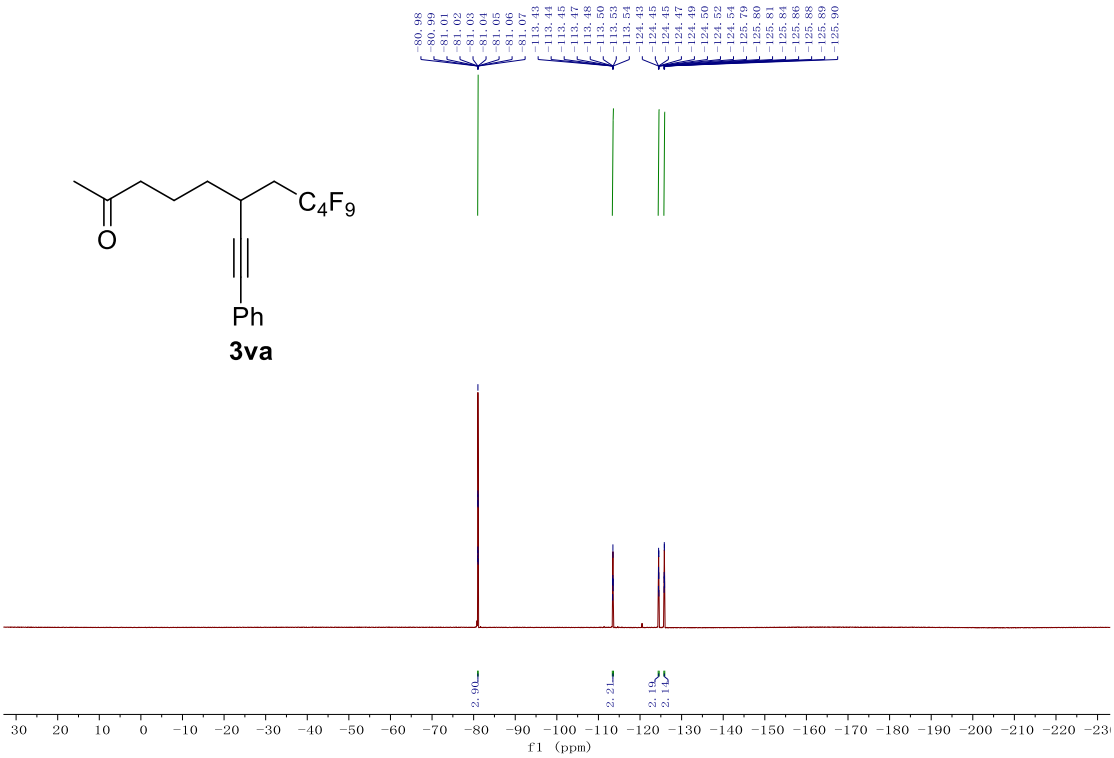

O
CF_2CF_2Cl
Ph
3z
f1 (ppm)
Mar07-2017.504.fid — TXJ-710-H — proton CDCl3 /opt/topspin av1 38


207.51
131.58
128.26
128.14
123.00
89.39
83.28
77.42
77.00
76.58
40.91
36.30
36.02
35.74
30.09
29.03
25.11
25.08
25.04
O
CF2CF2Cl
Ph
3z
f1 (ppm)
Mar07-2017.501.fid — TXJ-710-C — carbon CDCl3 /opt/topspin av1 38

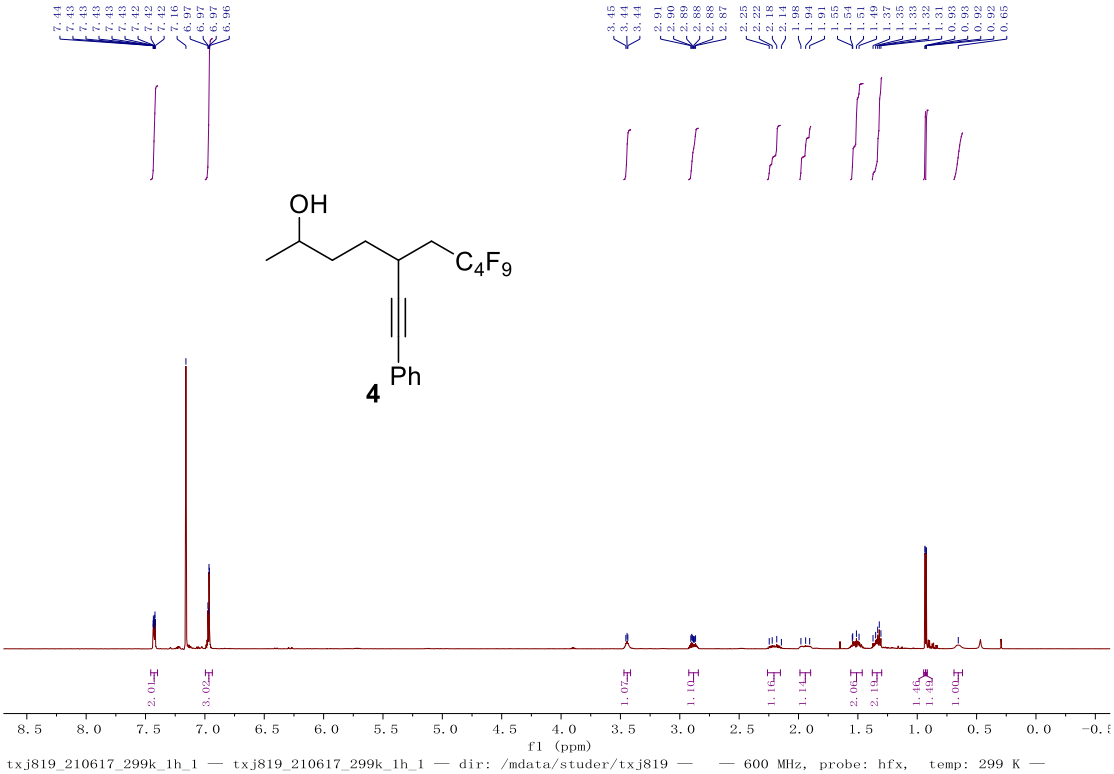

-71.44
-71.45
-71.46
-71.47
-113.04
-113.05
-113.06
-113.07
O
CF2CF2Cl
Ph
3z
2.00
2.10
f1 (ppm)
Mar07-2017.505.fid — TXJ-710-F — f19cpd CDCl3 /opt/topspin av1 38


7.41
7.40
7.40
7.39
7.39
7.39
7.38
7.30
7.29
7.28
7.26
3.10
3.08
3.07
3.07
3.06
3.04
3.04
3.03
3.01
2.55
2.54
2.52
2.52
2.52
2.50
2.49
2.43
2.37
2.30
2.24
2.16
1.95
1.89
1.82
1.79
1.68
1.65
1.57
O
C4F9
Ph
3va
2.10
3.08
1.00
4.12
2.99
1.07
1.31
2.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.
f1 (ppm)
Feb23-2017.124.fid — TXJ-700-H — proton CDCl3 /opt/topspin av1 32

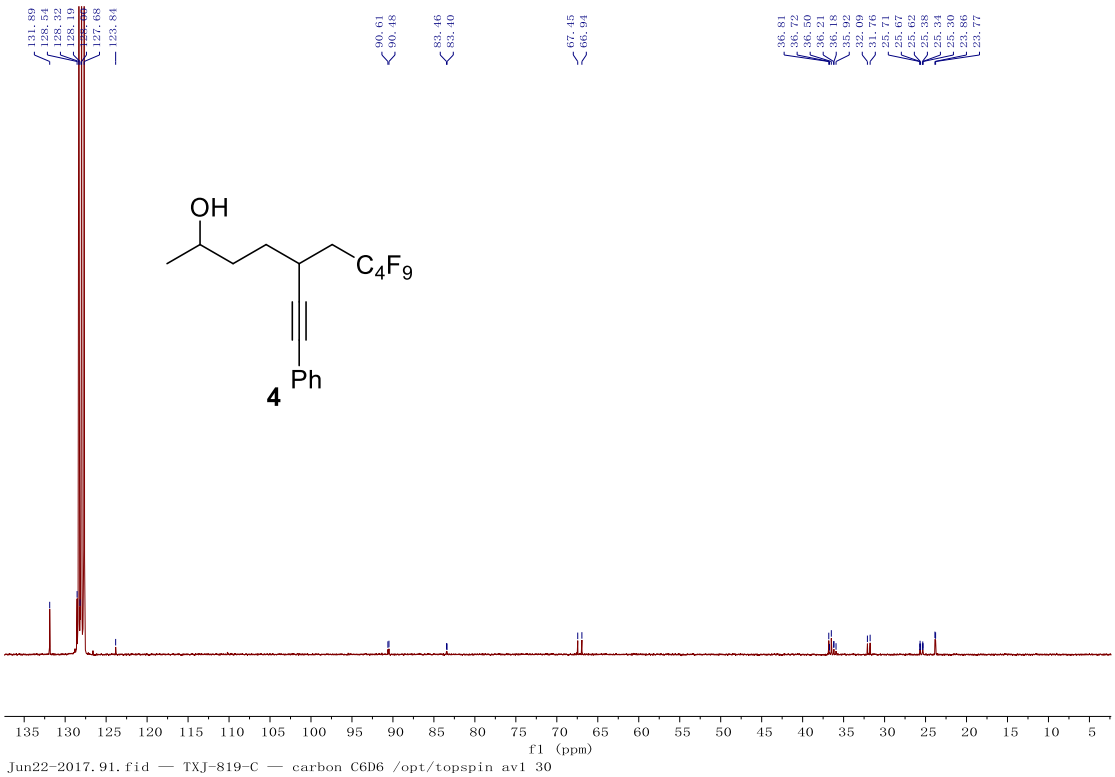

208.11
131.60
128.23
128.03
123.15
89.79
82.88
77.42
77.00
76.58
43.01
36.24
35.96
35.68
34.69
29.87
25.19
25.15
25.10
21.15
O
C4F9
Ph
3va
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Feb23-2017.121.fid — TXJ-700-C — carbon CDCl3 /opt/topspin av1 32

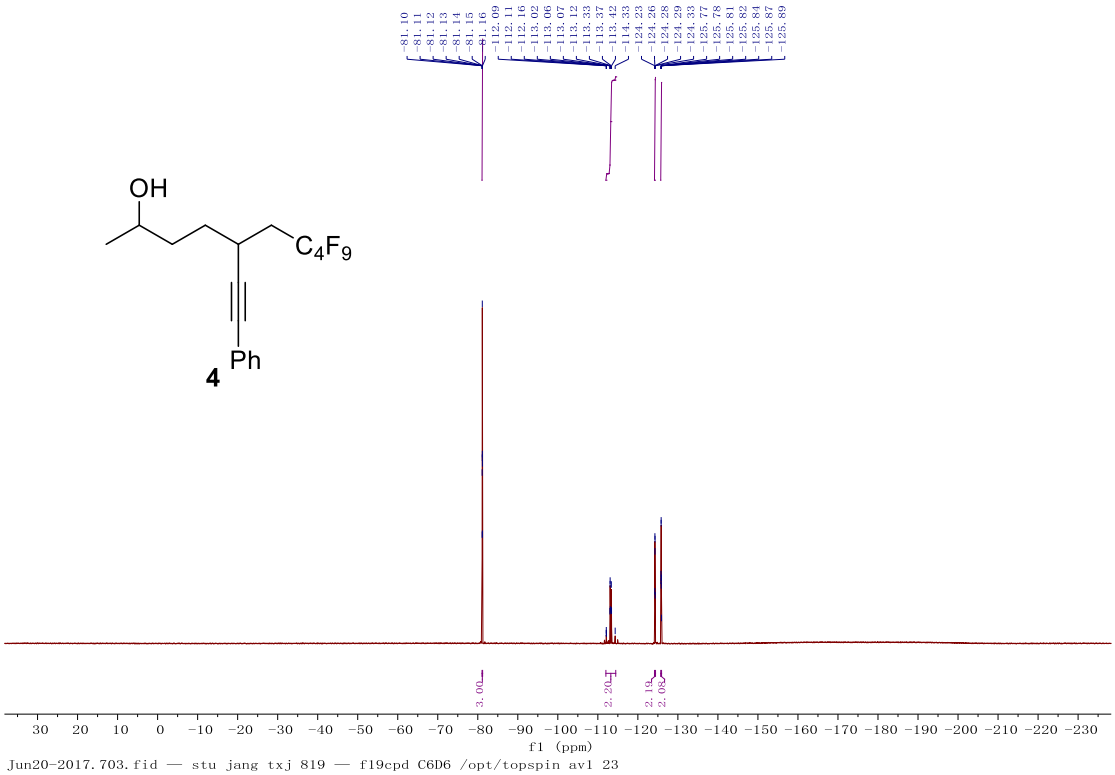


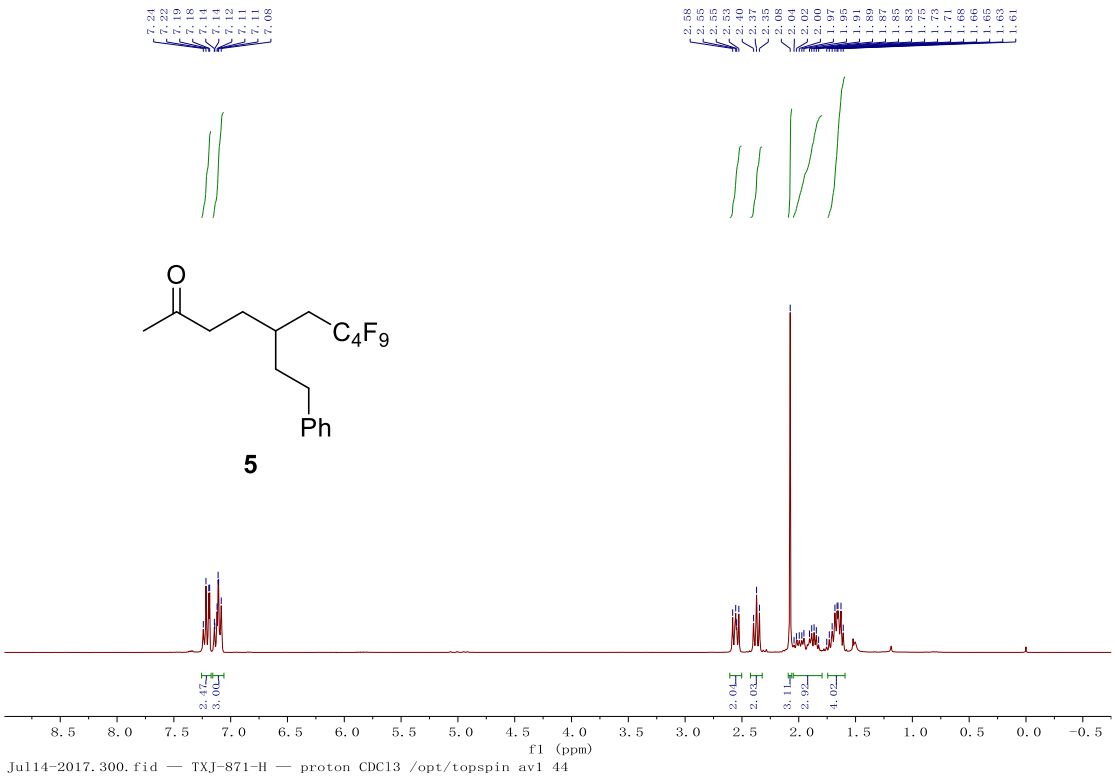
Feb23-2017.125.fid — TXJ-700-C — f19cpd CDCl3 /opt/topspin av1 32

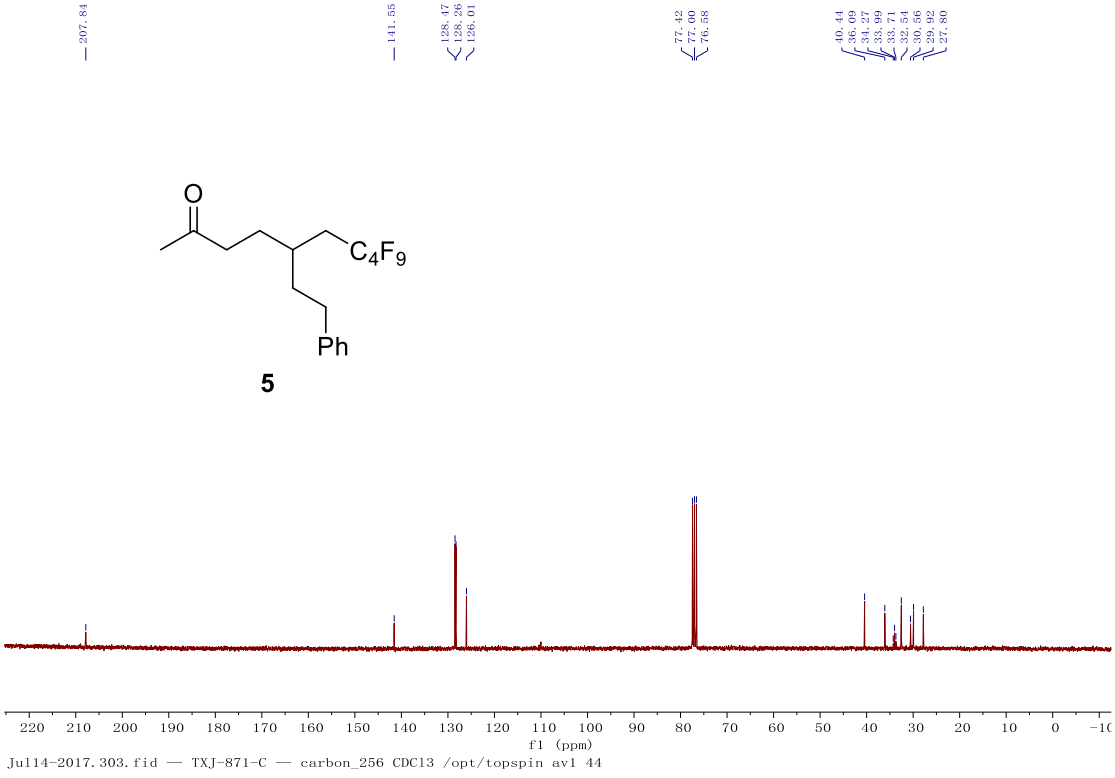


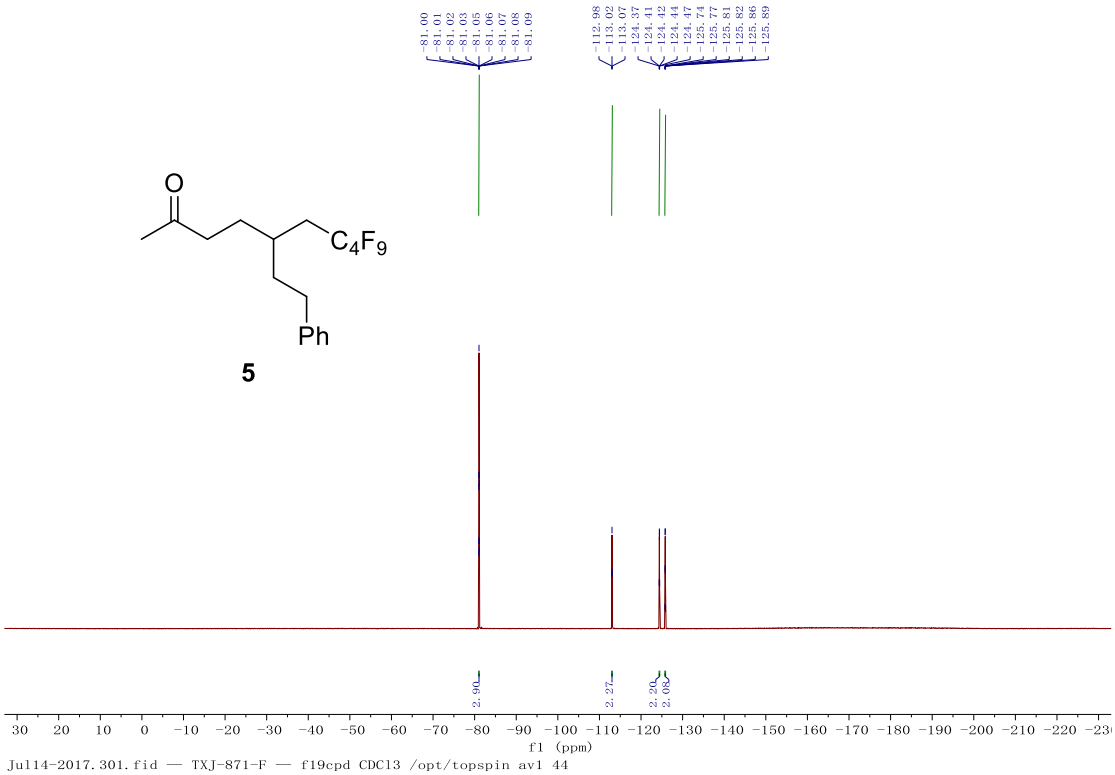
txj819_210617_299k_1h_1 — txj819_210617_299k_1h_1 — dir: /mdata/studer/txj819 — — 600 MHz, probe: hfx, temp: 299 K —


OH
C_4F_9
Ph
4
f1 (ppm)
Jun22-2017.91.fid — TXJ-819-C — carbon C6D6 /opt/topspin av1 30

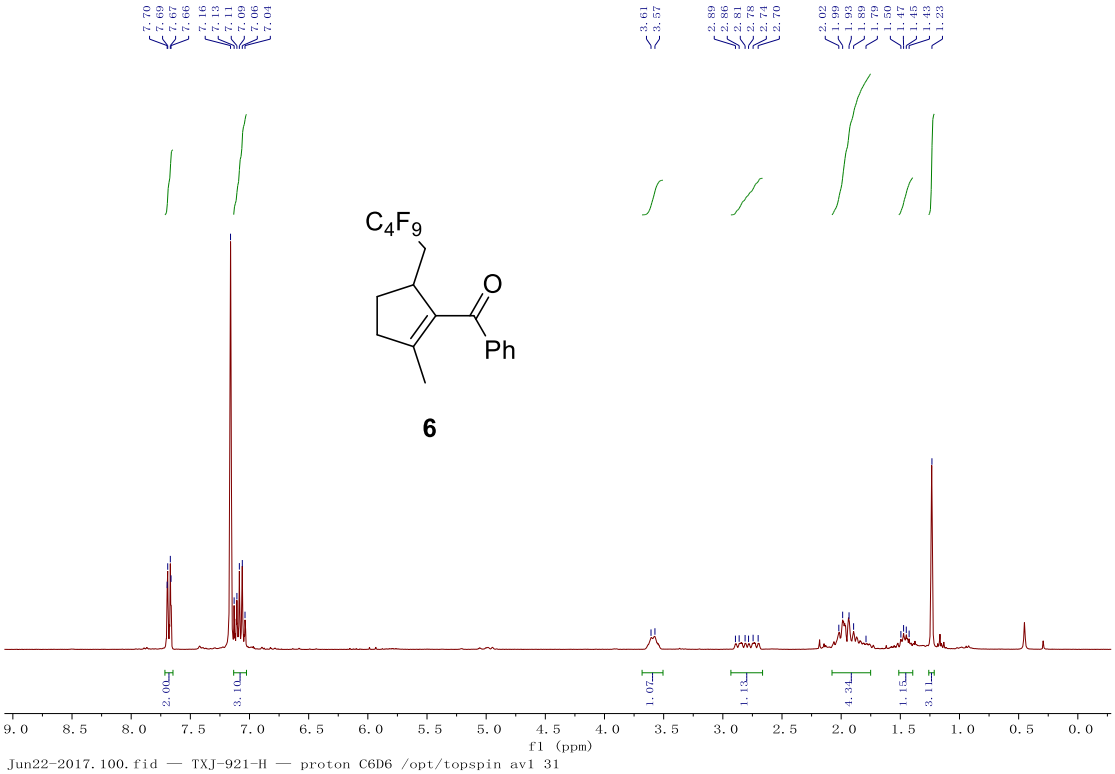

OH
C_4F_9
Ph
4
3.00
2.20
2.13
2.05
f1 (ppm)
Jun20-2017.703.fid — stu jang txj 819 — f19cpd C6D6 /opt/topspin av1 23


O
C4F9
Ph
5
f1 (ppm)
Jul14-2017.300.fid — TXJ-871-H — proton CDCl3 /opt/topspin av1 44

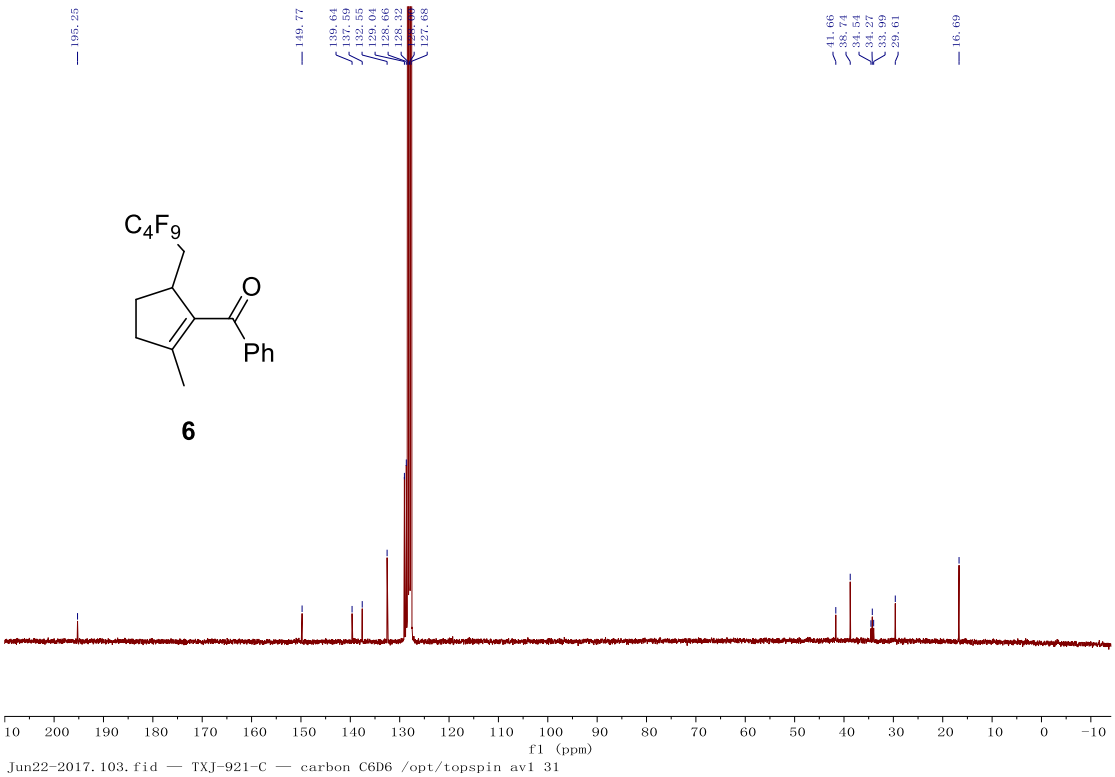

O
C4F9
Ph
5
f1 (ppm)
Jul14-2017.303.fid — TXJ-871-C — carbon_256 CDCl3 /opt/topspin av1 44

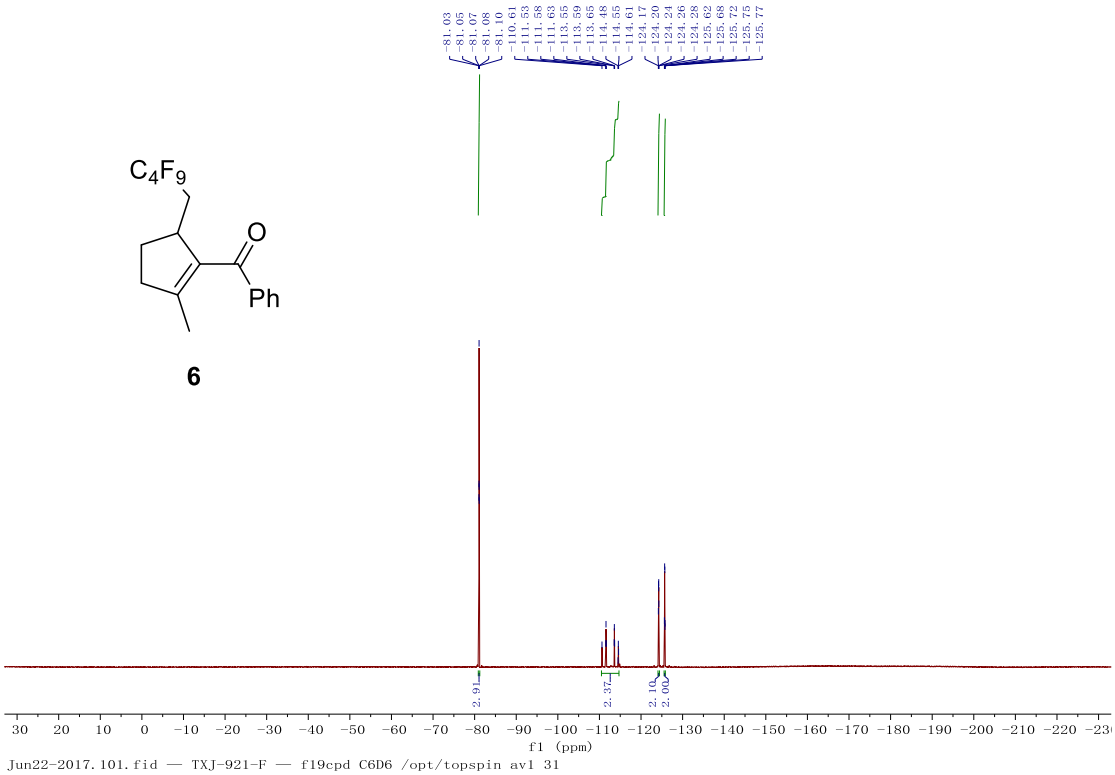

-81.00
-81.01
-81.02
-81.03
-81.05
-81.06
-81.07
-81.08
-81.09
-112.98
-113.02
-113.07
-124.37
-124.41
-124.42
-124.44
-124.47
-125.74
-125.77
-125.81
-125.82
-125.86
-125.89
O
C4F9
Ph
2.90
2.27
2.20
2.08
f1 (ppm)
Jul14-2017.301.fid — TXJ-871-F — f19cpd CDCl3 /opt/topspin av1 44

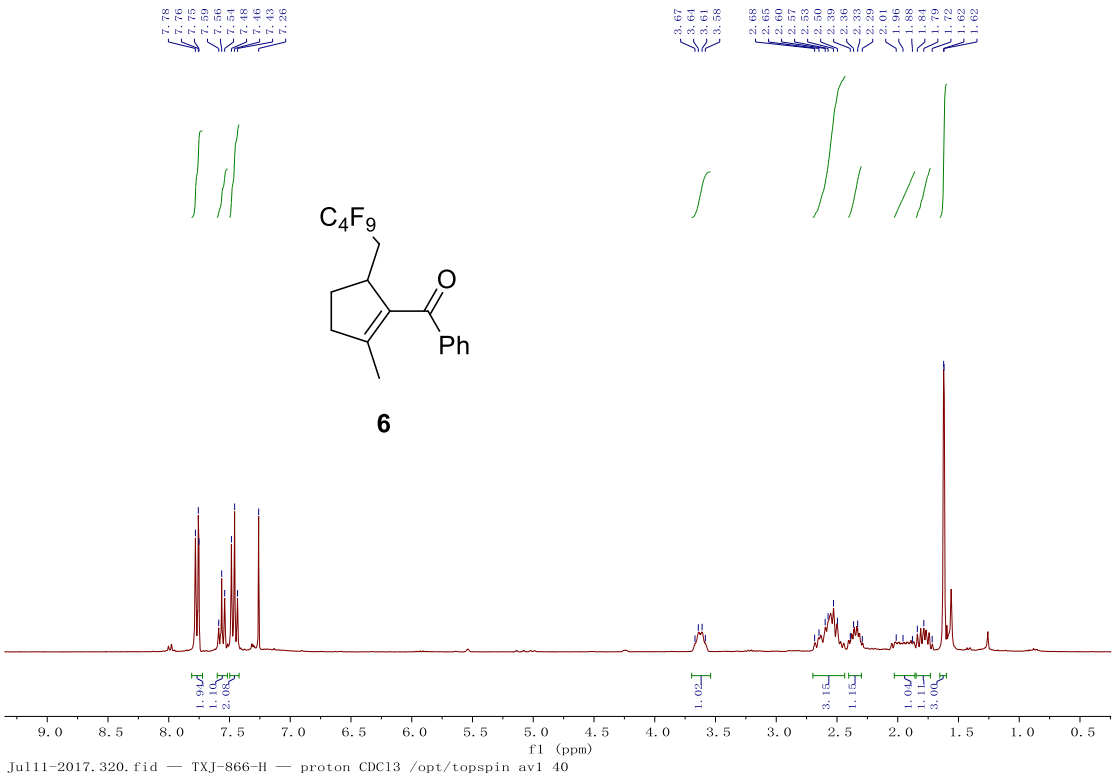
5


7.70
7.69
7.67
7.66
7.16
7.13
7.11
7.09
7.06
7.04
3.61
3.57
2.89
2.86
2.81
2.78
2.74
2.70
2.02
1.99
1.93
1.89
1.79
1.50
1.47
1.45
1.43
1.23
C4F9
O
Ph
2.00
3.10
1.07
1.13
4.34
1.15
3.11
f1 (ppm)
Jun22-2017.100.fid — TXJ-921-H — proton C6D6 /opt/topspin av1 31

6

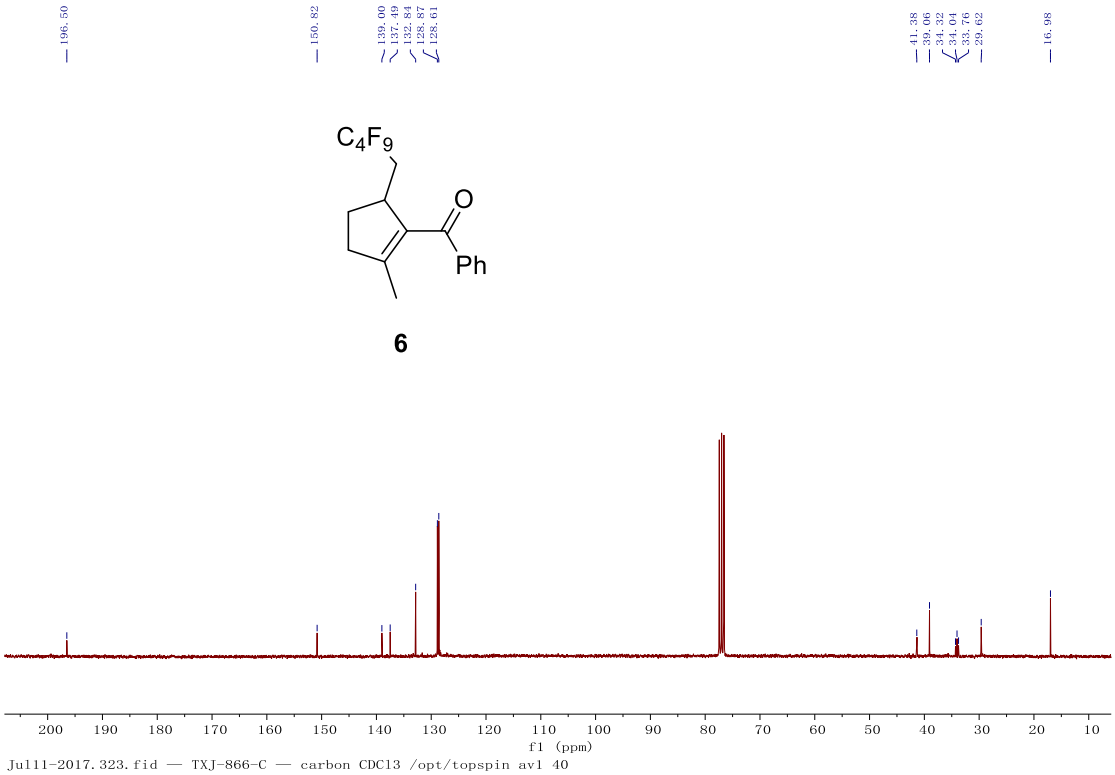

195.25
149.77
139.64
137.59
132.55
129.04
128.66
128.32
127.68
41.66
38.74
34.54
34.27
33.99
29.61
16.69
C4F9
O
Ph
6
f1 (ppm)
Jun22-2017.103.fid — TXJ-921-C — carbon C6D6 /opt/topspin av1 31


C4F9
O
Ph
6
2.91
2.37
2.10
2.00
f1 (ppm)
Jun22-2017.101.fid — TXJ-921-F — f19cpd C6D6 /opt/topspin av1 31



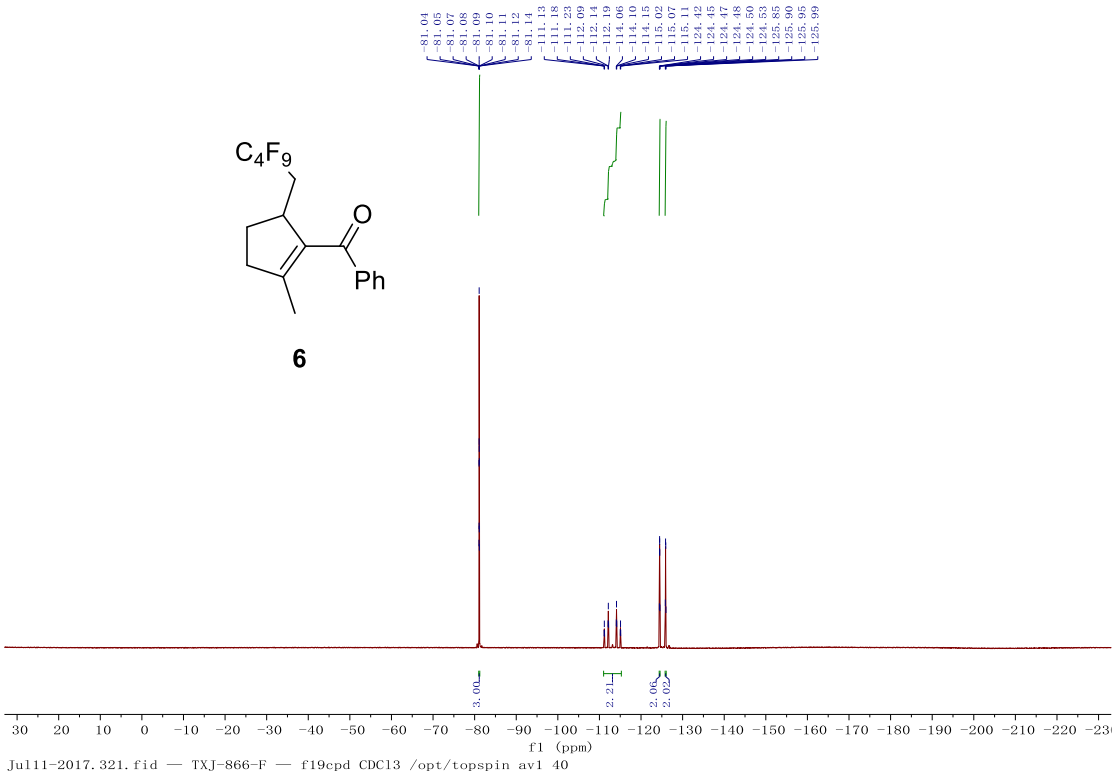
6

Jul11-2017.320.fid — TXJ-866-H — proton CDCl3 /opt/topspin av1 40



6

Jul11-2017.323.fid — TXJ-866-C — carbon CDCl3 /opt/topspin av1 40


C4F9
O
Ph
6
-81.04
-81.05
-81.07
-81.08
-81.09
-81.10
-81.11
-81.12
-81.14
-111.13
-111.18
-111.23
-112.09
-112.14
-112.19
-114.06
-114.10
-114.15
-115.02
-115.07
-115.11
-124.42
-124.45
-124.47
-124.48
-124.50
-124.53
-125.85
-125.90
-125.95
-125.99
3.00
2.21
2.06
2.02
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -23
f1 (ppm)
Jul11-2017.321.fid — TXJ-866-F — f19cpd CDCl3 /opt/topspin av1 40