Supporting Information

Pd(II)-SDP-Catalyzed enantioselective 5-*exo-dig* cyclization of γ-alkynoic acids: application to the synthesis of functionalized dihydofuran-2(3*H*)-ones containing a chiral quaternary carbon center

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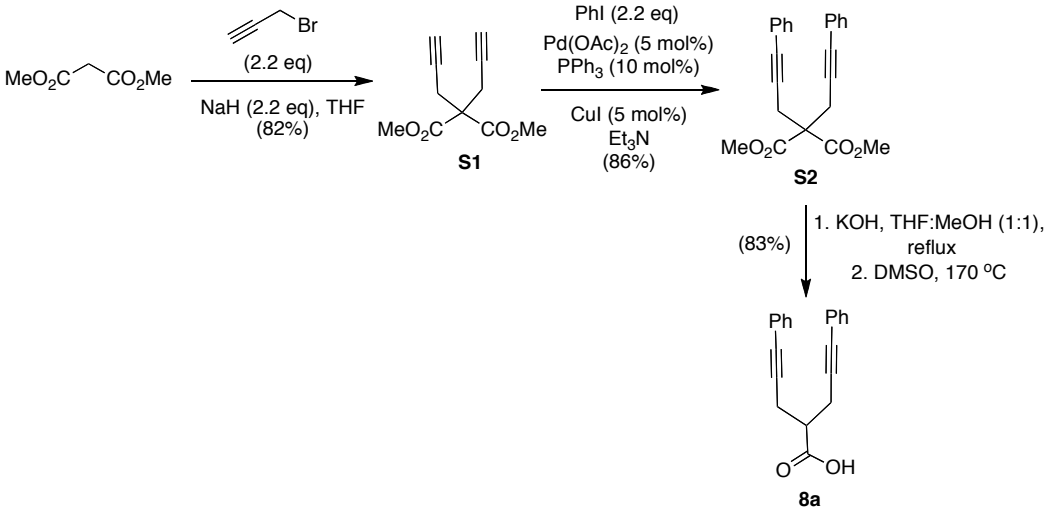
Table of Contents

Preparation of γ-alkynoic acids 8

Preparation of compound 8a[1]

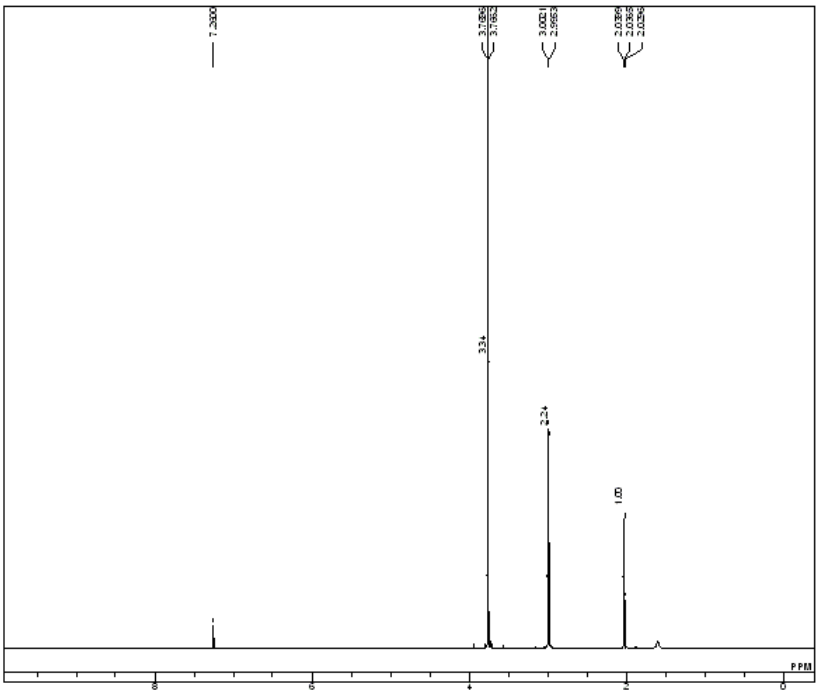


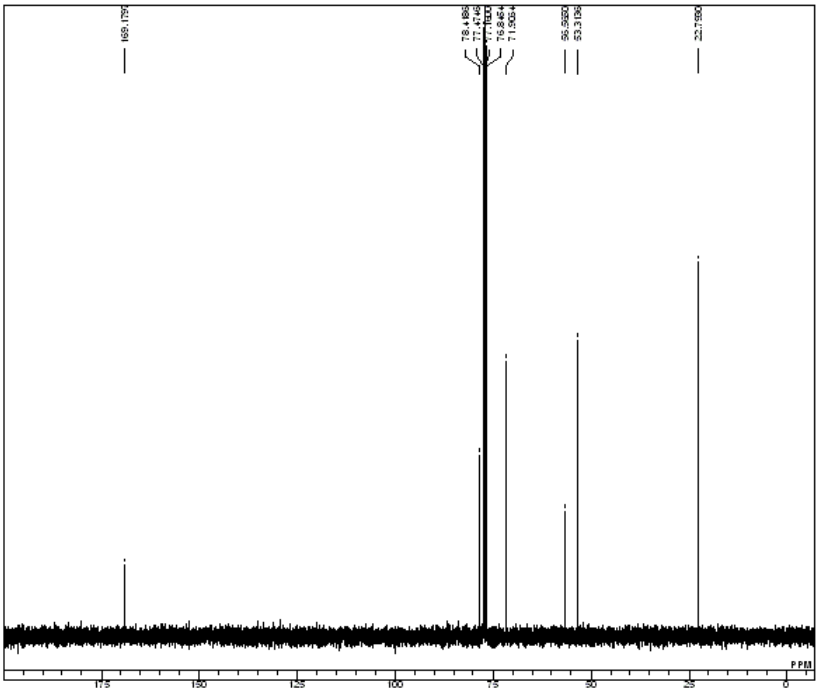
Dimethyl 2,2-di(prop-2-ynyl)malonate (S1)

To a stirred suspension of NaH (66 mmol) in THF (60 mL) at -10 °C under nitrogen atmosphere was added diethyl malonate (30 mmol) dropwise and the mixture was stirred for additional 30 min. Propargyl bromide (66 mmol) was then added again in dropwise and the reaction temperature was slowly raised and the reaction mixture was stirred overnight at room temperature. The reaction was quenched with saturated NH_4Cl solution, extracted with ether, washed with brine, dried over anhydrous Na_2SO_4 and evaporated. The crude product was purified through silica column chromatography using hexane/ethyl acetate mixture as eluent to furnish compound **S1**.

Yield: 82%; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.03-2.04 (m, 2H), 3.00 (d, J = 2.7 Hz, 4H), 3.77 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 22.8, 53.3, 56.6, 71.9, 78.4, 169.2.

[1] S. Li, W. Jia and N. Jiao, *Adv. Synth. Catal.*, 2009, **351**, 569-575.



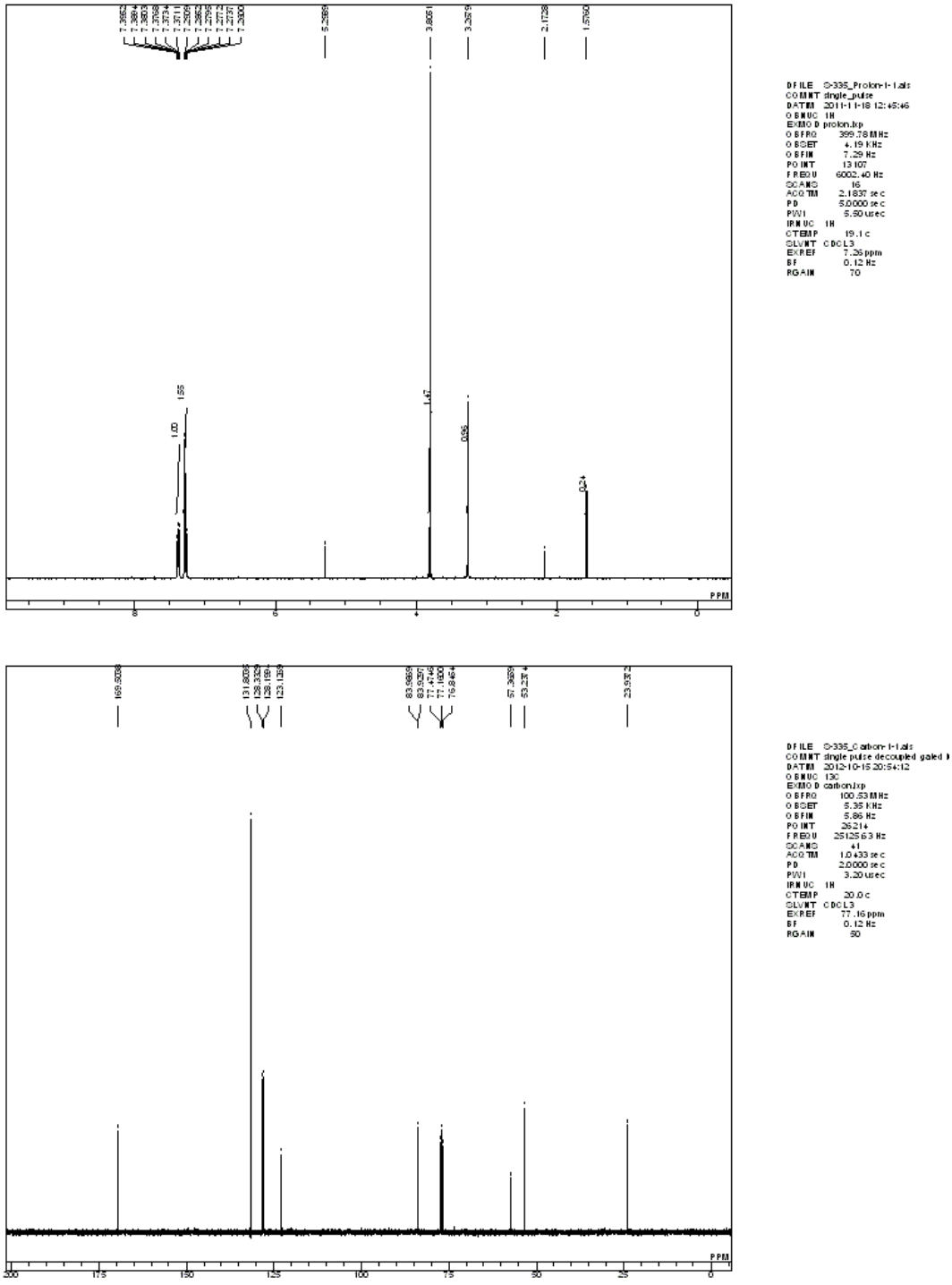


Dimethyl 2,2-bis(3-phenylprop-2-ynyl)malonate (S2)

To a stirred solution of **S1** (3 mmol), iodobenzene (6.6 mmol) in Et_3N (20 mL) was added $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%) and CuI (5 mol%) and the mixture was stirred at 60 ^oC. After completion of the reaction (2 h), the mixture was cooled to room temperature and diluted with CH_2Cl_2. To this mixture water was added and the organic layer was separated and the aqueous layer was extracted twice with CH_2Cl_2.

The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified through silica column chromatography using hexane/ethyl acetate mixture as eluent to afford compound **S2**.

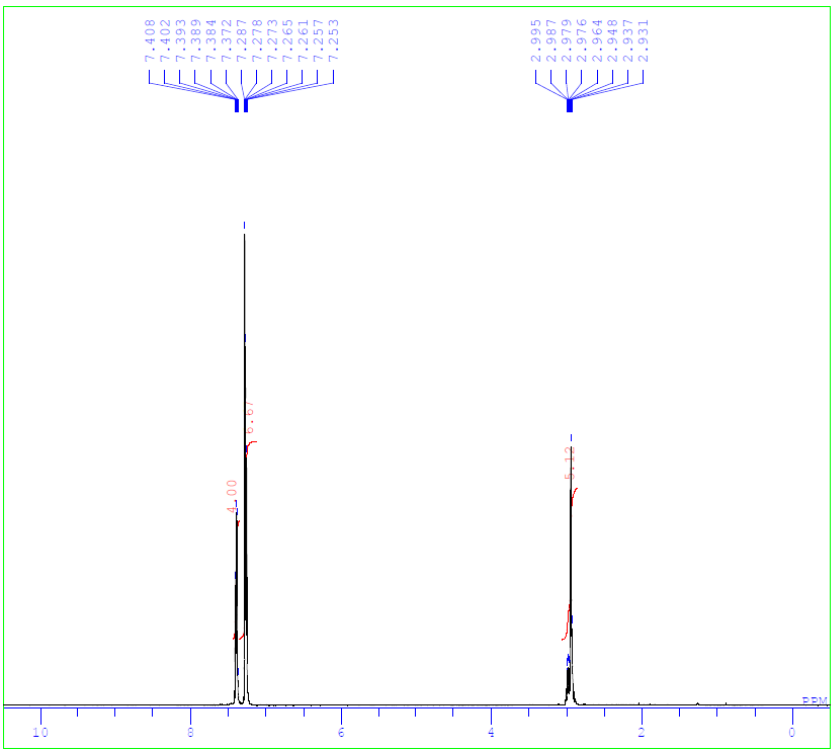
Yield: 86%; pale yellow solid; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.27 (s, 4H), 3.81 (s, 6H), 7.27-7.29 (m, 6H), 7.37-7.40 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 23.9, 53.2, 57.4, 83.9, 84.0, 123.1, 128.2, 128.3, 131.8, 169.5.



5-Phenyl-2-(3-phenylprop-2-ynyl)pent-4-ynoic acid (8a)

Compound **S2** (2 mmol) was dissolved in 1:1 mixture of THF/MeOH (10 mL). To this solution, KOH (8 mmol) in THF/H_2O (4 mL, 3:1 ratio) was added and the mixture was refluxed for 24 h. After cooling, the reaction mixture was diluted with water and acidified with 2N HCl. The mixture was then extracted with CH_2Cl_2, washed with water, brine and dried over anhydrous Na_2SO_4. The solvent was evaporated and DMSO (5 mL) was added to the crude mixture and heated at 170 ^oC with stirring for 6 h. The mixture was cooled to room temperature, diluted with water and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over anhydrous Na_2SO_4 and the solvent was evaporated. Purification of the crude mixture through silica column chromatography using hexane/ethyl acetate mixture as eluent afforded compound **8a**.

Yield: 83%; pale yellow solid; mp: 109-111 ^oC; IR (KBr): ν = 3500-2500 (broad), 3030, 2923, 2617, 2361, 1704, 1600, 1489, 1425, 1342, 1287, 1225, 1078 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.93-3.00 (m, 5H), 7.25-7.29 (m, 6H), 7.37-7.41 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.0, 43.8, 83.0, 85.9, 123.4, 128.1, 128.4, 131.80, 131.81, 178.9; HRMS (ESI): calcd for $C_{20}H_{16}NaO_2$, m/z 311.1048 ($[M+Na]^+$); found, m/z 311.1037.

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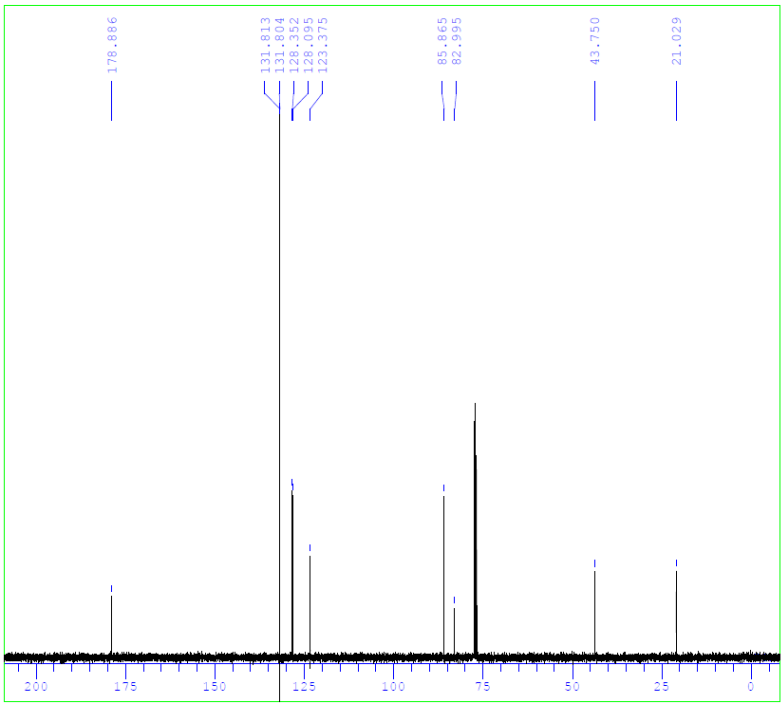


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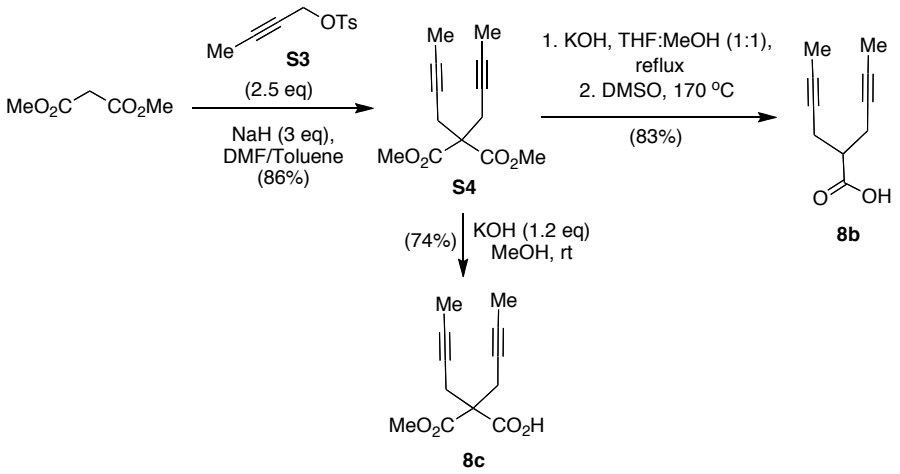
Preparation of compounds 8b[2] and 8c[2]



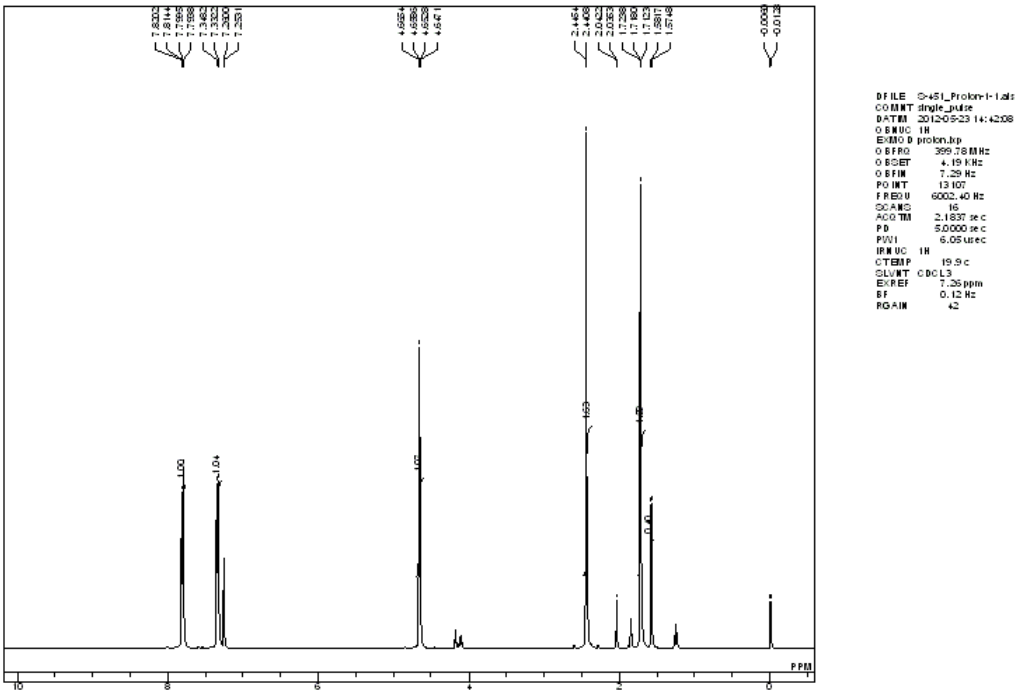
But-2-ynyl 4-methylbenzenesulfonate (S3)

Tosyl chloride (24 mmol) followed by powdered KOH (240 mmol) were added in portions to a stirred solution of but-2-yn-1-ol (20 mmol) in ether (40 mL) at 0 °C. The reaction mixture was warmed to room temperature gradually and stirred overnight. Water was added, the organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried

[2] E. Tomás-Mendivil, P. Y. Toullec, J. Díez, S. Conejero, V. Michelet and V. Cadierno, *Org. Lett.*, 2012, **14**, 2520-2523

over anhydrous Na_2SO_4 and evaporated. The crude product was used as such for the next step without further purification.

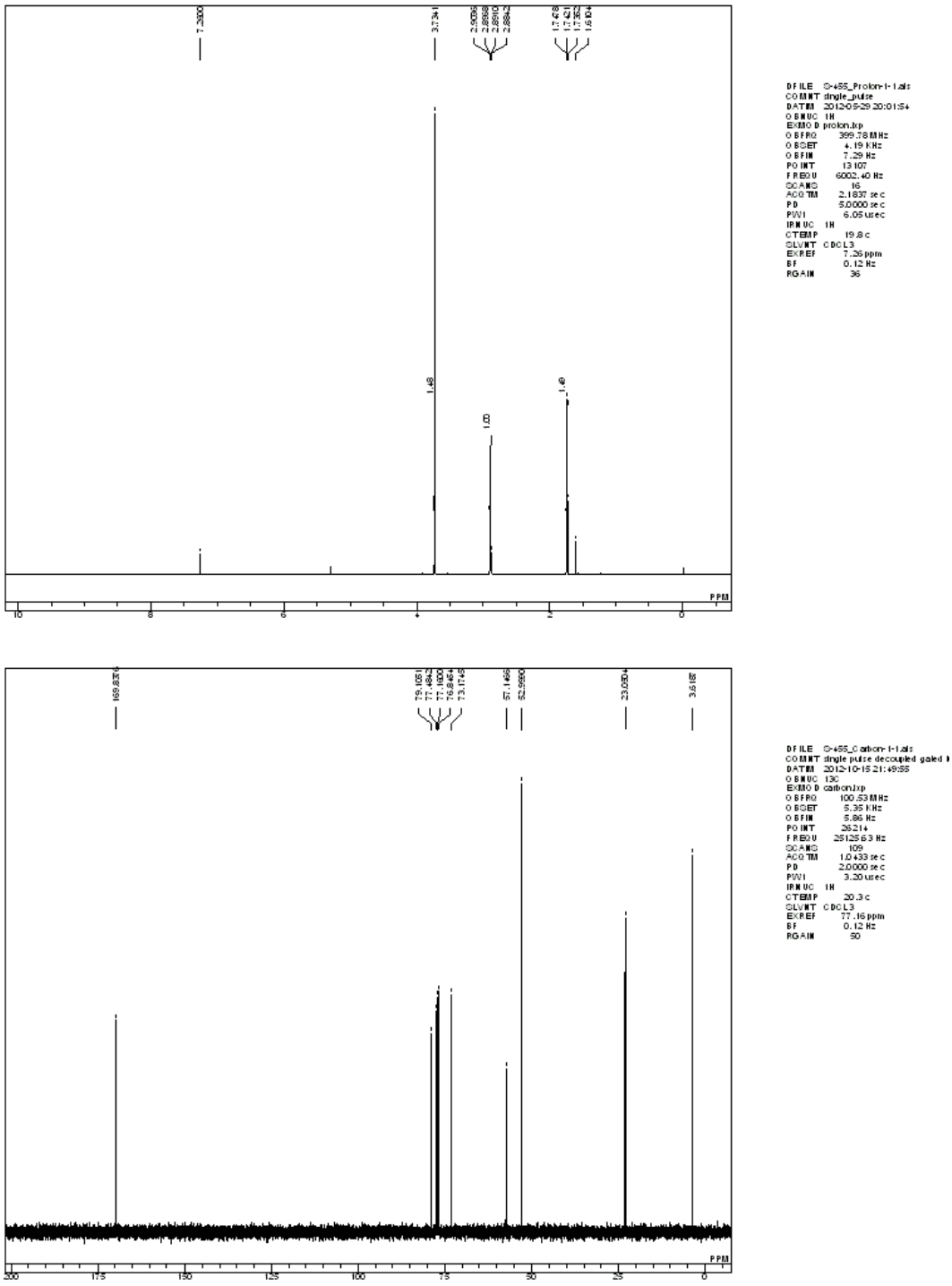
Yield: 94% (crude).



Dimethyl 2,2-di(but-2-ynyl)malonate (S4)

To a suspension of NaH (33 mmol) in DMF/toluene mixture (75 mL, 2:1) was added diethyl malonate (11 mmol) at 0 ^oC. After 1 h stirring, a solution of **S3** (27.5 mmol) in DMF (20 mL) was added dropwise. The reaction temperature was increased slowly to room temperature and the mixture was stirred for 12 h. After quenching the reaction with saturated NH_4Cl solution additional 50 mL of toluene was added and the layers were separated. Aqueous layer was extracted with toluene and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and evaporated. Crude mixture was purified through silica column chromatography using hexane/ethyl acetate mixture as eluent to furnish compound **S4**.

Yield: 86%; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.74 (t, *J* = 2.7 Hz, 6H), 2.88-2.90 (m, 4H), 3.73 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 3.6, 23.1, 53.0, 57.2, 73.2, 79.1, 169.8.

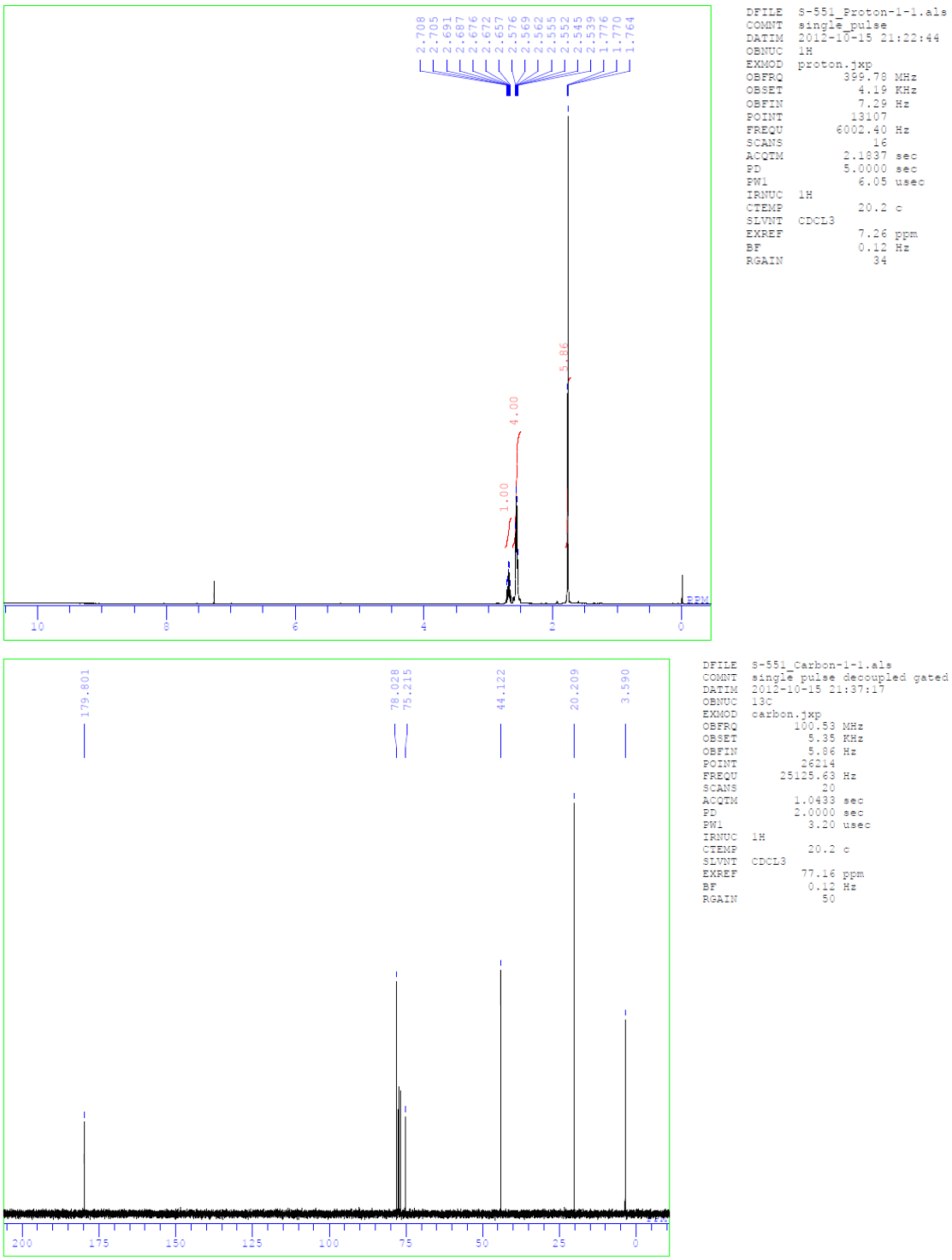


2-(But-2-ynyl)hex-4-ynoic acid (8b)

The procedure used for the preparation of acid **8a** from diester **S2** was employed to obtain compound **8b** from **S4**.

Yield: 83%; pale yellow solid; mp: 70-72 ^{o}C; IR (KBr): ν = 3500-2500 (broad) 3033, 2916, 2617, 2360, 1703, 1435, 1287, 1224, 1076, 1025, cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.76-1.78 (m, 6H), 2.54-2.58 (m, 4H), 2.66-2.71 (m, 1H); ^{13}C-NMR (100

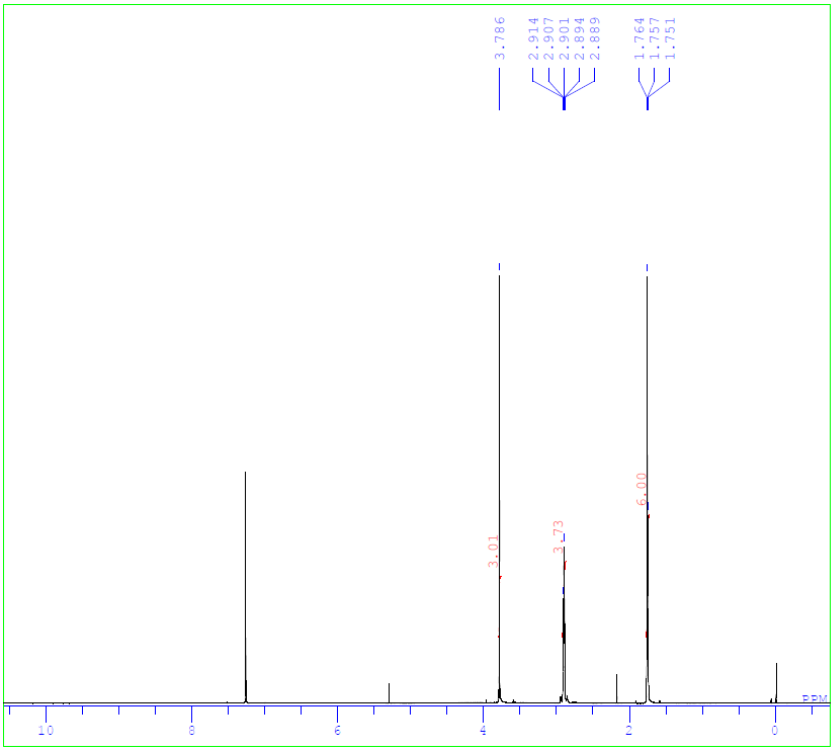
MHz, $CDCl_3$): δ = 3.6, 20.2, 44.1, 75.2, 78.0, 179.8; HRMS (ESI): calcd for $C_{10}H_{12}NaO_2$, m/z 187.0735 ([M+Na]$^+$); found, m/z 187.0726.



2-(But-2-ynyl)-2-(methoxycarbonyl)hex-4-ynoic acid (8c)

A mixture of diester **S4** (2 mmol) in MeOH (10 mL) and KOH (2.4 mmol) in MeOH (3 mL) was stirred at room temperature for 4 days. The mixture was added ether and washed with saturated $NaHCO_3$ solution. The basic aqueous solution was neutralized

with 2N HCl and extracted with CH_2Cl_2, washed with brine, dried over anhydrous Na_2SO_4 and evaporated. The crude material was purified through silica column chromatography using hexane/ethyl acetate mixture as eluent to afford compound **8c**. Yield: 74%; colorless solid; mp: 119-121 ^oC; IR (KBr): ν = 3500-2500 (broad band), 2924, 2678, 2360, 1718, 1434, 1304, 1211, 1061 cm^{-1}; ^1H-NMR (400 MHz, $CDCl_3$): δ = 1.76 (t, *J* = 2.3 Hz, 6H), 2.89-2.91 (m, 4H), 3.79 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 3.6, 23.1, 53.2, 57.2, 72.9, 79.5, 169.6, 175.1; HRMS (ESI): calcd for $C_{12}H_{14}NaO_4$, m/z 245.0790 ($[M+Na]^+$); found, m/z 245.0782.

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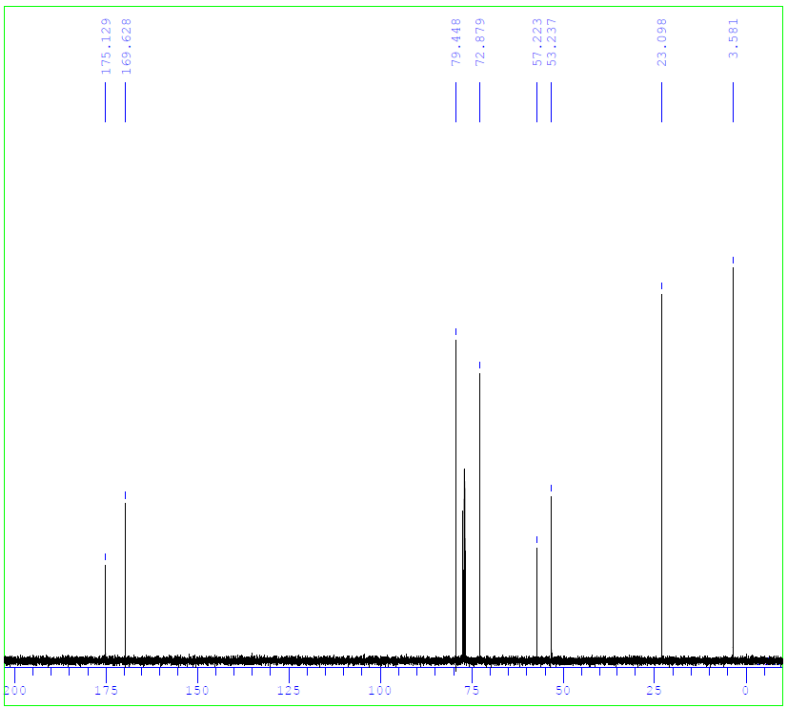


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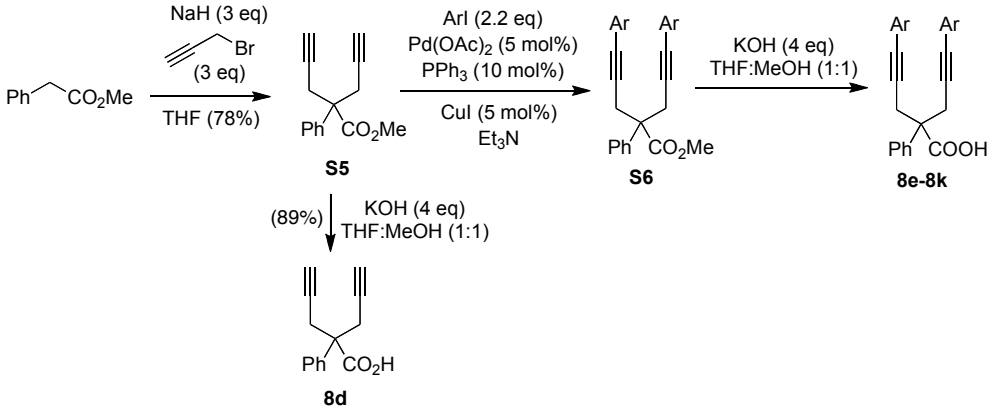
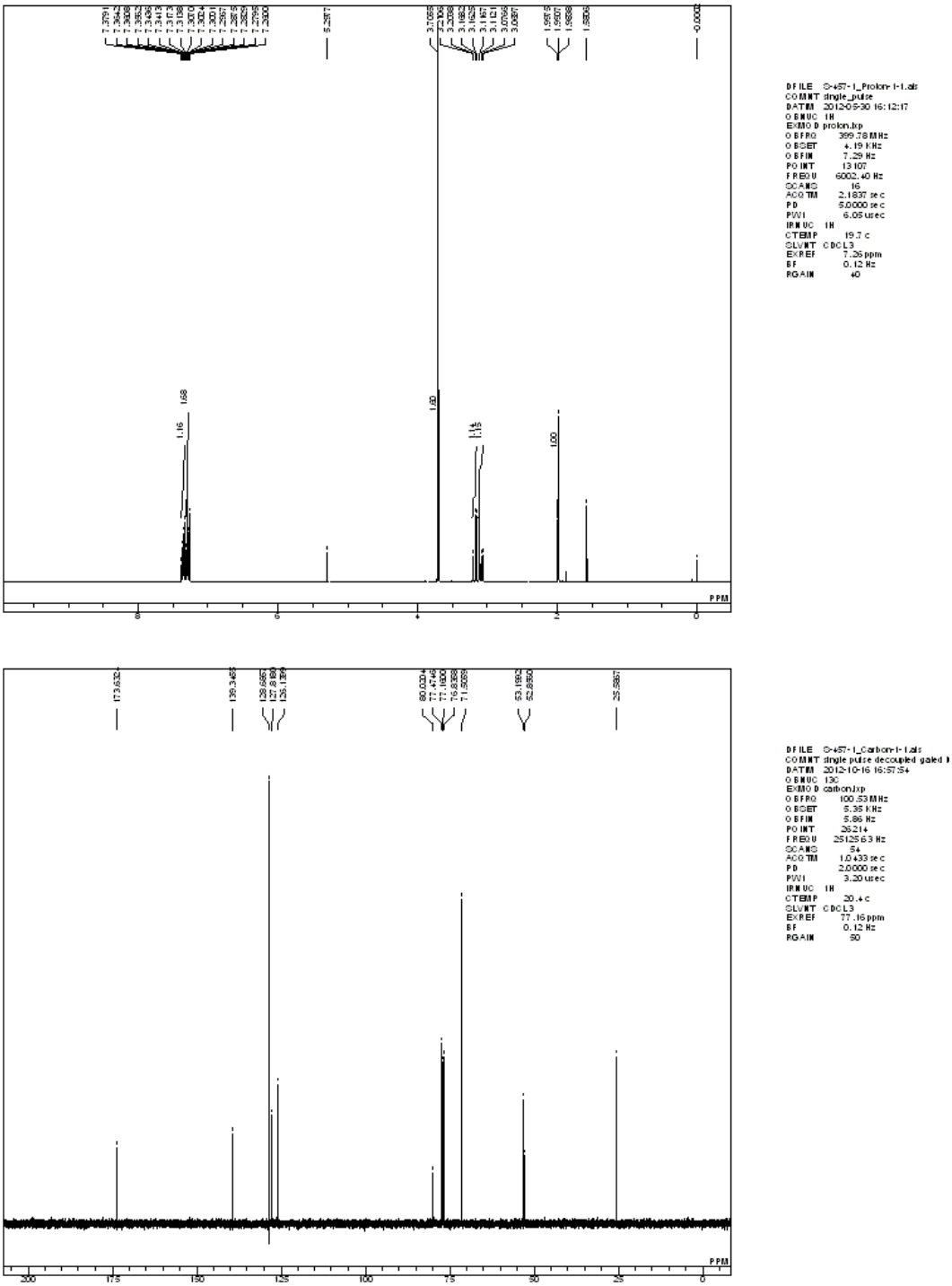
Preparation of compounds 8d,[2] 8e, 8f, 8g, 8h, 8i, 8j, 8k



Methyl 2-phenyl-2-(prop-2-ynyl)pent-4-ynoate (S5)

To a stirred suspension of NaH (30 mmol) in THF (30 mL) at 0 ^{o}C under nitrogen atmosphere was added methyl 2-phenylacetate (10 mmol) dropwise and the mixture was stirred for additional 1 h at room temperature. The reaction mixture was again cooled to 0 ^{o}C and propargyl bromide (30 mmol) was added dropwise. After the addition was complete the mixture was heated at 50 ^{o}C for 24 h. The reaction was quenched with saturated NH_4Cl solution, extracted with CH_2Cl_2, washed with brine, dried over anhydrous Na_2SO_4 and evaporated. The crude product was purified through silica column chromatography using hexane/ethyl acetate mixture as eluent to furnish compound **S5**.

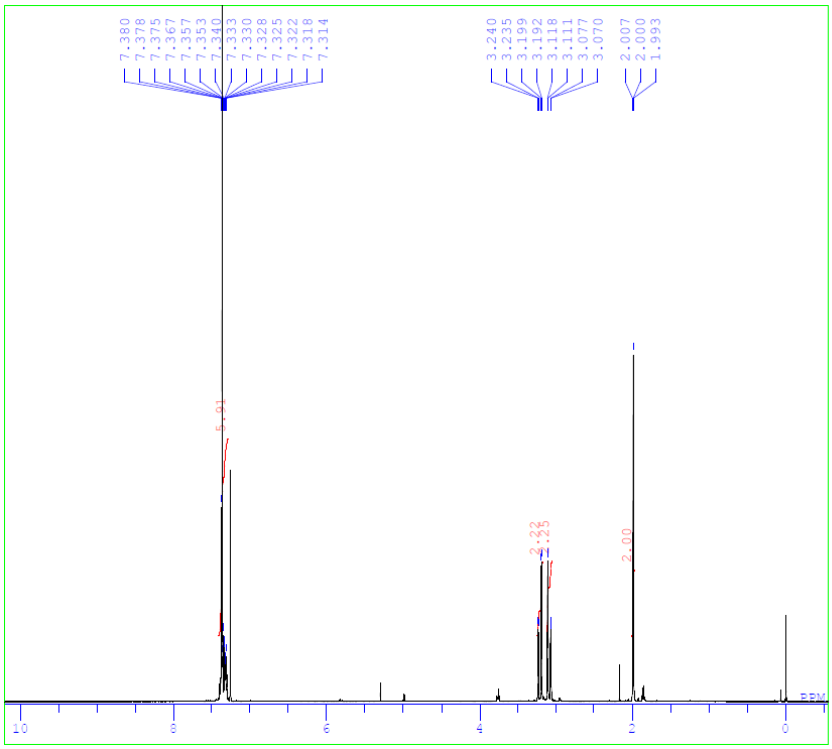
Yield: 78%; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.99 (t, *J* = 2.7 Hz, 2H), 3.10 (dd, *J* = 16.9, 2.7 Hz, 2H), 3.19 (dd, *J* = 16.5, 2.3 Hz, 2H), 3.71 (s, 3H), 7.28-7.32 (m, 3H), 7.34-7.38 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 25.6, 52.9, 53.2, 71.5, 80.0, 126.1, 127.8, 128.7, 139.4, 173.6.



2-Phenyl-2-(prop-2-ynyl)pent-4-ynoic acid (8d)

To a solution of **S5** (2 mmol) in 1:1 mixture of THF/MeOH (10 mL) was added KOH (8 mmol) in THF/H_2O (4 mL, 3:1 ratio) and the mixture was refluxed for 6 h. After cooling, the reaction mixture was diluted with water and acidified with 2N HCl. The mixture was then extracted with CH_2Cl_2, washed with water, brine, dried over anhydrous Na_2SO_4 and evaporated. Purification of the crude mixture through silica column chromatography using hexane/ethyl acetate mixture as eluent afforded compound **8d**.

Yield: 89%; pale yellow solid; mp: 116-118 ^oC; IR (KBr): ν = 3500-2500 (broad), 3281, 3078, 2361, 1711, 1596, 1496, 1397, 1282, 1225 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.00 (t, *J* = 2.7 Hz, 2H), 3.10 (dd, *J* = 16.5, 2.7 Hz, 2H), 3.22 (dd, *J* = 16.9, 2.7 Hz, 2H), 7.31-7.38 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 25.2, 53.0, 71.7, 79.8, 126.3, 128.1, 128.8, 138.5, 179.1; HRMS (ESI): calcd for $C_{14}H_{12}NaO_2$, m/z 235.0735 ($[M+Na]^+$); found, m/z 235.0728.

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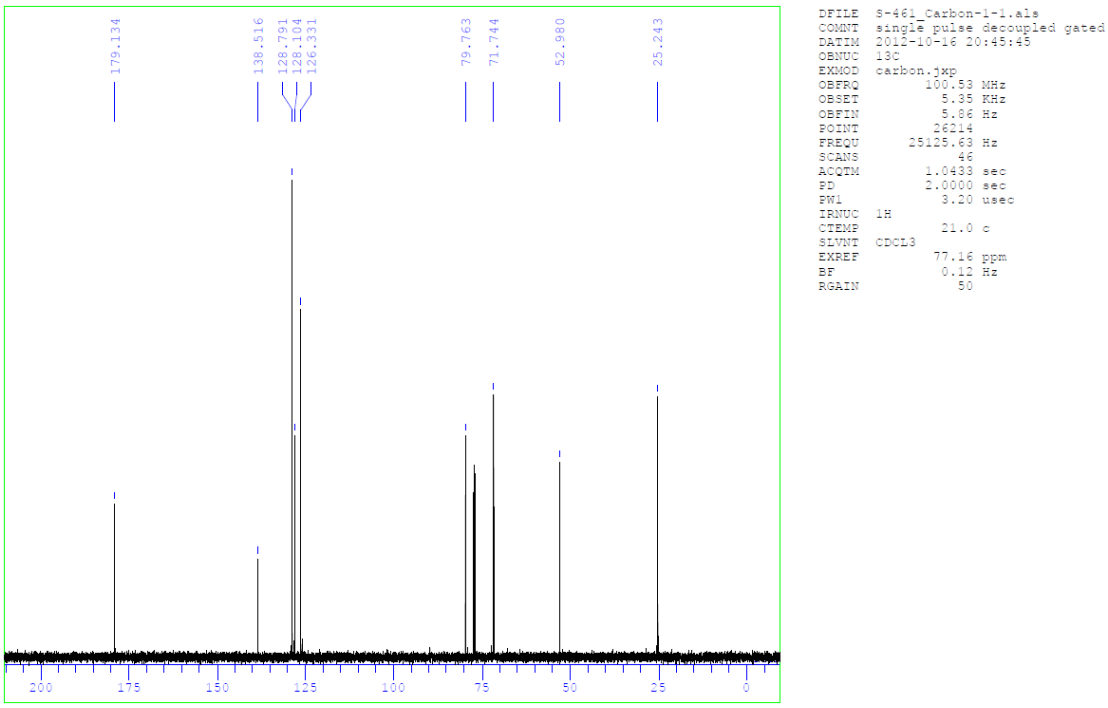


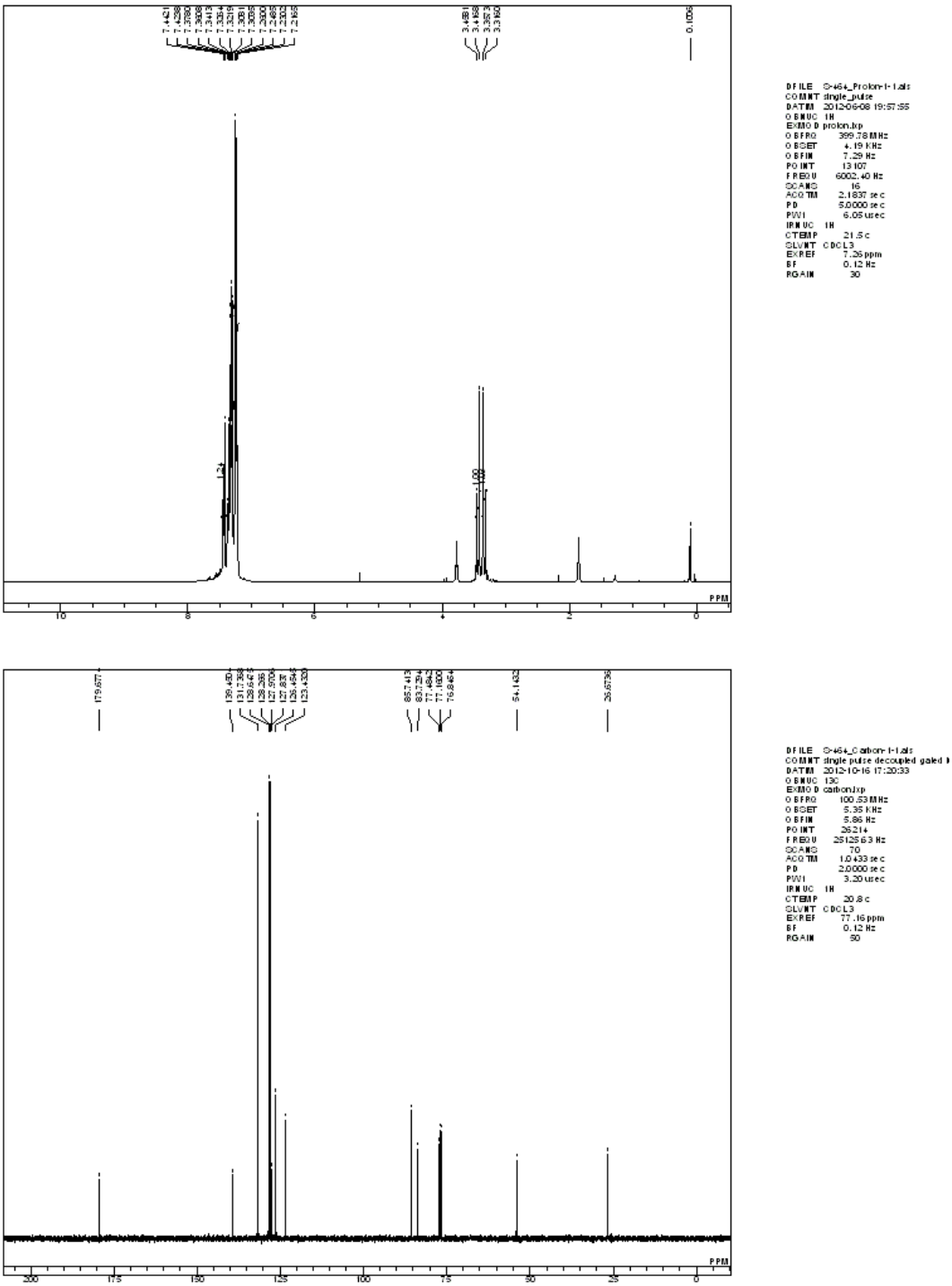
Methyl 2-phenyl-(5-aryl-2-(3-arylprop-2-ynyl)pent-4-ynoate (S6)

To a stirred solution of **S5** (3 mmol), aryl iodide (6.6 mmol) in Et_3N (20 mL) was added $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%) and CuI (5 mol%) and the mixture was stirred at 60 ^oC. After completion of the reaction (2-6 h), the mixture was cooled to room temperature and diluted with CH_2Cl_2. To this mixture water was added and the organic layer was separated and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4 and the solution was filtered through a short pad of silica gel to afford the crude products **S6**.

8e-8k

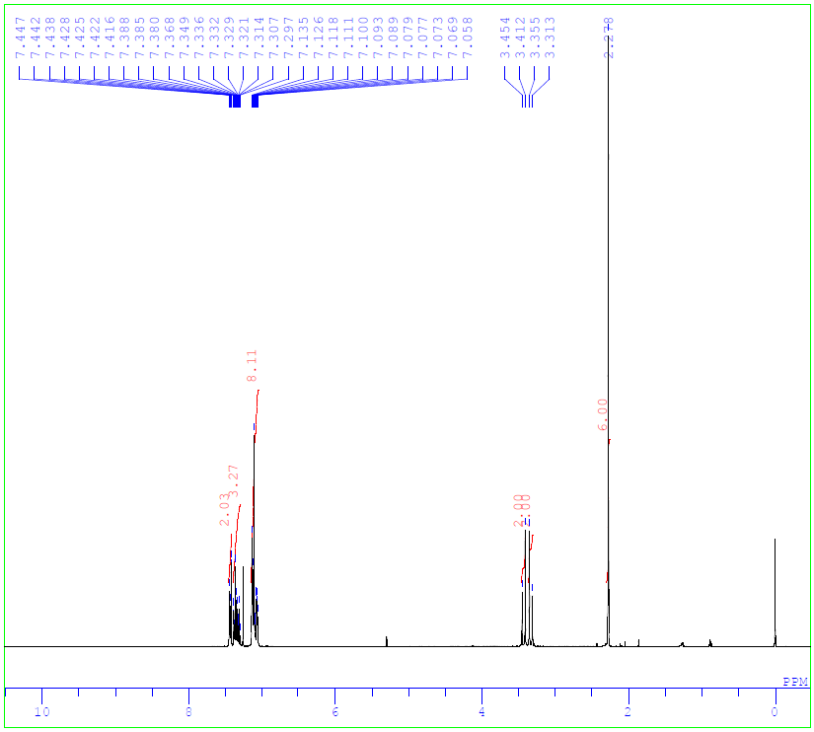
The conditions used for the hydrolysis of compound **S5** was employed for the preparation of compounds **8e-8k** from previously obtained esters **S6**.

2,5-Diphenyl-2-(3-phenylprop-2-ynyl)pent-4-ynoic acid (8e): Yield: 75% (two steps); pale yellow solid; mp: 142-144 ^oC; IR (KBr): ν = 3500-2500 (broad), 3025, 2361, 1698, 1594, 1492, 1437, 1287, 1232, 1065 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.34 (d, *J* = 16.5 Hz, 2H), 3.44 (d, *J* = 16.5 Hz, 2H), 7.22-7.38 (m, 13H), 7.43 (d, *J* = 7.3 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 54.1, 83.7, 85.7, 123.4, 126.5, 127.8, 128.0, 128.3, 128.6, 131.7, 139.5, 179.7; HRMS (ESI): calcd for $C_{26}H_{20}NaO_2$, m/z 387.1361 ($[M+Na]^+$); found, m/z 387.1352.



2-Phenyl-5-*m*-tolyl-2-(3-*m*-tolylprop-2-ynyl)pent-4-ynoic acid (8f): Yield: 42% (two steps); colorless solid; mp: 135-137 ^{o}C; IR (KBr): ν = 3500-2500 (broad), 3022, 2915, 2600, 2362, 1703, 1596, 1490, 1403, 1286, 1231 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 6H), 2.34 (d, *J* = 16.9 Hz, 2H), 3.43 (d, *J* = 16.9 Hz, 2H), 7.06-7.14 (m, 8H), 7.30-7.39 (m, 3H), 7.42-7.45 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.3, 26.7, 54.1, 83.9, 85.2, 123.2, 126.5, 127.9, 128.2, 128.7, 128.8, 128.9, 132.4,

137.9, 139.3, 179.1; HRMS (ESI): calcd for $C_{28}H_{24}NaO_2$, m/z 415.1674 ($[M+Na]^+$); found, m/z 415.1663.

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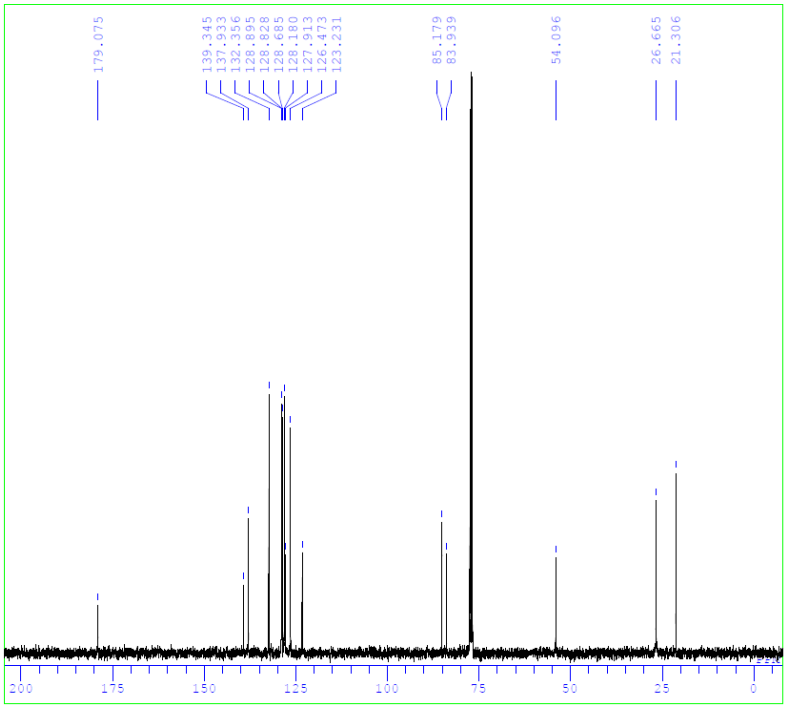


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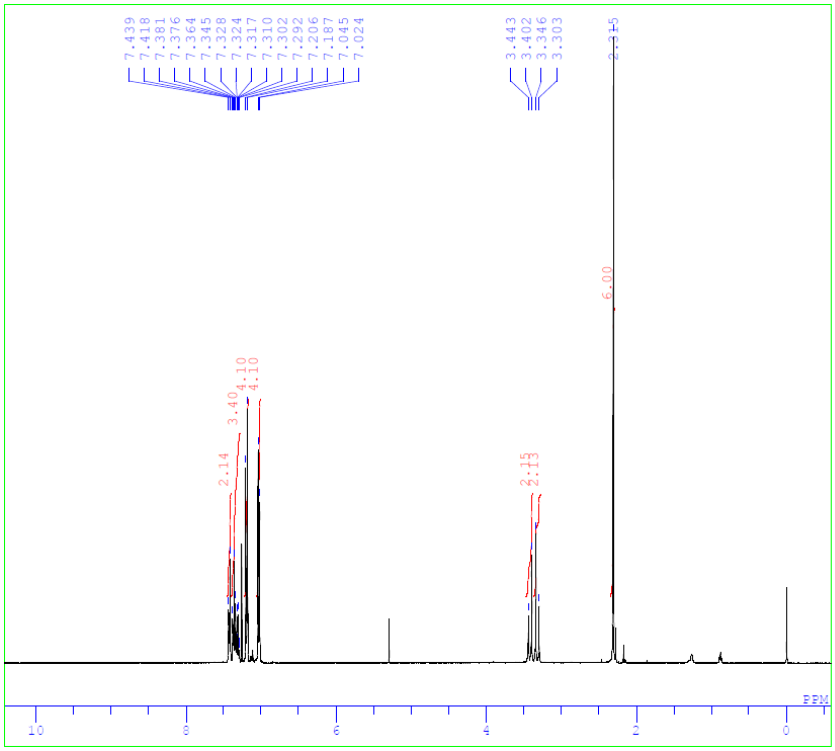
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             8.20 usec
IRNUC  1H
CTEMP          19.8 c
SLVNT  CDCL3
EXREF         77.16 ppm
BF             9.12 Hz
RGAIN            50
```

2-Phenyl-5-*p*-tolyl-2-(3-*p*-tolylprop-2-ynyl)pent-4-ynoic acid (8g): Yield: 35% (two steps); colorless solid; mp: 119-121 ^oC; IR (KBr): ν = 3500-2500 (broad), 3033, 2918, 1698, 1503, 1438, 1285, 1225 cm^{-1}; ^1H-NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 6H), 3.33 (d, *J* = 16.5 Hz, 2H), 3.42 (d, *J* = 16.5 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 4H),

7.20 (d, J = 7.8 Hz, 4H), 7.29-7.38 (m, 3H), 7.43 (d, J = 7.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.6, 26.7, 54.1, 83.8, 84.8, 120.4, 126.5, 127.9, 128.7, 129.0, 131.6, 138.0, 139.4, 178.7; HRMS (ESI): calcd for $C_{28}H_{24}NaO_2$, m/z 415.1674 ($[M+Na]^+$); found, m/z 415.1665.

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DFILE  282-6_Proton-1-2.als
COMNT  single_pulse
DATIM  2012-10-19 20:20:45
OBNUC  1H
EXMOD  proton.jxp
OBFRQ         399.78 MHz
OBSET           4.19 KHz
OBFIN           7.29 Hz
POINT          16384
FREQU        7503.00 Hz
SCANS                8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.50 usec
IRNUC  1H
CTEMP           19.4 c
SLVNT  CDCL3
EXREF           7.26 ppm
BF              9.12 Hz
RGAIN             44
```
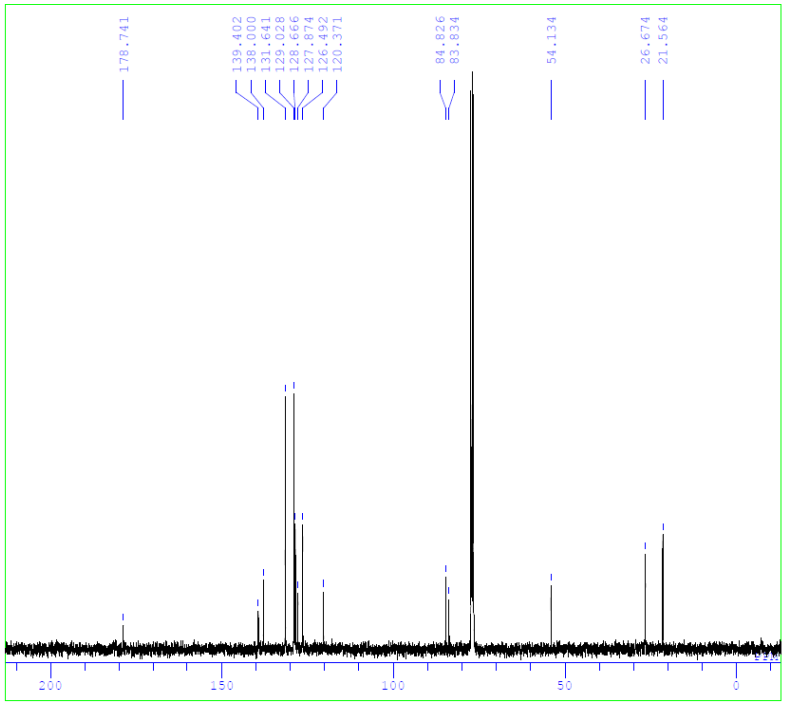
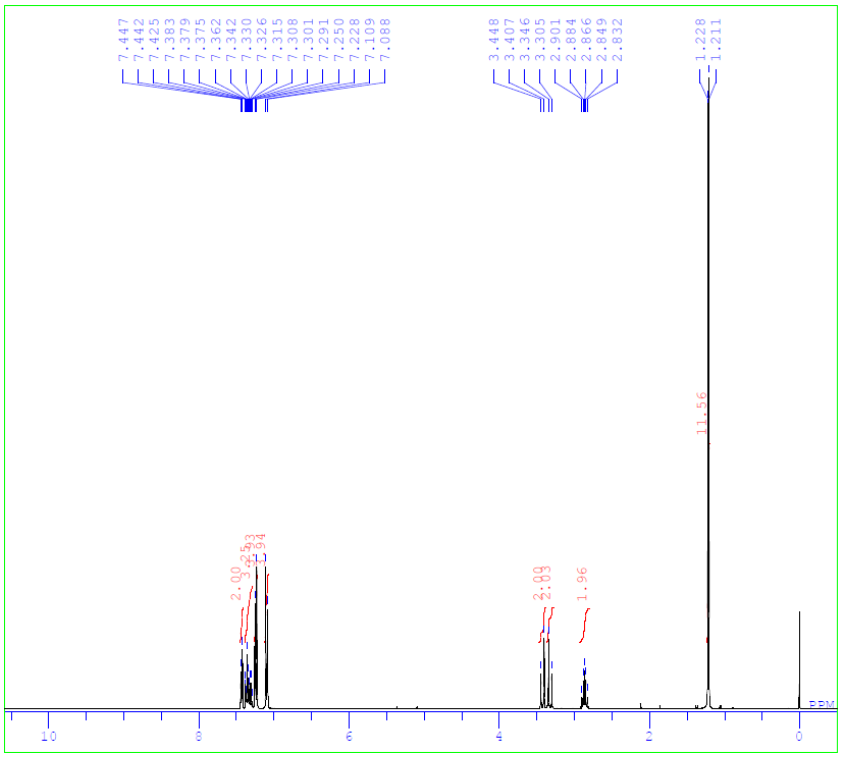
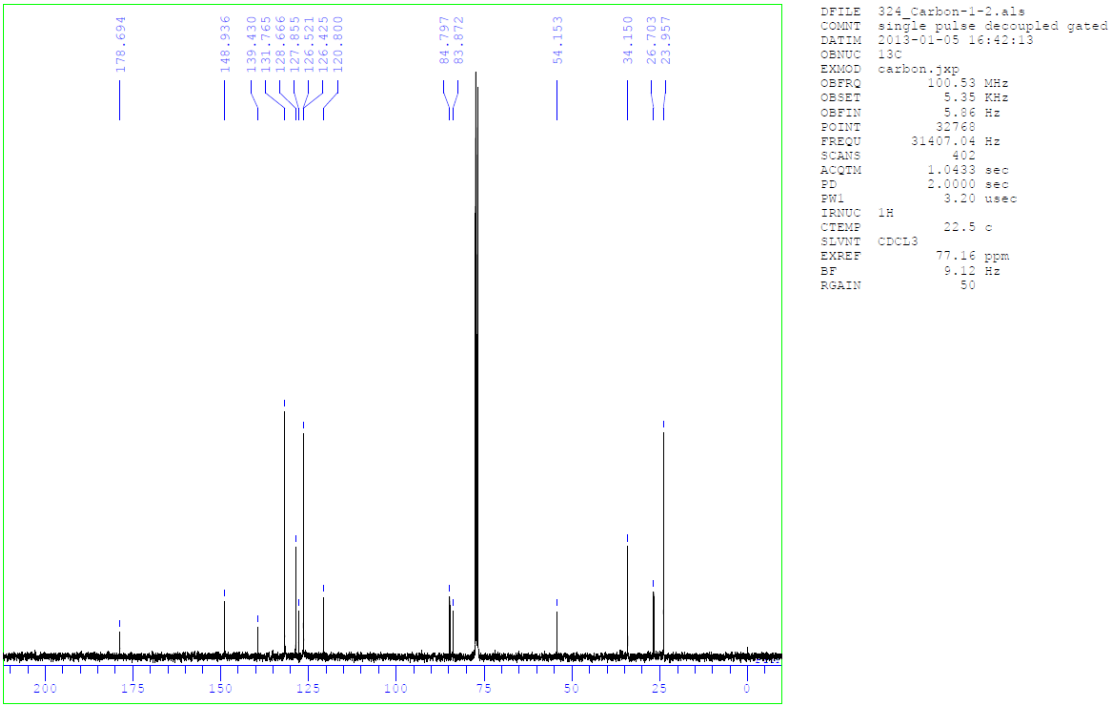




```
DFILE  282-5_Carbon-1-2.als
COMNT  single pulse decoupled gated
DATIM  2012-10-19 18:05:27
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ         100.53 MHz
OBSET           5.35 KHz
OBFIN           5.86 Hz
POINT          32768
FREQU       31407.04 Hz
SCANS            1024
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.20 usec
IRNUC  1H
CTEMP           20.3 c
SLVNT  CDCL3
EXREF          77.16 ppm
BF              9.12 Hz
RGAIN             50
```

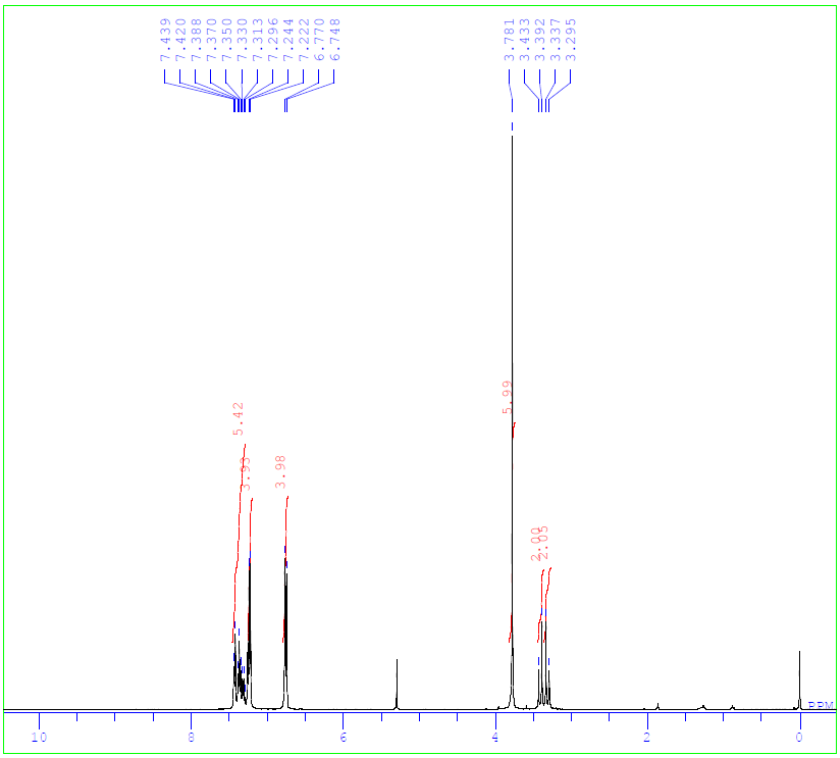
5-(4-Isopropylphenyl)-2-(3-(4-isopropylphenyl)prop-2-ynyl)-2-phenylpent-4-ynoic acid (8h): Yield: 46% (two steps); colorless solid; mp: 137-139 ^{o}C; IR (KBr): ν = 3500-2500 (broad), 2964, 2372, 2317, 1698, 1504, 1407, 1281, 1232 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.22 (d, *J* = 6.9 Hz, 12H), 2.87 (m, 2H), 3.33 (d, *J* = 16.5 Hz, 2H), 3.43 (d, *J* = 16.5 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 4H), 7.24 (d, *J* = 8.2 Hz, 4H), 7.29-7.38 (m, 3H), 7.42-7.45 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 24.0, 26.7, 34.5, 54.2, 83.9, 84.8, 120.8, 126.4, 126.5, 127.9, 128.7, 131.8, 139.4, 148.9, 178.7; HRMS (ESI): calcd for $C_{32}H_{32}NaO_2$, m/z 471.2300 ([M+Na]$^{+}$); found, m/z 471.2289.



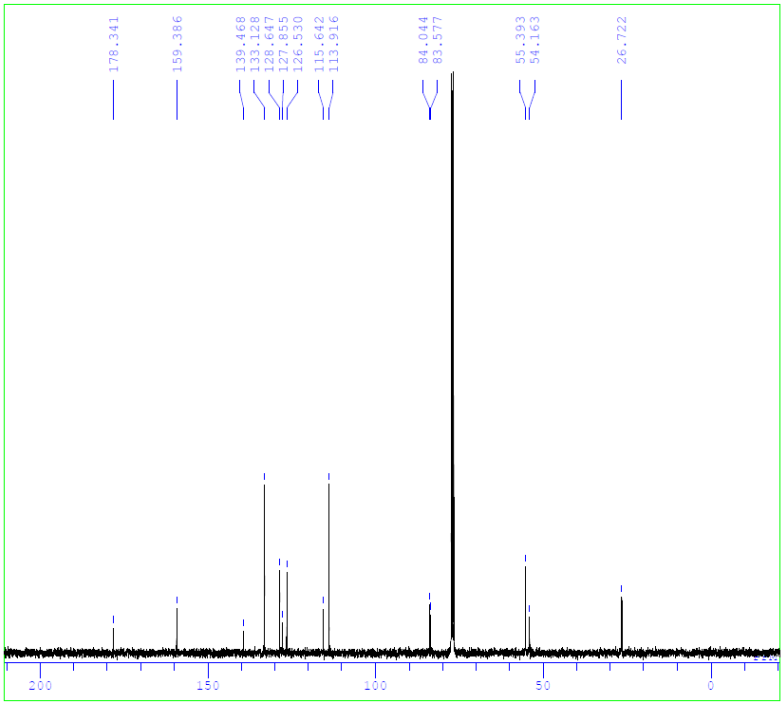

```
DFILE   324_Proton-1-2.als
COMNT   single_pulse
DATIM   2013-01-05 16:40:28
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         399.78 MHz
OBSET           4.19 KHz
OBFIN           7.29 Hz
POINT          16384
FREQU        7503.00 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.50 usec
IRNUC   1H
CTEMP          22.2 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             9.12 Hz
RGAIN            38
```



5-(4-Methoxyphenyl)-2-(3-(4-methoxyphenyl)prop-2-ynyl)-2-phenylpent-4-ynoic acid (8i): Yield: 28% (two steps); pale yellow solid; mp: 103-104 ^{o}C; IR (KBr): ν = 3500-2500 (broad), 2958, 2839, 2361, 1701, 1605, 1507, 1442, 1290, 1249, 1177, 1033 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.32 (d, *J* = 16.5 Hz, 2H), 3.41 (d, *J* = 16.5 Hz, 2H), 3.78 (s, 6H), 6.76 (d, *J* = 7.8 Hz, 4H), 7.23 (d, *J* = 7.8 Hz, 4H), 7.30-7.44 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 26.7, 54.2, 55.4, 83.6, 84.0, 113.9, 115.6, 126.5, 127.9, 128.7, 133.1, 139.5, 159.4, 178.3; HRMS (ESI): calcd for $C_{28}H_{24}NaO_4$, m/z 447.1572 ($[M+Na]^+$); found, m/z 447.1561.



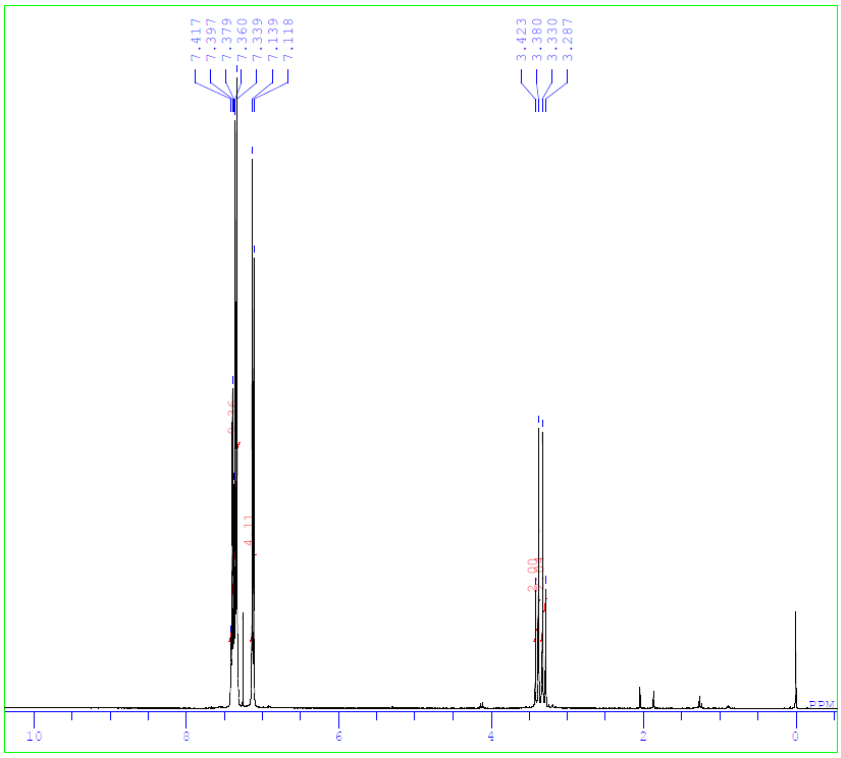

```
DFILE   351_Proton-1-2.als
COMNT   single_pulse
DATIM   2013-02-05 12:44:45
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         399.78 MHz
OBSET           4.19 KHz
OBFIN           7.29 Hz
POINT          16384
FREQU        7503.00 Hz
SCANS             16
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             6.05 usec
IRNUC   1H
CTEMP           23.3 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              9.12 Hz
RGAIN             44
```



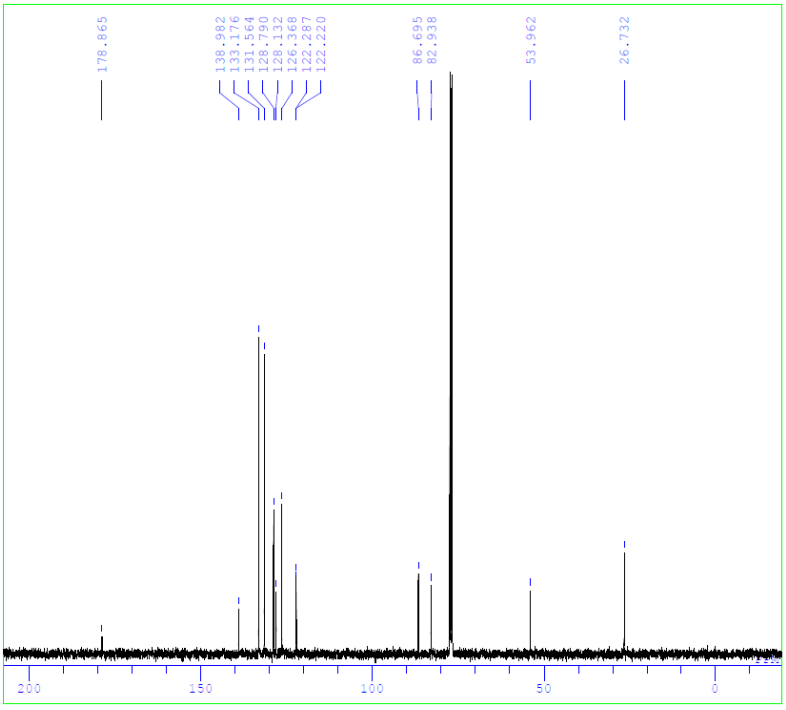

```
DFILE   351_Carbon-1-2.als
COMNT   single_pulse_decoupled_gated
DATIM   2013-02-05 12:47:16
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         100.53 MHz
OBSET           5.35 KHz
OBFIN           5.86 Hz
POINT          32768
FREQU       31407.04 Hz
SCANS            469
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.20 usec
IRNUC   1H
CTEMP           23.6 c
SLVNT   CDCL3
EXREF          77.16 ppm
BF              9.12 Hz
RGAIN             50
```

5-(4-Bromophenyl)-2-(3-(4-bromophenyl)prop-2-ynyl)-2-phenylpent-4-ynoic acid (8j): Yield: 41% (two steps); colorless solid; mp: 171-173 ^{o}C; IR (KBr): ν = 3500-2500 (broad), 3056, 2905, 2595, 2368, 1702, 1593, 1486, 1401, 1291, 1231, 1066, 1006 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.31 (d, *J* =16.9 Hz, 2H), 3.40 (d, *J* = 16.9 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 4H), 7.34-7.42 (m, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 26.7, 54.0, 82.9, 86.7, 122.2, 122.3, 126.4, 128.1, 128.8, 131.6, 133.2,

139.0, 178.9; HRMS (ESI): calcd for $C_{26}H_{18}Br_2NaO_2$, m/z 542.9571 ($[M+Na]^+$); found, m/z 542.9556.



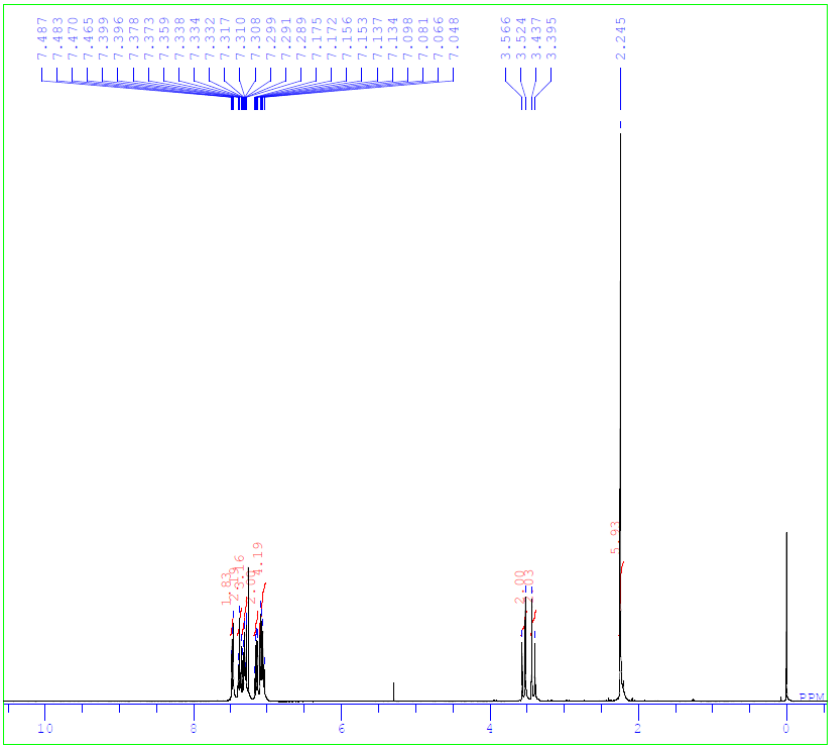

```
DFILE  330_Proton-1-2.als
COMNT  single_pulse
DATIM  2013-01-23 11:59:50
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16384
FREQU       7503.00 Hz
SCANS            16
ACQTM        2.1837 sec
PD           5.0000 sec
PW1            6.05 usec
IRNUC  1H
CTEMP         22.8 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             9.12 Hz
RGAIN            42
```



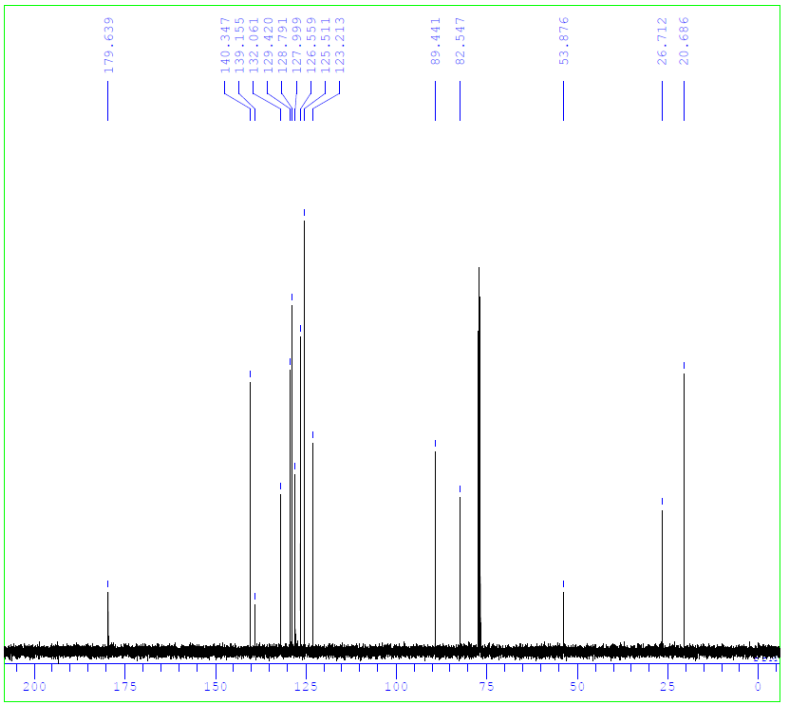

```
DFILE  330_Carbon-1-2.als
COMNT  single pulse decoupled gated
DATIM  2013-01-23 12:02:35
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32768
FREQU      31407.04 Hz
SCANS           268
ACQTM        1.0433 sec
PD           2.0000 sec
PW1            3.20 usec
IRNUC  1H
CTEMP         23.1 c
SLVNT  CDCL3
EXREF         77.16 ppm
BF             9.12 Hz
RGAIN            50
```

2-Phenyl-5-*o*-tolyl-2-(3-*o*-tolylprop-2-ynyl)pent-4-ynoic acid (8k): Yield: 57% (two steps); pale yellow solid; mp: 148-150 ^oC; IR (KBr): ν = 3500-2500 (broad), 3025, 2917, 2678, 2605, 2361, 1704, 1600, 1489, 1414, 1288, 1224, 1113, 1038 cm^{-1}; ^1H-NMR (400 MHz, $CDCl_3$): δ = 2.24 (s, 6H), 3.42 (d, *J* = 16.9 Hz, 2H), 3.55 (d, *J* =

16.5 Hz, 2H), 7.05-7.10 (m, 4H), 7.13-7.18 (m, 2H), 7.29-7.34 (m, 3H), 7.36-7.40 (m, 2H), 7.47-7.49 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 20.7, 26.7, 53.9, 82.6, 89.4, 123.2, 125.5, 126.6, 128.0, 128.8, 129.4, 132.1, 139.2, 140.4, 179.6; HRMS (ESI): calcd for $C_{28}H_{24}NaO_2$, m/z 415.1674 ([M+Na]$^+$); found, m/z 415.1661.

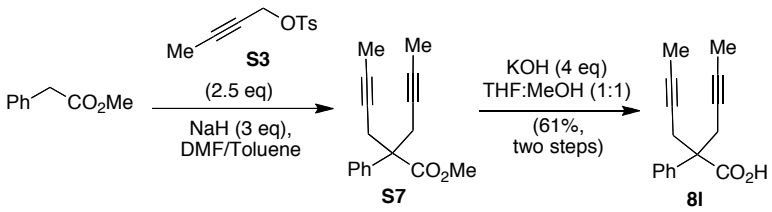



```
DFILE   S-476_Proton-2-1.als
COMNT   single_pulse
DATIM   2012-08-22 19:48:52
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         399.78 MHz
OBSET           4.19 KHz
OBFIN           7.29 Hz
POINT          13107
FREQU        6002.40 Hz
SCANS             16
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             6.05 usec
IRNUC   1H
CTEMP          24.1 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            44
```




```
DFILE   S-476_Carbon-1-1.als
COMNT   single pulse decoupled gated
DATIM   2012-10-17 14:43:54
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         100.53 MHz
OBSET           5.35 KHz
OBFIN           5.86 Hz
POINT          26214
FREQU       25125.63 Hz
SCANS            128
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.20 usec
IRNUC   1H
CTEMP          19.9 c
SLVNT   CDCL3
EXREF          77.16 ppm
BF              0.12 Hz
RGAIN             50
```

Preparation of compound 8l



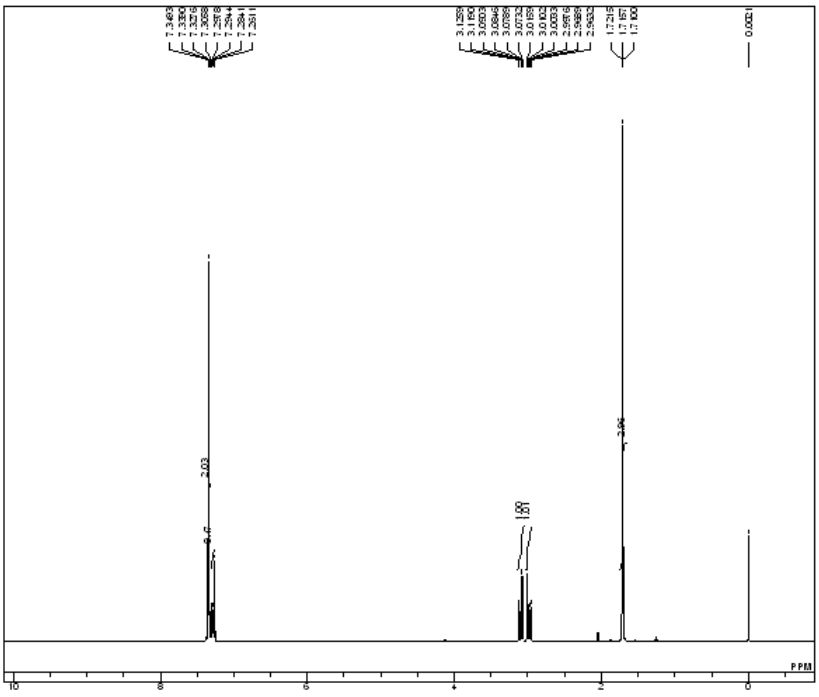
Methyl 2-(but-2-ynyl)-2-phenylhex-4-ynoate (S7)

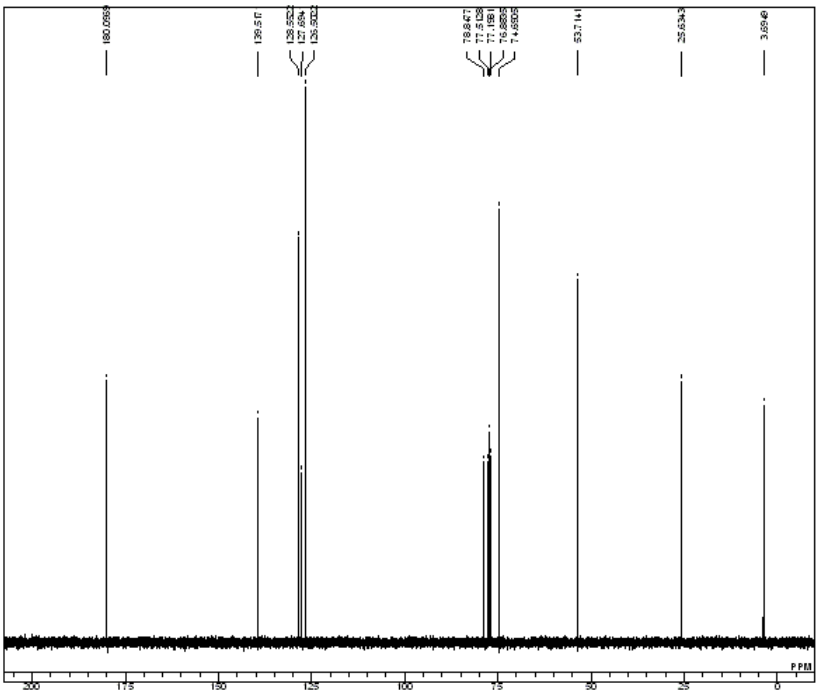
The procedure used for the preparation of compound **S4** was employed for the synthesis of compound **S7** from methyl 2-phenylacetate and tosylate **S3**. The crude product was used for the next step without further purification.

2-(But-2-ynyl)-2-phenylhex-4-ynoic acid (8l)

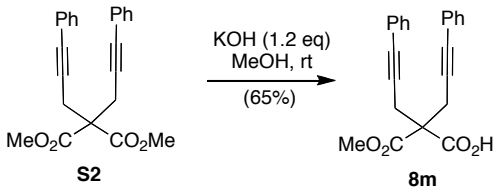
The conditions used for the hydrolysis of compound **S5** was employed for the preparation of carboxylic acid **8l** from the crude ester **S7**.

Yield: 61% (two steps); colorless solid; mp: 151-153 ^{o}C; IR (KBr): ν = 3500-2500 (broad), 2916, 2361, 1699, 1495, 1410, 1284, 1237 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.72 (t, *J* = 2.3 Hz, 6H), 2.96-3.02 (m, 2H), 3.07-3.13 (m, 2H), 7.27-7.32 (m, 1H), 7.33-7.36 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 3.7, 25.6, 53.7, 74.7, 78.8, 126.5, 127.7, 128.5, 139.5, 180.1; HRMS (ESI): calcd for $C_{16}H_{16}NaO_2$, m/z 263.1048 ($[M+Na]^+$); found, m/z 263.1040





Preparation of compound 8m[2]

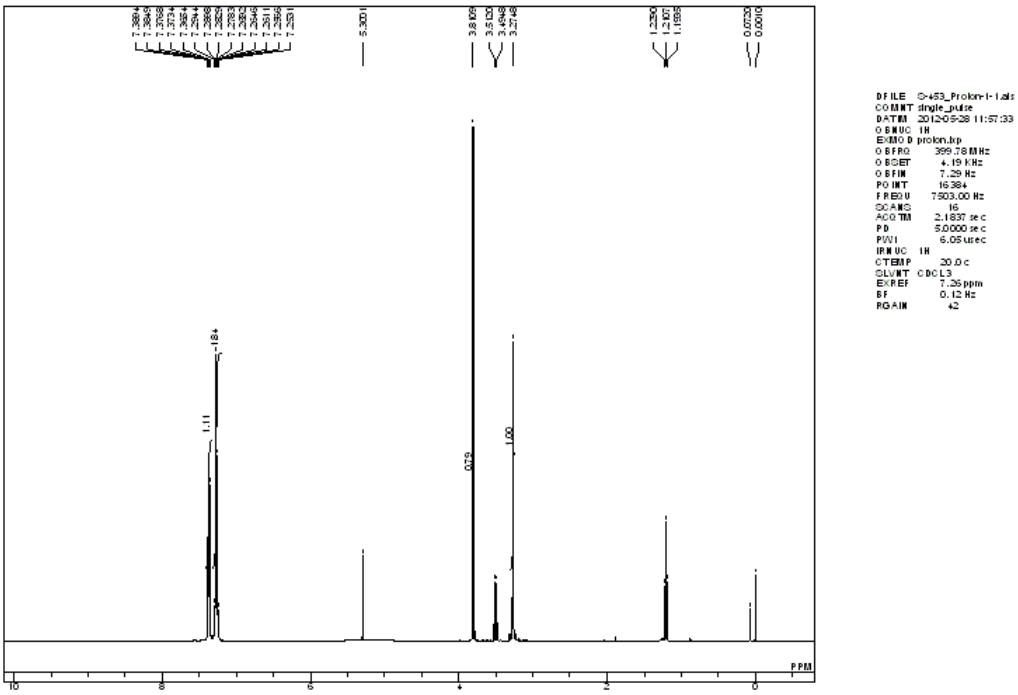


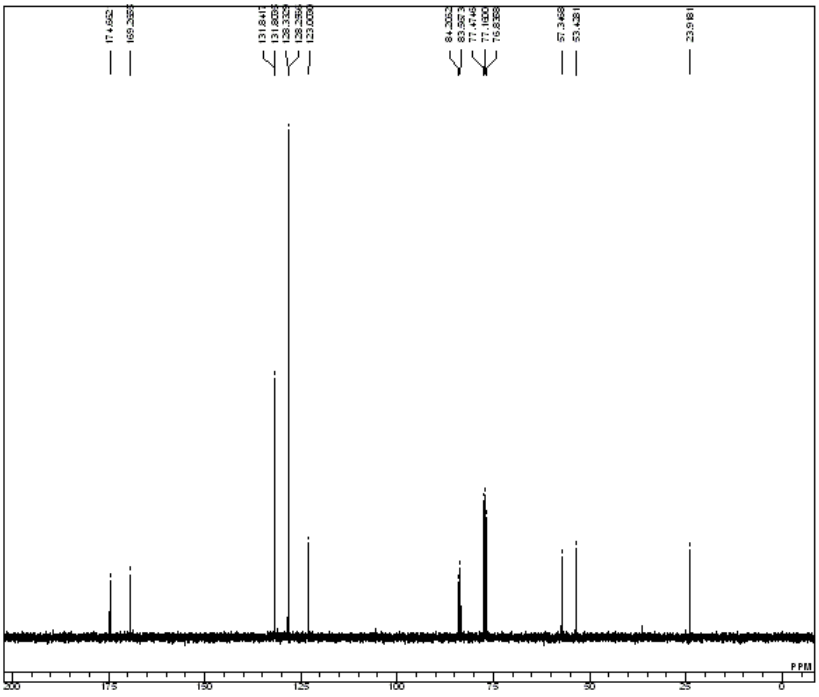
S2 **8m**

2-(Methoxycarbonyl)-5-phenyl-2-(3-phenylprop-2-ynyl)pent-4-ynoic acid (8m)

The procedure used for the partial hydrolysis of diester **S4** to carboxylic acid **8c** was employed to access compound **8m** from **S2**.

Yield: 65%; yellow oil; IR (KBr): ν = 3500-2500 (broad band), 3058, 2956, 2361, 1735, 1489, 1435, 1212, 1116 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.27 (s, 4H), 3.81 (s, 3H), 7.25-7.29 (m, 6H), 7.37-7.39 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 23.9, 53.4, 57.4, 83.6, 84.2, 123.0, 128.26, 128.33, 131.80, 131.84, 169.3, 174.7; HRMS (ESI): calcd for $C_{22}H_{18}NaO_4$, m/z 369.1103 ($[M+Na]^+$); found, m/z 369.1095.

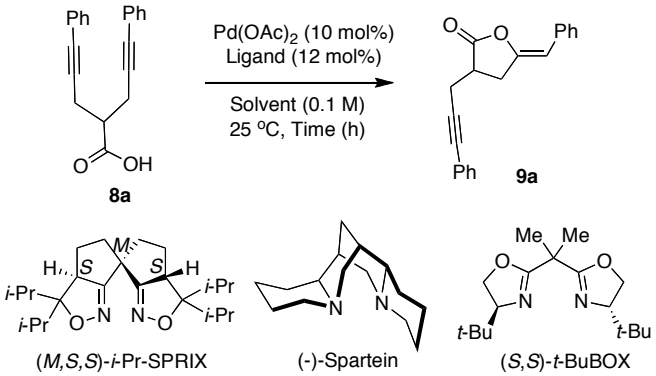





```
FILE   C:\453_Carbon-1-1.als
COMMNT single pulse decoupled gated
DATIM  2012-10-16 16:48:53
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ      100.53 MHz
OBSET        5.35 kHz
OBFIN        5.86 Hz
POINT       26214
FREQU    25125.63 Hz
SCANS          37
ACQTM       1.0433 sec
PD          2.0000 sec
PW1         3.20 usec
IRNUC       1H
CTEMP       20.2 c
SLVNT       CDCL3
EXREF       77.16 ppm
BF           0.12 Hz
RGAIN          50
```

General optimization of reaction conditions

Table S1. Screening of bidentate nitrogen ligands



Entry	Ligand	Solvent	Reaction time (h)	Yield of **9a** (%)[a]	Ee of **9a** (%)
1	(*M,S,S*)-*i*-Pr-SPRIX	Dioxane	4	88	*rac*
2	(*M,S,S*)-*i*-Pr-SPRIX	DCM	4	93	5
3	(*M,S,S*)-*i*-Pr-SPRIX	Toluene	4	91	5
4	(*M,S,S*)-*i*-Pr-SPRIX	MeCN	4	93	*rac*
5	(*M,S,S*)-*i*-Pr-SPRIX	MeOH	4	84	5
6	(*M,S,S*)-*i*-Pr-SPRIX	AcOH	4	81	*rac*
7	(-)-Spartein	DCM	3	92	*rac*
8	(*S,S*)-*t*-BuBOX	DCM	3	94	*rac*

[a] Isolated yield

Stability of *i*-Pr-SPRIX-Pd(OAc)$_2$ complex in the presence of alkynoic acid 8a

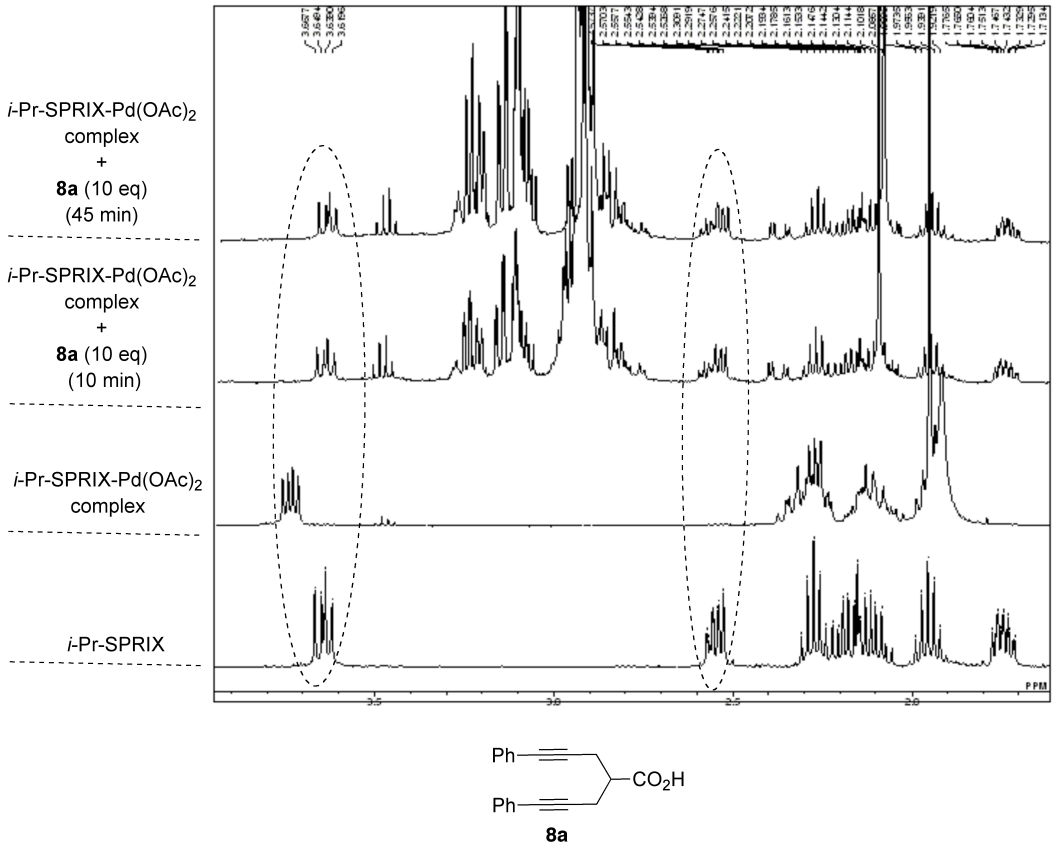
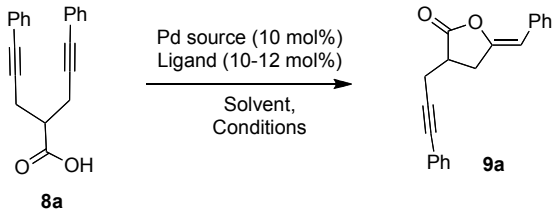


Table S2. Screening of bidentate phosphine ligands

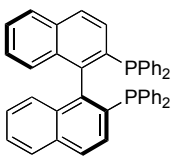


Entry	Pd source	Ligand (Additive)	Solvent	Temp (^{o}C)	Reaction time (h)	Yield of **9a** (%)[a]	ee of **9a** (%)
1	Pd(OAc)$_2$	(*S*)-BINAP	CH_2Cl_2	25	24	86	19
2	-	(*S*)-BINAP	CH_2Cl_2	25	48	0	-
3	Pd(OAc)$_2$	(*S*)-BINAP	CH_2Cl_2	10	24	41[b]	12
4	Pd(OAc)$_2$	(*S*)-BINAP	CH_2Cl_2	0	24	23[b]	13
5	Pd(OAc)$_2$	(*S*)-BINAP	CH_2Cl_2	-20	96	21[b]	9
6	Pd(OAc)$_2$	(*S*)-BINAP	CH_2Cl_2	-40	96	18[b]	14
7	Pd(OAc)$_2$	(*S*)-BINAP	CH_2Cl_2	45 ^{o}C	18	89	8
8	Pd(OAc)$_2$	(*R*)-BINAP	CH_2Cl_2	25	24	87	-8
9	Pd(OAc)$_2$	(*S*)-BINAP	Toluene	25	96	16[b]	8
10	Pd(OAc)$_2$	(*S*)-BINAP	$CHCl_3$	25	24	89	9
11	Pd(OAc)$_2$	(*S*)-BINAP	MeCN	25	2	86	4
12	Pd(OAc)$_2$	(*S*)-BINAP	MeOH	25	2	88	10

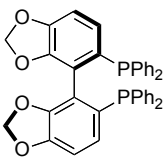
13	$Pd(OAc)_2$	(*S*)-BINAP	Dioxane	25	96	37[b]	14
14	$Pd(OAc)_2$	(*S*)-BINAP	Et_2O	25	96	79	10
15	$Pd(TFA)_2$	(*S*)-BINAP	CH_2Cl_2	25	72	71[b]	0
16	$PdCl_2$	(*S*)-BINAP	CH_2Cl_2	25	72	9[b]	-6
17	$PdCl_2$-(S)-BINAP[c]	-	CH_2Cl_2	25	72	8[b]	-4
18[d]	$[(\eta 3\text{-}C_3H_5)PdCl]_2$	(*S*)-BINAP	CH_2Cl_2	25	72	16[b]	0
19	$Pd(OAc)_2$	(*R*)-SEGPHOS	CH_2Cl_2	25	36	83	8
20	$Pd(OAc)_2$	(*R*)-DIFLUORPHOS	CH_2Cl_2	25	24	18[b]	13
21	$Pd(OAc)_2$	(*R*)-SYNPHOS	CH_2Cl_2	25	12	83	0
22	$Pd(OAc)_2$	(*S*)-MOP	CH_2Cl_2	25	8	86	0
23	$Pd(OAc)_2$	(*S*)-BINAP (K_2CO_3, 1 eq)	CH_2Cl_2	25	24	23[b]	9
24	$Pd(OAc)_2$	(*S*)-BINAP (KOH, 1 eq)	CH_2Cl_2	25	24	26[b]	8
25	$Pd(OAc)_2$	(*S*)-BINAP (Et_3N, 1 eq)	CH_2Cl_2	25	24	29[b]	12
26[e]	$Pd(OAc)_2$	(*S*)-BINAP (AcOH)	CH_2Cl_2	25	10	92	11
27[f]	$Pd(OAc)_2$	(*S*)-BINAP	CH_2Cl_2	25	12	88	17
28[g]	$Pd(OAc)_2$	(*S*)-BINAP	CH_2Cl_2	25	1	12	12
29[h]	$Pd(OAc)_2$	(*S*)-BINAP	CH_2Cl_2	25	15	90	15
30[i]	$Pd(OAc)_2$	(*S*)-BINAP	CH_2Cl_2	25	24	85	11

All reactions were carried out in 0.1M solution (in entries 1 to 18, 10 mol% of ligand was used and in entries 19 to 30, 12 mol% of ligand was used)

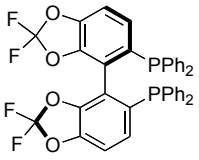
[a] Isolated yield; [b] Remaining unreacted starting material was recovered; [c] 10 mol% of isolated complex was used; [d] 5 Mol% of Pd reagent was used; [e] Reaction was carried out in 9:1 DCM:AcOH solution; [f] Reaction was carried out in 0.5 M solution; [g] Reaction was quenched after 1 h; [h] 30 Mol% of catalyst was used; [i] 40 Mol% of ligand was used



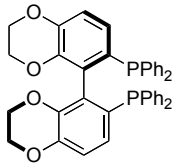
(*S*)-BINAP



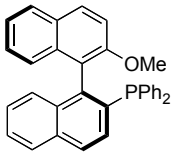
(*R*)-SEGPHOS



(*R*)-DIFLUORPHOS



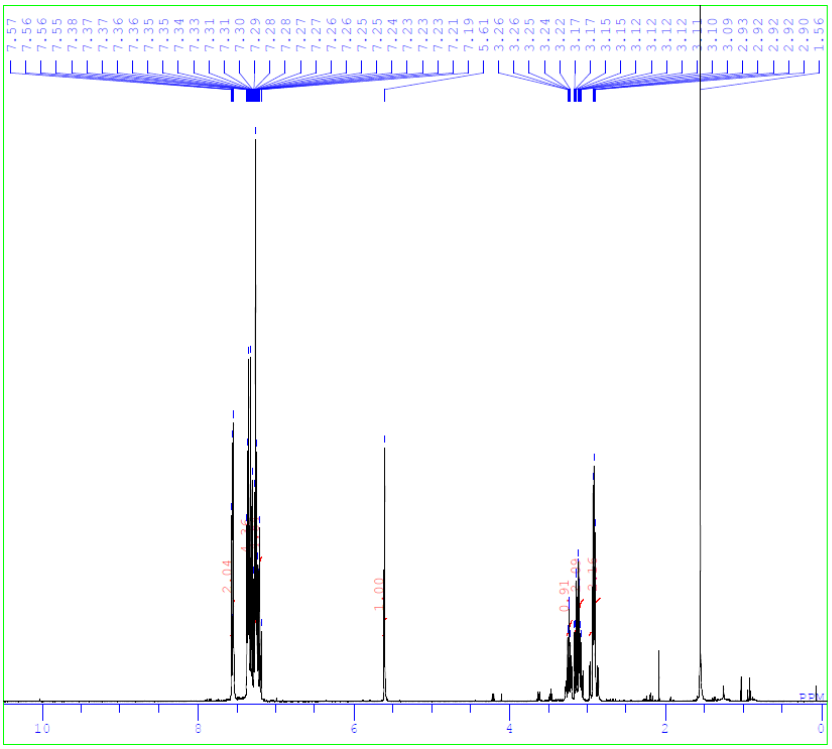
(*R*)-SYNPHOS



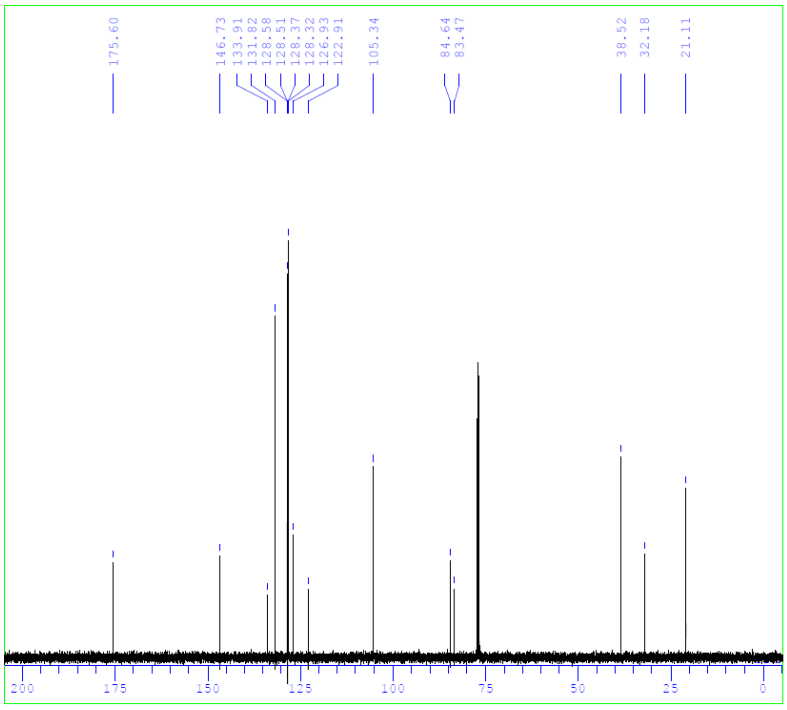
(*S*)-MOP

^{1}H, ^{13}C-NMR spectra and HPLC data of compounds 9

(*Z*)-5-Benzylidene-3-(3-phenylprop-2-ynyl)dihydrofuran-2(3*H*)-one (9a)

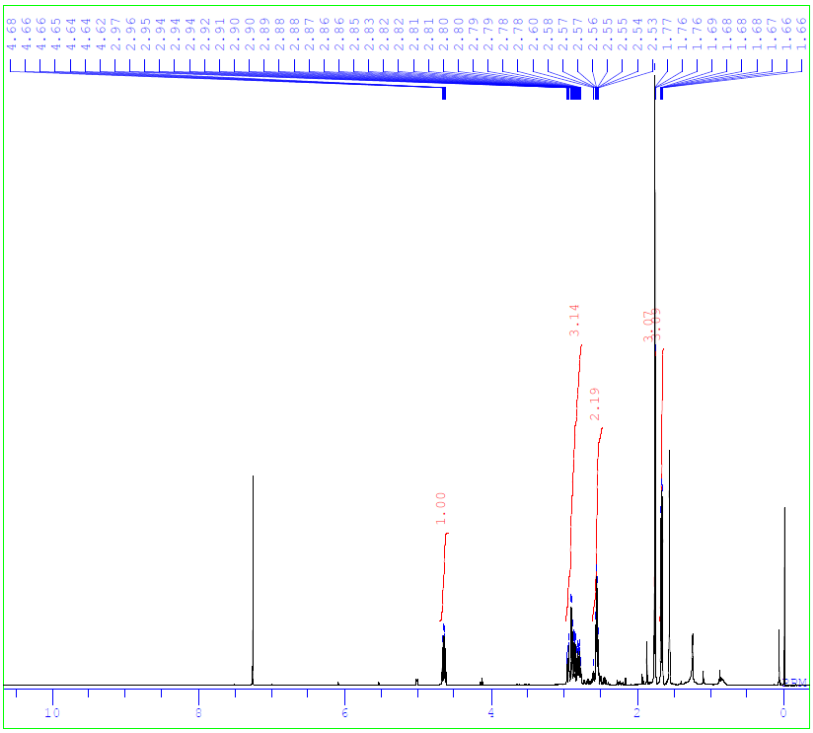



```
DFILE   S-354_Proton-1-1.als
COMNT   single_pulse
DATIM   2011-12-01 12:12:35
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         399.78 MHz
OBSET           4.19 KHz
OBFIN           7.29 Hz
POINT          13107
FREQU        6002.40 Hz
SCANS             16
ACQTM          2.1837 sec
PD             5.0000 sec
PW1              6.00 usec
IRNUC   1H
CTEMP           22.9 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             46
```

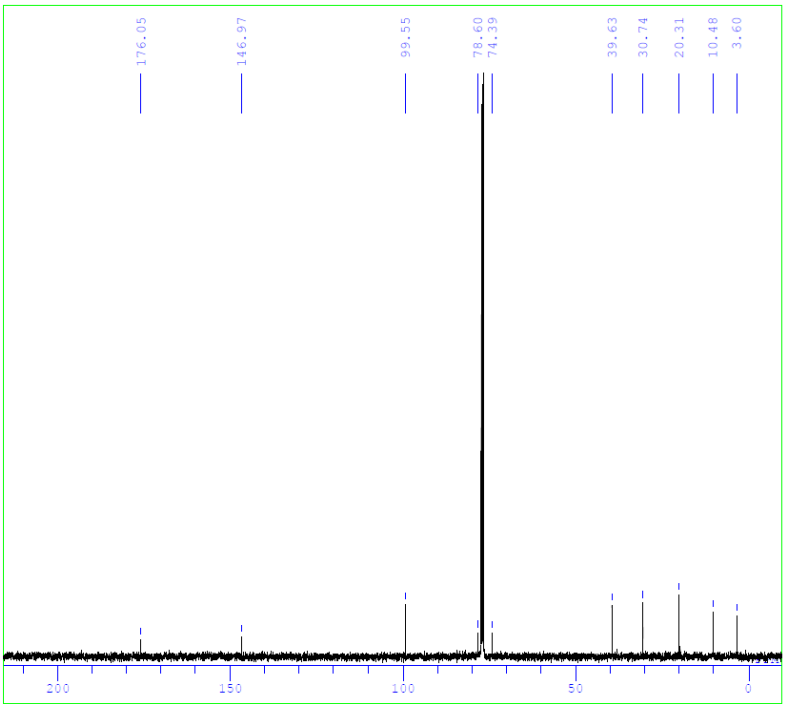



```
DFILE   S-354_Carbon-2-1.als
COMNT   single pulse decoupled gated
DATIM   2011-12-01 12:34:00
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         100.53 MHz
OBSET           5.35 KHz
OBFIN           5.86 Hz
POINT          26214
FREQU       25125.63 Hz
SCANS            132
ACQTM          1.0433 sec
PD             2.0000 sec
PW1              3.17 usec
IRNUC   1H
CTEMP           23.2 c
SLVNT   CDCL3
EXREF           77.16 ppm
BF              0.12 Hz
RGAIN             50
```

(*Z*)-3-(But-2-ynyl)-5-ethylidenedihydrofuran-2(3*H*)-one (9b)

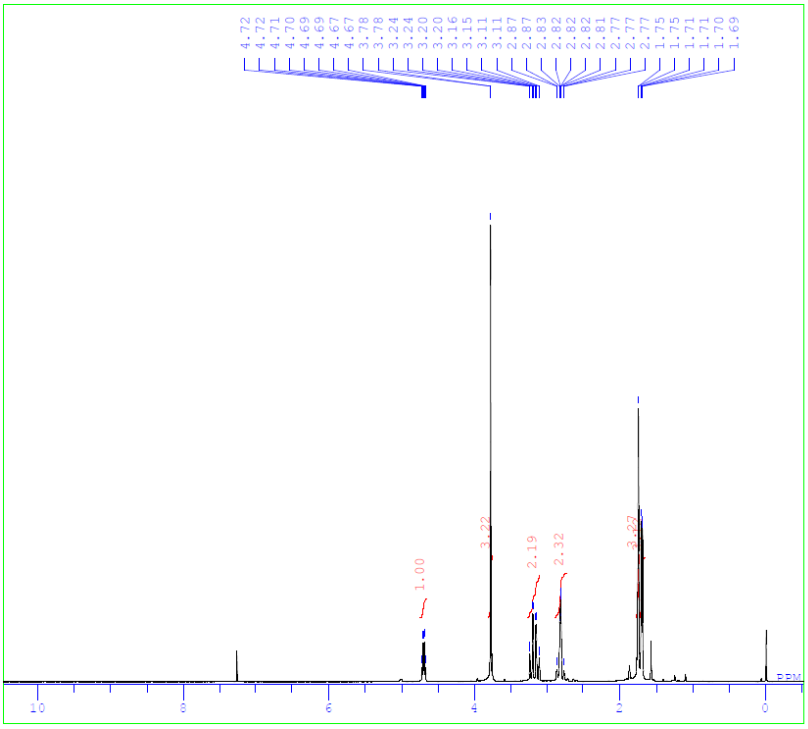



```
DFILE  428-pure_Proton-1-2.jdf
COMNT  single_pulse
DATIM  2013-05-13 21:19:38
OBNUC  1H
EXMOD  proton.jxp
OBFRQ         399.78 MHz
OBSET           4.19 KHz
OBFIN           7.29 Hz
POINT          20480
FREQU        9378.75 Hz
SCANS             16
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             6.05 usec
IRNUC  1H
CTEMP           23.6 c
SLVNT  CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             46
```

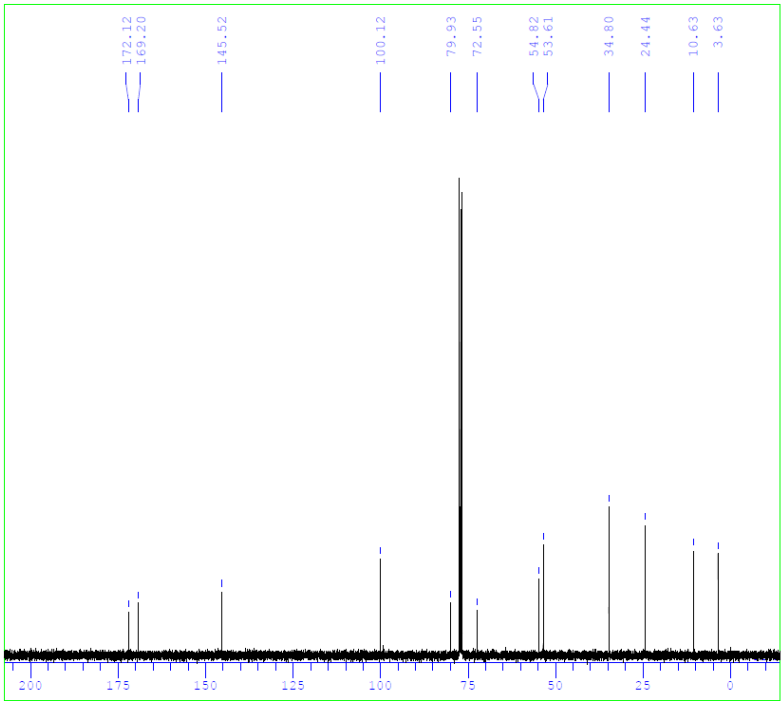



```
DFILE  428-pure_Carbon-1-2.jdf
COMNT  single pulse decoupled gated
DATIM  2013-05-13 21:22:25
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ         100.53 MHz
OBSET           5.35 KHz
OBFIN           5.86 Hz
POINT          40960
FREQU       39258.79 Hz
SCANS            403
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.20 usec
IRNUC  1H
CTEMP           23.9 c
SLVNT  CDCL3
EXREF          77.16 ppm
BF              0.12 Hz
RGAIN             50
```

(*Z*)-Methyl 3-(but-2-ynyl)-5-ethylidene-2-oxotetrahydrofuran-3-carboxylate (9c)

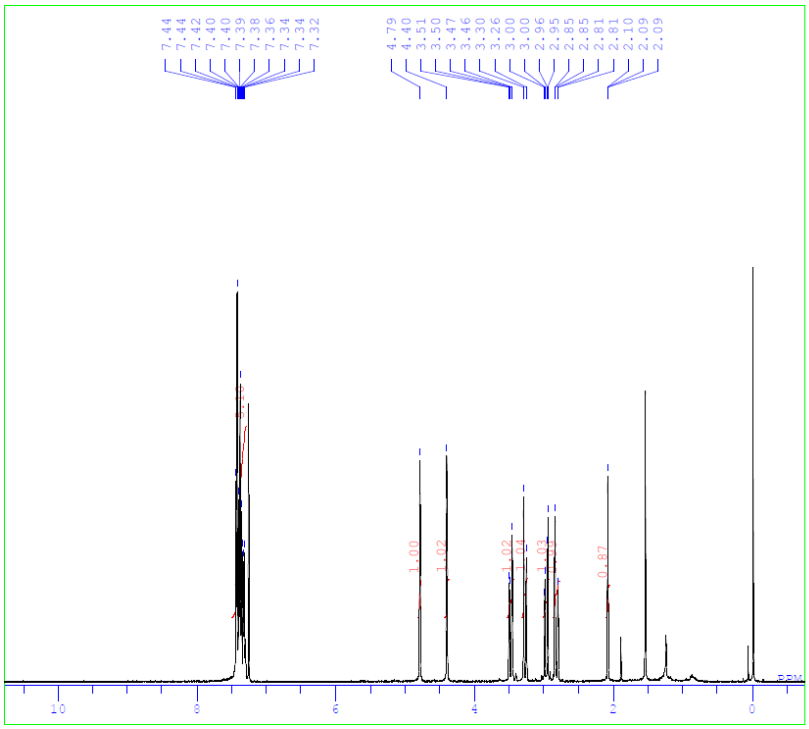



```
DFILE   S-537 rac_Proton-1-1.als
COMNT   single_pulse
DATIM   2012-10-03 16:53:25
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         399.78 MHz
OBSET           4.19 KHz
OBFIN           7.29 Hz
POINT          13107
FREQU        6002.40 Hz
SCANS             16
ACQTM          2.1837 sec
PD             5.0000 sec
PW1              6.05 usec
IRNUC   1H
CTEMP            21.5 c
SLVNT   CDCL3
EXREF            7.26 ppm
BF               0.12 Hz
RGAIN              40
```

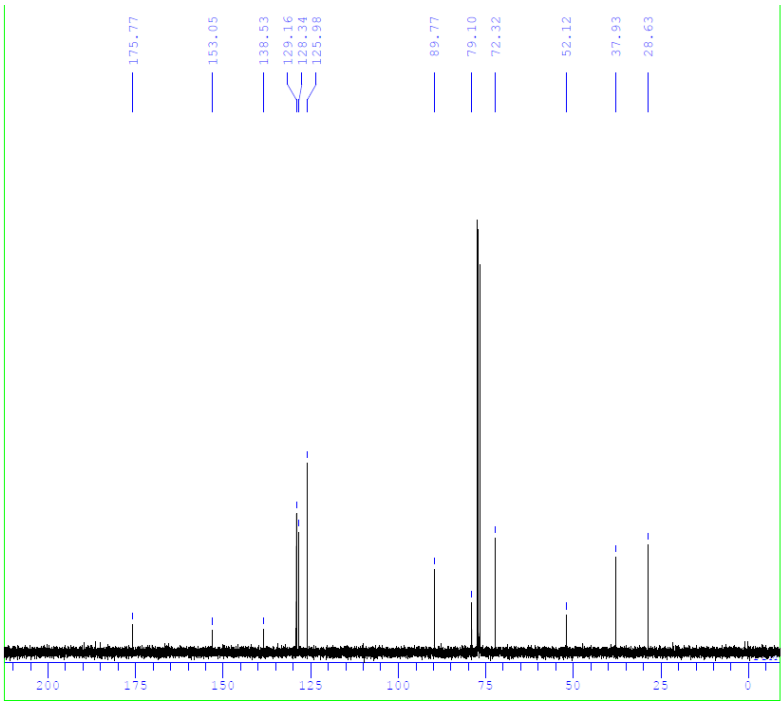



```
DFILE   S-537_Carbon-1-1.als
COMNT   single pulse decoupled gated
DATIM   2012-10-05 19:26:33
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         100.53 MHz
OBSET           5.35 KHz
OBFIN           5.86 Hz
POINT          26214
FREQU       25125.63 Hz
SCANS            742
ACQTM          1.0433 sec
PD             2.0000 sec
PW1              3.20 usec
IRNUC   1H
CTEMP            21.1 c
SLVNT   CDCL3
EXREF           77.16 ppm
BF               0.12 Hz
RGAIN              50
```

5-Methylene-3-phenyl-3-(prop-2-ynyl)dihydrofuran-2(3*H*)-one (9d)

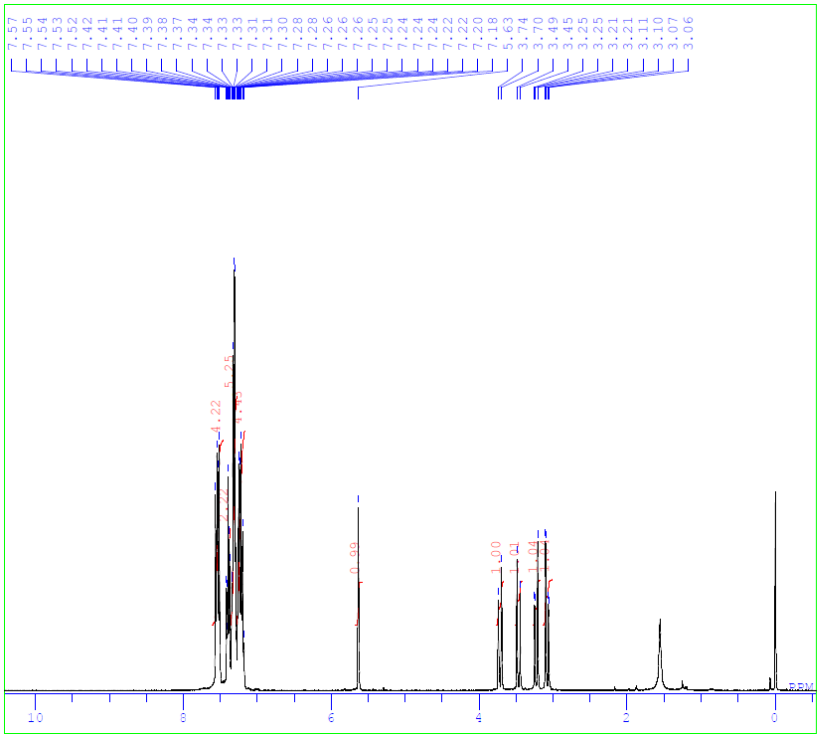



```
DFILE   S-539 Rac_Proton-1-1.als
COMNT   single_pulse
DATIM   2012-10-03 17:10:04
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         399.78 MHz
OBSET           4.19 KHz
OBFIN           7.29 Hz
POINT          13107
FREQU        6002.40 Hz
SCANS             16
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             6.05 usec
IRNUC   1H
CTEMP          21.6 c
SLVNT   CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            50
```

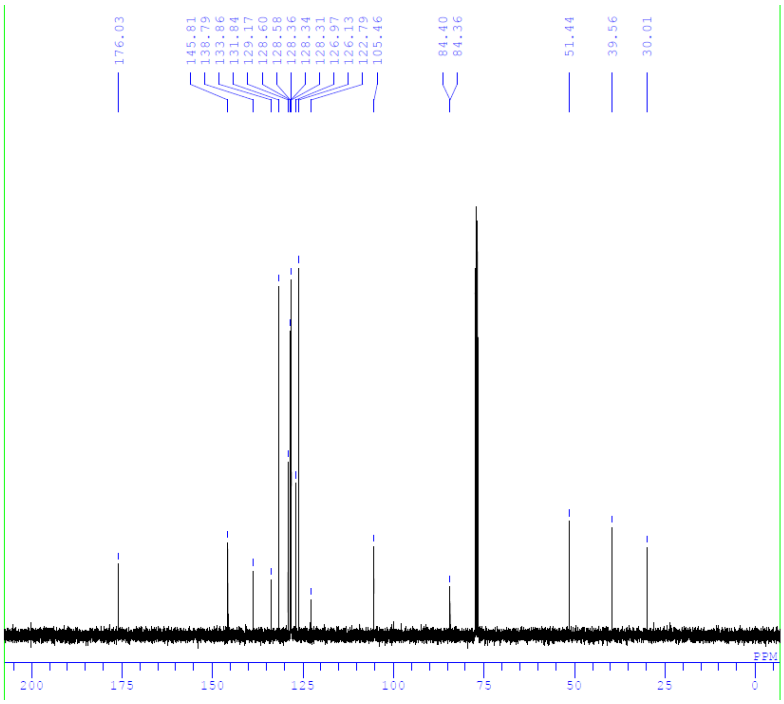



```
DFILE   S-539_Carbon-2-1.als
COMNT   single_pulse decoupled gated
DATIM   2012-10-10 16:23:03
OBNUC   13c
EXMOD   carbon.jxp
OBFRQ         100.53 MHz
OBSET           5.35 KHz
OBFIN           5.86 Hz
POINT          26214
FREQU        25125.63 Hz
SCANS            317
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.20 usec
IRNUC   1H
CTEMP          20.9 c
SLVNT   CDCL3
EXREF          77.16 ppm
BF             0.12 Hz
RGAIN            50
```

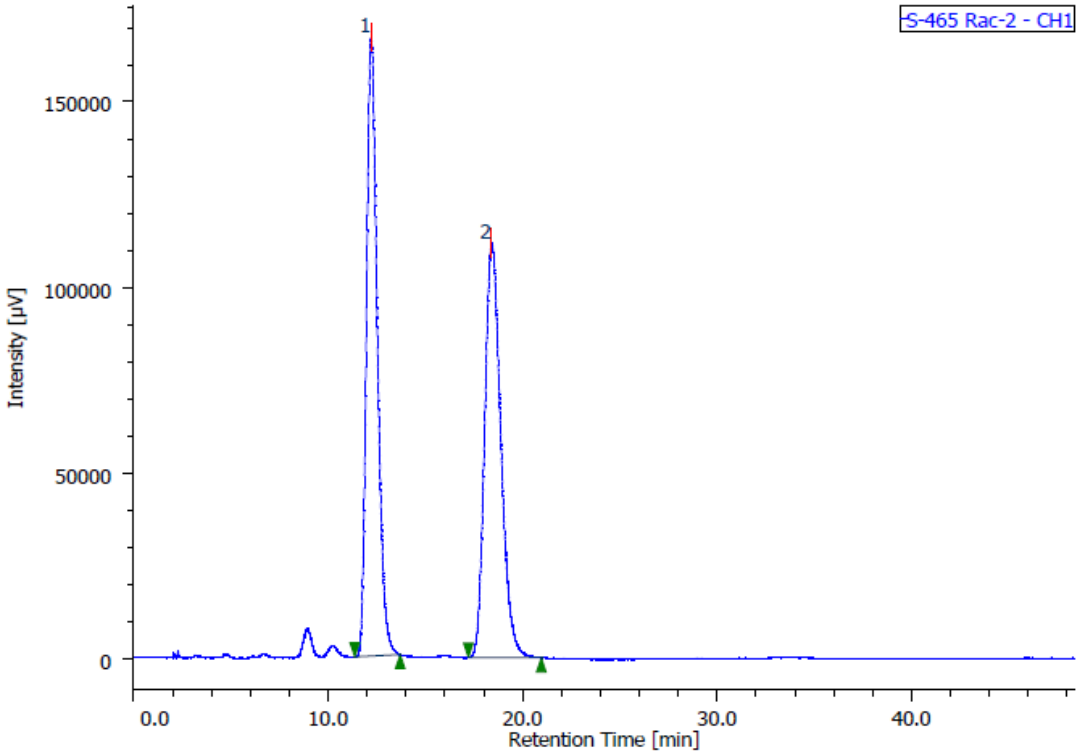
(*Z*)-5-Benzylidene-3-phenyl-3-(3-phenylprop-2-ynyl)dihydrofuran-2(3*H*)-one (9e)

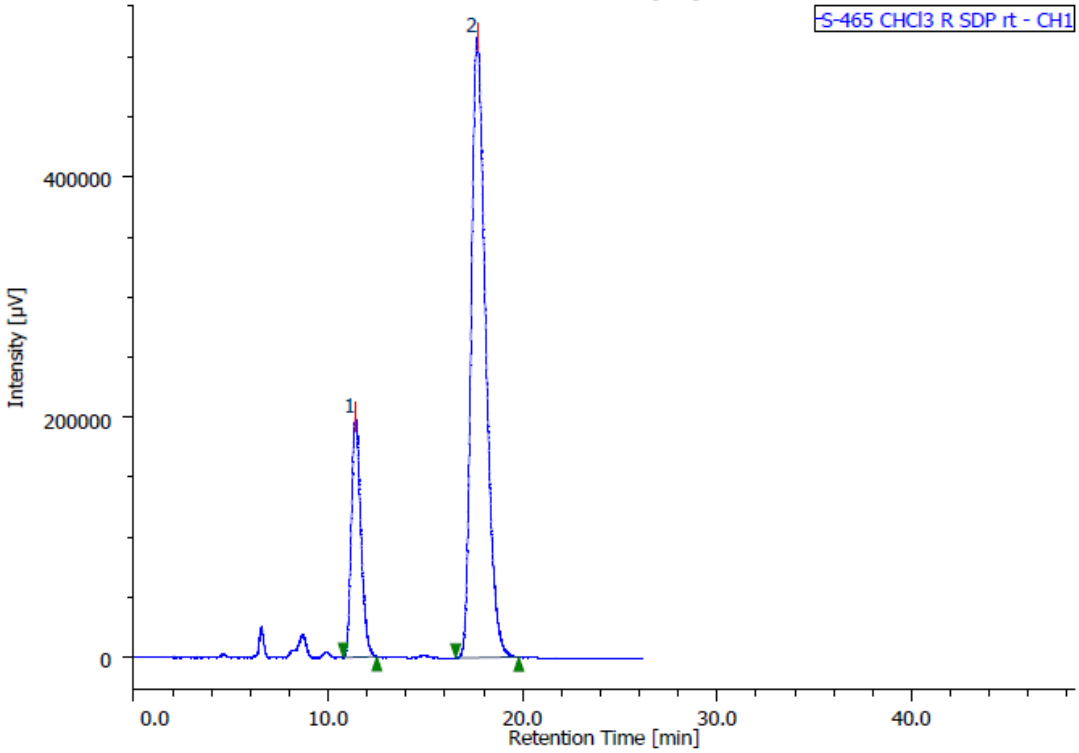


```
DFILE   S-465-1_Proton-1-1.als
COMNT   single_pulse
DATIM   2012-10-16 20:39:15
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         399.78 MHz
OBSET           4.19 KHz
OBFIN           7.29 Hz
POINT          13107
FREQU        6002.40 Hz
SCANS             16
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             6.05 usec
IRNUC   1H
CTEMP           21.0 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             44
```



```
DFILE   S-465-1_Carbon-1-1.als
COMNT   single pulse decoupled gated
DATIM   2012-10-16 20:55:06
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         100.53 MHz
OBSET           5.35 KHz
OBFIN           5.86 Hz
POINT          26214
FREQU       25125.63 Hz
SCANS            195
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.20 usec
IRNUC   1H
CTEMP           20.9 c
SLVNT   CDCL3
EXREF          77.16 ppm
BF              0.12 Hz
RGAIN             50
```





Channel & Peak Information Table

Chromatogram Name S-465 Rac-2-CH1

Sample Name

Channel Name UV-2075

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	12.208	6422085	166621	49.882	59.885	N/A	2382	4.975	1.306	
2	Unknown	1	18.417	6452530	111615	50.118	40.115	N/A	2405	N/A	1.241	

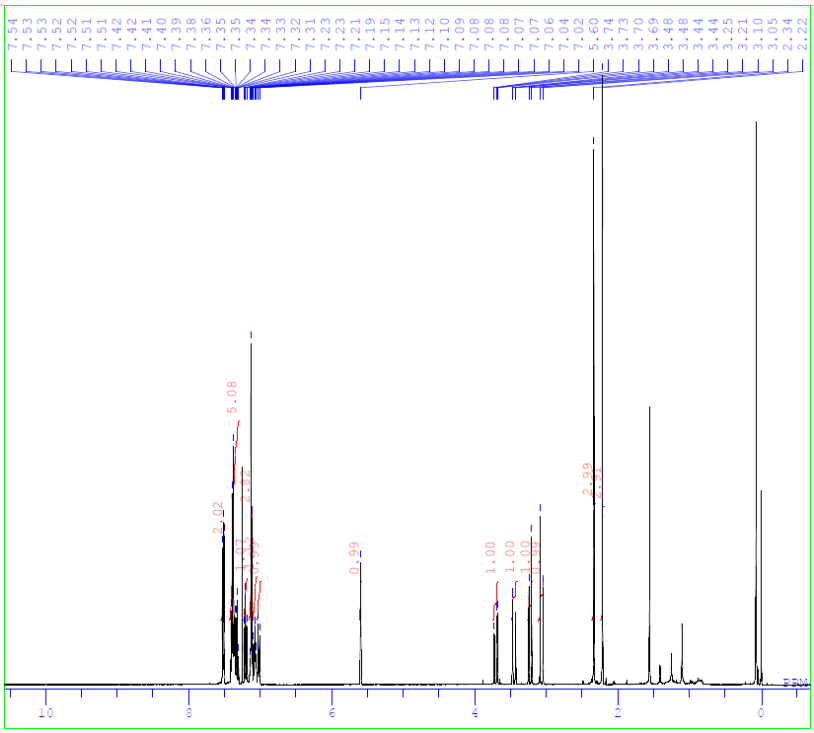
Chromatogram Name S-465 CHCl3 R SDP rt-CH1

Sample Name

Channel Name UV-2075

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	11.408	6750922	199546	20.230	27.881	N/A	2651	5.613	1.256	
2	Unknown	1	17.658	26620015	516166	79.770	72.119	N/A	2752	N/A	1.363	

(*E*)-5-(3-Methylbenzylidene)-3-phenyl-3-(3-*m*-tolylprop-2-ynyl)dihydrofuran-2(3*H*)-one (9f)



```
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COMNT  single_pulse
DATIM  2012-10-25 16:31:48
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16384
FREQU       7503.00 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.50 usec
IRNUC  1H
CTEMP          19.2 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.10 Hz
RGAIN            40
```
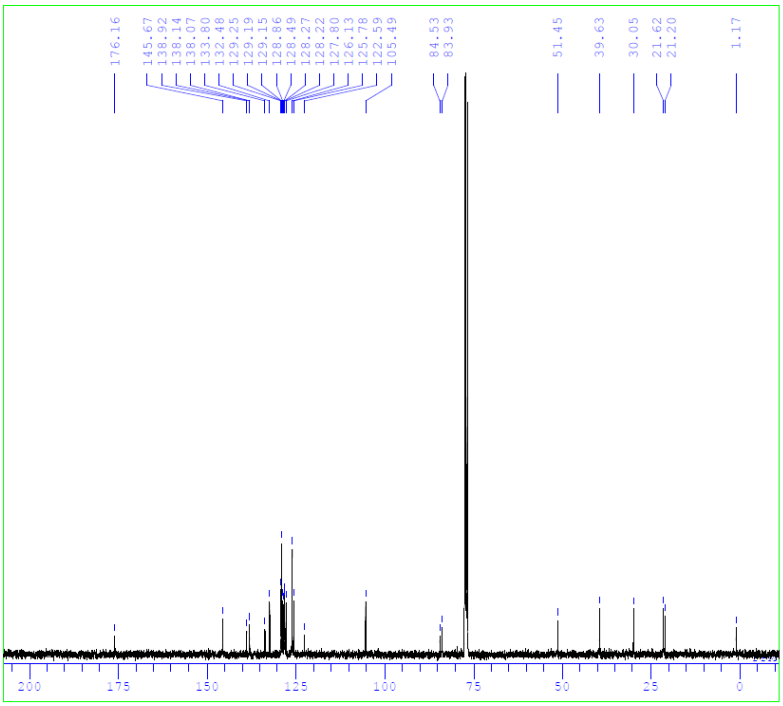
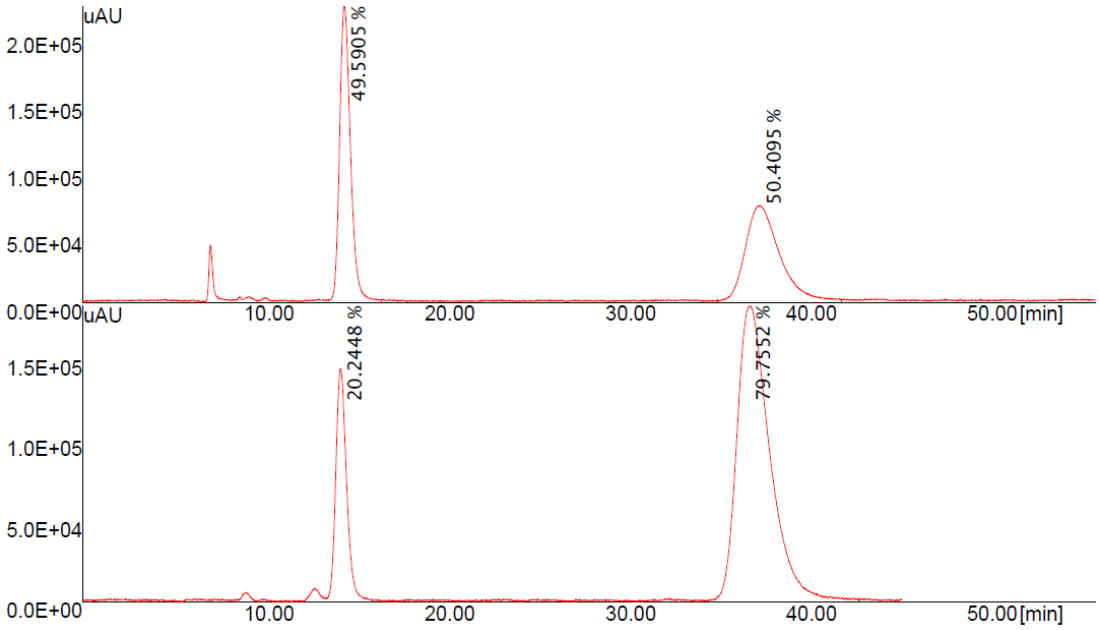



```
DFILE  286_Carbon-1-2.als
COMNT  single pulse decoupled gated
DATIM  2012-10-23 19:57:13
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32768
FREQU      31407.04 Hz
SCANS           744
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.20 usec
IRNUC  1H
CTEMP          18.7 c
SLVNT  CDCL3
EXREF         77.16 ppm
BF             0.10 Hz
RGAIN            50
```



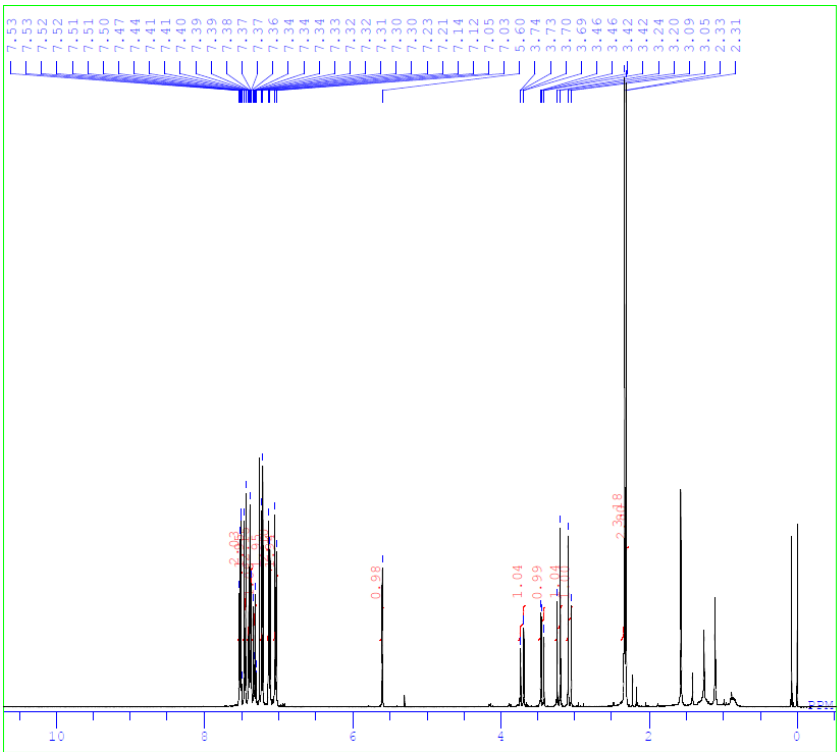
#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		14.453	220364	9068189.447	49.59
2		37.440	71524	9217969.737	50.41

Total Area of Peak = 18286159.184 [uAU. Sec]

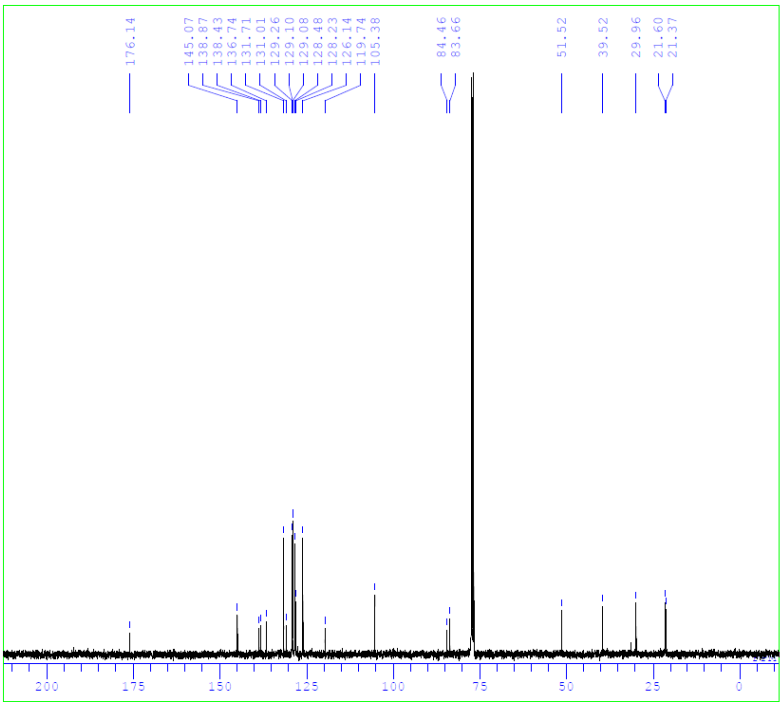
#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		14.267	143165	5813376.887	20.24
2		36.853	182558	22902061.941	79.76

Total Area of Peak = 28715438.828 [uAU. Sec]

(*E*)-5-(4-Methylbenzylidene)-3-phenyl-3-(3-*p*-tolylprop-2-ynyl)dihydrofuran-2(3*H*)-one (9g)



```
DFILE  289_Proton-1-2.als
COMNT  single_pulse
DATIM  2012-10-26 21:10:13
OBNUC  1H
EXMOD  proton.jxp
OBFRQ          399.78 MHz
OBSET            4.19 KHz
OBFIN            7.29 Hz
POINT           16384
FREQU         7503.00 Hz
SCANS               8
ACQTM          2.1837 sec
PD             5.0000 sec
PW1              5.50 usec
IRNUC  1H
CTEMP           19.4 c
SLVNT  CDCL3
EXREF            7.26 ppm
BF               0.10 Hz
RGAIN              40
```



```
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COMNT  single_pulse decoupled gated
DATIM  2012-10-26 21:11:50
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ          100.53 MHz
OBSET            5.35 KHz
OBFIN            5.86 Hz
POINT           26224
FREQU        25125.63 Hz
SCANS             422
ACQTM          1.0433 sec
PD             2.0000 sec
PW1              3.20 usec
IRNUC  1H
CTEMP           19.7 c
SLVNT  CDCL3
EXREF           77.16 ppm
BF               0.10 Hz
RGAIN              50
```
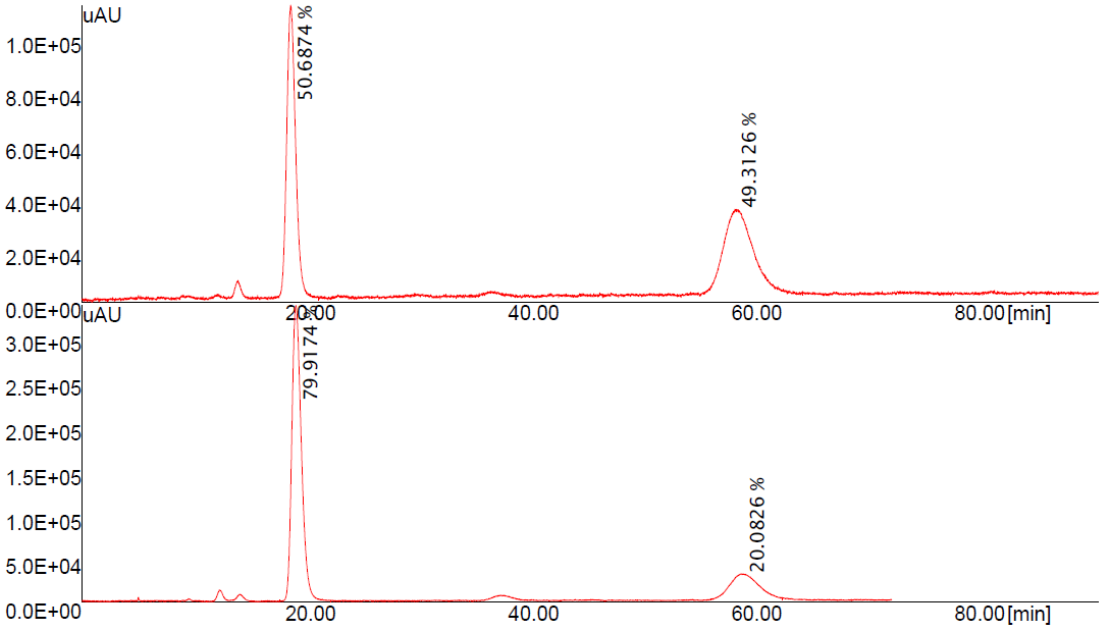



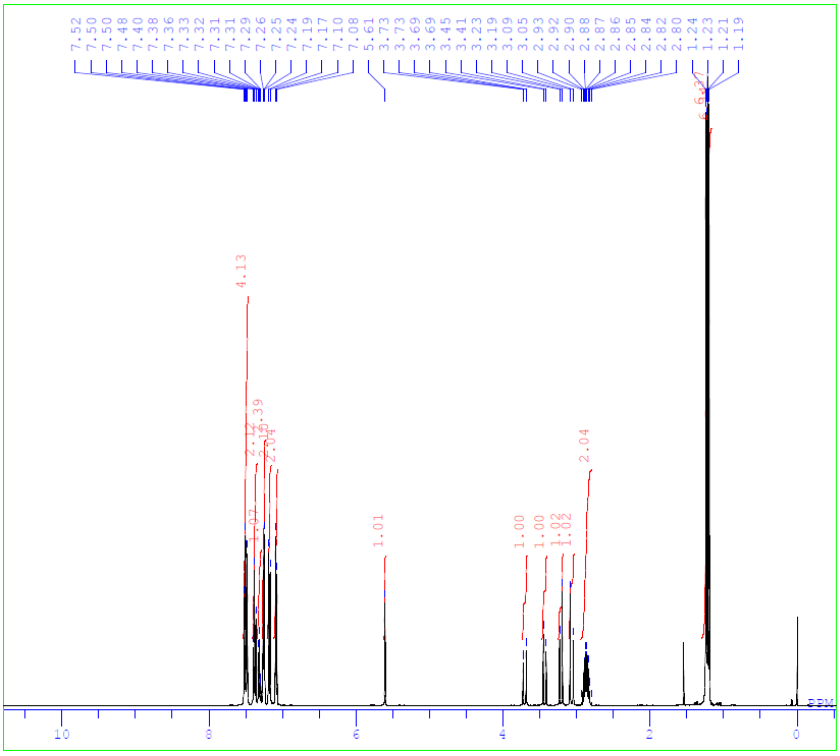
#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		18.707	110856	6200333.692	50.69
2		58.533	32408	6032165.910	49.31

Total Area of Peak = 12232499.603 [uAU. Sec]

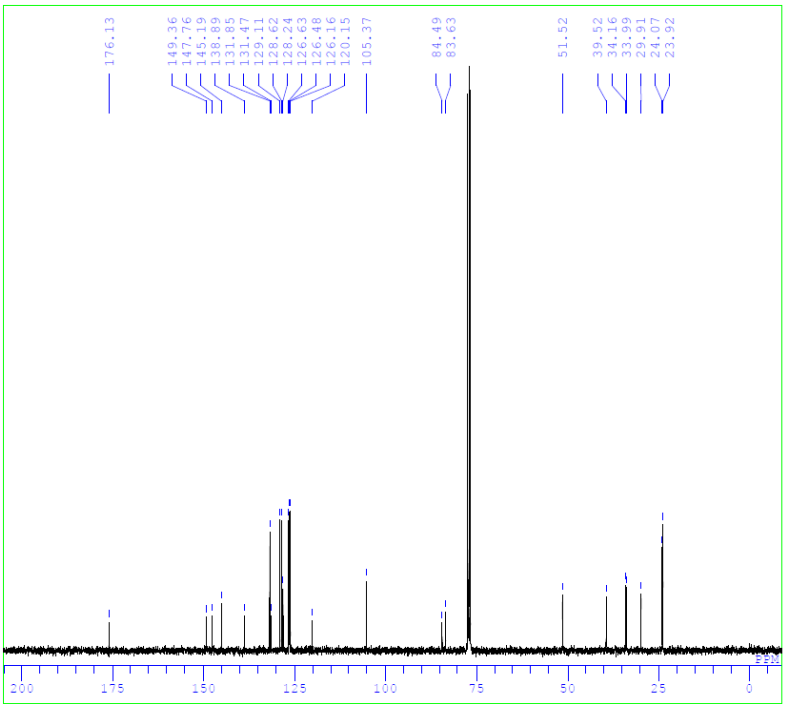
#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		19.200	331749	19759039.494	79.92
2		59.280	28326	4965288.474	20.08

Total Area of Peak = 24724327.968 [uAU. Sec]

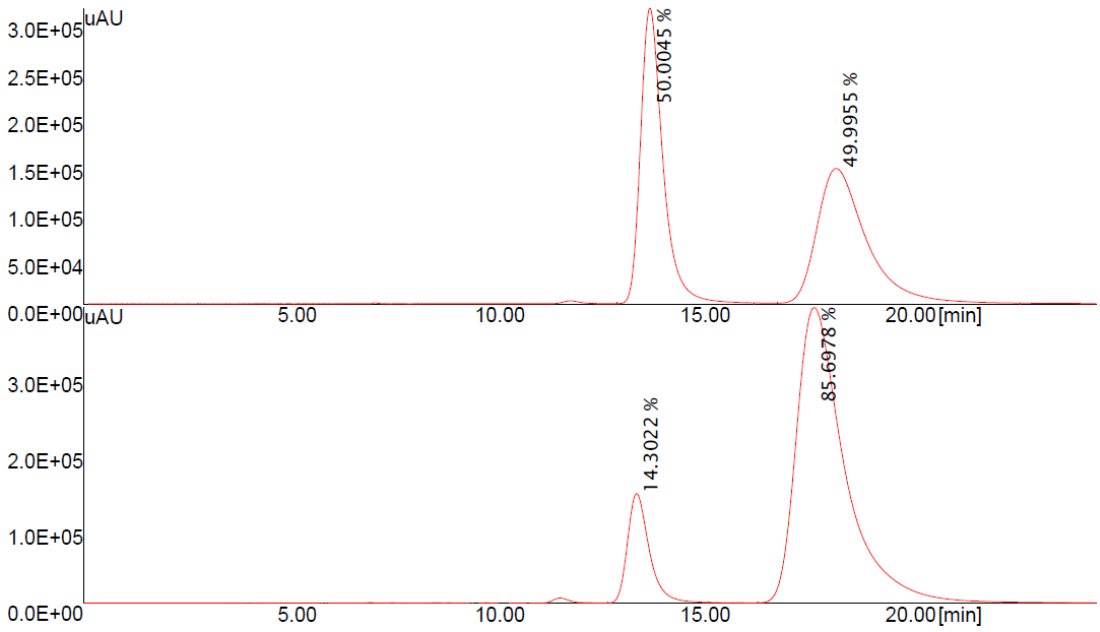
(*E*)-5-(4-Isopropylbenzylidene)-3-(3-(4-isopropylphenyl)prop-2-ynyl)-3-phenyldihydrofuran-2(3*H*)-one (9h)



DFILE 334_Proton-1-2.als
COMNT single_pulse
DATIM 2013-01-25 22:16:16
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16384
FREQU 7503.00 Hz
SCANS 16
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 6.05 usec
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 9.12 Hz
RGAIN 40



DFILE 334_Carbon-1-2.als
COMNT single pulse decoupled gated
DATIM 2013-01-25 22:19:02
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32768
FREQU 31407.04 Hz
SCANS 464
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.20 usec
IRNUC 1H
CTEMP 21.6 c
SLVNT CDCL3
EXREF 77.16 ppm
BF 9.12 Hz
RGAIN 50



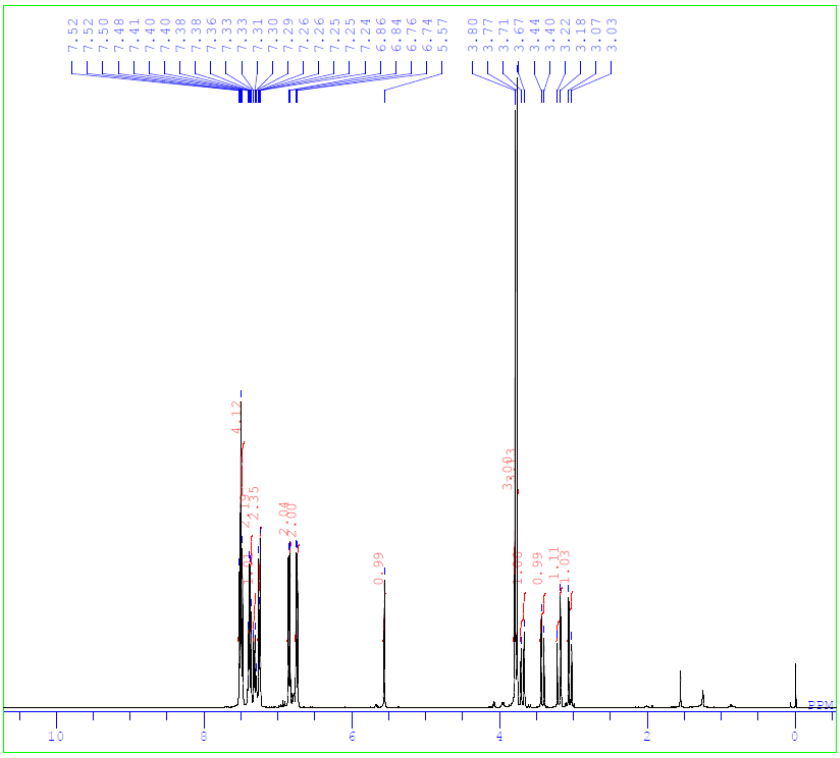
#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		13.787	312071	11806612.576	50.00
2		18.320	142388	11804488.576	50.00

Total Area of Peak = 23611101.152 [uAU. Sec]

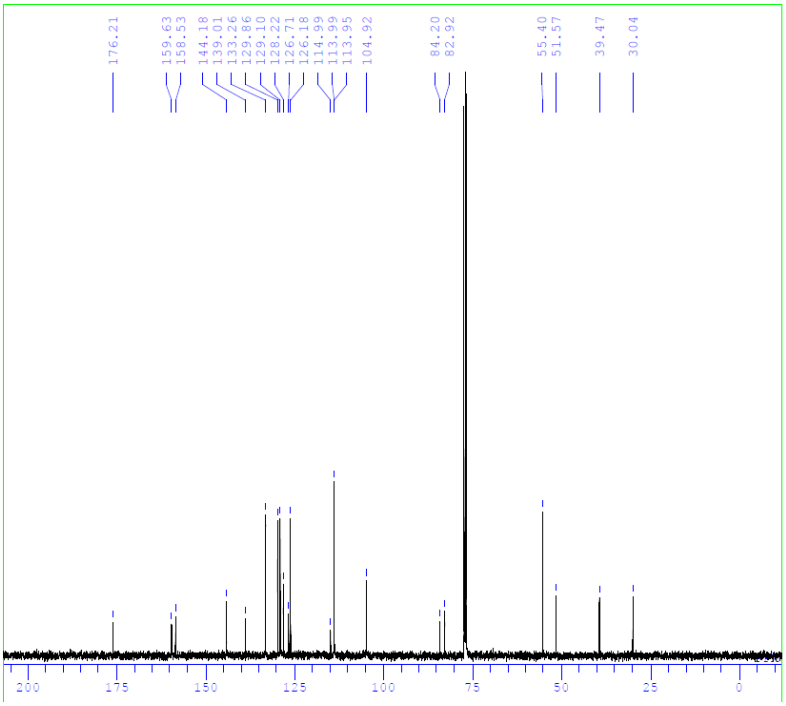
#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		13.480	143728	5256252.078	14.30
2		17.800	388291	31495098.869	85.70

Total Area of Peak = 36751350.948 [uAU. Sec]

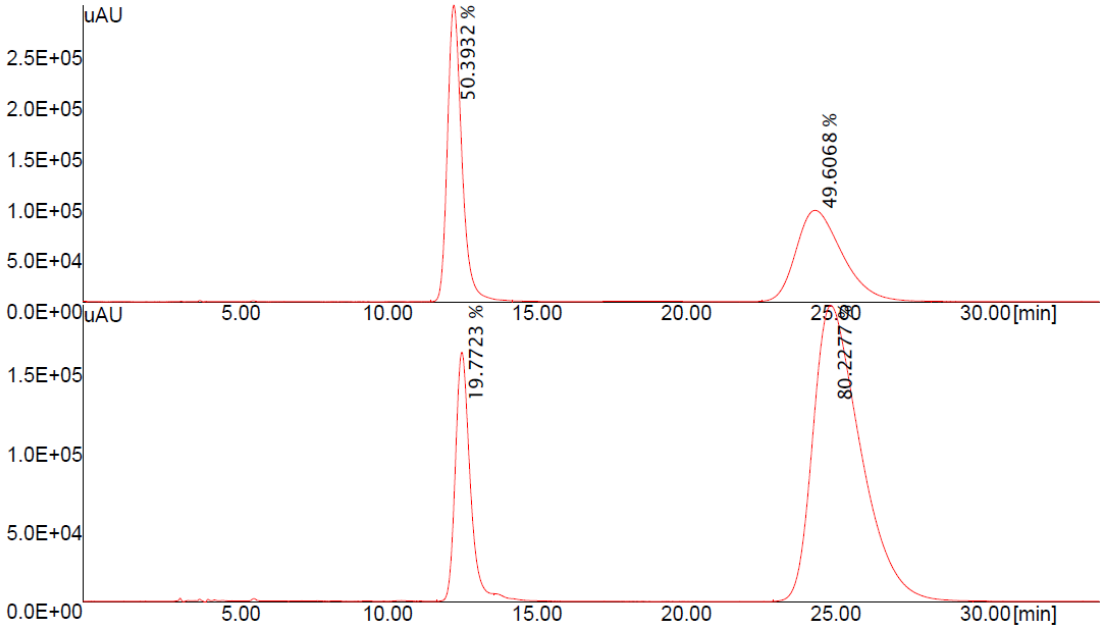
(*E*)-5-(4-Methoxybenzylidene)-3-(3-(4-methoxyphenyl)prop-2-ynyl)-3-phenyldihydrofuran-2(3*H*)-one (9i)




```
DFILE   360_Proton-1-2.als
COMNT   single_pulse
DATIM   2013-02-08 18:08:51
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         399.78 MHz
OBSET           4.19 KHz
OBFIN           7.29 Hz
POINT          16384
FREQU        7503.00 Hz
SCANS             16
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             6.05 usec
IRNUC   1H
CTEMP           21.8 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              9.12 Hz
RGAIN             38
```




```
DFILE   360_Carbon-1-2.als
COMNT   single_pulse_decoupled_gated
DATIM   2013-02-08 17:12:06
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         100.53 MHz
OBSET           5.35 KHz
OBFIN           5.86 Hz
POINT          32768
FREQU       31407.04 Hz
SCANS            378
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.20 usec
IRNUC   1H
CTEMP           22.8 c
SLVNT   CDCL3
EXREF          77.16 ppm
BF              9.12 Hz
RGAIN             50
```



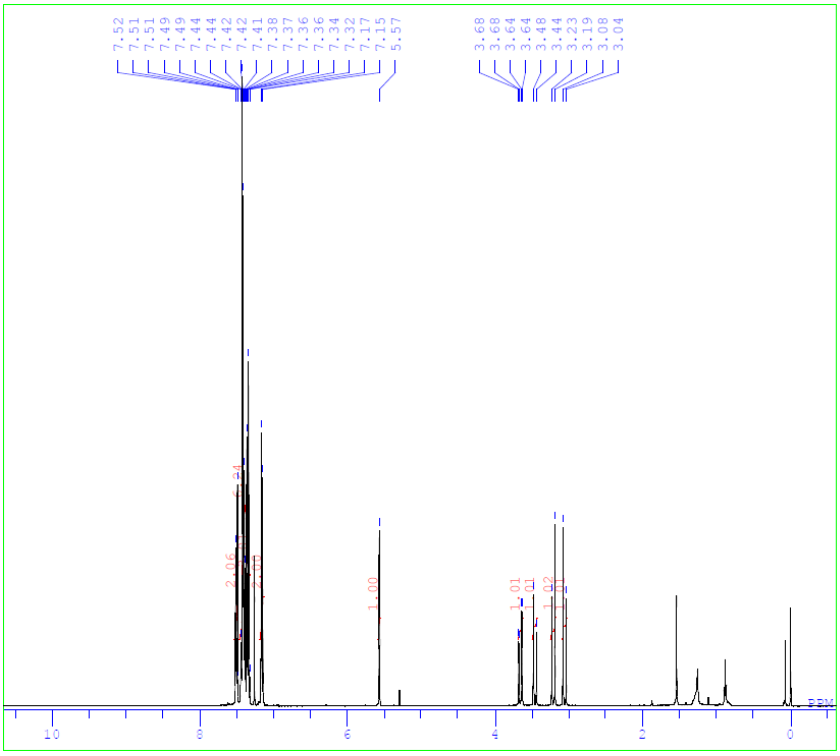
#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		12.400	291614	9671192.944	50.39
2		24.493	89501	9520267.742	49.61

Total Area of Peak = 19191460.686 [uAU. Sec]

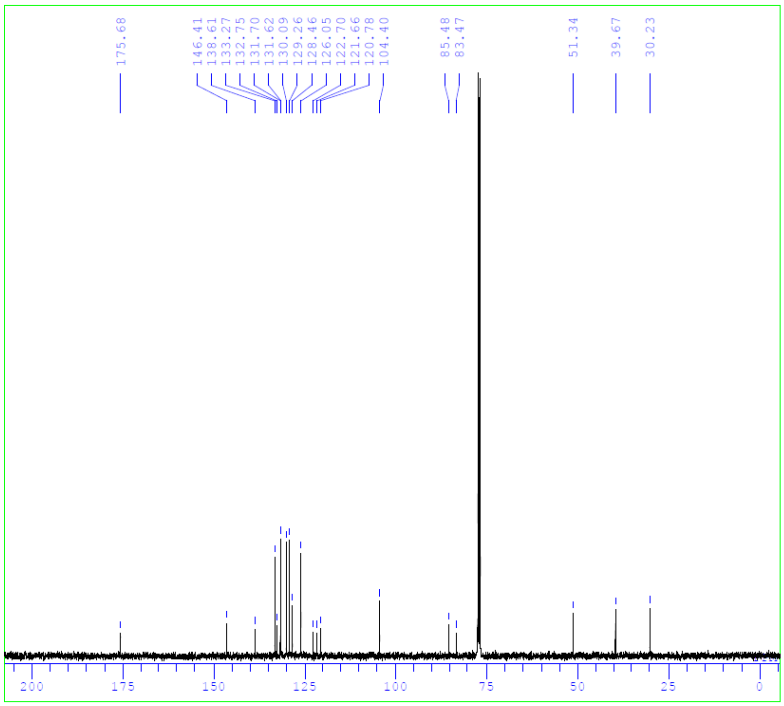
#	Name	RT	Height [uAU]	Area [uAU. Sec]	%Area
1		12.680	156170	5085732.842	19.77
2		25.027	187963	20635803.508	80.23

Total Area of Peak = 25721536.349 [uAU. Sec]

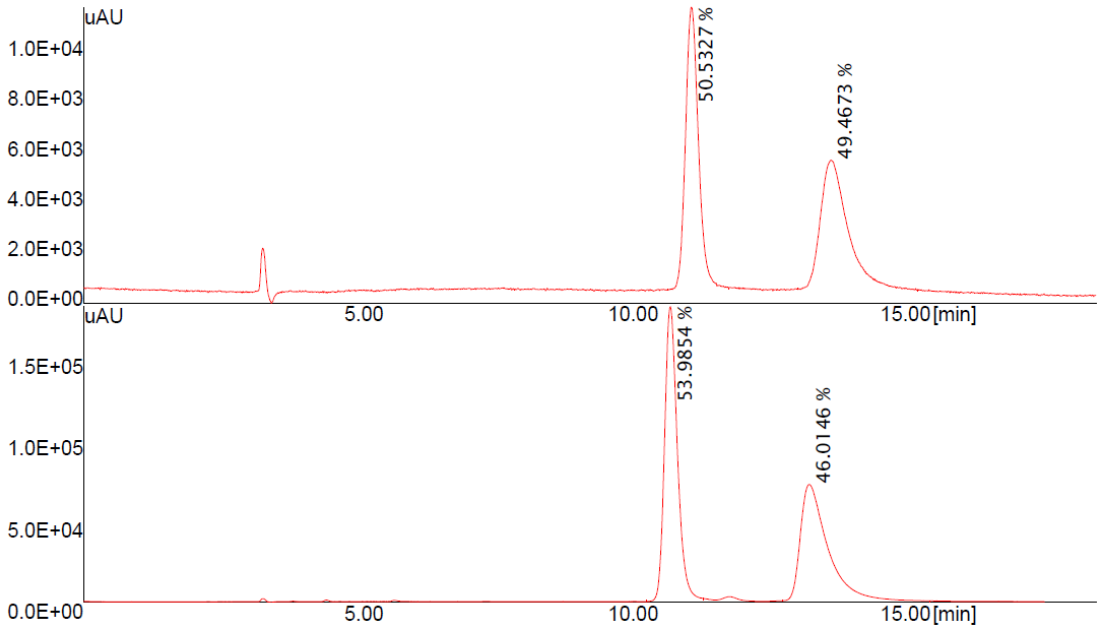
(*E*)-5-(4-Bromobenzylidene)-3-(3-(4-bromophenyl)prop-2-ynyl)-3-phenyldihydrofuran-2(3*H*)-one (9j)




```
DFILE   344_Proton-1-2.als
COMNT   single_pulse
DATIM   2013-02-01 22:08:16
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         399.78 MHz
OBSET           4.19 KHz
OBFIN           7.29 Hz
POINT          16384
FREQU        7503.00 Hz
SCANS             16
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             6.05 usec
IRNUC   1H
CTEMP           23.5 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              9.12 Hz
RGAIN             44
```




```
DFILE   344_Carbon-1-2.als
COMNT   single_pulse decoupled gated
DATIM   2013-02-01 22:10:49
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         100.53 MHz
OBSET           5.35 KHz
OBFIN           5.86 Hz
POINT          32768
FREQU       31407.04 Hz
SCANS            749
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.20 usec
IRNUC   1H
CTEMP           23.8 c
SLVNT   CDCL3
EXREF           77.16 ppm
BF              9.12 Hz
RGAIN             50
```



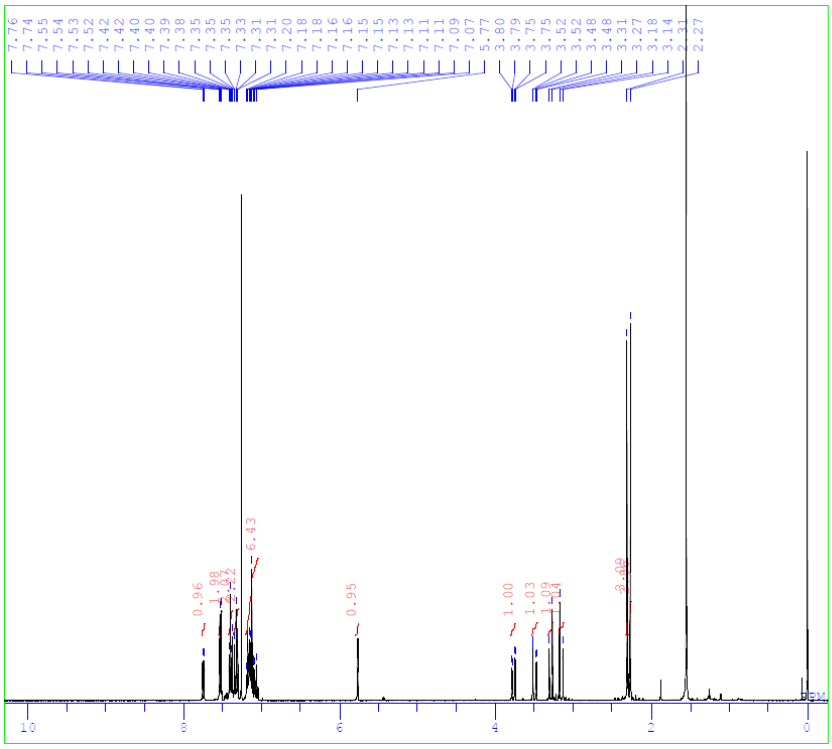
#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
1		11.173	11264	186216.003	50.53
2		13.733	5177	182290.003	49.47

Total Area of Peak = 368506.005 [uAU.Sec]

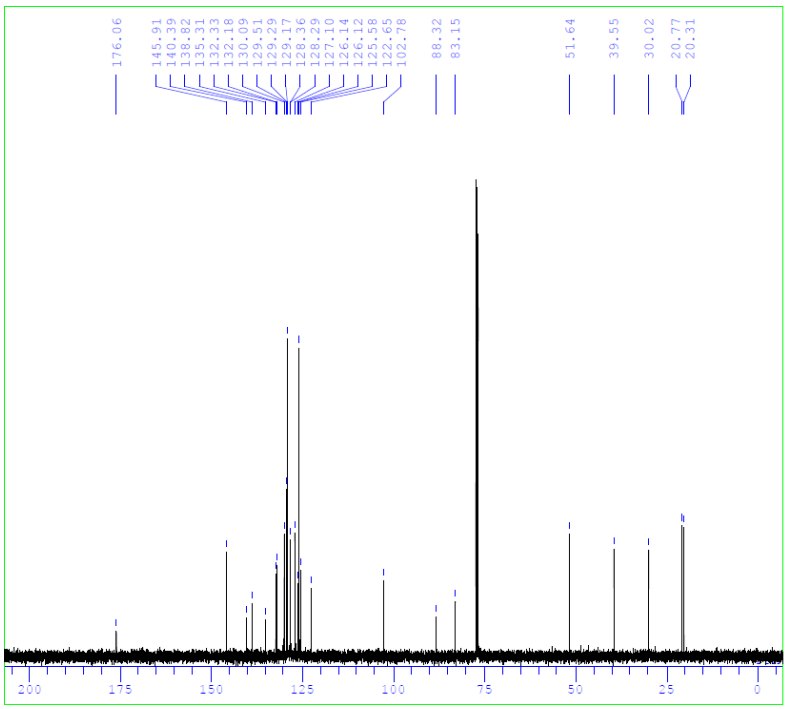
#	Name	RT	Height[uAU]	Area[uAU.Sec]	%Area
1		10.800	179953	2905727.643	53.99
2		13.347	71395	2476708.037	46.01

Total Area of Peak = 5382435.680 [uAU.Sec]

(*E*)-5-(2-Methylbenzylidene)-3-phenyl-3-(3-*o*-tolylprop-2-ynyl)dihydrofuran-2(3*H*)-one (9k)

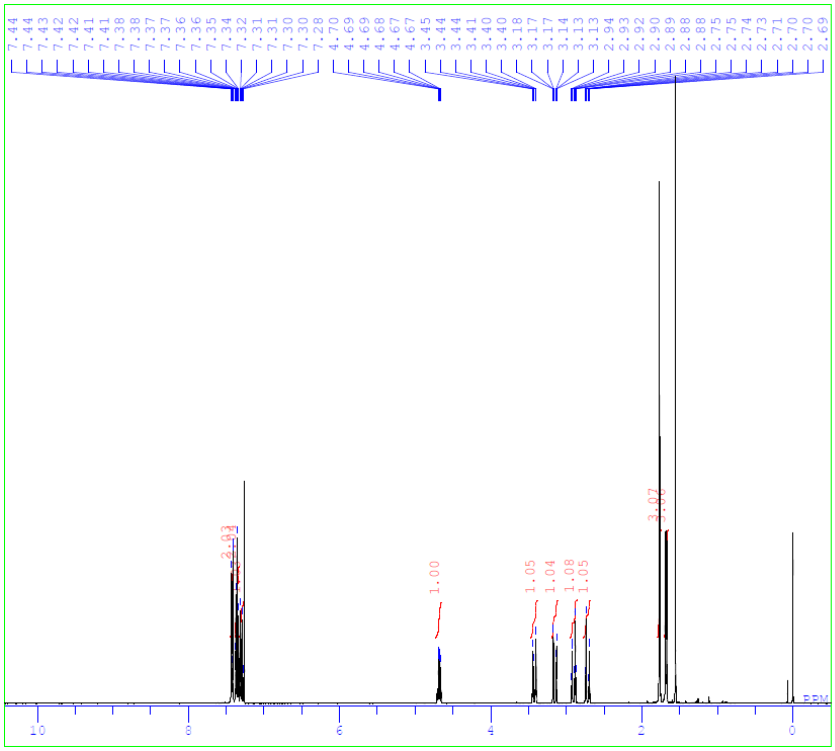



```
DFILE   S-518_Proton-1-1.als
COMNT   single_pulse
DATIM   2012-09-03 16:14:46
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         399.78 MHz
OBSET           4.19 KHz
OBFIN           7.29 Hz
POINT          13107
FREQU        6002.40 Hz
SCANS             16
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.50 usec
IRNUC   1H
CTEMP           25.3 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             50
```

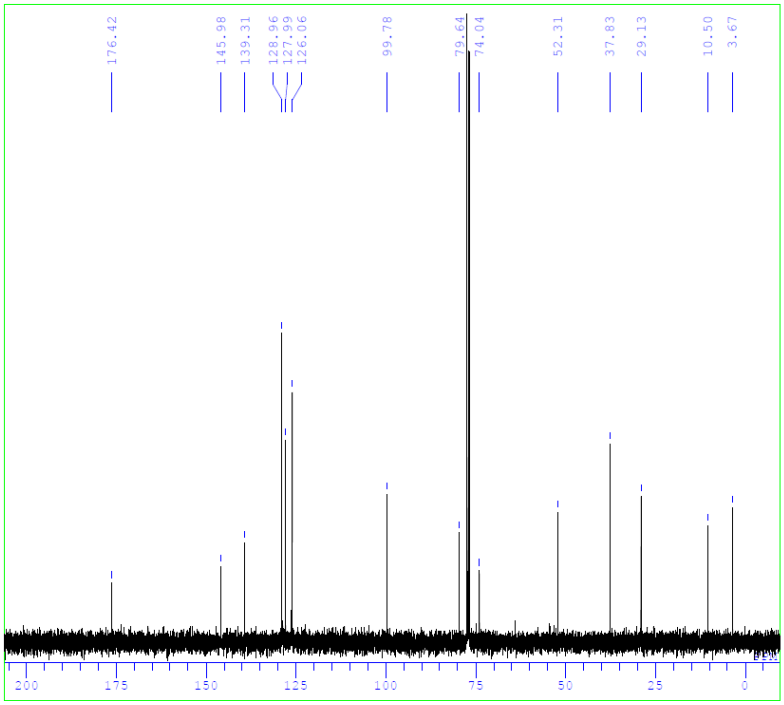



```
DFILE   S-552_Carbon-1-1.als
COMNT   single pulse decoupled gated
DATIM   2012-10-17 15:32:44
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         100.53 MHz
OBSET           5.35 KHz
OBFIN           5.86 Hz
POINT          26214
FREQU       25125.63 Hz
SCANS            284
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.20 usec
IRNUC   1H
CTEMP           20.2 c
SLVNT   CDCL3
EXREF          77.16 ppm
BF              0.12 Hz
RGAIN             50
```

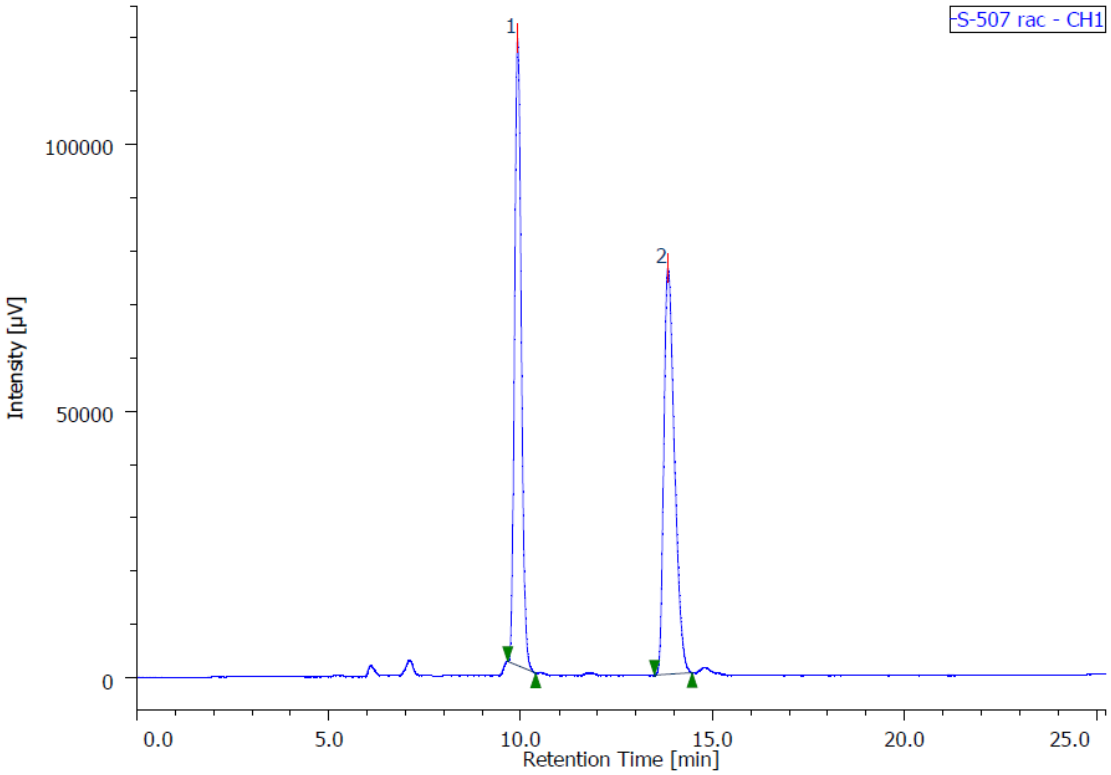
(*Z*)-3-(But-2-ynyl)-5-ethylidene-3-phenyldihydrofuran-2(3*H*)-one (9l)

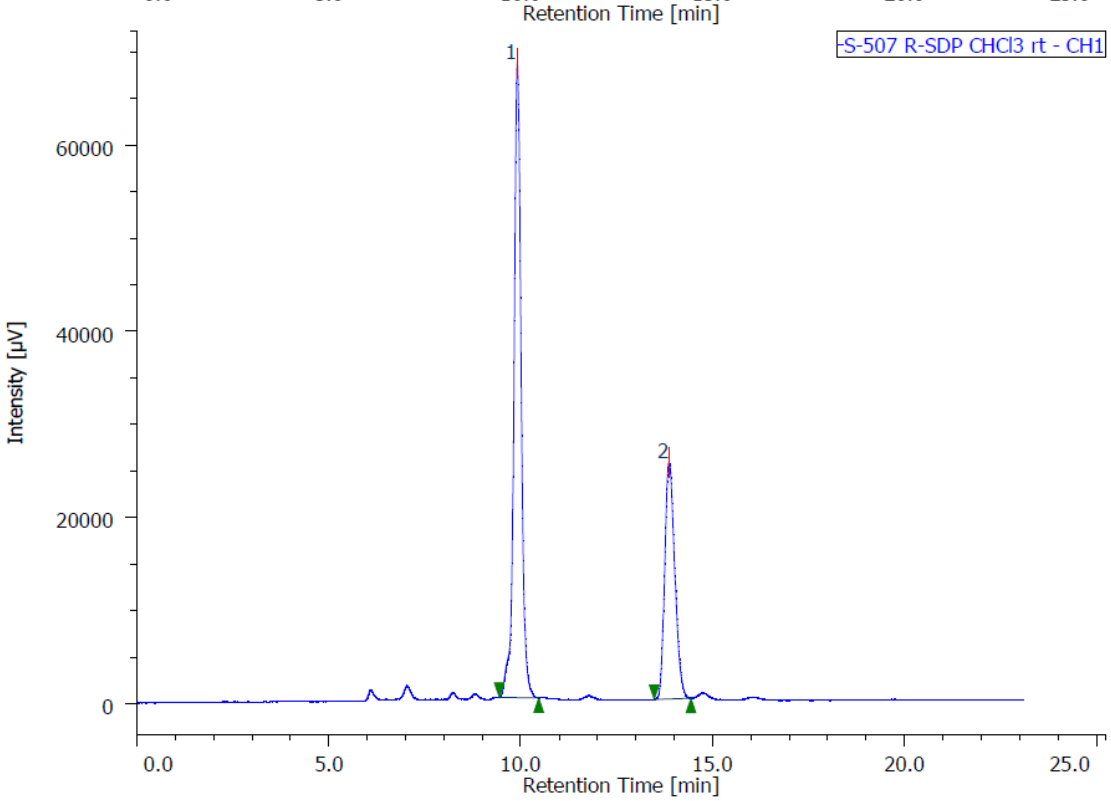



```
DFILE   S-507_Proton-1-1.als
COMNT   single_pulse
DATIM   2012-08-25 11:57:29
OBNUC   1H
EXMOD   proton.jxp
OBFRQ         399.78 MHz
OBSET           4.19 KHz
OBFIN           7.29 Hz
POINT          13107
FREQU        6002.40 Hz
SCANS             16
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.50 usec
IRNUC   1H
CTEMP           26.0 c
SLVNT   CDCL3
EXREF           7.26 ppm
BF              0.12 Hz
RGAIN             44
```




```
DFILE   S-507_Carbon-1-1.als
COMNT   single pulse decoupled gated
DATIM   2012-10-16 21:21:00
OBNUC   13C
EXMOD   carbon.jxp
OBFRQ         100.53 MHz
OBSET           5.35 KHz
OBFIN           5.86 Hz
POINT          26214
FREQU       25125.63 Hz
SCANS            176
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.20 usec
IRNUC   1H
CTEMP           20.8 c
SLVNT   CDCL3
EXREF          77.16 ppm
BF              0.12 Hz
RGAIN             50
```


-S-507 rac - CH1
1
2
100000
50000
0
Intensity [µV]
0.0
5.0
10.0
15.0
20.0
25.0
Retention Time [min]


-S-507 R-SDP CHCl3 rt - CH1
1
2
60000
40000
20000
0
Intensity [µV]
0.0
5.0
10.0
15.0
20.0
25.0
Retention Time [min]

Channel & Peak Information Table

Chromatogram Name S-507 rac-CH1

Sample Name

Channel Name UV-2075

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	9.917	1428453	117484	49.290	60.680	N/A	15384	9.472	1.175	
2	Unknown	1	13.833	1469589	76128	50.710	39.320	N/A	11800	N/A	1.451	

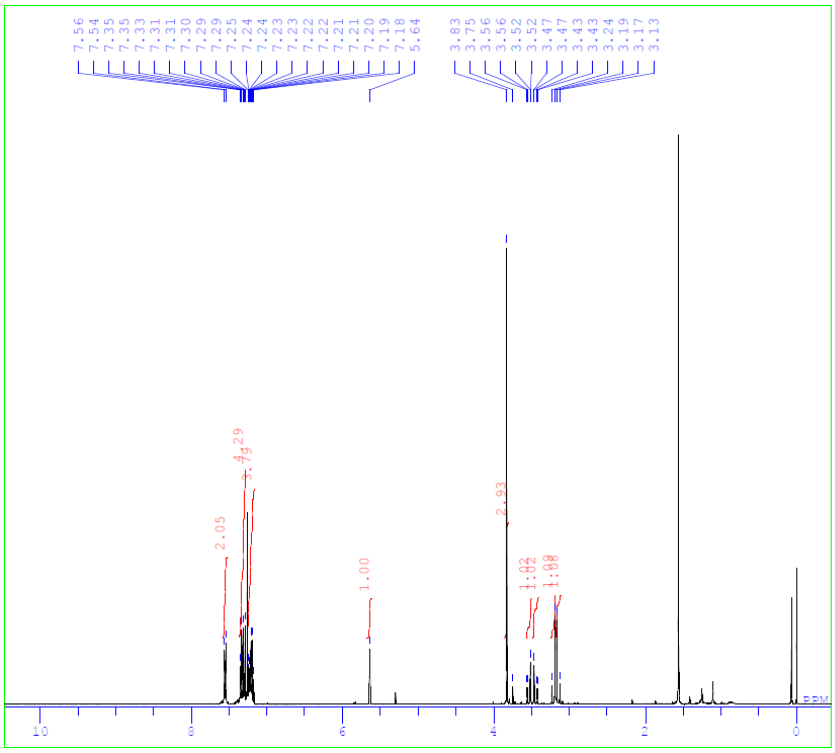
Chromatogram Name S-507 R-SDP CHCl3 rt-CH1

Sample Name

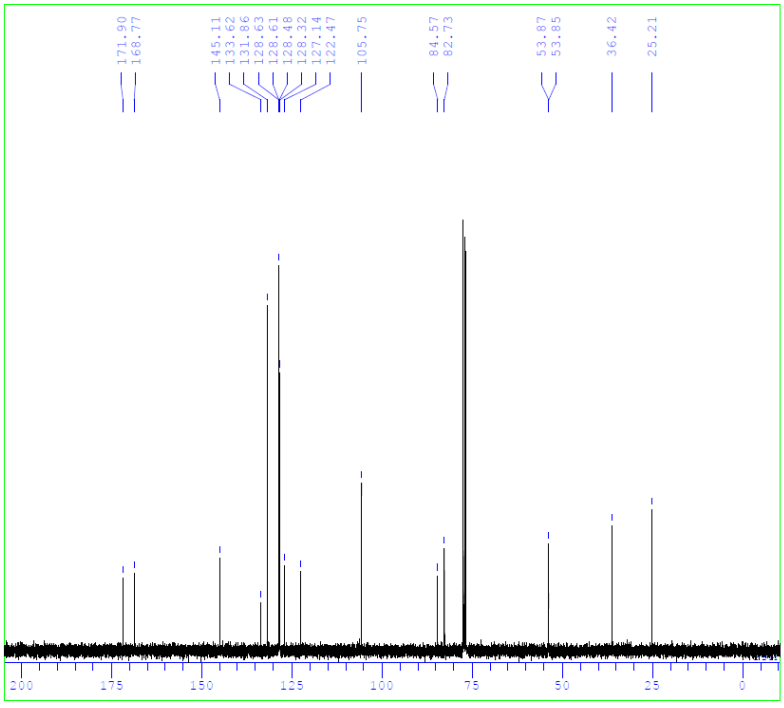
Channel Name UV-2075

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	9.908	893899	68089	65.841	72.844	N/A	15061	9.856	0.941	
2	Unknown	1	13.867	463766	25383	34.159	27.156	N/A	13218	N/A	1.224	

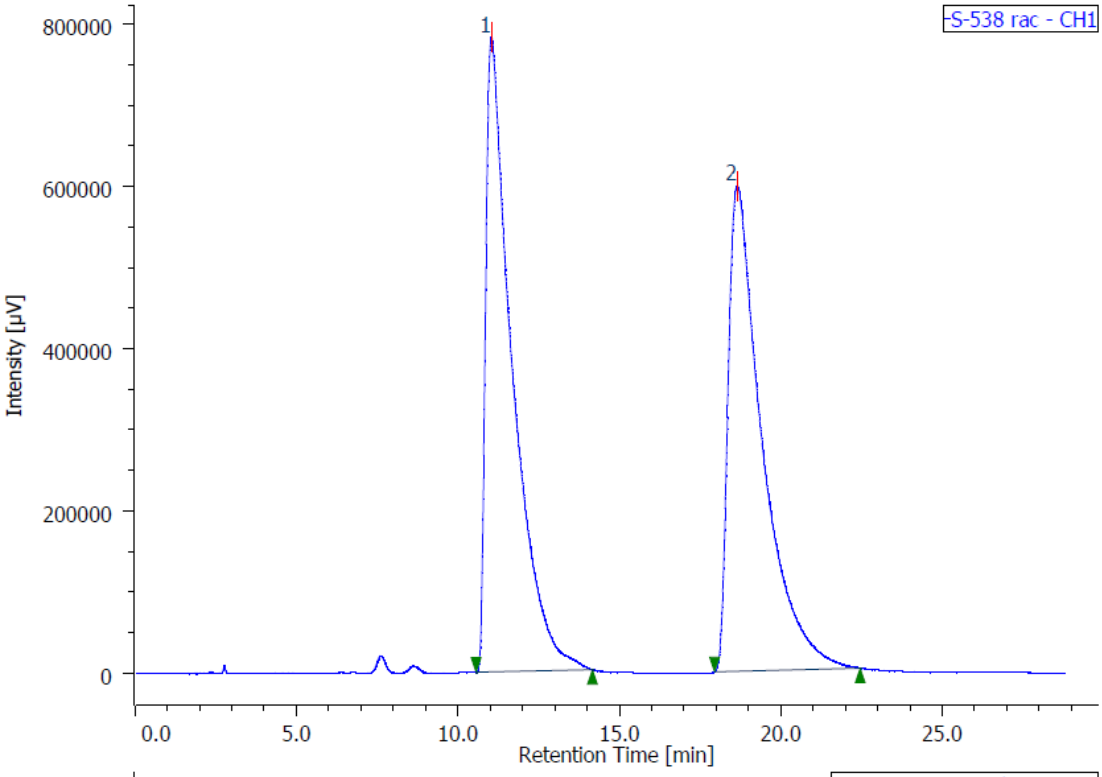
(*Z*)-Methyl 5-benzylidene-2-oxo-3-(3-phenylprop-2-ynyl)tetrahydrofuran-3-carboxylate (9m)

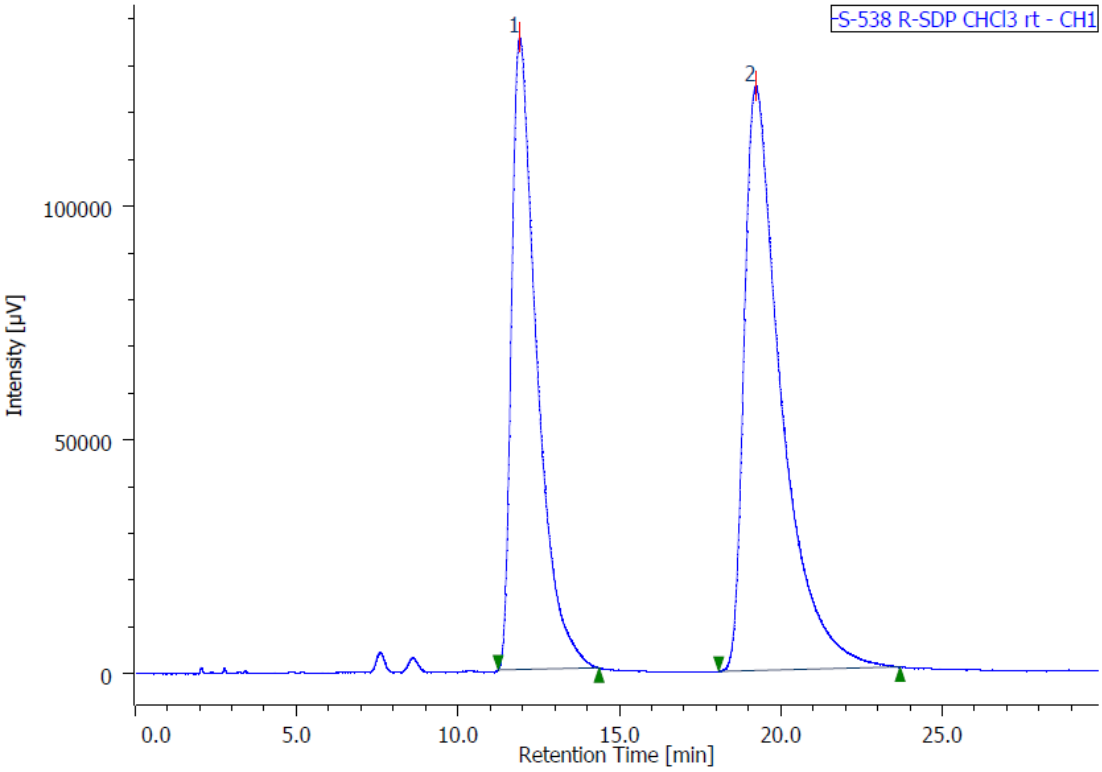



```
DFILE  S-538_Proton-1-1.als
COMNT  single_pulse
DATIM  2012-09-27 15:07:29
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         13107
FREQU       6002.40 Hz
SCANS            16
ACQTM        2.1837 sec
PD           5.0000 sec
PW1            5.50 usec
IRNUC  1H
CTEMP          22.8 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            46
```




```
DFILE  S-538_Carbon-1-1.als
COMNT  single pulse decoupled gated
DATIM  2012-10-10 15:57:49
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26214
FREQU      25125.63 Hz
SCANS           284
ACQTM        1.0433 sec
PD           2.0000 sec
PW1            3.20 usec
IRNUC  1H
CTEMP          20.8 c
SLVNT  CDCL3
EXREF         77.16 ppm
BF             0.12 Hz
RGAIN            50
```





Channel & Peak Information Table

Chromatogram Name S-538 rac-CH1

Sample Name

Channel Name UV-2075

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	11.042	44897648	781318	50.712	56.645	N/A	1022	4.862	3.232	
2	Unknown	1	18.650	43636146	597999	49.288	43.355	N/A	1804	N/A	2.656	

Chromatogram Name S-538 R-SDP CHCl3 rt-CH1

Sample Name

Channel Name UV-2075

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	11.917	7348401	134999	42.537	51.953	N/A	1229	4.480	2.004	
2	Unknown	1	19.225	9926962	124847	57.463	48.047	N/A	1618	N/A	2.140	