Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

A facile copper(I)-catalyzed homocoupling of terminal alkynes to 1,3-diynes with diaziridinone under mild conditions

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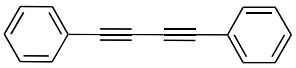
Supporting Information

General methods. All commercially available reagents were used without further purification. Column chromatography was performed on silica gel (200-400 mesh). ^{1}H NMR spectra were recorded on a 300 MHz NMR spectrometer and ^{13}C NMR spectra were recorded on a 75 MHz NMR spectrometer. IR spectra were recorded on a FT-IR spectrometer. Melting points were uncorrected.

Representative procedure for oxidative homocoupling of terminal alkynes (Table 2, entry 4): To a 50 mL single-necked flask equipped with a stir bar were added CuBr (0.0717 g, 0.50 mmol) and CH_3CN (15 mL). After the mixture was stirred at rt for 3 min, 1-ethynyl-4-(trifluoromethyl)benzene (**3e**) (1.701 g, 10.0 mmol) was added, followed by the addition of di-*tert*-butyldiazridinone (**1**) (1.532 g, 9.0 mmol). The reaction mixture was vigorously stirred at rt for 2 h, concentrated, and purified by flash chromatography (silica gel, hexanes:ethyl acetate = 200:1) to give 1,3-diyne **4e** as a white solid (1.399 g, 83%).

Characterization data

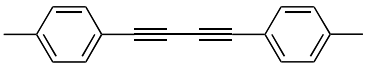
Table 2, entry 1



1,4-Diphenylbuta-1,3-diyne: White solid; mp 85-87 ^{o}C (lit. mp 88-89 ^{o}C); IR (film) 3050, 2150, 1592, 1485, 1439, 915, 756 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.48 (m, 4H), 7.43-7.29 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.7, 129.4, 128.6, 122.0, 81.8, 74.2.

S. Zhang, X. Liu and T. Wang, *Adv. Synth. Catal.*, 2011, **353**, 1463–1466.

Table 2, entry 2

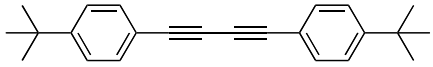


1,4-Di-*p*-tolylbuta-1,3-diyne: White solid; mp 183-184 ^{o}C (lit. mp 182-183 ^{o}C); IR (film) 2136, 1897, 1637, 1503, 1406, 809 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J*

= 8.1 Hz, 4H), 7.15 (d, J = 8.1 Hz, 4H), 2.37 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 132.6, 129.4, 119.0, 81.8, 73.7, 21.8.

S. Zhang, X. Liu and T. Wang, *Adv. Synth. Catal.*, 2011, **353**, 1463–1466.

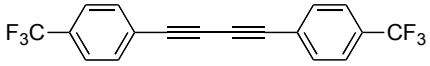
Table 2, entry 3



1,4-Bis(4-*tert*-butylphenyl)buta-1,3-diyne: Off-white solid; mp 195-196 °C; IR (film) 2959, 1462, 1364, 1267, 1103, 835 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, J = 8.1 Hz, 4H), 7.37 (d, J = 8.1 Hz, 4H), 1.34 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 132.5, 125.7, 119.1, 81.7, 73.7, 35.1, 31.3.

(*a*) Z. Chen, H. Jiang, A. Wang and S. Yang, *J. Org. Chem.*, 2010, **75**, 6700–6703; (*b*) W. Susanto, C.-Y. Chu, W. J. Ang, T.-C. Chou, L.-C. Lo and Y. Lam, *J. Org. Chem.*, 2012, **77**, 2729−2742.

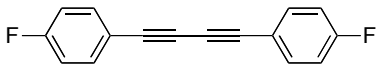
Table 2, entry 4



1,4-Bis[4-(trifluoromethyl)phenyl]buta-1,3-diyne: White solid; mp 165-167 °C (lit. mp 166-168 °C); IR (film) 2923, 1609, 1406, 1318, 1176, 1129, 1106, 1065, 839 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J = 9.0 Hz, 4H), 7.61 (d, J = 9.0 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.0, 131.3 (q, J = 32.8 Hz), 125.7 (q, J = 3.7 Hz), 125.5, 123.9 (q, J = 270.8 Hz), 81.2, 75.9.

(*a*) S. V. Damle, D. Seomoon and P. H. Lee, *J. Org. Chem.*, 2003, **68**, 7085–7087; (*b*) K. Kude, S. Hayase, M. Kawatsura and T. Itoh, *Heteroat. Chem.*, 2011, **22**, 397–404.

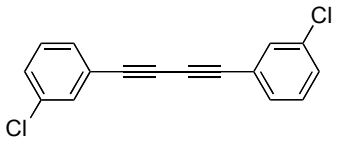
Table 2, entry 5



1,4-Bis(4-fluorophenyl)buta-1,3-diyne: White solid; mp 188-190 °C (lit. mp 194-195 °C); IR (film) 1888, 1595, 1502, 1225, 1158, 828 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57-7.45 (m, 4H), 7.10-6.98 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3 (d, J = 250.1 Hz), 134.8 (d, J = 8.6 Hz), 118.1 (d, J = 3.5 Hz), 116.1 (d, J = 22.2 Hz), 80.7, 73.8.

(*a*) A. Kusuda, X.-H. Xu, X. Wang, E. Tokunaga and N. Shibata, *Green Chem.*, 2011, **13**, 843–846; (*b*) S. Zhang, X. Liu and T. Wang, *Adv. Synth. Catal.*, 2011, **353**, 1463–1466.

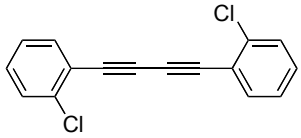
Table 2, entry 6



1,4-Bis(3-chlorophenyl)buta-1,3-diyne: Off-white solid; mp 71-72 ^{o}C (lit. mp 73 ^{o}C); IR (film) 1586, 1560, 1469, 1403, 876, 784 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.46 (m, 2H), 7.44-7.32 (m, 4H), 7.31-7.21 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.6, 132.5, 130.9, 129.9, 123.5, 80.8, 74.9.

(*a*) K. Kamata, S. Yamaguchi, M. Kotani, K. Yamaguchi and N. Mizuno, *Angew. Chem. Int. Ed.*, 2008, **47**, 2407–2410; (*b*) E. Merkul, D. Urselmann and T. J. J. Müller, *Eur. J. Org. Chem.*, 2011, 238–242.

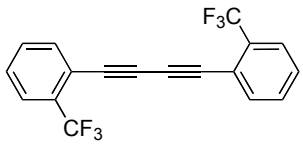
Table 2, entry 7



1,4-Bis(2-chlorophenyl)buta-1,3-diyne: White solid; mp 137-138 ^{o}C (lit. mp 138-140 ^{o}C); IR (film) 2924, 1559, 1465, 1071, 750 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, J = 7.8, 2.0 Hz, 2H), 7.42 (dd, J = 7.8, 1.5 Hz, 2H), 7.31 (td, J = 7.8, 2.0 Hz, 2H), 7.24 (td, J = 7.8, 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 134.6, 130.5, 129.7, 126.8, 122.0, 79.6, 78.6.

(*a*) S. V. Damle, D. Seomoon and P. H. Lee, *J. Org. Chem.*, 2003, **68**, 7085–7087; (*b*) S.-N. Chen, W.-Y. Wu and F.-Y. Tsai, *Green Chem.*, 2009, **11**, 269–274.

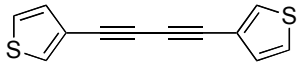
Table 2, entry 8



1,4-Bis[2-(trifluoromethyl)phenyl]buta-1,3-diyne: White solid; mp 70-71 ^{o}C (lit. mp 70.8-71.7 ^{o}C); IR (film) 1600, 1487, 1449, 1318, 1164, 1125, 1108, 762 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.63 (m, 4H), 7.57-7.43 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.4, 132.8 (q, J = 30.8 Hz), 131.7, 129.4, 126.3 (q, J = 5.1 Hz), 123.5 (q, J = 271.7 Hz), 119.9 (q, J = 2.3 Hz), 78.9, 78.8; HRMS Calcd for $C_{18}H_{12}F_6N$ ($M+NH_4^+$): 356.0868. Found: 356.0859.

T. Kurita, M. Abe, T. Maegawa, Y. Monguchi and H. Sajiki, *Synlett*, 2007, 2521–2524.

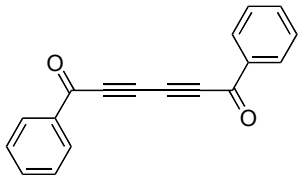
Table 2, entry 9



1,4-Di(thiophen-3-yl)buta-1,3-diyne: White solid; mp 109-111 ^{o}C (lit. mp 111.5-112.5 ^{o}C); IR (film) 3104, 2145, 1352, 1216, 1078, 929, 868, 783 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (dd, J = 3.0, 1.2 Hz, 2H), 7.28 (dd, J = 5.1, 3.0 Hz, 2H), 7.18 (dd, J = 5.1, 1.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.4, 130.4, 125.8, 121.1, 76.8, 73.7.

(*a*) J.-P. Beny, S. N. Dhawan, J. Kagan and S. Sundlass, *J. Org. Chem.*, 1982, **47**, 2201–2204; (*b*) A. Kusuda, X.-H. Xu, X. Wang, E. Tokunaga and N. Shibata, *Green Chem.*, 2011, **13**, 843–846.

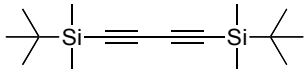
Table 2, entry 10



1,6-Diphenylhexa-2,4-diyne-1,6-dione: Yellow solid; mp 135-137 ^{o}C (lit. mp 136-138 ^{o}C); IR (film) 2135, 1638, 1450, 1236, 994, 697 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18-8.06 (m, 4H), 7.72-7.62 (m, 2H), 7.58-7.47 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 136.1, 135.3, 129.9, 129.1, 80.6, 74.2; HRMS Calcd for $C_{18}H_{11}O_2$ ($M+H^+$): 259.0754. Found: 259.0755.

D. R. M. Walton and F. Waugh, *J. Organomet. Chem.*, 1972, **37**, 45–56.

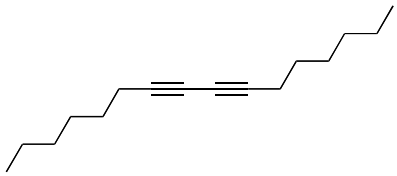
Table 2, entry 11



1,4-Bis(*tert*-butyldimethylsilyl)buta-1,3-diyne: White solid; mp 189-191 ^{o}C; IR (film) 2951, 2931, 2858, 2067, 1470, 1264, 809, 741 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (s, 18H), 0.13 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 89.1, 84.2, 26.3, 17.0, –4.6.

M. Blangetti, A. Deagostino, H. Rosso, C. Prandi, C. Zavattaro and P. Venturello, *Eur. J. Org. Chem.*, 2007, 5867–5874.

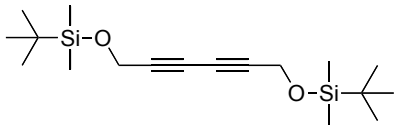
Table 2, entry 12



Hexadeca-7,9-diyne: Colorless oil; IR (film) 2957, 2932, 2860, 2234, 1710, 1459, 1239, 725 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.24 (t, *J* = 6.9 Hz, 4H), 1.58-1.19 (m, 16H), 0.88 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 77.7, 65.5, 31.5, 28.7, 28.5, 22.7, 19.4, 14.2.

S. Zhang, X. Liu and T. Wang, *Adv. Synth. Catal.*, 2011, **353**, 1463–1466.

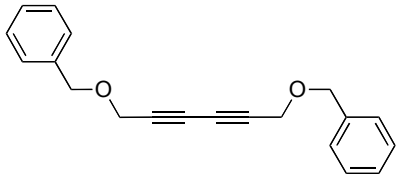
Table 2, entry 13



2,2,3,3,12,12,13,13-Octamethyl-4,11-dioxa-3,12-disilatetradeca-6,8-diyne: White solid; mp 38-39 ^{o}C; IR (film) 2957, 2931, 2859, 1472, 1363, 1256, 1091, 836, 778 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.37 (s, 4H), 0.90 (s, 18H), 0.12 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 77.8, 69.4, 52.3, 26.0, 18.5, –5.0; HRMS Calcd for $C_{18}H_{35}O_2Si_2$ ($M+H^+$): 339.2170. Found: 339.2162.

C. H. Oh and V. R. Reddy, *Tetrahedron Lett.*, 2004, **45**, 5221–5224.

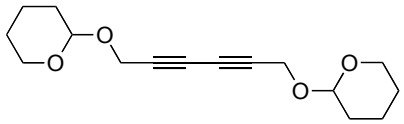
Table 2, entry 14



1,6-Bis(benzyloxy)hexa-2,4-diyne: Light yellow oil; IR (film) 3032, 2863, 2243, 1727, 1454, 1348, 1073, 739, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.29 (m, 10H), 4.63 (s, 4H), 4.28 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 128.7, 128.3, 128.2, 75.6, 72.0, 70.8, 57.7.

W. Yin, C. He, M. Chen, H. Zhang and A. Lei, *Org. Lett.*, 2009, **11**, 709–712.

Table 2, entry 15



1,6-Bis(tetrahydro-2*H*-pyran-2-yloxy)hexa-2,4-diyne: Light yellow oil; IR (film) 2944, 1729, 1343, 1202, 1120, 1026, 902 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.78 (t, *J* = 3.0 Hz, 2H), 4.30 (s, 4H), 3.86-3.72 (m, 2H), 3.57-3.45 (m, 2H), 1.88-1.43 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 97.1, 75.4, 70.2, 62.2, 54.6, 30.3, 25.5, 19.1.

(*a*) F. Nador, L. Fortunato, Y. Moglie, C. Vitale and G. Radivoy, *Synthesis*, 2009, 4027–4031; (*b*) W. Yin, C. He, M. Chen, H. Zhang and A. Lei, *Org. Lett.*, 2009, **11**, 709–712.

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
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INOVA-500 "epoxide"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.598 sec
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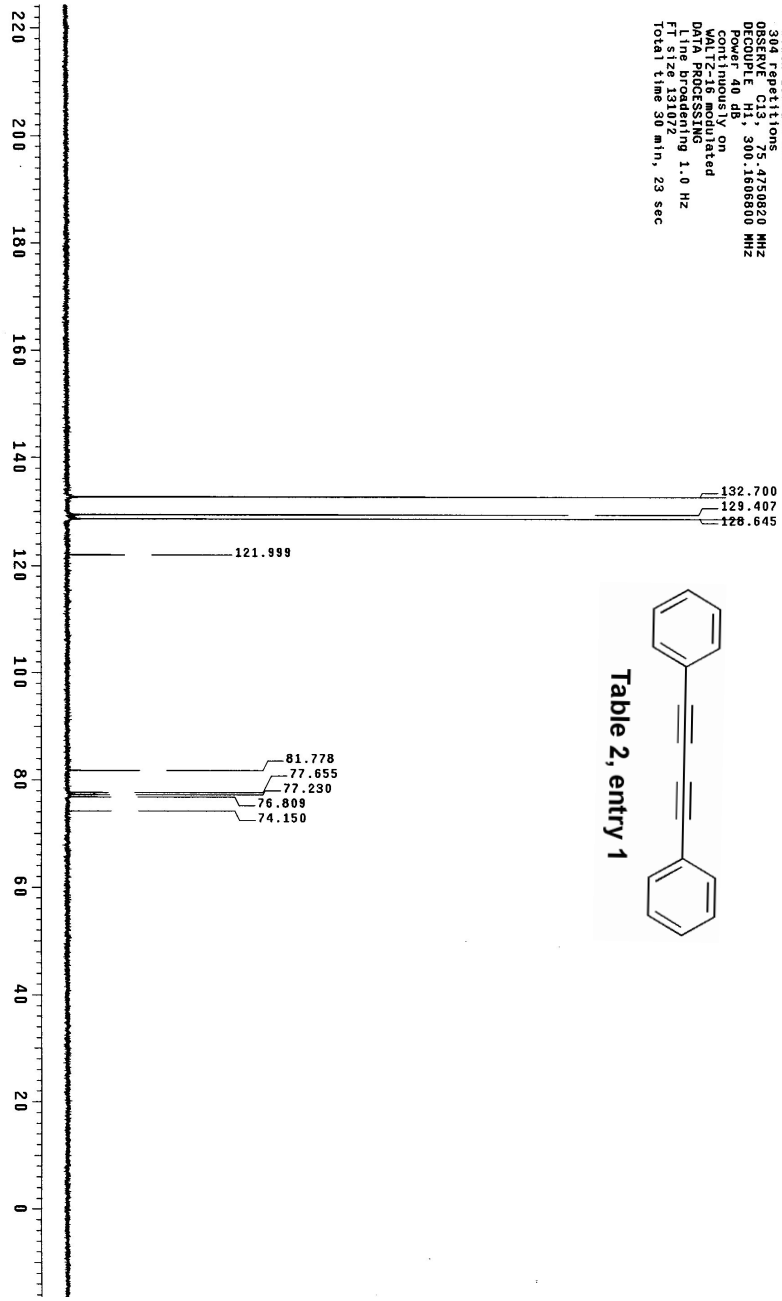
4 repetitions
OBSERVE H1, 300.1592196 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 12 sec

Table 2, entry 1



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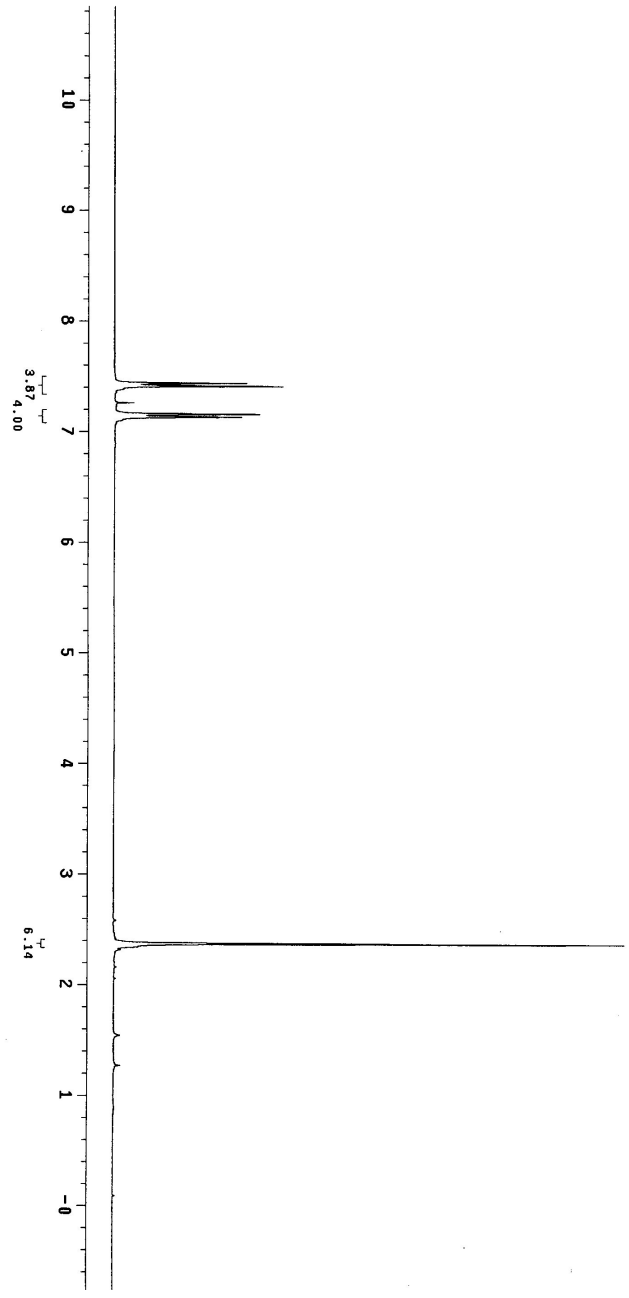

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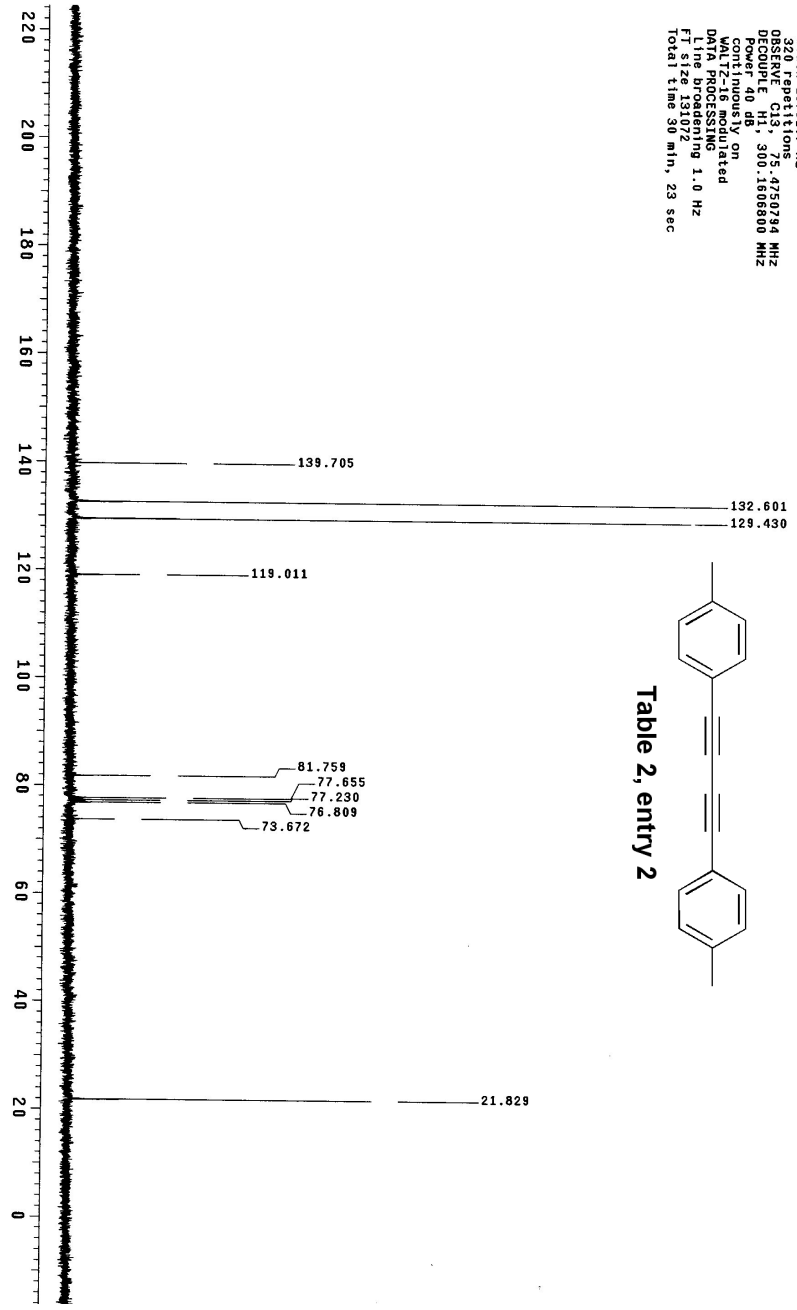

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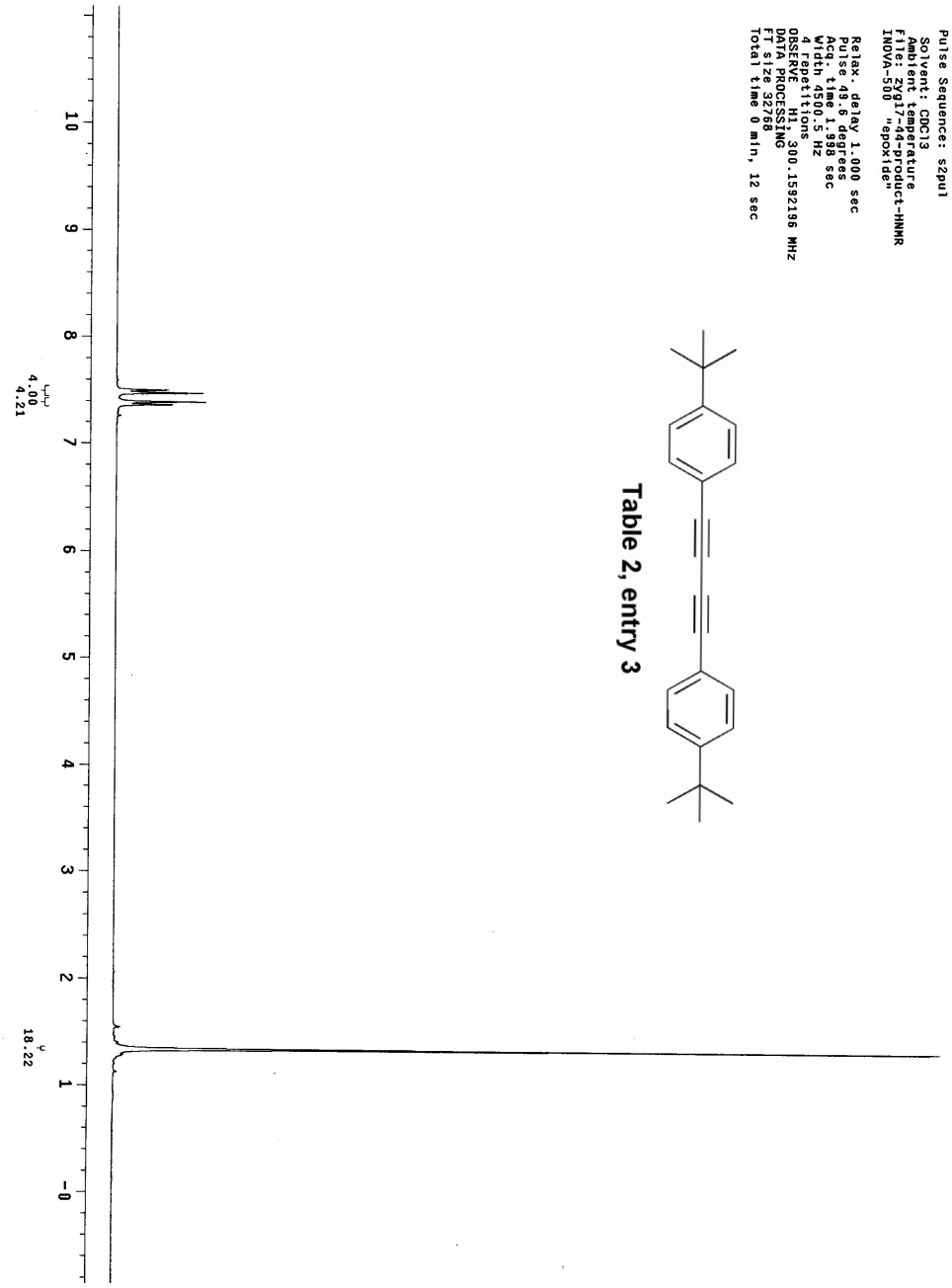

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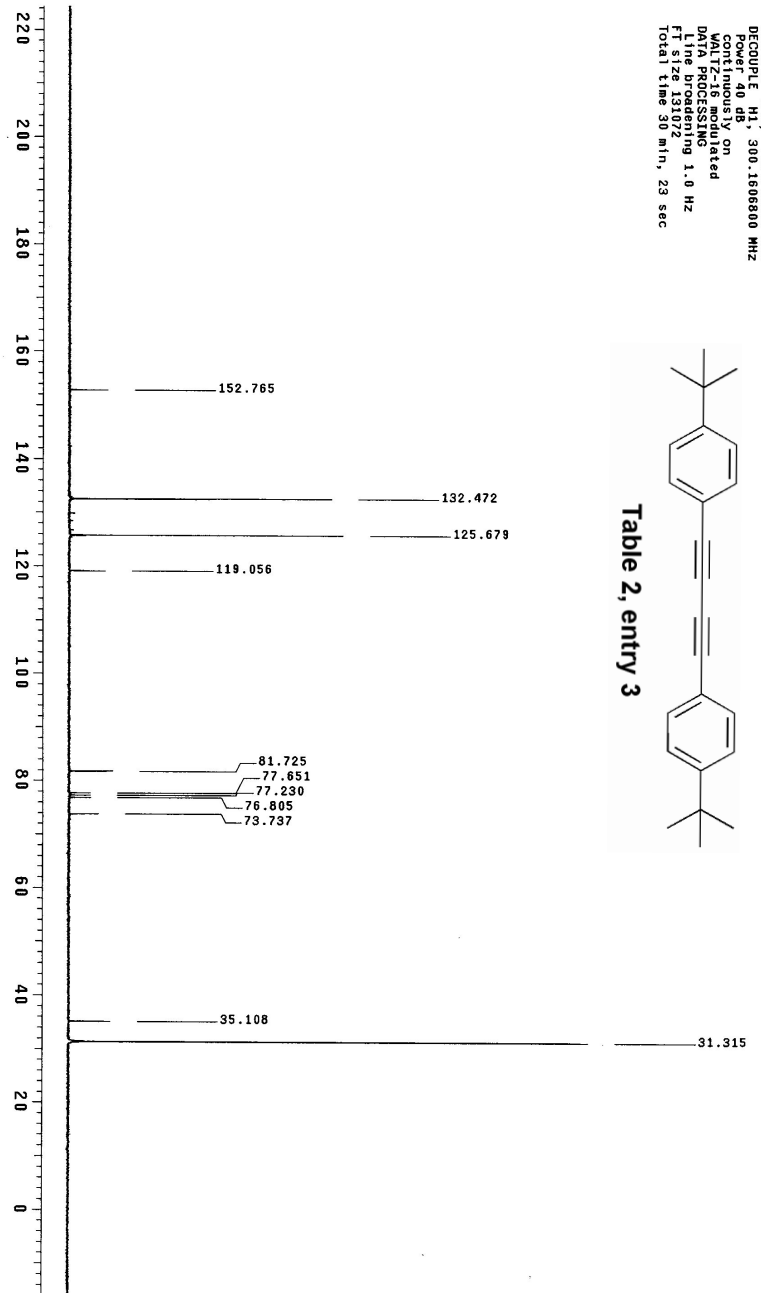
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Width 18761.7 Hz
33554 repetitions
OBSERVE C13, 75.4750808 MHz
DECOUPLE H1, 300.1606800 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 30 min, 23 sec
Table 2, entry 3
152.765
132.472
125.679
119.056
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35.108
31.315
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200
180
160
140
120
100
80
60
40
20
0

STANDARD 1H OBSERVE

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File: zyg22-12-product-HNMR
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Relax. delay 1.000 sec
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DATA PROCESSING
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Total time 0 min, 30 sec

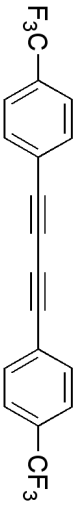
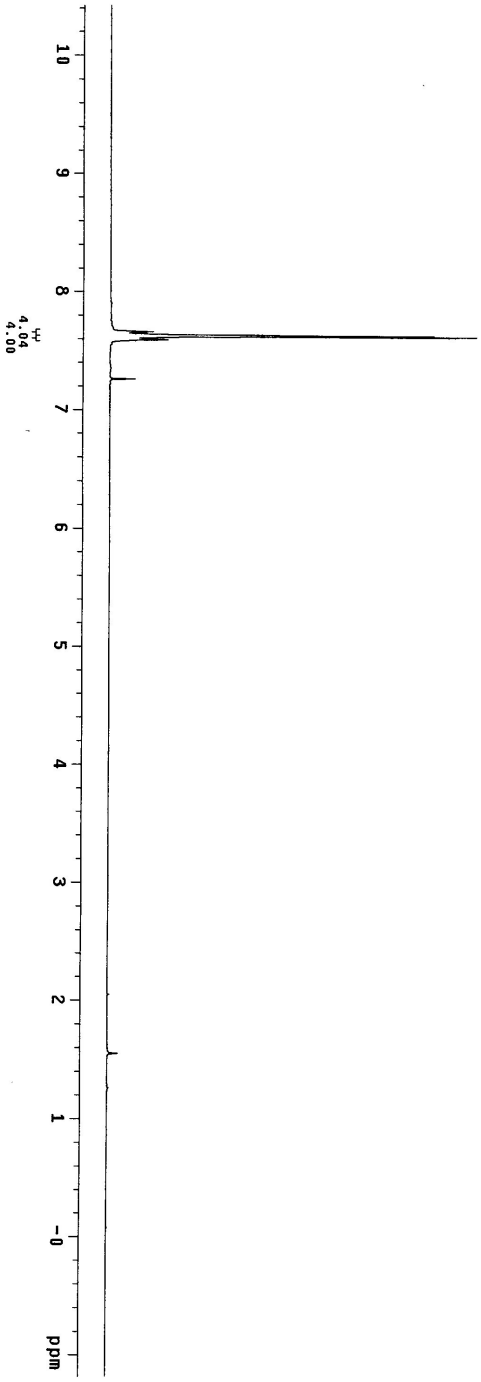
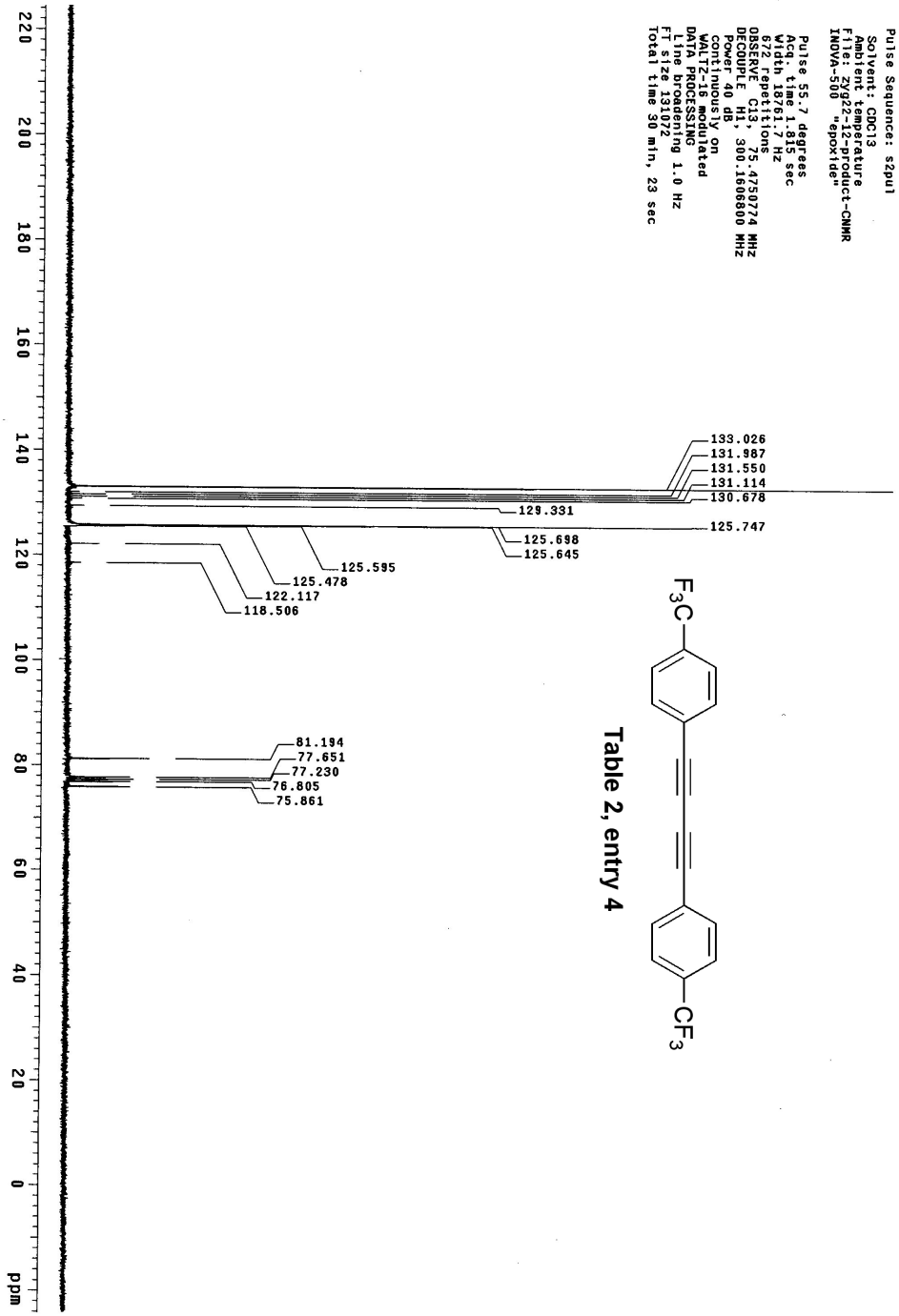


Table 2, entry 4





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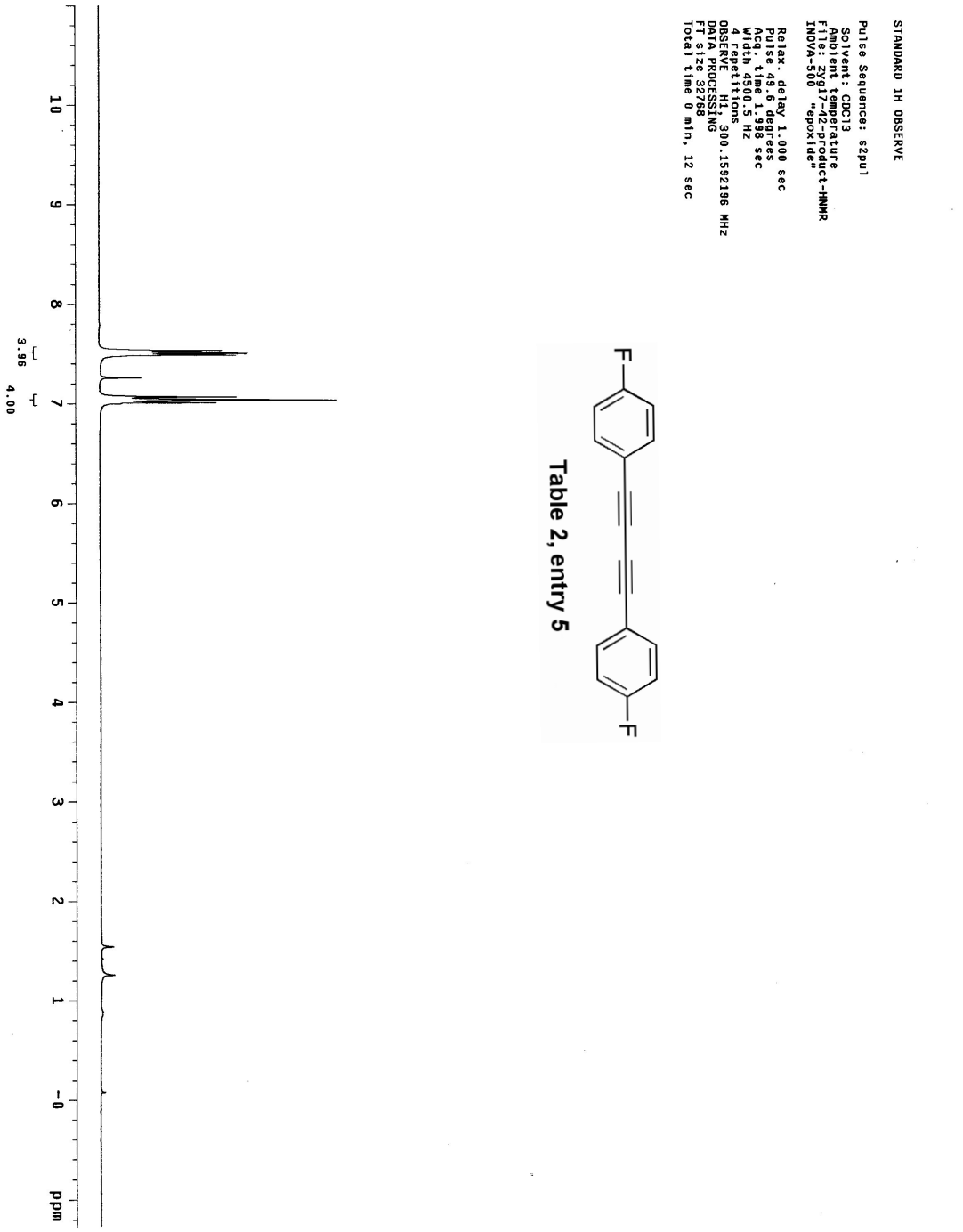

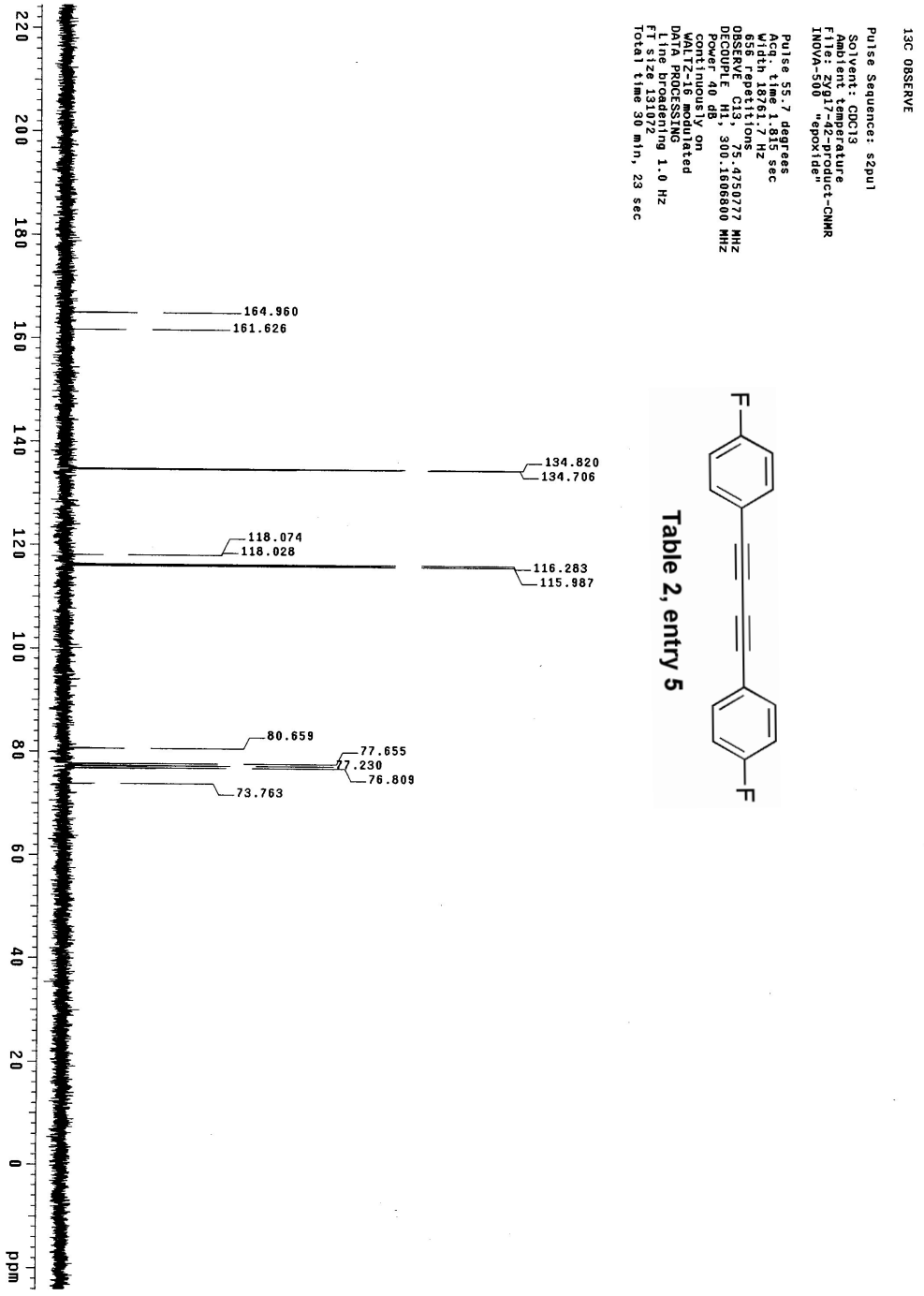

STANDARD 1H OBSERVE

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INOVA-500 "epoxide"

Relax. delay 1.000 sec
Pulse 49.6 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
8 repetitions
OBSERVE H1, 300.1592196 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 12 sec

Table 2, entry 6

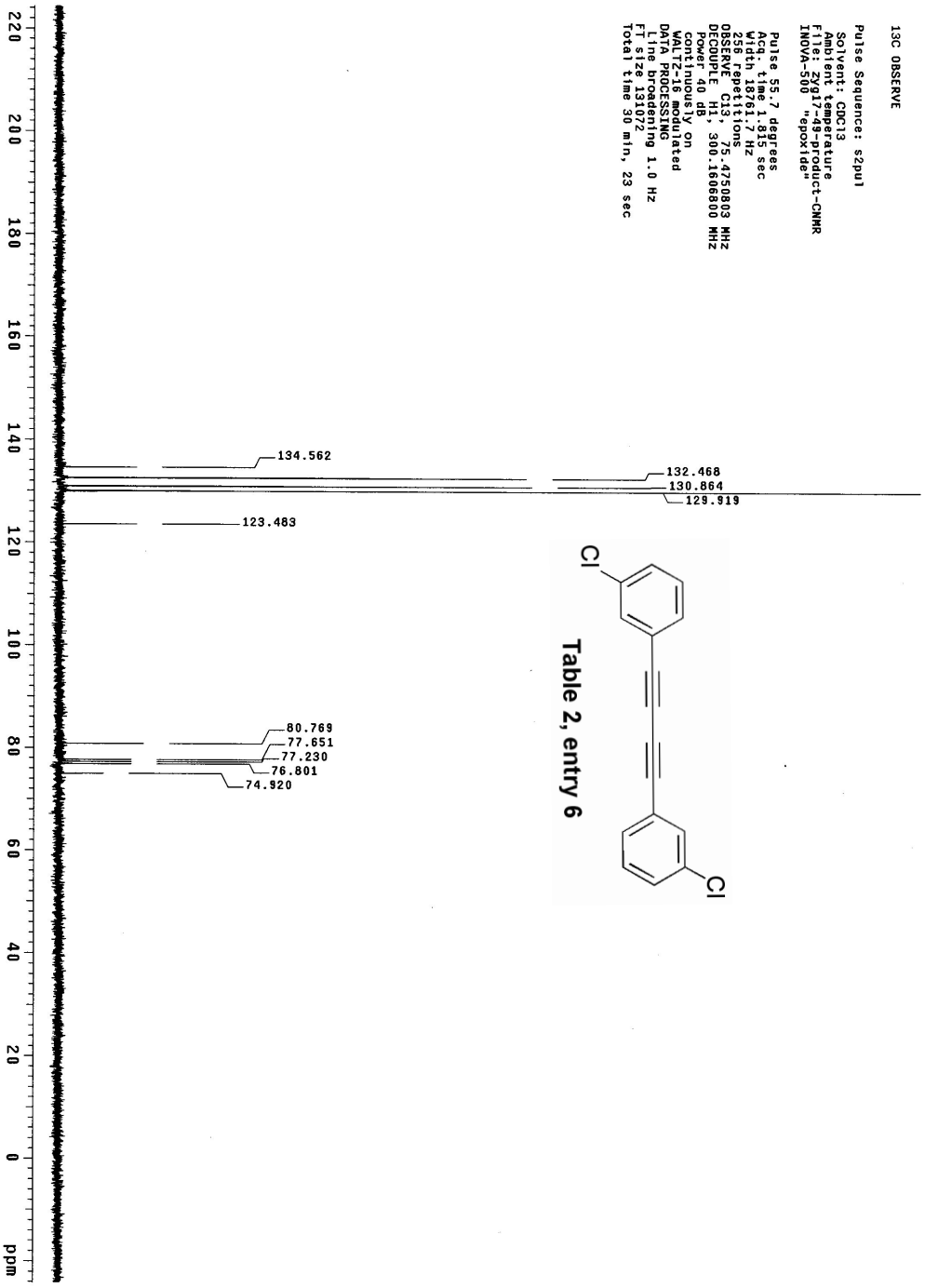


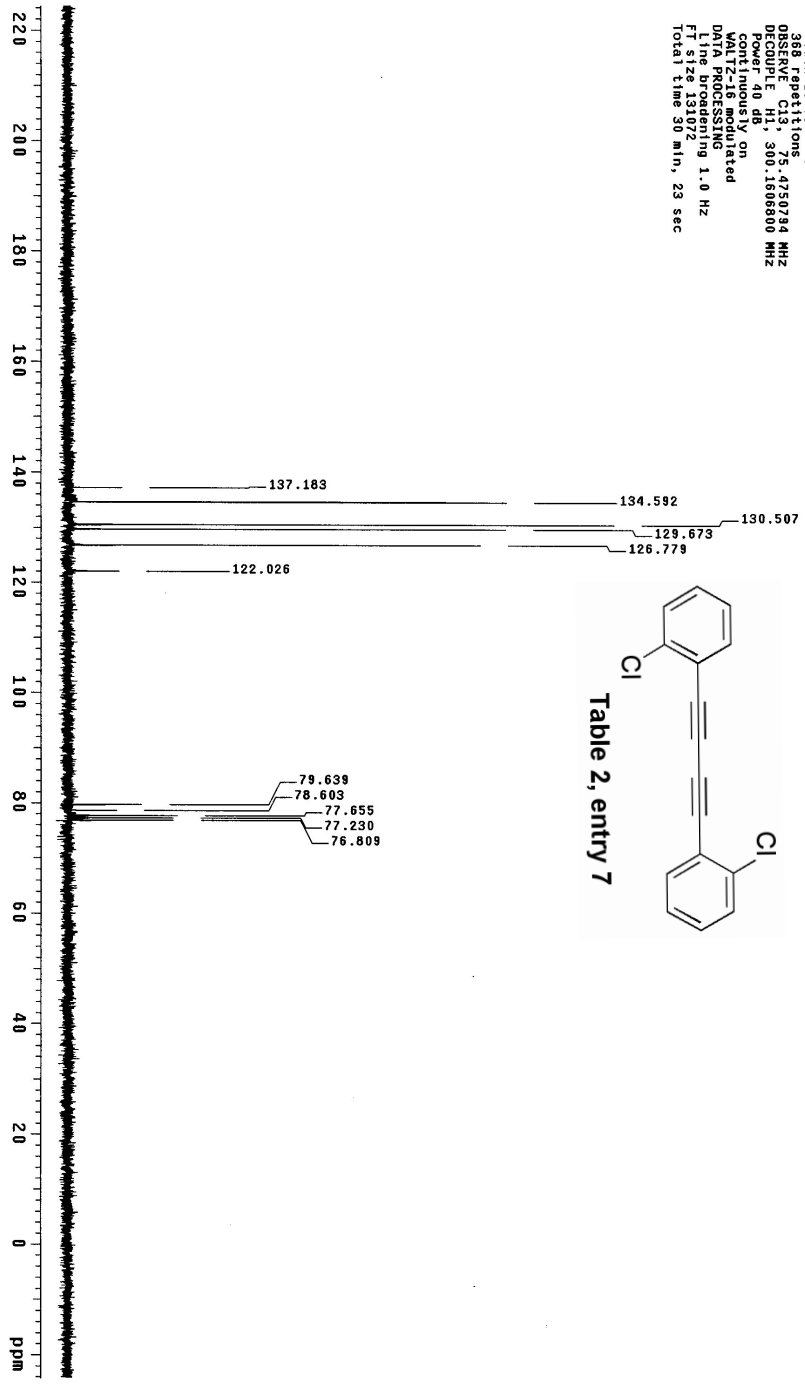
Table 2, entry 6

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: zyg17-48-2-HNMR
INOVA-500 "epoxide"

Relax. delay 1.000 sec
Pulse 49.6 degrees
Acq. time 1.998 sec
width 4500.5 Hz
4 repetitions
OBSERVE H1, 300.1592196 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 12 sec

Table 2, entry 7


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: ZYg17-48-2-CNMR
INOVA-500 "epoxide"
Pulse 55.7 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
368 repetitions
OBSERVE C13, 75.4750794 MHz
DECOUPLE H1, 300.1606800 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 30 min, 23 sec
137.183
134.592
130.507
129.673
126.779
122.026
79.639
78.603
77.655
77.230
76.809
220
200
180
160
140
120
100
80
60
40
20
0
ppm
Cl
Cl
Table 2, entry 7

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: zyg18-13-1-HNMR
INOVA-500 "epoxide"

Relax. delay 1.000 sec
Pulse 49.6 degrees
Acq. time 1.998 sec
Width 4500.5 Hz
4 repetitions
OBSERVE H1, 300.1592196 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 12 sec

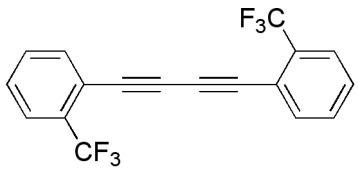
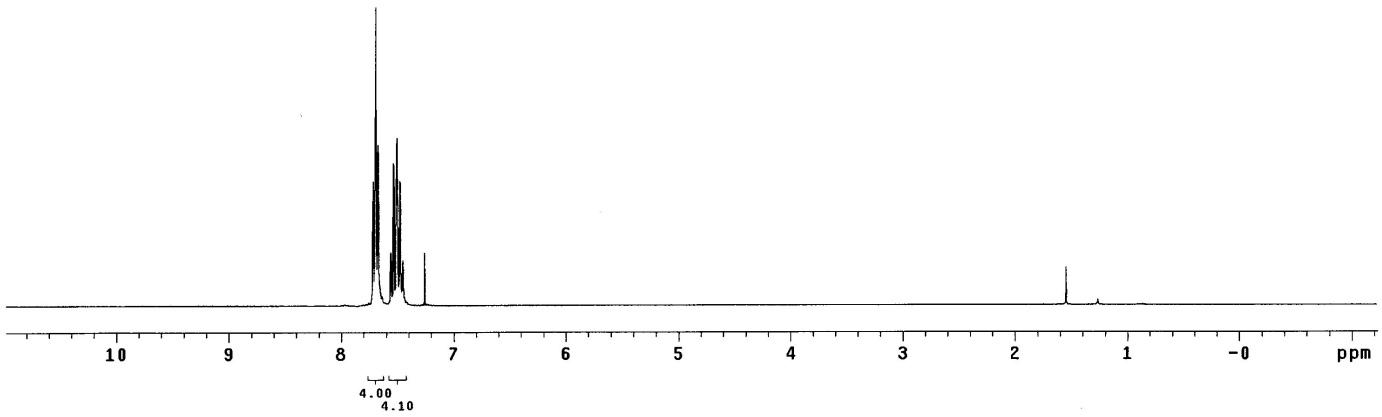


Table 2, entry 8



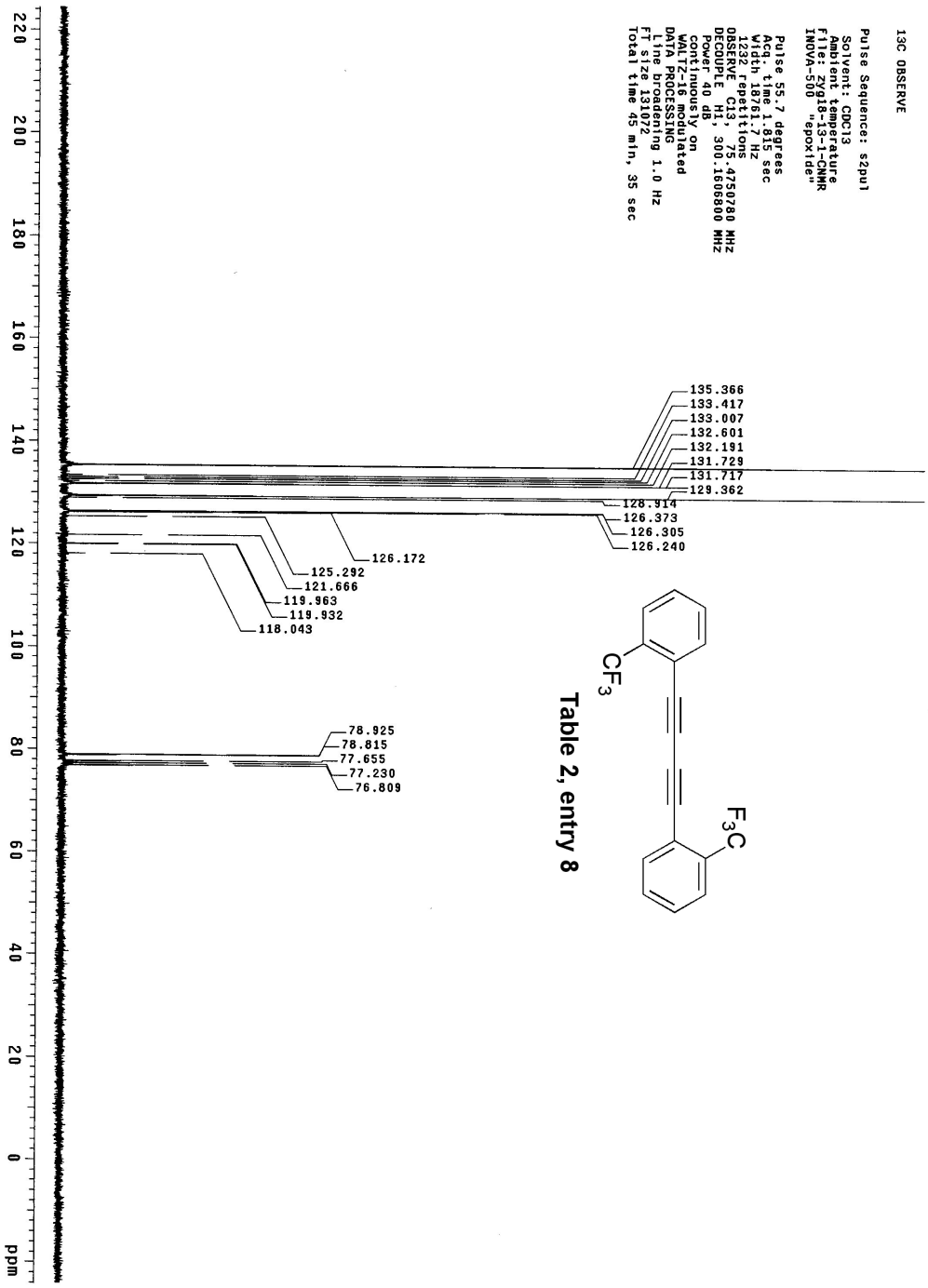


Table 2, entry 8

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
File: zyg17-26-product-HNMR
INOVA-500 "epoxide"

 Relax. delay 1.000 sec
 Pulse 49.6 degrees
 Acq. time 1.998 sec
 Width 4500.5 Hz
 10 repetitions
OBSERVE H1, 300.1592196 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 30 sec

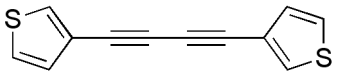
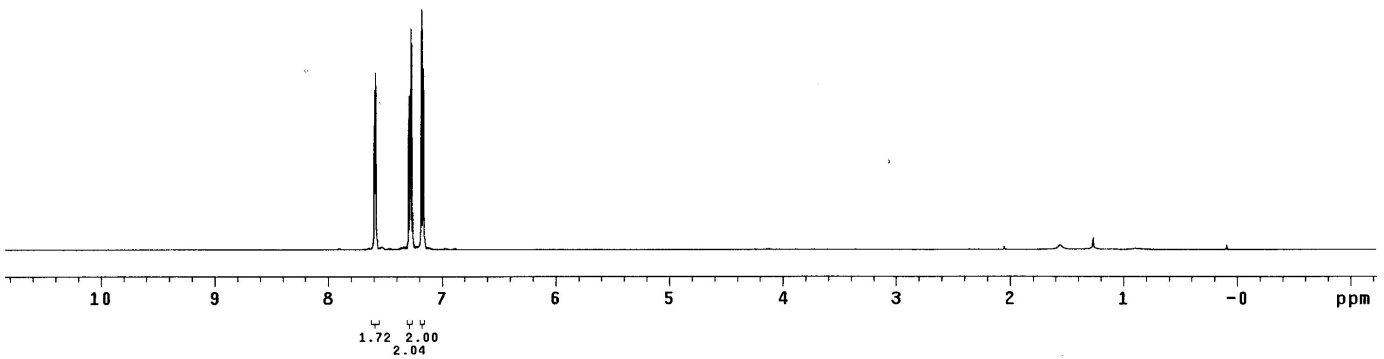


Table 2, entry 9



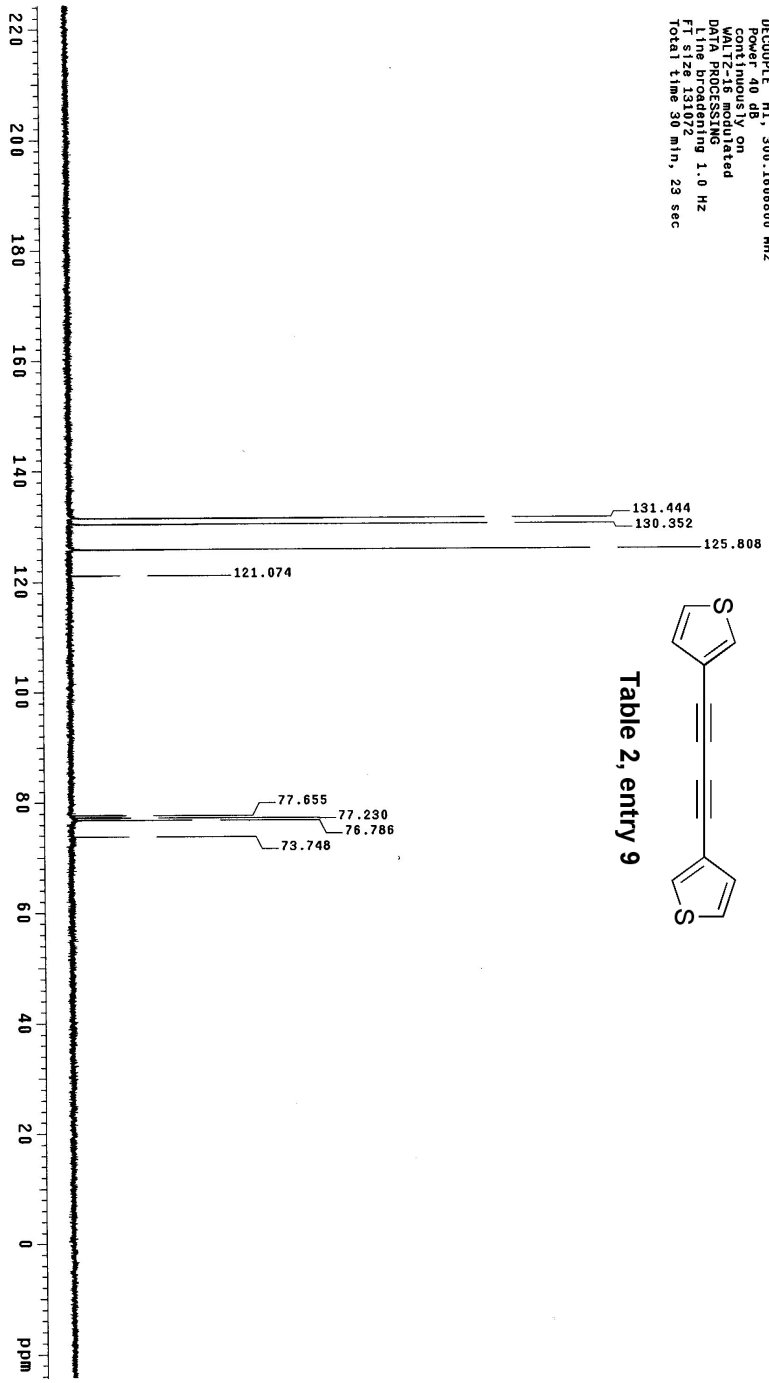
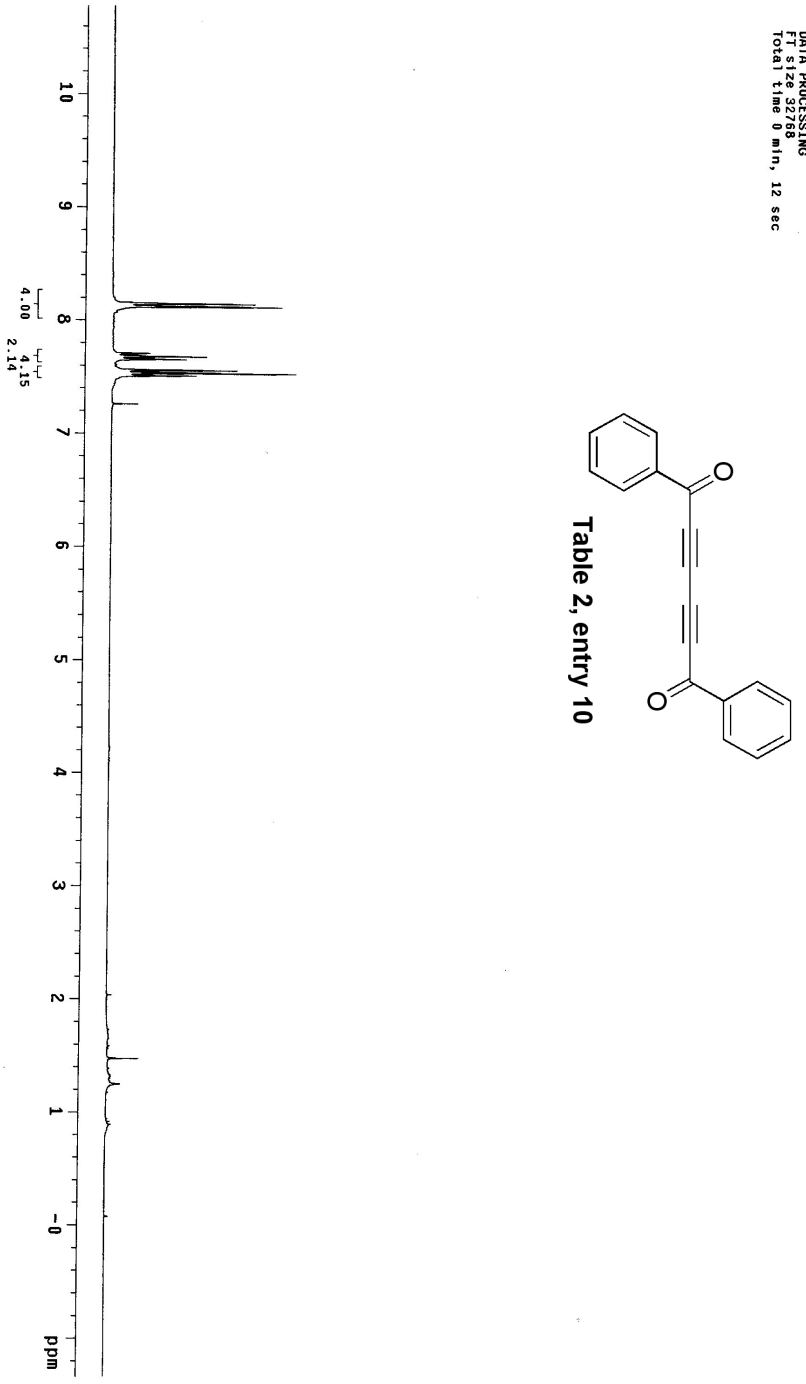


Table 2, entry 9



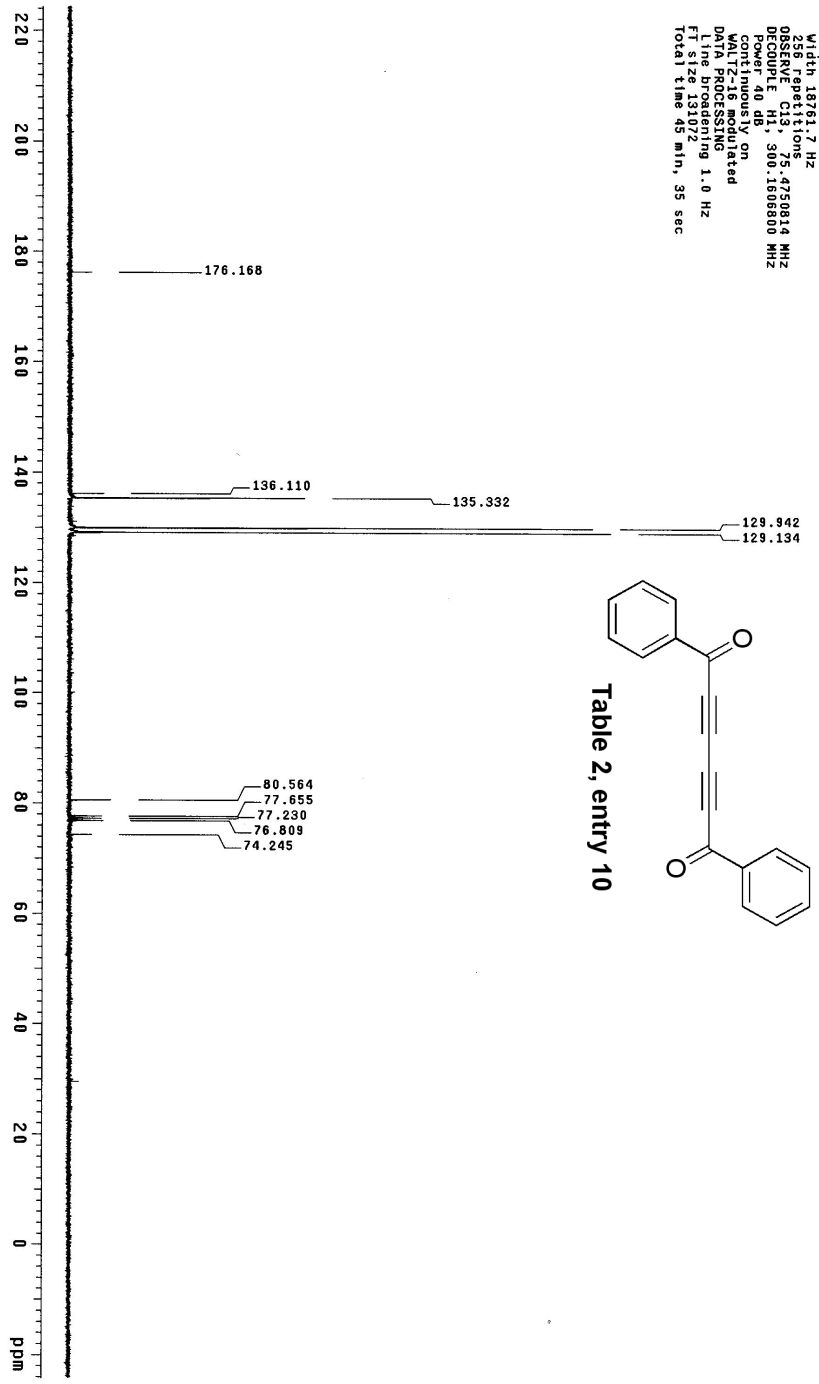
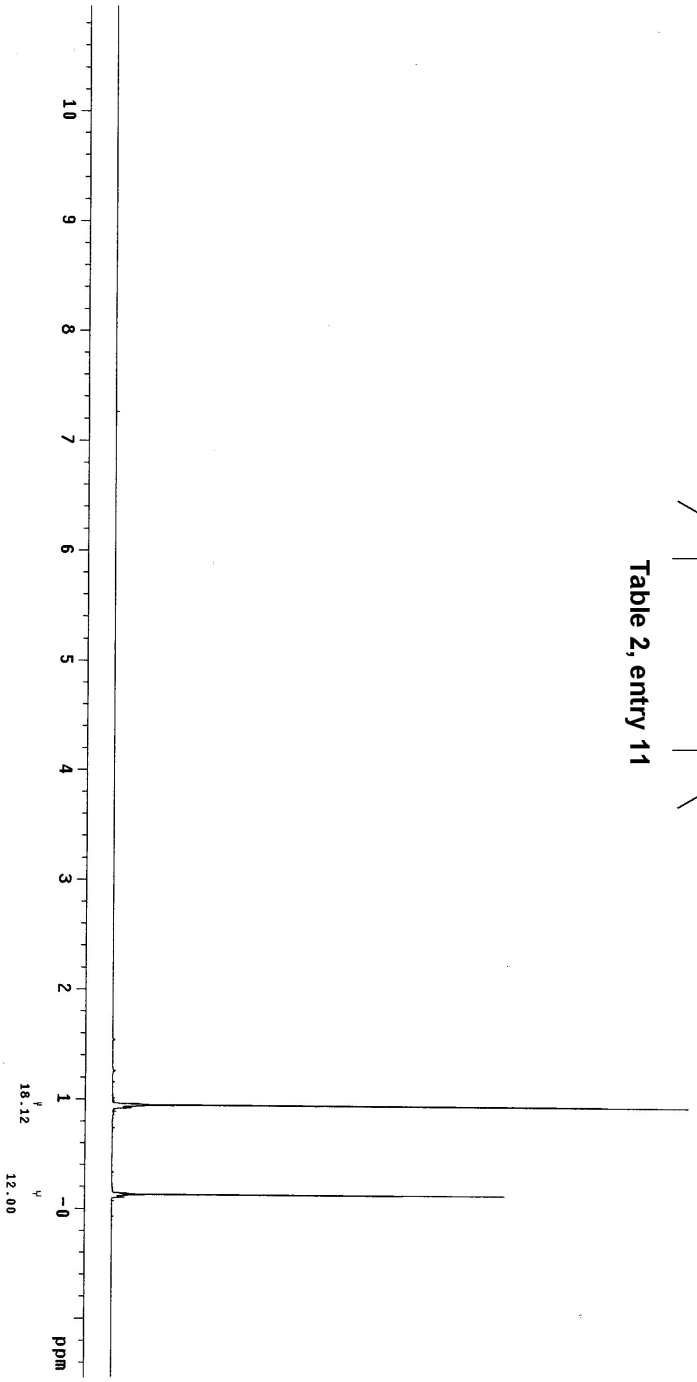
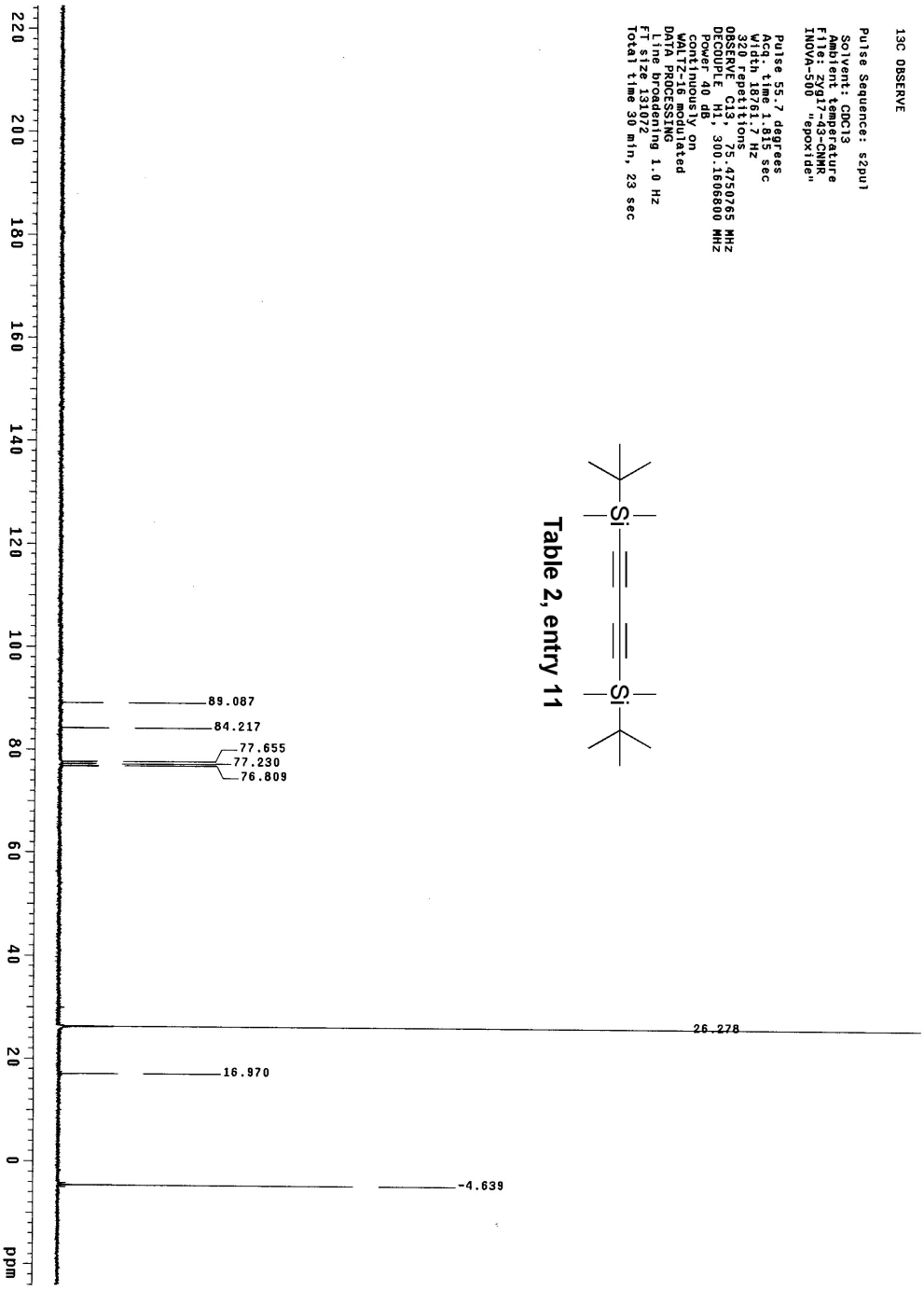


Table 2, entry 10




13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: zyq17-43-CNMR
INOVA-500 "epoxide"
Pulse 55.7 degrees
Acq. time 1.885 sec
Width 18761.7 Hz
320 repetitions
OBSERVE C13, 75.4750765 MHz
DECOUPLE H1, 300.1606800 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 30 min, 23 sec
Si
Si
Table 2, entry 11
89.087
84.217
77.655
77.230
76.809
26.278
16.970
-4.639
ppm

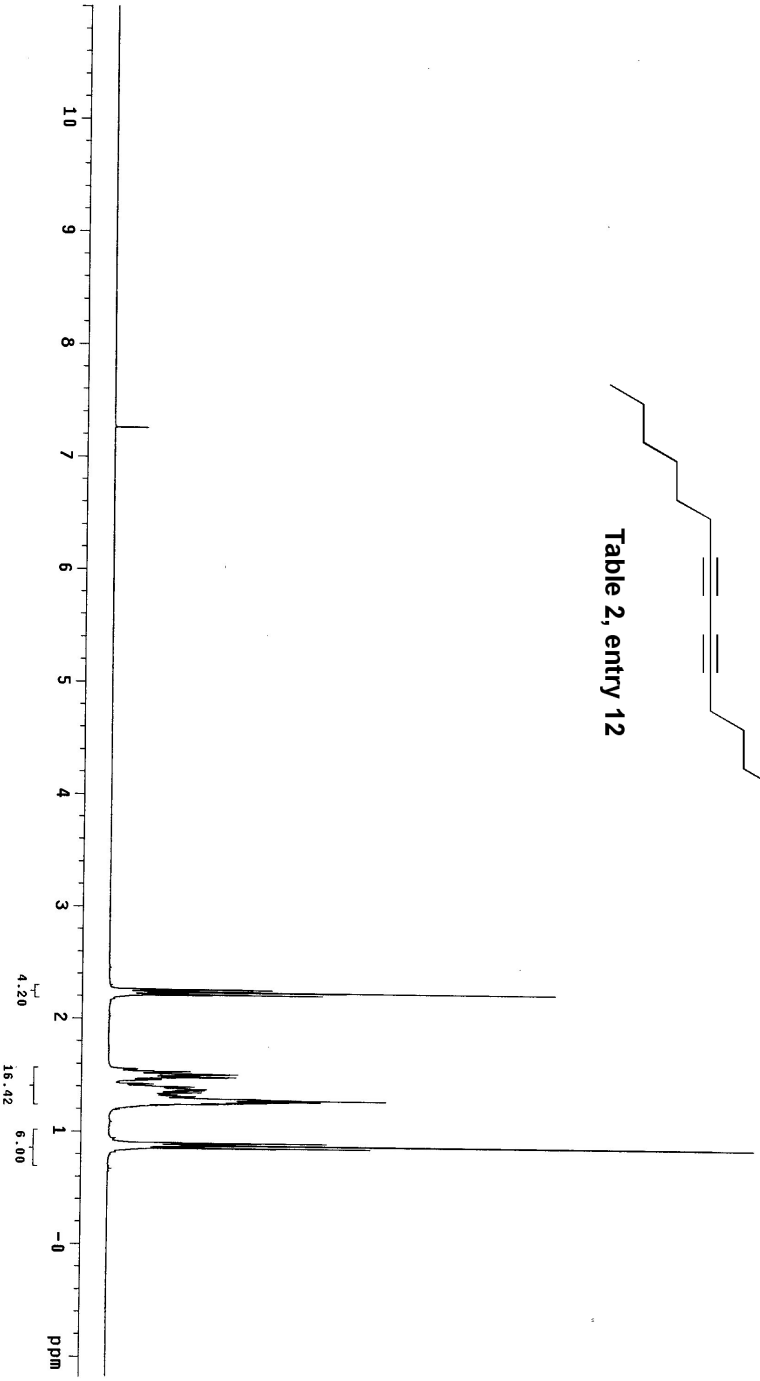
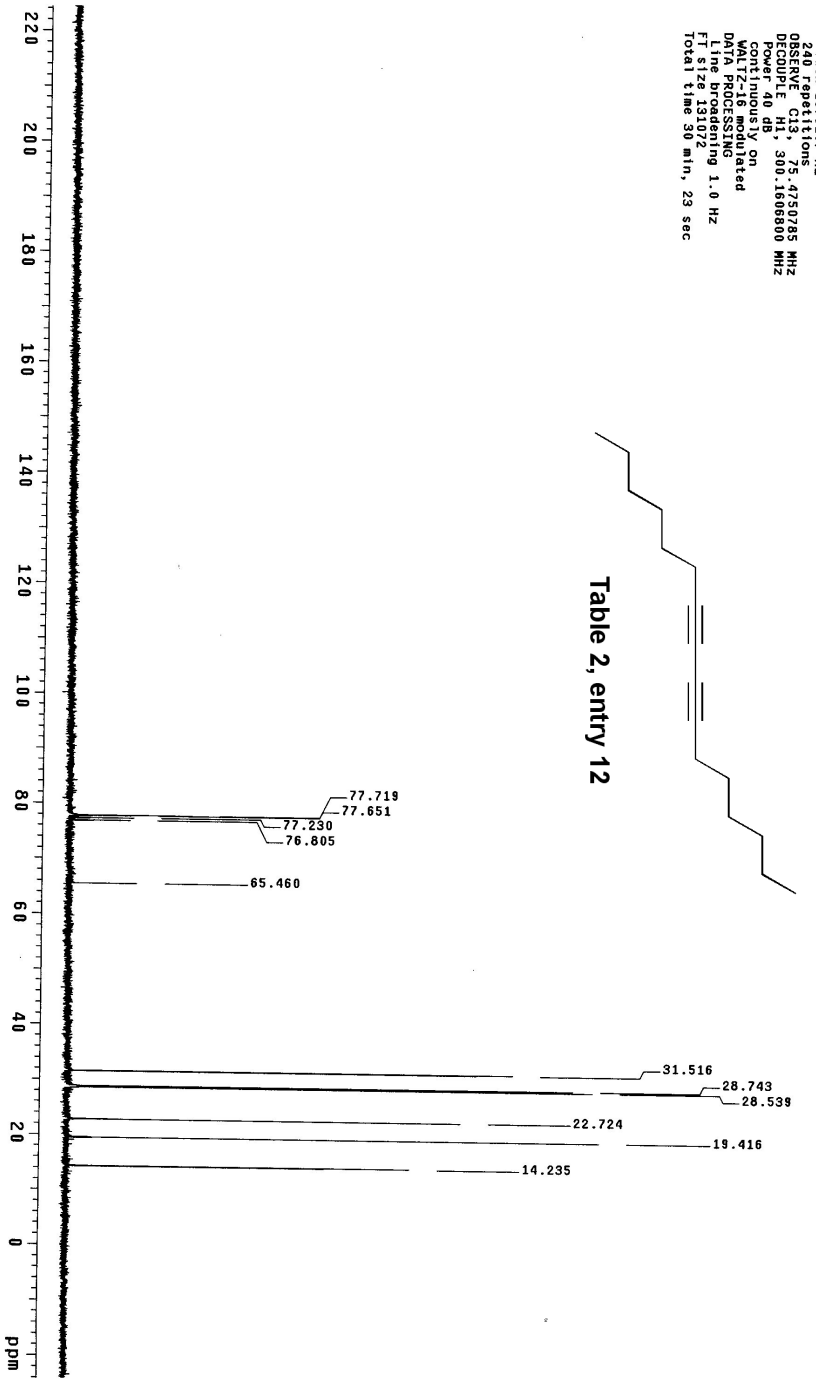
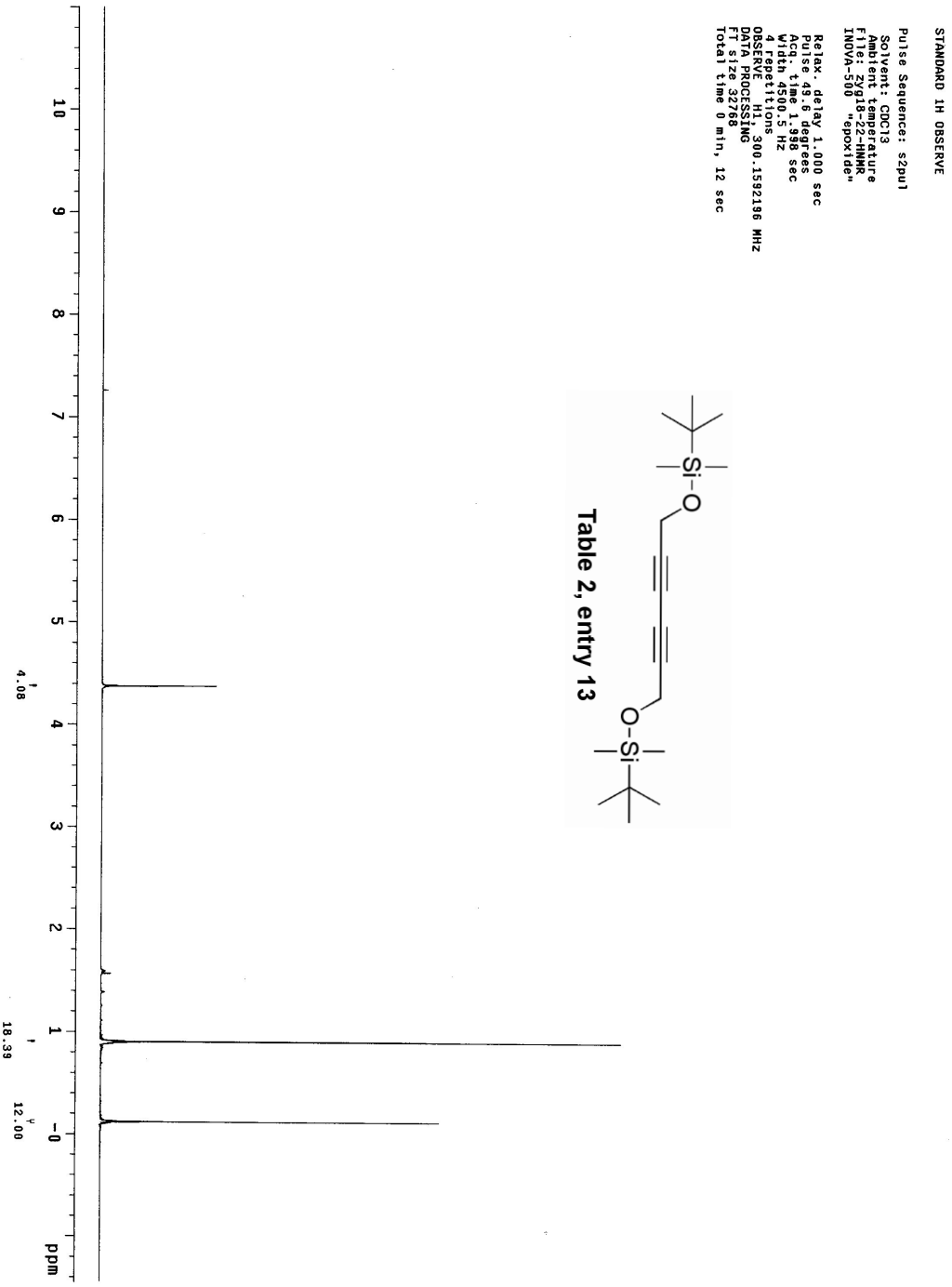
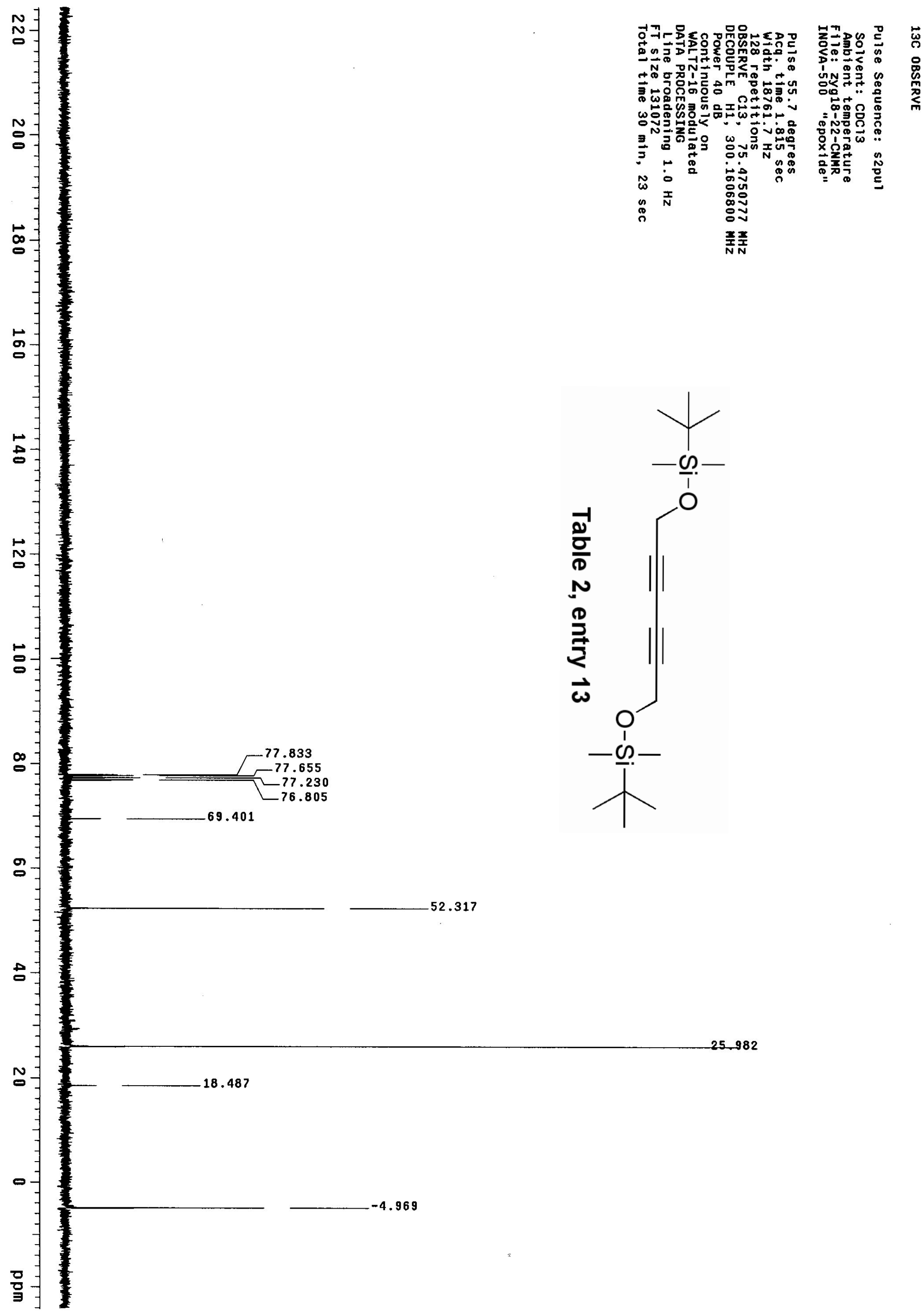


Table 2, entry 12


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: zyg18-2-product-CNMR
INOVA-500 "epoxide"
Pulse 55.7 degrees
Acq. time 1.615 sec
Width 18061.7 Hz
240 repetitions
OBSERVE C13, 75.4750785 MHz
DECOUPLE H1, 300.1606800 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 30 min, 23 sec
Table 2, entry 12
77.719
77.651
77.230
76.805
65.460
31.516
28.743
28.539
22.724
19.416
14.235
220
200
180
160
140
120
100
80
60
40
20
0
ppm




13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: zyg18-22-CNMR
INOVA-500 "epoxide"
Pulse 55.7 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
128 repetitions
OBSERVE C13, 75.4750777 MHz
DECOUPLE H1, 300.1606800 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 30 min, 23 sec
Table 2, entry 13
O-Si
Si-O
77.833
77.655
77.230
76.805
69.401
52.317
25.982
18.487
-4.969
220
200
180
160
140
120
100
80
60
40
20
0
ppm