Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A co-operative Ni-Cu system for C_{sp}-C_{sp} and C_{sp}-C_{sp2} cross-coupling providing a direct access to unsymmetrical 1,3-diynes and en-ynes

Nirmalya Mukherjee, Debasish Kundu and Brindaban C. Ranu*

Table of contents

Page No.

Experimental procedure

IR spectra were taken as KBr pellets for solids. NMR spectra were recorded at 300, 400 and 500 MHz for ^{1}H spectra and at 75, 100 and 125 MHz for ^{13}C spectra in $CDCl_3$ solutions. $Ni(acac)_2$, CuI and vinyl halides were procured commercially and all styrenyl and alkynyl halides were prepared following reported procedures.

Representative experimental procedure for the cross-coupling of 1-(2-bromoethynyl)benzene and 4-ethynylanisole to 1-Methoxy-4-(4-phenylbuta-1,3-diynyl)benzene (Scheme 2, 3aa): In a 10 mL round bottom flask a mixture of 1-(2-bromoethynyl)benzene (181 mg, 1 mmol), 4-ehthynylanisole (158 mg, 1.2 mmol), Cs_2CO_3 (650 mg, 2 mmol), $Ni(acac)_2$ (13 mg, 0.05 mmol), CuI (10 mg, 0.05 mmol) and NMP (3 mL) was heated at 100 ^{o}C under argon for 9 h (TLC). The reaction mixture was then allowed to cool and was extracted with diethyl ether (3 x 20 mL). The extract was washed with water (10 mL) and brine (10 mL). Then the organic phase was dried over Na_2SO_4 and evaporated to leave the crude product, which was purified by column chromatography over silica gel (hexane/diethyl ether 98:2) to provide the pure 1-methoxy-4-(4-phenylbuta-1,3-diynyl)benzene as a white solid (206 mg, 89%), Mp (^{o}C) = 88-90; IR (KBr): 2966, 2939, 2839, 2207, 1605, 1509, 1431 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 3H), 6.85 (d, J = 9 Hz, 2H), 7.33 (d, J = 6.3 Hz, 3H), 7.46-7.53 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.35, 72.87, 7431, 81.16, 81.96, 113.86 (2C), 114.29 (2C), 122.16, 128.54 (2C), 129.18, 132.60, 134.29 (2C), 160.52 ppm; HRMS: m/z calcd. for $C_{17}H_{12}O$: 233.0961 $[M+H]^{+}$; found: 233.0964.

This procedure was followed for all the reactions listed in Table 2, Table 3, and Scheme 2. All of the known compounds are characterized by their spectroscopic data (^{1}H NMR and ^{13}C NMR) and the data are consistent with those reported earlier. Similarly all of the unknown compounds are well characterized by their spectroscopic and spectrometric data (IR, ^{1}H NMR, ^{13}C NMR, HRMS and elemental analysis). All these data are provided bellow.

1-(4-(2-Trifluoromethyl)phenyl)buta-1,3-diynyl)benzene (Table 2, 3ae): White solid, Mp (^oC) = 91-93, IR (KBr): 3066, 3018, 2968, 2927, 2399, 2219, 1600, 1572, 1487, 1452, 1442, 1317, 1261, 1215 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.32-7.40 (m, 3H), 7.44-7.47 (m, 1H), 7.50-7.56 (m, 3H), 7.67- 7.72 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 73.7, 79.3, 81.7, 83.6, 121.6, 126.1, 128.6 (2C), 128.63, 128.9, 129.3, 129.6, 131.6, 132.6, 132.7, 135.2 ppm; anal. calcd. for $C_{17}H_9F_3$; C 75.55, H 3.36; found: C 75.59, H 3.38 %.

2,4-Dimethyl-1-(4-phenylbuta-1,3-diynyl)benzene (Table 2, 3ab): Off-white solid, Mp (^oC) = 82-84, IR (KBr): 2967, 2938, 2835, 2211, 1600 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.30 (s, 3H), 2.45 (s, 3H), 7.07-7.12 (m, 2H), 7.33-7.38 (m, 4H), 7.54 (d, J = 10 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.3, 20.8, 74.2, 77.4, 81.2, 81.8, 121.6, 122.0, 128.5, 129.2, 129.6, 130.2, 132.6, 133.4, 135.3, 138.7 ppm; anal. calcd. for $C_{18}H_{14}$: C 93.87, H 6.13; found: C 93.83, H 6.17 %.

1-(4-(4-*Tert*-butylphenyl)buta-1,3-diynyl)-4-pentylbenzene (Table 2, 3fh): White solid, Mp (^oC) = 91-93, IR (KBr): 2954,2926, 2856, 2216, 2144, 1726, 1600, 1500 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.88 (t, J = 7 Hz, 3H), 1.312 (s, 11H), 1.57-1.63 (m, 4H), 2.602 (t, J = 7.5 Hz, 2H), 7.14 (d, J = 8 Hz, 2H), 7.354 (d, J = 8 Hz, 2H), 7.394-7.470 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 22.6, 30.9, 31.2 (3C), 31.5, 35.0, 36.11, 73.62, 77.58 (2C), 81.7, 118.9, 119.1, 125.6 (2C), 128.7 (2C), 132.4 (2C), 132.5 (2C), 144.6, 152.7 ppm; HRMS: m/z calcd. for $C_{25}H_{28}$: 329.2269 $[M+H]^+$; found: 329.2266.

4-((2-(Trifluoromethyl)phenyl)buta-1,3-diynyl)biphenyl (Table 2, 3gi): White solid, Mp (^oC) = 88- 91; IR (KBr): 2920, 2851, 2214, 1319, 1263 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$); δ 7.37 (t, J = 7 Hz, 1H), 7.45 (t, J = 7.5 Hz, 3H), 7.52 (t, J = 7.5 Hz, 1H), 7.57-7.63 (m, 6H), 7.68 (t, J = 7 Hz, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 74.3, 77.5, 79.3, 83.6, 116.3, 120.4, 126.1 (d, J_{C-F} = 5.25 Hz, 1C), 127.2 (2C), 127.3 (2C), 128.0, 128.9, 129.0 (2C), 131.6, 132.8, 133.2 (2C), 135.2, 136.7, 140.1, 142.3 ppm; anal. calcd. for $C_{23}H_{13}F_3$: C 79.76, H 3.78; found: C 79.81, H 3.80 %.

1-((*E*)-Dec-1-en-3-ynyl)naphthalene (Table 3, 5ac): White solid, Mp (^oC) = 102-105; IR (KBr): 3056, 3041, 2954, 2926, 2856, 2210, 1589, 1510 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.89-0.94 (m, 3H), 1.32-1.38 (m, 4H), 1.44-1.50 (m, 2H), 1.58-1.64 (m, 2H), 2.40-2.43 (m, 2H), 6.21-6.25 (m, 1H), 7.42-7.48 (m, 1H), 7.49-7.54 (m, 2H), 7.60-7.62 (m, 1H), 7.66 (d, J = 16 Hz, 1H), 7.90-7.85 (m, 2H), 8.13 (d, J = 8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 19.8, 22.7, 28.8, 28.9, 31.5, 78.5, 80.1, 93.0, 111.8, 123.3, 123.7, 125.6, 126.0, 126.3, 128.6, 130.9, 133.8, 134.2, 137.1 ppm; anal. Calcd. for $C_{20}H_{22}$: C 91.55, H 8.45; found: C 91.59, H 8.41 %.

1-**((*E*)-4-(4-Methoxyphenyl)but-1-en-3-ynyl)naphthalene (Table 3, 5aa):** Yellow solid, Mp (^oC) = 107-111; IR (KBr): 3018, 2962, 2933, 2839, 2399, 2192, 1598, 1508 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 6.47 (d, J = 16 Hz, 1H), 6.90 (d, J = 8.4 Hz, 2H), 7.45-7.56 (m, 5H), 7.69 (d, J = 7.2 Hz, 1H), 7.80-7.88 (m, 3H), 8.19 (d, J = 8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 88.1, 91.8, 111.2, 114.2 (2C), 115.6, 123.4, 123.7, 125.7, 126.1, 126.4,

128.7, 128.9, 131.0, 132.2 (2C), 133.8, 134.0, 137.6, 159.8 ppm; anal. calcd. for $C_{21}H_{16}O$: C 88.70, H 5.67; found: C 88.72, H 5.70 %.

3-((*E*)-4-(Naphthalene-1-yl)but-3-en-1-ynyl)thiophene (Table 3, 5ag): Off white solid, Mp (^oC) = 115-118; IR (KBr): 3105, 3043, 2952, 2921, 2850, 1587 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.44 (d, *J* = 16 Hz, 1H), 7.20-7.21 (m, 1H), 7.30-7.32 (m, 1H), 7.45-7.57 (m, 4H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.82-7.89 (m, 3H), 8.17 (d, *J* = 8.4 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 86.8, 88.8, 110.8, 122.5, 123.5, 123.6, 125.5, 125.7, 126.1, 126.5, 126.6, 128.7, 129.1, 129.9, 131.0, 133.8, 133.9, 138.2 ppm; anal. calcd. for $C_{18}H_{12}S$: C 83.04, H 4.65; found: C 83.08, H 4.67 %.

1-Tert-butyl-4-(3-cyclohexylideneprop-1-ynyl)benzene (Table 3, 5bd): White solid, Mp (^oC) = 90-92; IR (KBr): 2950, 2927, 2854, 1512, 1500 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.30 (s, 9H), 1.59 (s, 6H), 2.21 (s, 2H), 2.48 (t, *J* = 5Hz, 2H), 5.41 (s, 1H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 10 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.5, 27.7, 28.4, 31.2 (2C), 31.8, 35.0, 36.2, 86.7, 91.5, 101.9, 121.2, 125.3 (2C), 131.16 (2C), 152.7, 156.0 ppm; anal. calcd. for $C_{19}H_{24}$: C 90.42, H 9.58; found: C 90.44, H 9.56 %.

1-((3*E*, 5*E*)-5-Benzylidenedec-3-en-1-ynyl)-4-methoxybenzene (Table 3, 5ca): Off white solid, Mp (^oC) = 101-102; IR (KBr): 3026, 2954, 2929, 2867, 2858, 2837, 2189, 1606, 1585, 1568, 1508 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.81-0.83 (m, 3H), 1.26-1.27 (m, 4H), 1.48-1.51 (m, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 3.7 (s, 3H), 5.84 (d, *J* = 16 Hz, 1H), 6.44 (s, 1H), 6.66 (d, *J* = 16 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 2H), 7.13-7.16 (m, 1H), 7.19- 7.21 (m, 2H), 7.24-7.31 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.5, 27.1, 28.9, 32.3, 55.3, 88.3, 92.2, 107.4, 114.1 (2C), 115.9, 127.1, 128.4 (2C), 129.0 (2C), 132.9, 133.0, 137.4 (2C), 140.5, 145.3, 159.6 ppm; anal. calcd. for $C_{24}H_{26}O$: C 87.23, H 7.93; found: C 87.25, H 7.96 %.

(*E*)-1,6-Bis(4-methoxyphenyl)hexa-1-en-3,5-diyne (Scheme 2, 7aa): White solid, Mp (^oC) = 119-121; IR (KBr): 3018, 2977, 2873, 2399, 1247, 1215 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.82 (s, 6H), 6.11 (d, *J* = 16.5 Hz, 1H), 6.84-6.87 (m, 4H), 7.05 (d, *J* = 16 Hz, 1H), 7.34 (d, *J* = 10 Hz, 2H), 7.43-7.45 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4 (2C), 73.3, 75.7, 81.4, 82.2, 104.5, 114.1, 114.2 (2C), 114.4 (2C), 128 (2C), 128.9, 134.1 (2C), 143.9, 160.4 (2C) ppm; HRMS: m/z calcd. for $C_{20}H_{16}O_2$: 289.1223 $[M+H]^+$; found: 289.1250.

1-((*E*)-6-(4-Chlorophenyl)hexa-5-en-1,3-diynyl)-2-methoxybenzene (Scheme 2, 7bj): Yellow solid, Mp (^oC) = 121-122; IR (KBr): 3068, 3018, 2978, 2935, 2873, 2401, 1215 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.92 (s, 3H), 6.26 (d, *J* = 16 Hz, 1H), 6.90-6.95 (m, 2H), 7.06 (d, *J* = 16.5 Hz, 1H), 7.32-7.37 (m, 5H), 7.48 (d, *J* = 5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.9, 77.4, 77.9, 79.3, 81.6, 107.8, 110.8, 111.2, 116.3, 120.7, 127.7 (2C), 129.2 (2C), 130.8, 134.5, 135.0, 142.8, 161.5 ppm; anal. calcd. for $C_{19}H_{13}ClO$: C 77.9, H 4.48; found: C 77.5, H 4.54 %.

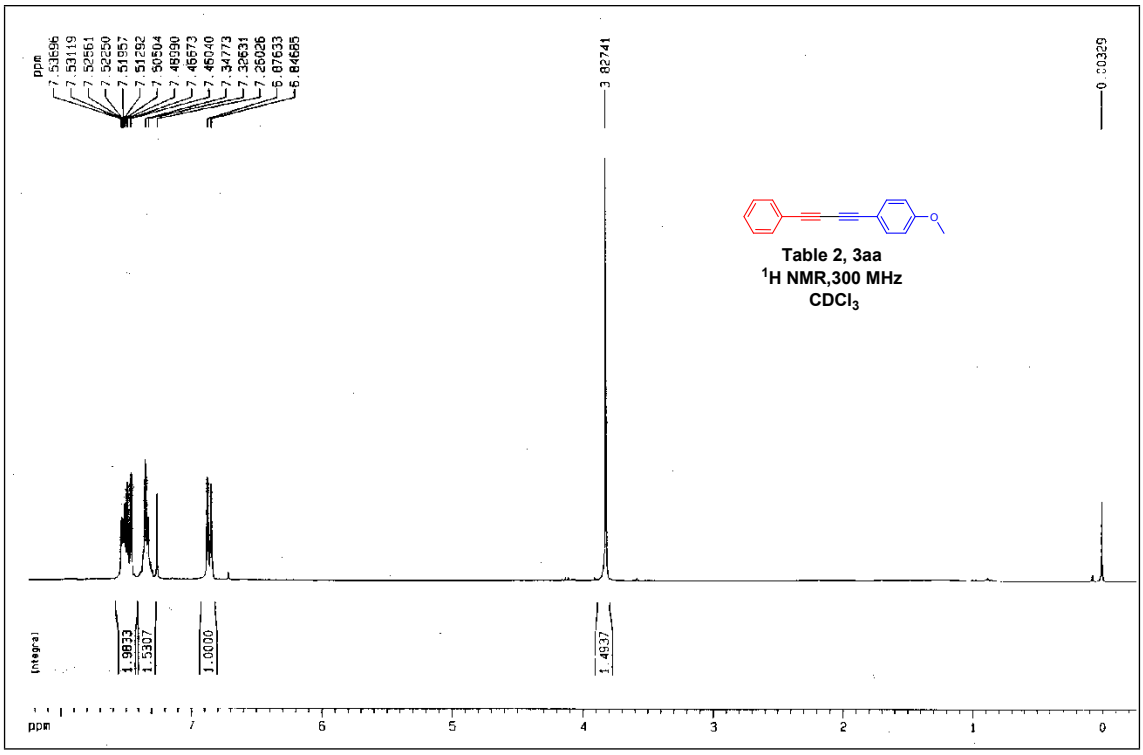


Table 2, 3aa
^{1}H NMR,300 MHz
$CDCl_3$

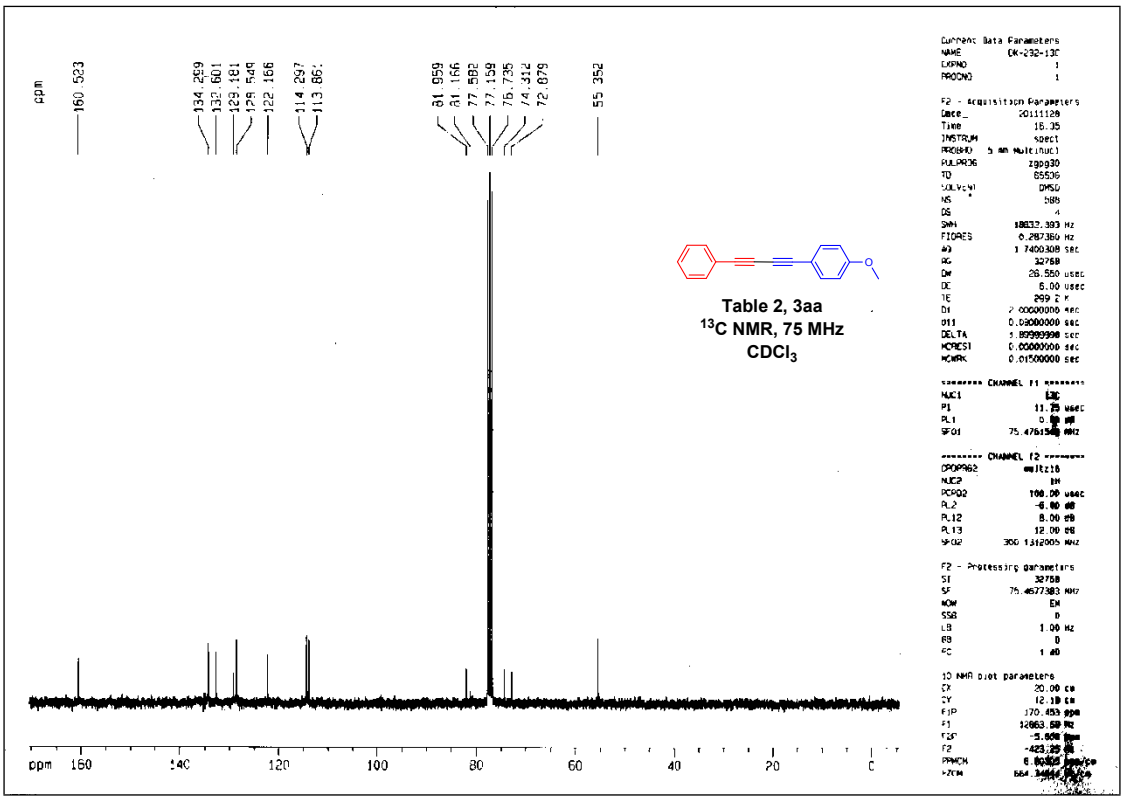
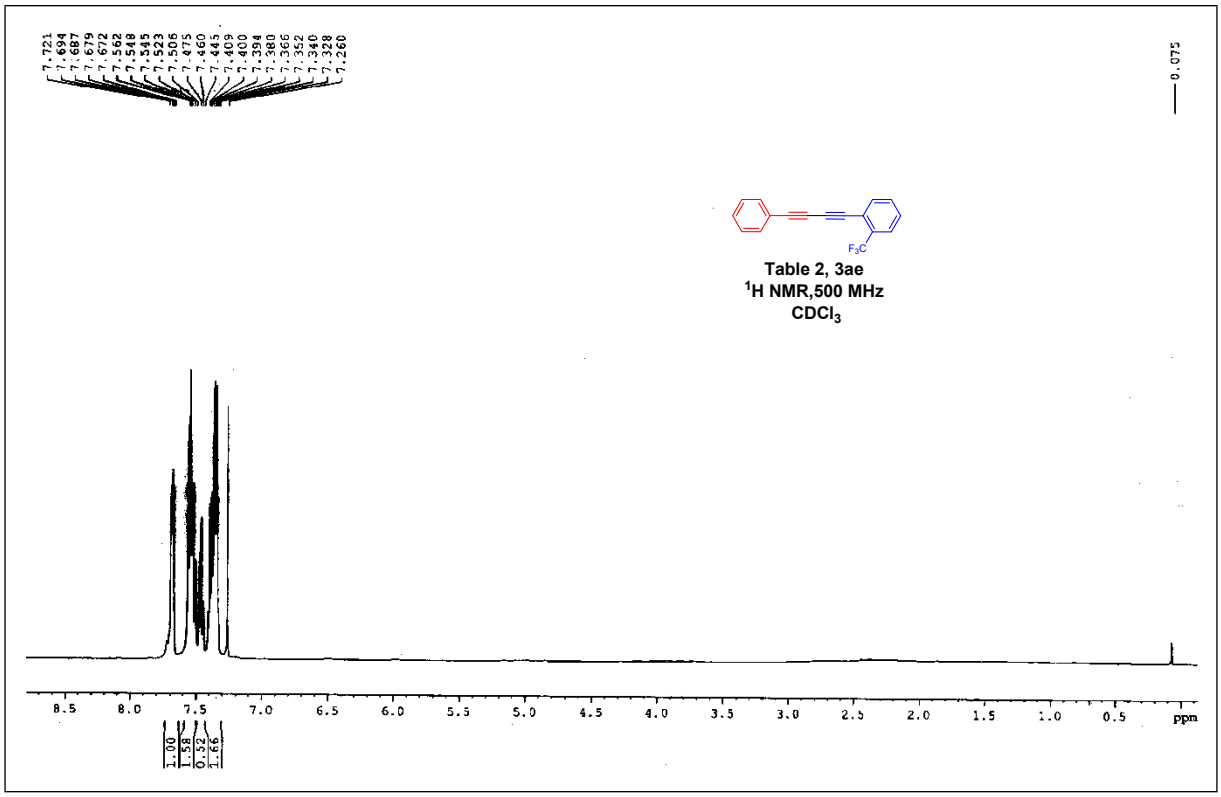
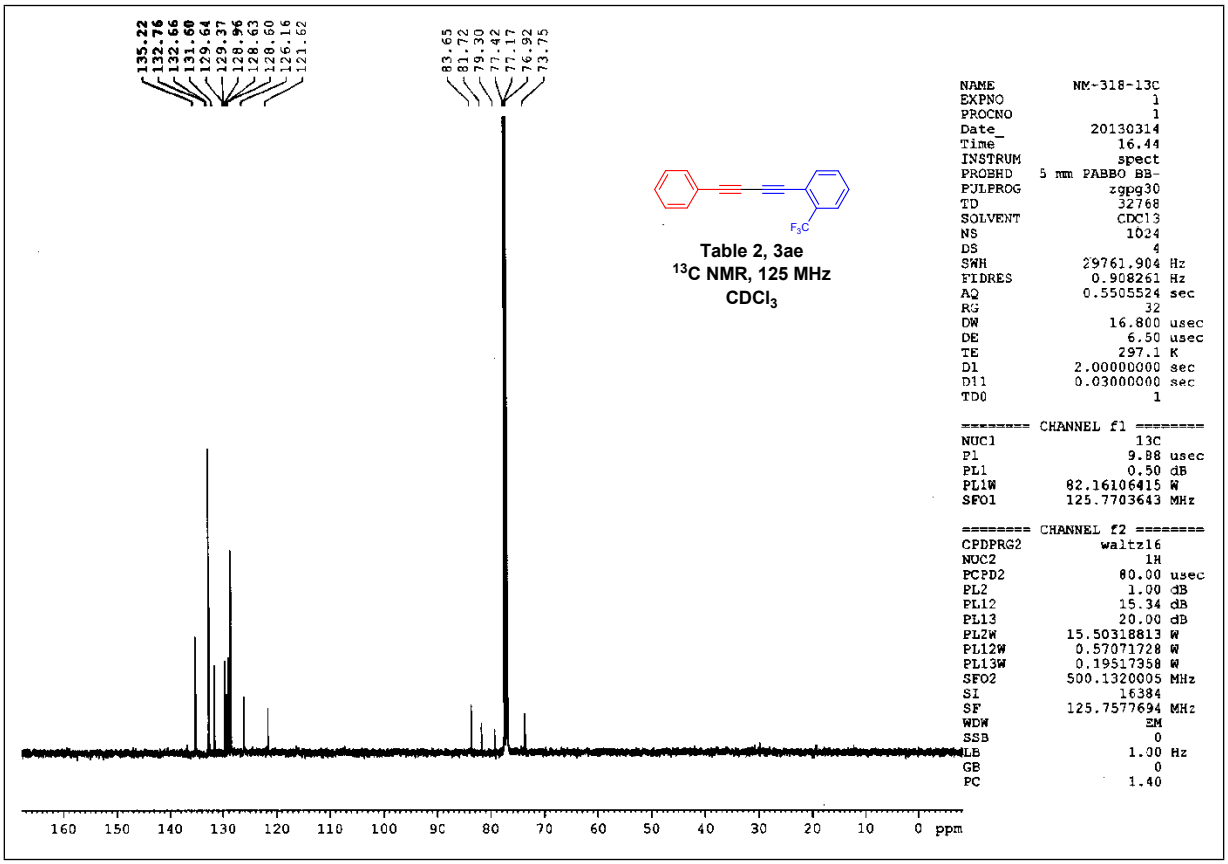
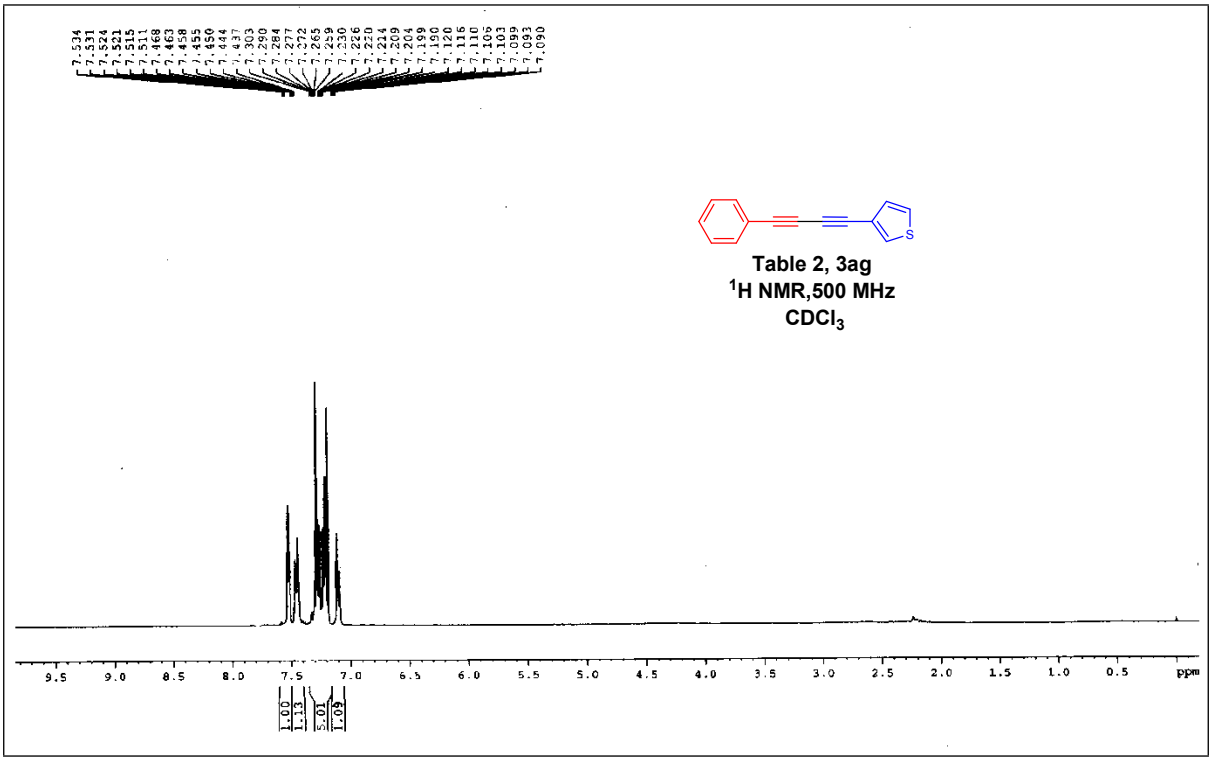
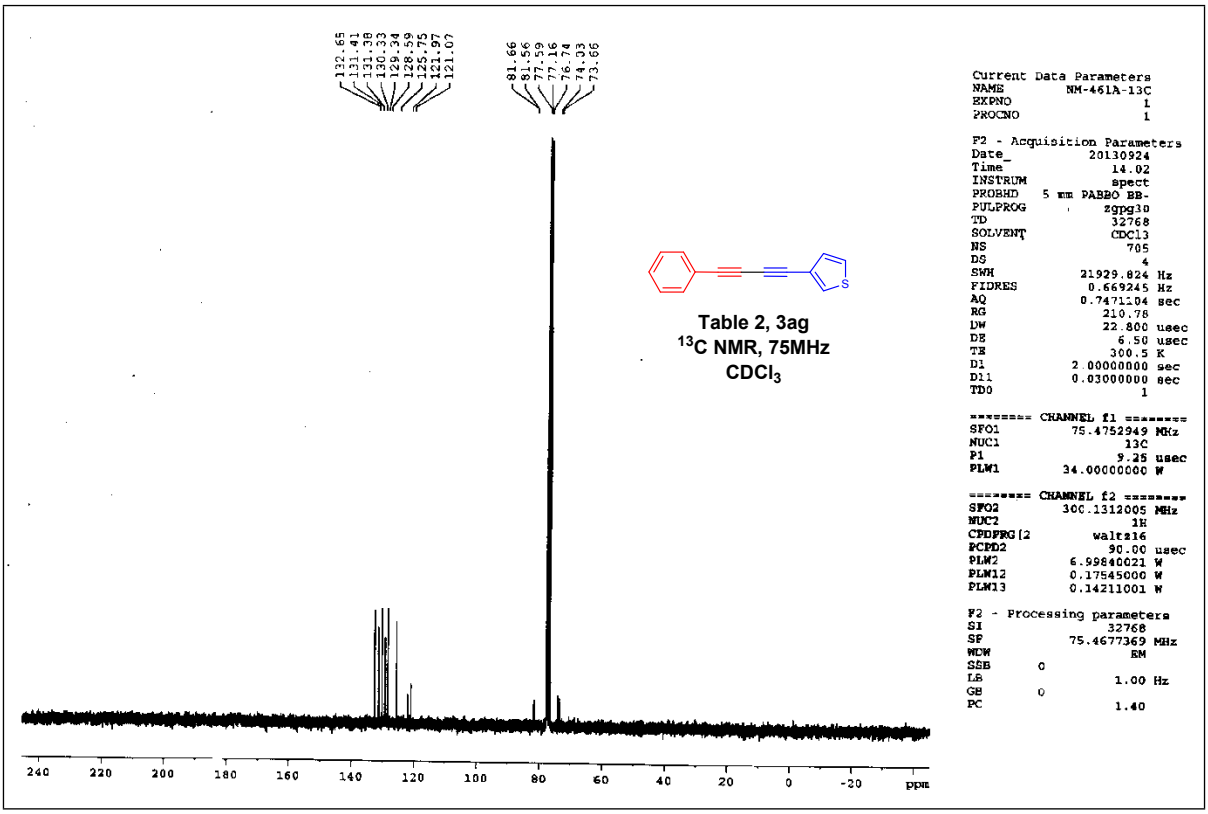


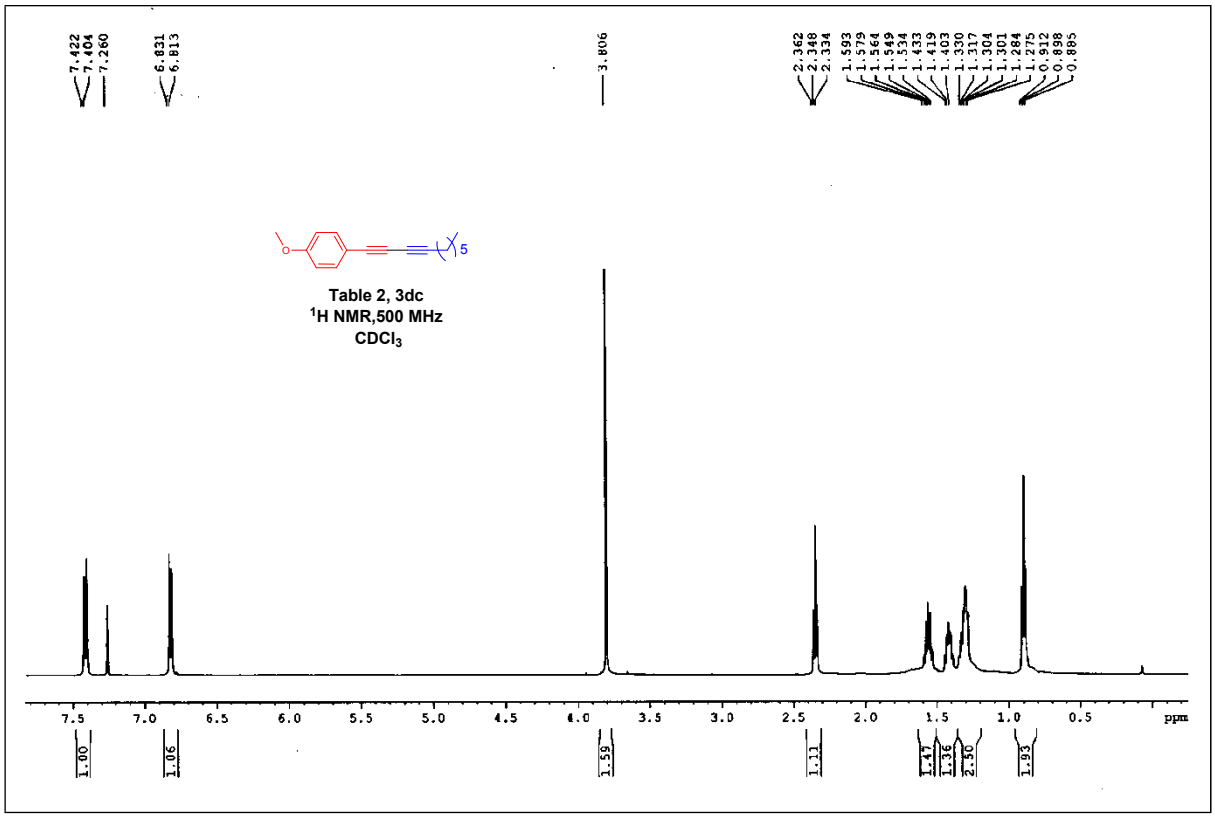
Table 2, 3aa
^{13}C NMR, 75 MHz
$CDCl_3$

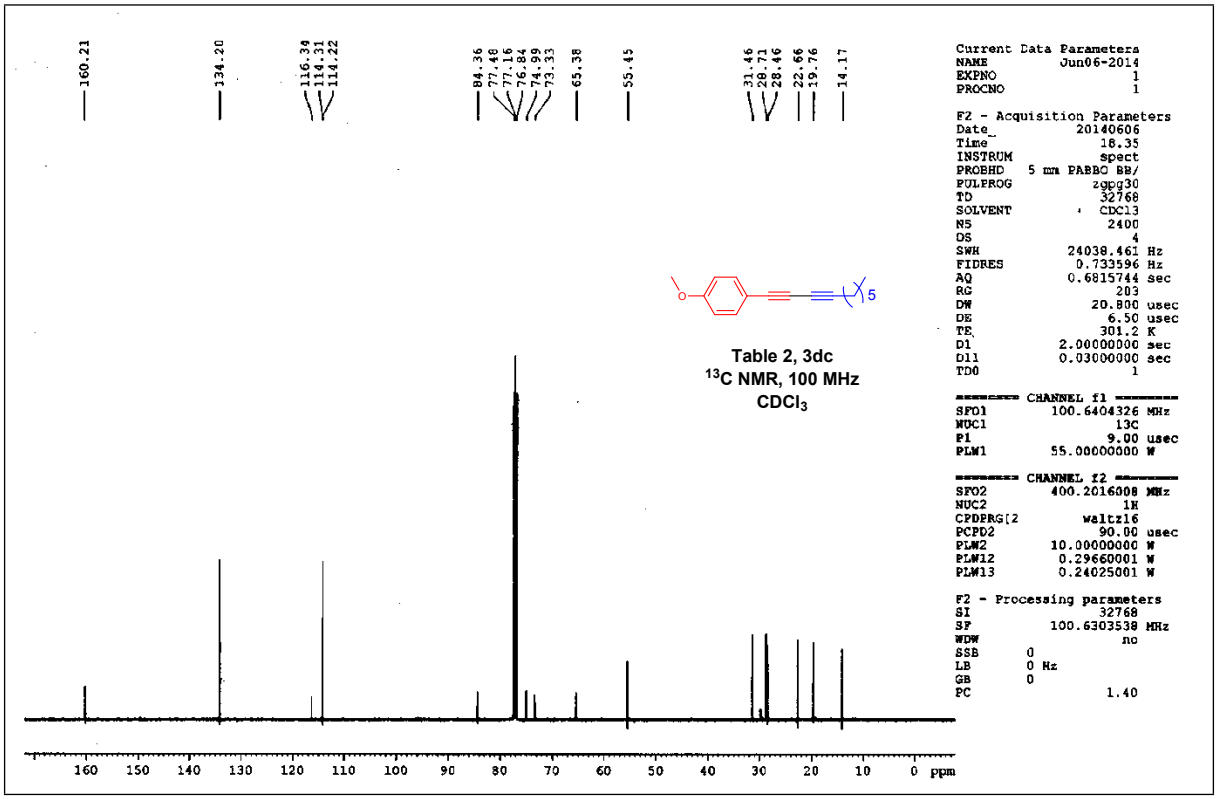

7.721
7.694
7.687
7.679
7.672
7.562
7.548
7.545
7.523
7.506
7.475
7.460
7.445
7.409
7.400
7.394
7.380
7.366
7.352
7.340
7.328
7.260
0.075
F3C
Table 2, 3ae
1H NMR,500 MHz
CDCl3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.58
0.52
0.22
1.16

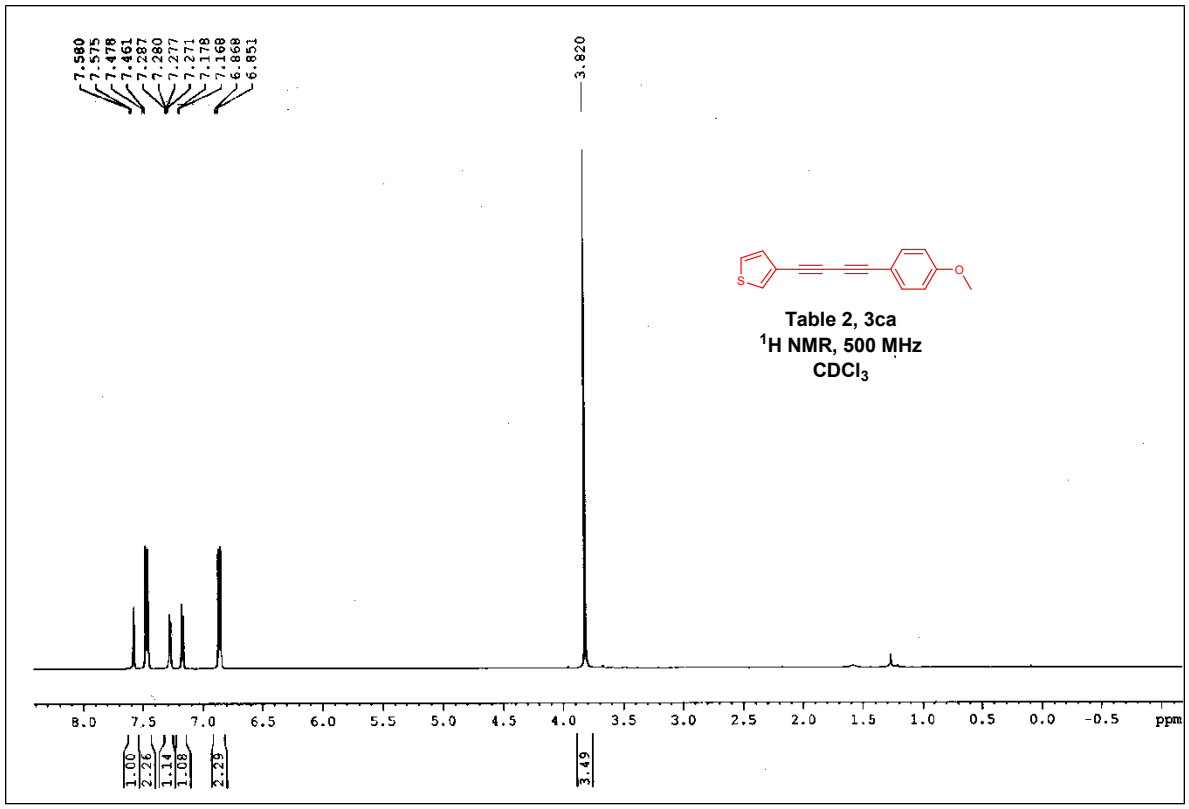

135.22
132.76
132.66
131.60
129.64
129.37
128.96
128.63
128.60
126.16
121.62
83.65
81.72
79.30
77.42
77.17
76.92
73.75
F3C
Table 2, 3ae
13C NMR, 125 MHz
CDCl3
NAME NM-318-13C
EXPNO 1
PROCNO 1
Date_ 20130314
Time 16.44
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 0.5505524 sec
RG 32
DW 16.800 usec
DE 6.50 usec
TE 297.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.88 usec
PL1 0.50 dB
PL1W 82.16106415 W
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 15.34 dB
PL13 20.00 dB
PL2W 15.50318813 W
PL12W 0.57071728 W
PL13W 0.19517358 W
SFO2 500.1320005 MHz
SI 16384
SF 125.7577694 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

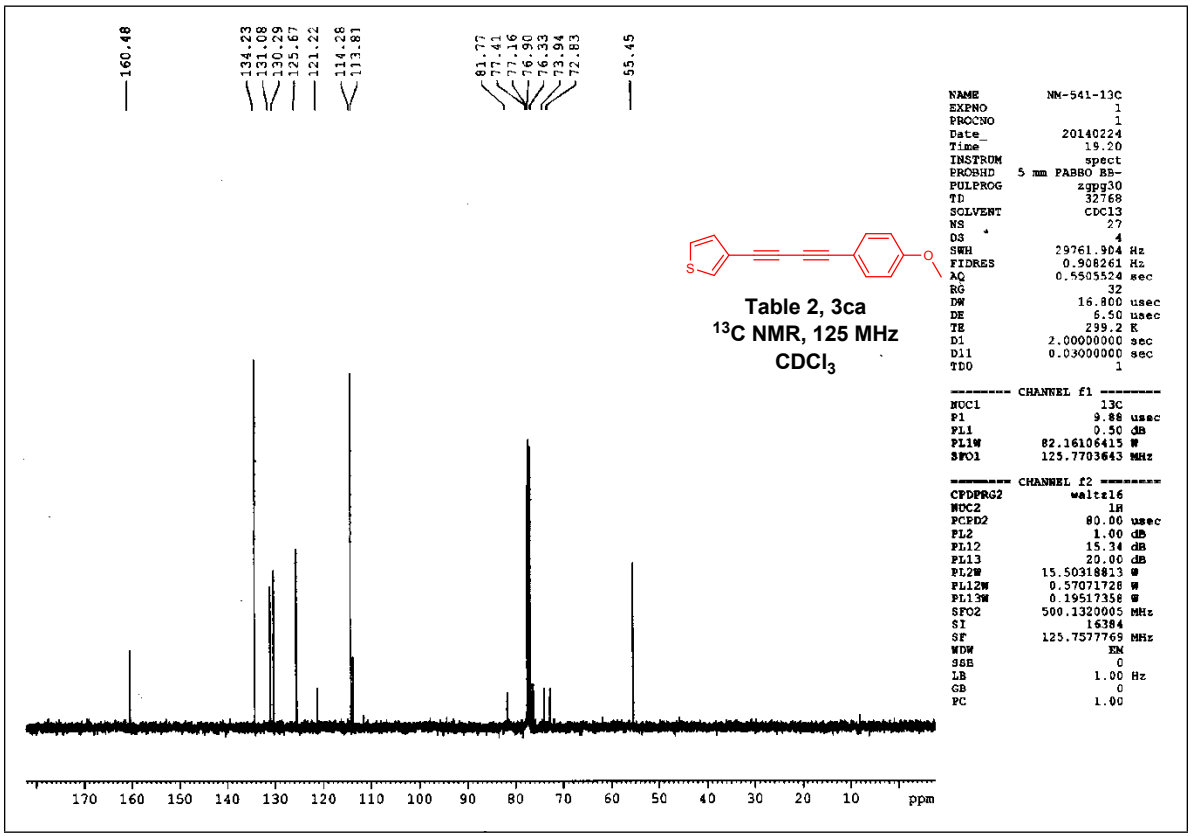

7.534
7.531
7.524
7.521
7.515
7.511
7.468
7.463
7.458
7.455
7.450
7.444
7.437
7.303
7.290
7.284
7.277
7.272
7.265
7.259
7.230
7.226
7.220
7.214
7.209
7.204
7.199
7.150
7.120
7.116
7.110
7.106
7.103
7.099
7.093
7.090
S
Table 2, 3ag
1H NMR,500 MHz
CDCl3
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.13
5.01
1.09

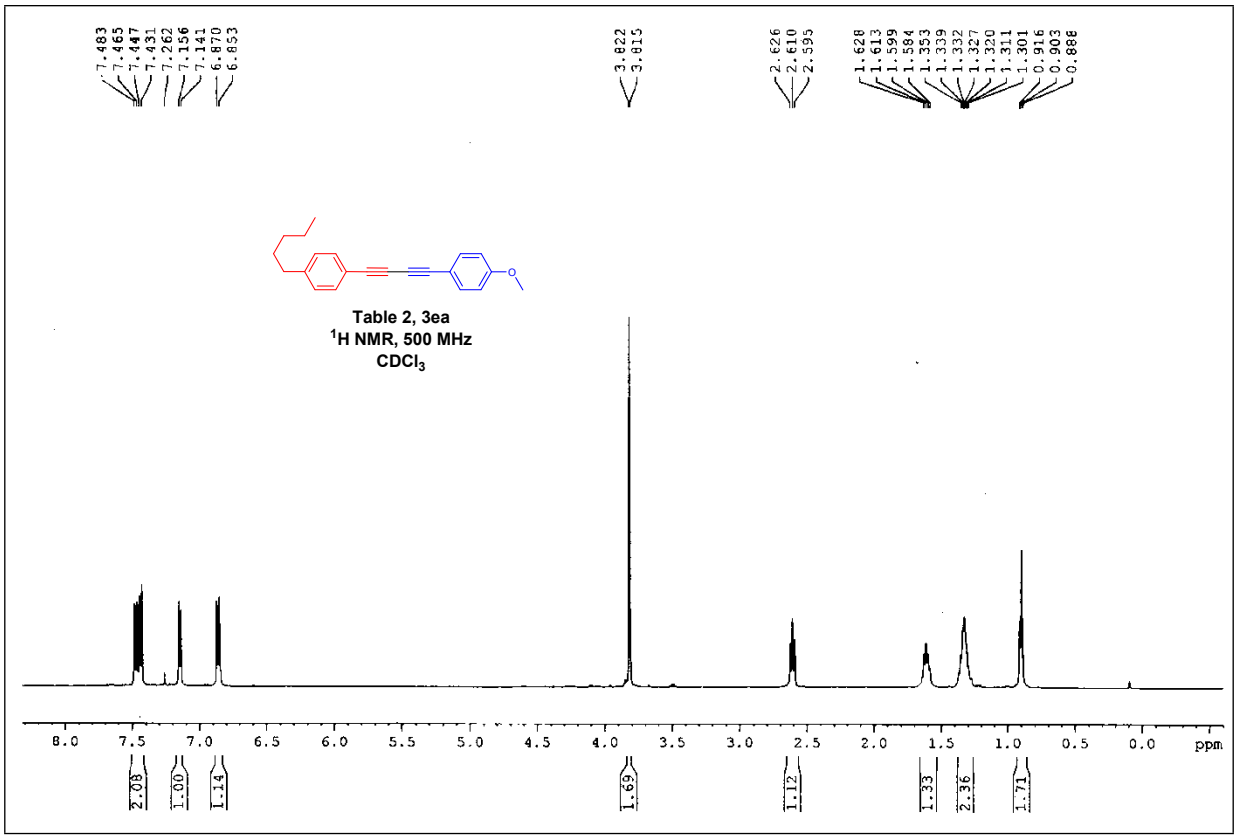

132.65
131.41
131.38
130.33
129.34
128.59
125.75
121.97
121.07
81.66
81.56
77.59
77.16
76.74
74.33
73.66
S
Table 2, 3ag
13C NMR, 75MHz
CDCl3
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm
Current Data Parameters
NAME NM-461A-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130924
Time 14.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 705
DS 4
SWH 21929.824 Hz
FIDRES 0.669245 Hz
AQ 0.7471104 sec
RG 210.78
DW 22.800 usec
DE 6.50 usec
TE 300.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 75.4752949 MHz
NUC1 13C
P1 9.25 usec
PLW1 34.00000000 W
======== CHANNEL f2 ========
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 6.99840021 W
PLW12 0.17545000 W
PLW13 0.14211001 W
F2 - Processing parameters
SI 32768
SF 75.4677369 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

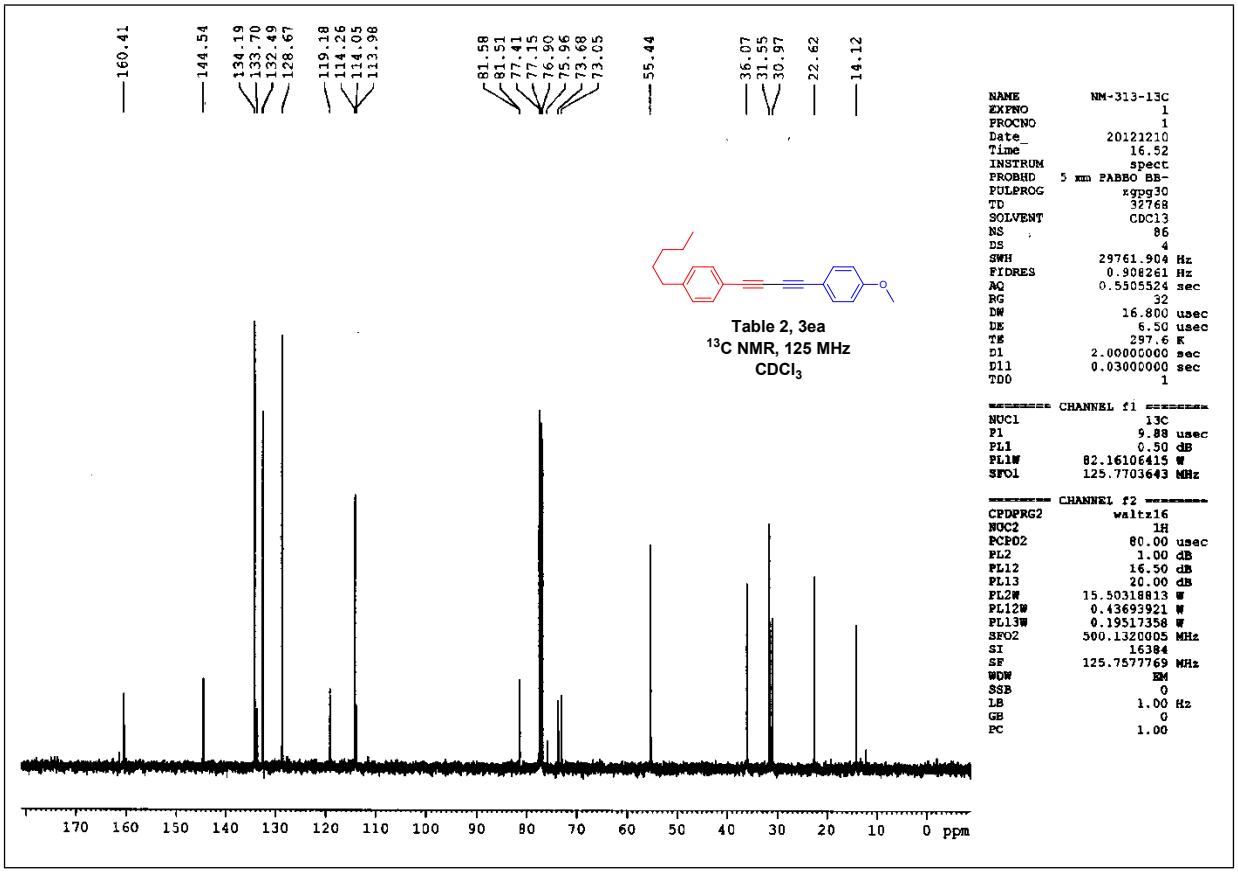

7.422
7.404
7.260
6.831
6.813
3.806
2.362
2.348
2.334
1.593
1.579
1.564
1.549
1.534
1.433
1.419
1.403
1.330
1.317
1.304
1.301
1.284
1.275
0.912
0.898
0.885
Table 2, 3dc
1H NMR,500 MHz
CDCl3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.06
1.59
1.11
1.47
1.36
2.50
1.93

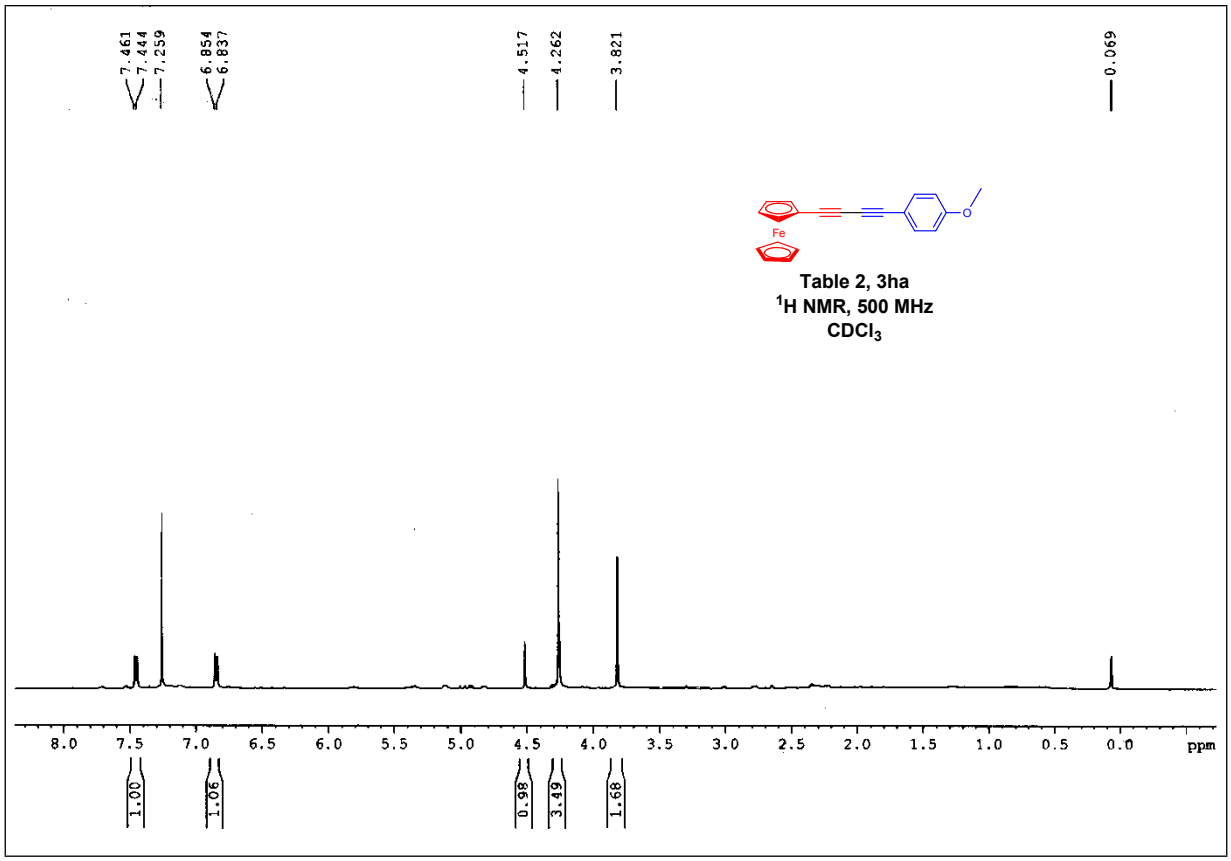

160.21
134.20
116.34
114.31
114.22
84.36
77.48
77.16
76.84
74.99
73.33
65.38
55.45
31.46
28.71
28.46
22.66
19.76
14.17
Table 2, 3dc
13C NMR, 100 MHz
CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Current Data Parameters
NAME Jun06-2014
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140606
Time 18.35
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 2400
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 301.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
SFO1 100.6404326 MHz
NUC1 13C
P1 9.00 usec
PLW1 55.00000000 W
CHANNEL f2
SFO2 400.2016008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 10.00000000 W
PLW12 0.29660001 W
PLW13 0.24025001 W
F2 - Processing parameters
SI 32768
SF 100.6303538 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.40

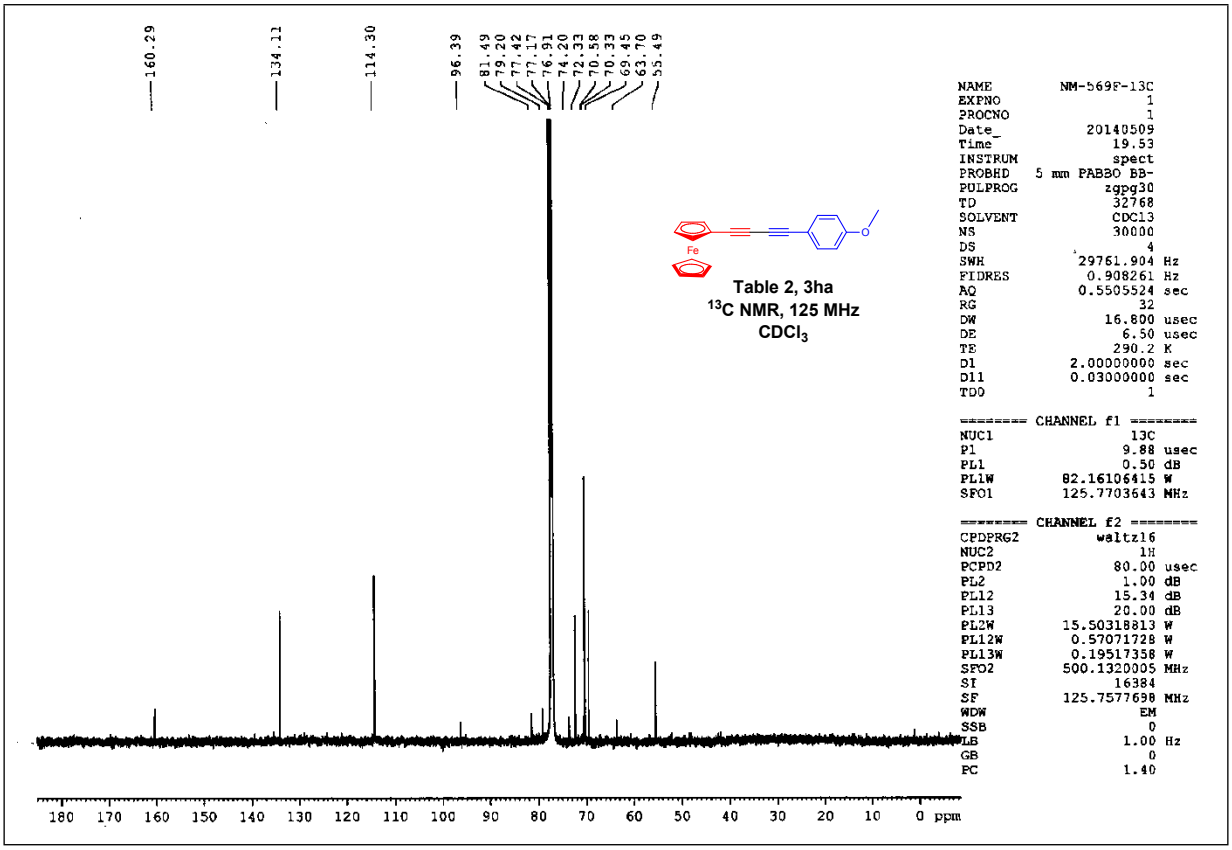

7.580
7.575
7.478
7.461
7.287
7.280
7.277
7.271
7.178
7.168
6.868
6.851
3.820
Table 2, 3ca
^{1}H NMR, 500 MHz
$CDCl_3$
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.00
2.26
1.14
1.08
2.29
3.49


160.48
134.23
131.08
130.29
125.67
121.22
114.28
113.81
81.77
77.41
77.16
76.90
76.33
73.94
72.83
55.45
Table 2, 3ca
^{13}C NMR, 125 MHz
$CDCl_3$
NAME NM-541-13C
EXPNO 1
PROCNO 1
Date_ 20140224
Time 19.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 27
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 0.5505524 sec
RG 32
DW 16.800 usec
DE 6.50 usec
TE 239.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 9.88 usec
PL1 0.50 dB
PL1W 82.16106415 W
SFO1 125.7703643 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 15.34 dB
PL13 20.00 dB
PL2W 15.50318813 W
PL12W 0.57071728 W
PL13W 0.19517358 W
SFO2 500.1320005 MHz
SI 16384
SF 125.7577769 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.483
7.465
7.447
7.431
7.262
7.156
7.141
6.870
6.853
3.822
3.815
2.626
2.610
2.595
1.628
1.613
1.599
1.584
1.353
1.339
1.332
1.327
1.320
1.311
1.301
0.916
0.903
0.888
Table 2, 3ea
1H NMR, 500 MHz
CDCl3
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
ppm
2.08
1.00
1.14
1.69
1.12
1.33
2.36
1.71


160.41
144.54
134.19
133.70
132.49
128.67
119.18
114.26
114.05
113.98
81.58
81.51
77.41
77.15
76.90
75.96
73.68
73.05
55.44
36.07
31.55
30.97
22.62
14.12
Table 2, 3ea
13C NMR, 125 MHz
CDCl3
NAME NM-313-13C
EXPNO 1
PROCNO 1
Date_ 20121210
Time 16.52
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 86
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 0.5505524 sec
RG 32
DW 16.800 usec
DE 6.50 usec
TE 297.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 9.88 usec
PL1 0.50 dB
PL1W 82.16106415 W
SFO1 125.7703643 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.50 dB
PL13 20.00 dB
PL2W 15.50318813 W
PL12W 0.43693921 W
PL13W 0.19517358 W
SFO2 500.1320005 MHz
SI 16384
SF 125.7577769 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


7.461
7.444
7.259
6.854
6.837
4.517
4.262
3.821
0.069
Fe
O
Table 2, 3ha
^{1}H NMR, 500 MHz
$CDCl_3$
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
ppm
1.00
1.06
0.98
3.49
1.68


160.29
134.11
114.30
96.39
81.49
79.20
77.42
77.17
76.91
74.20
72.33
70.58
70.33
69.45
63.70
55.49
Fe
O
Table 2, 3ha
^{13}C NMR, 125 MHz
$CDCl_3$
NAME NM-569F-13C
EXPNO 1
PROCNO 1
Date_ 20140509
Time 19.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 30000
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 0.5505524 sec
RG 32
DW 16.800 usec
DE 6.50 usec
TE 290.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.88 usec
PL1 0.50 dB
PL1W 82.16106415 W
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 15.34 dB
PL13 20.00 dB
PL2W 15.50318813 W
PL12W 0.57071728 W
PL13W 0.19517358 W
SFO2 500.1320005 MHz
SI 16384
SF 125.7577698 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

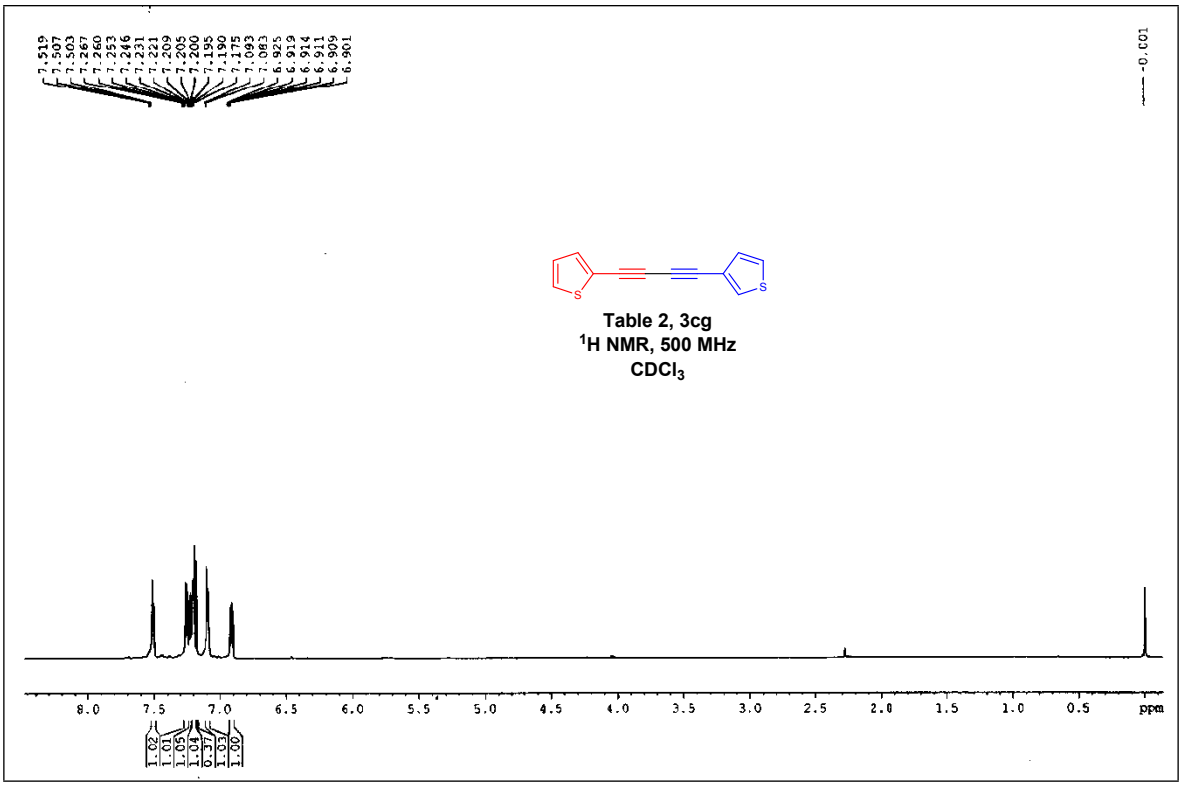


Table 2, 3cg
^{1}H NMR, 500 MHz
$CDCl_3$

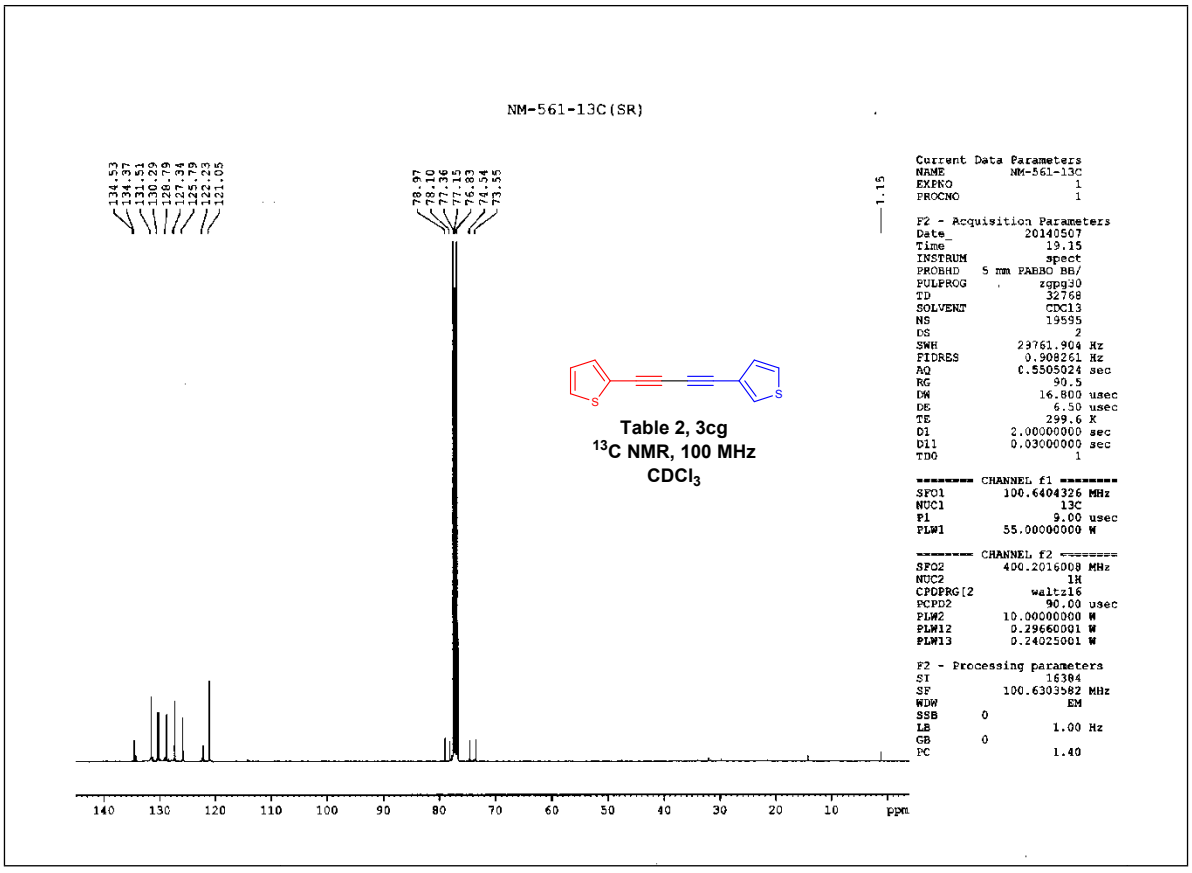
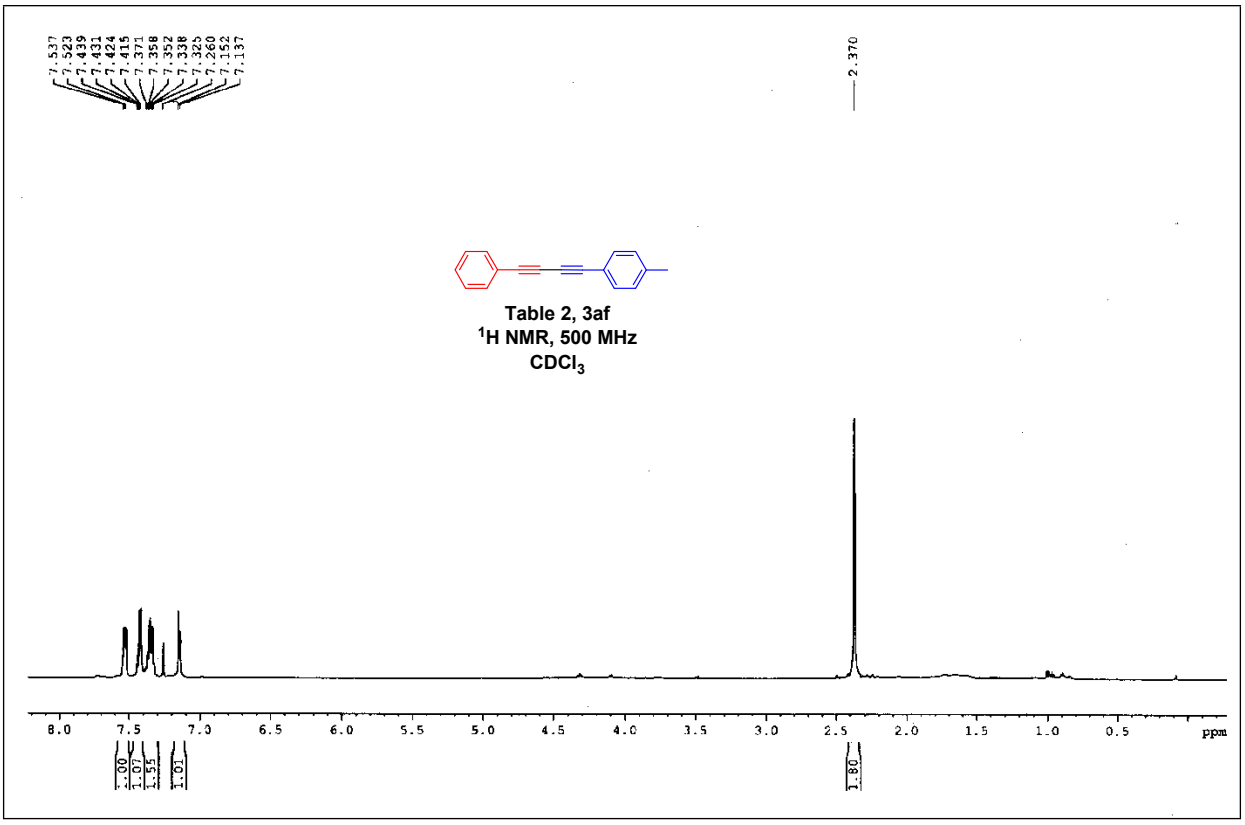
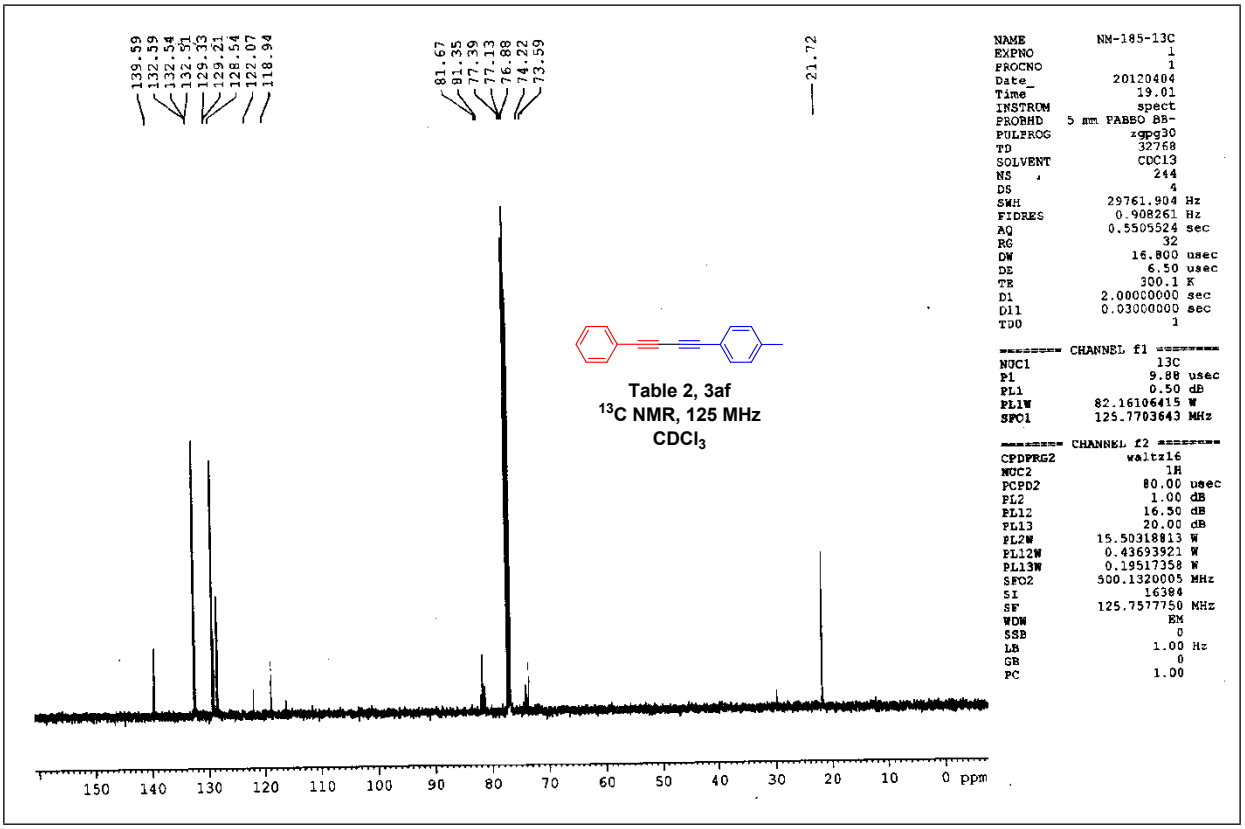
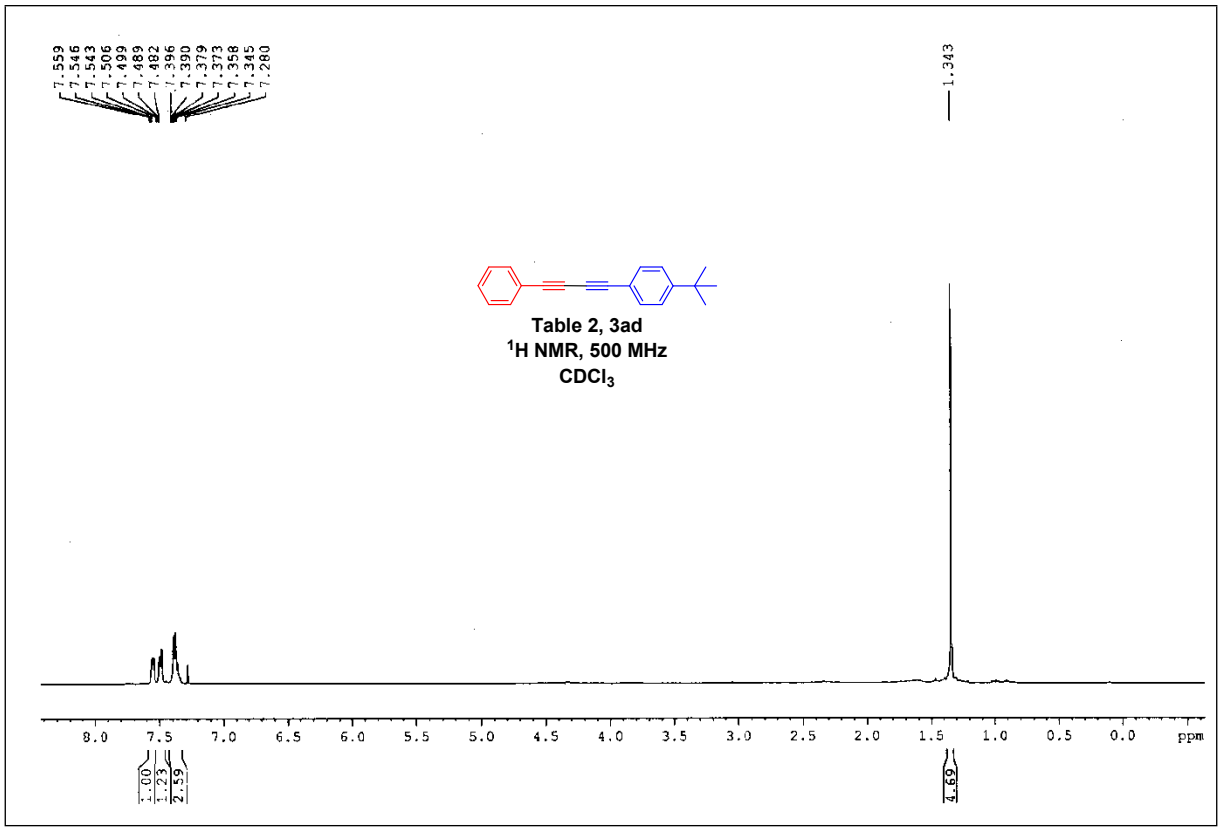
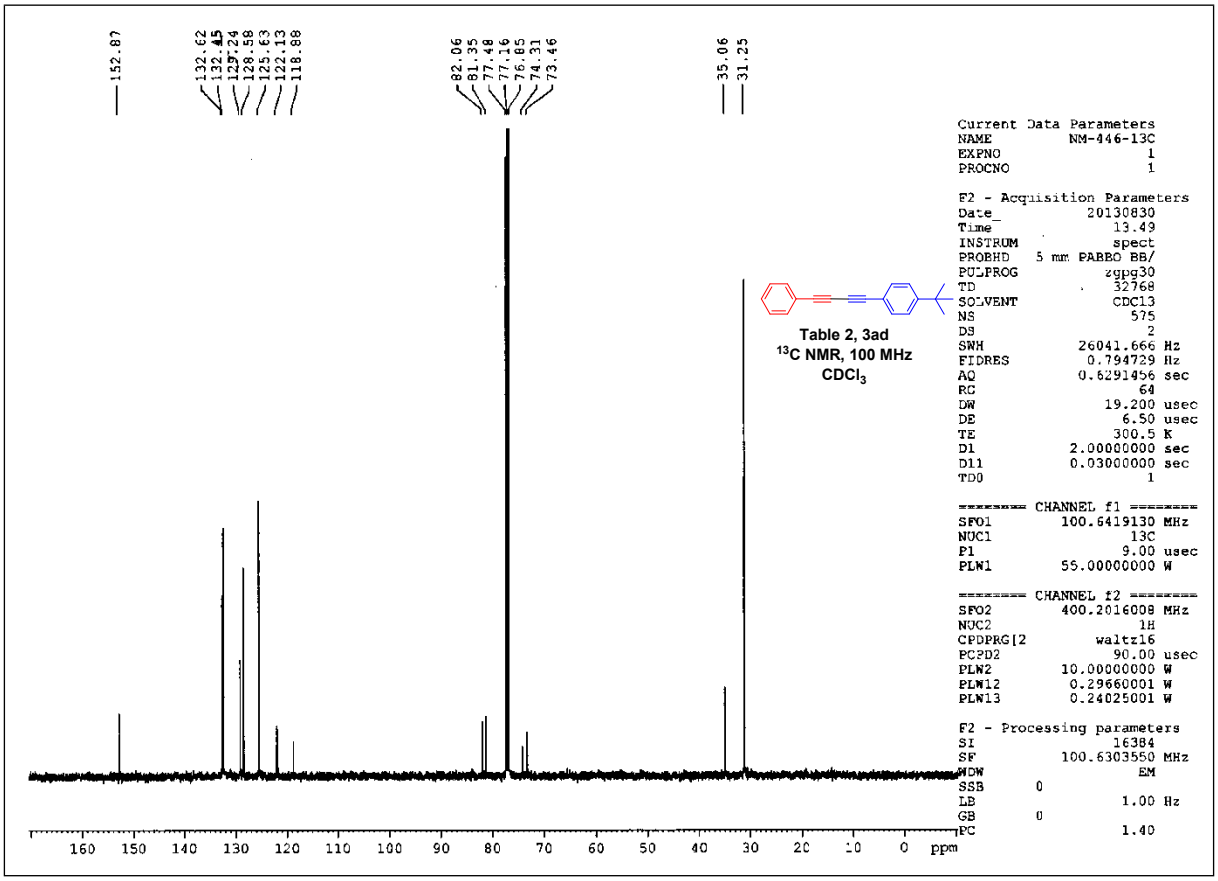


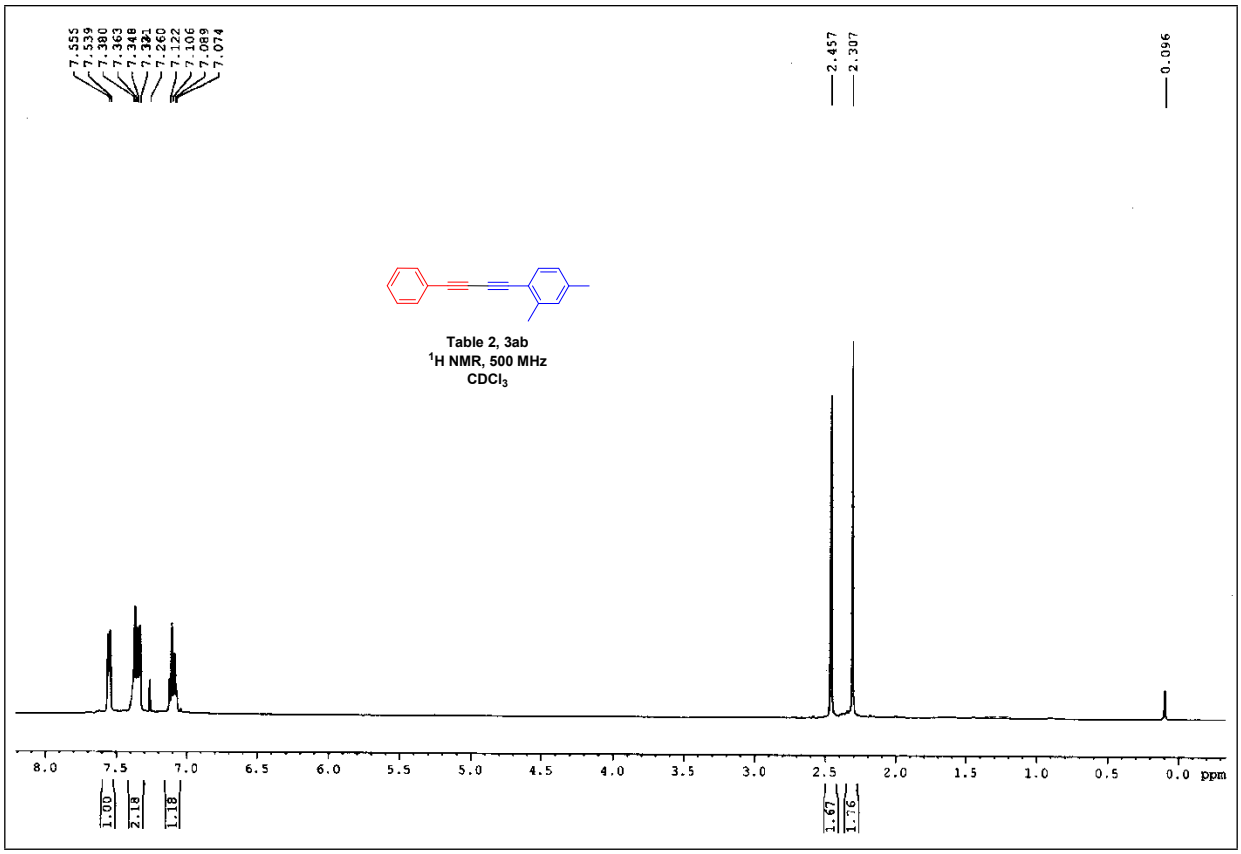
Table 2, 3cg
^{13}C NMR, 100 MHz
$CDCl_3$

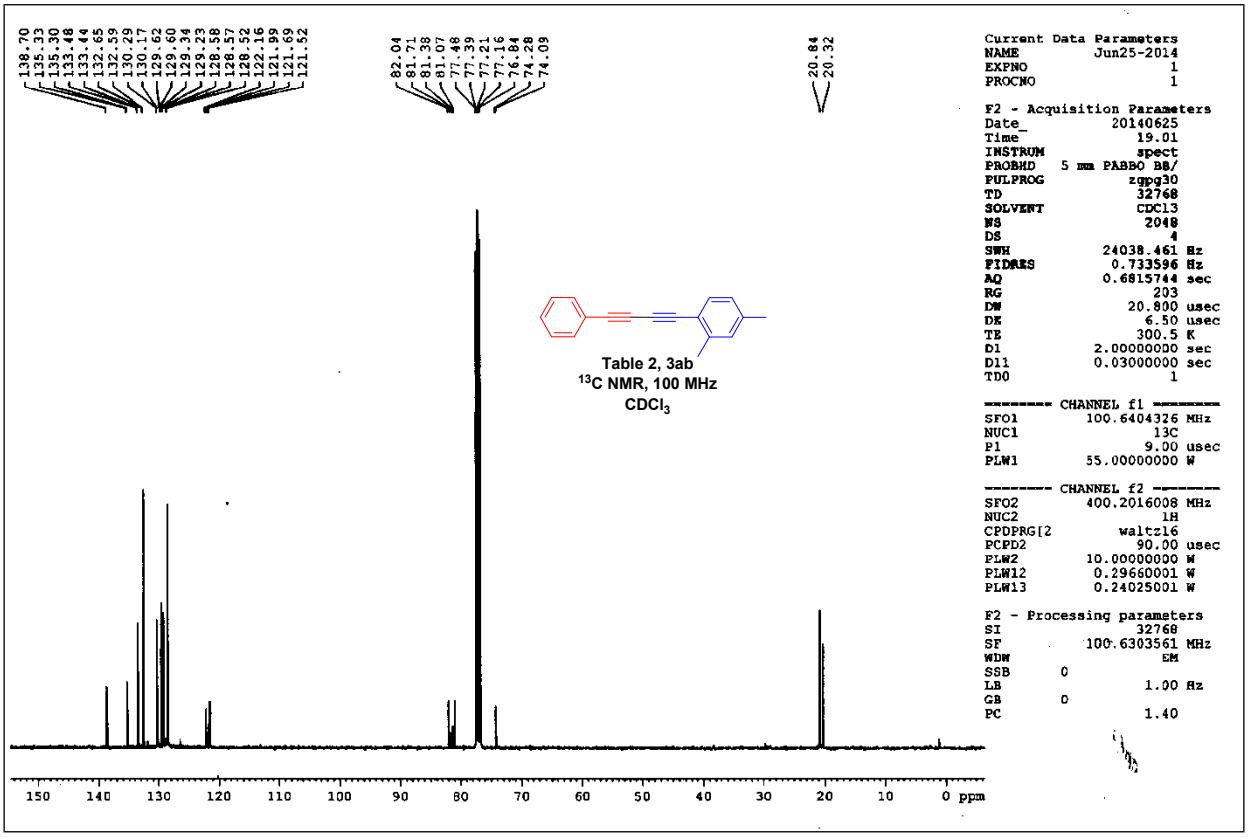

7.537
7.523
7.439
7.431
7.424
7.415
7.371
7.358
7.352
7.338
7.325
7.260
7.152
7.137
2.370
Table 2, 3af
1H NMR, 500 MHz
CDCl3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.07
1.55
1.01
1.80


139.59
132.59
132.54
132.51
129.33
129.21
128.54
122.07
118.94
81.67
81.35
77.39
77.13
76.88
74.22
73.59
21.72
Table 2, 3af
13C NMR, 125 MHz
CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm
NAME NM-185-13C
EXPNO 1
PROCNO 1
Date_ 20120404
Time 19.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 244
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 0.5505524 sec
RG 32
DW 16.800 usec
DE 6.50 usec
TE 300.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.88 usec
PL1 0.50 dB
PL1W 82.16106415 W
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 16.50 dB
PL13 20.00 dB
PL2W 15.50318813 W
PL12W 0.43693921 W
PL13W 0.19517358 W
SFO2 500.1320005 MHz
SI 16384
SF 125.7577750 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00


7.559
7.546
7.543
7.506
7.499
7.489
7.482
7.396
7.390
7.379
7.373
7.358
7.345
7.280
1.343
Table 2, 3ad
1H NMR, 500 MHz
CDCl3
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
ppm
1.00
1.23
2.59
4.69


152.87
132.62
132.45
129.24
128.58
125.63
122.13
118.88
82.06
81.35
77.48
77.16
76.85
74.31
73.46
35.06
31.25
Table 2, 3ad
13C NMR, 100 MHz
CDCl3
Current Data Parameters
NAME NM-446-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130830
Time 13.49
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 575
DS 2
SWH 26041.666 Hz
FIDRES 0.794729 Hz
AQ 0.6291456 sec
RG 64
DW 19.200 usec
DE 6.50 usec
TE 300.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6419130 MHz
NUC1 13C
P1 9.00 usec
PLW1 55.00000000 W
======== CHANNEL f2 ========
SFO2 400.2016008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 10.00000000 W
PLW12 0.29660001 W
PLW13 0.24025001 W
F2 - Processing parameters
SI 16384
SF 100.6303550 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.555
7.539
7.380
7.363
7.348
7.321
7.260
7.122
7.106
7.089
7.074
2.457
2.307
0.096
Table 2, 3ab
1H NMR, 500 MHz
CDCl3
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 ppm
1.00
2.18
1.18
1.67
1.76


138.70
135.33
135.30
133.48
133.44
132.65
132.59
130.29
130.17
129.62
129.60
129.34
129.23
128.58
128.57
128.52
122.16
121.99
121.69
121.52
82.04
81.71
81.38
81.07
77.48
77.39
77.21
77.16
76.84
74.28
74.09
20.84
20.32
Table 2, 3ab
13C NMR, 100 MHz
CDCl3
Current Data Parameters
NAME Jun25-2014
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140625
Time 19.01
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 2048
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
SFO1 100.6404326 MHz
NUC1 13C
P1 9.00 usec
PLW1 55.00000000 W
CHANNEL f2
SFO2 400.2016008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 10.00000000 W
PLW12 0.29660001 W
PLW13 0.24025001 W
F2 - Processing parameters
SI 32768
SF 100.6303561 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

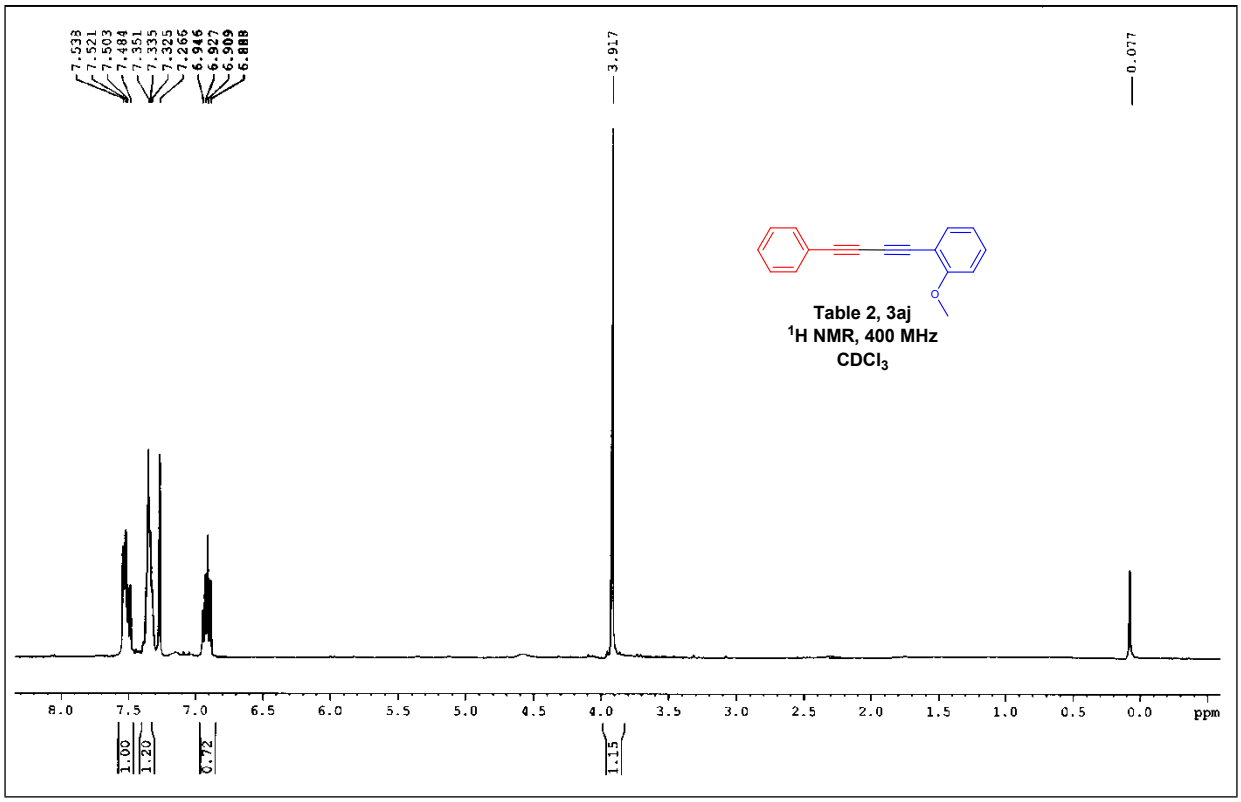


Table 2, 3aj
^{1}H NMR, 400 MHz
$CDCl_3$

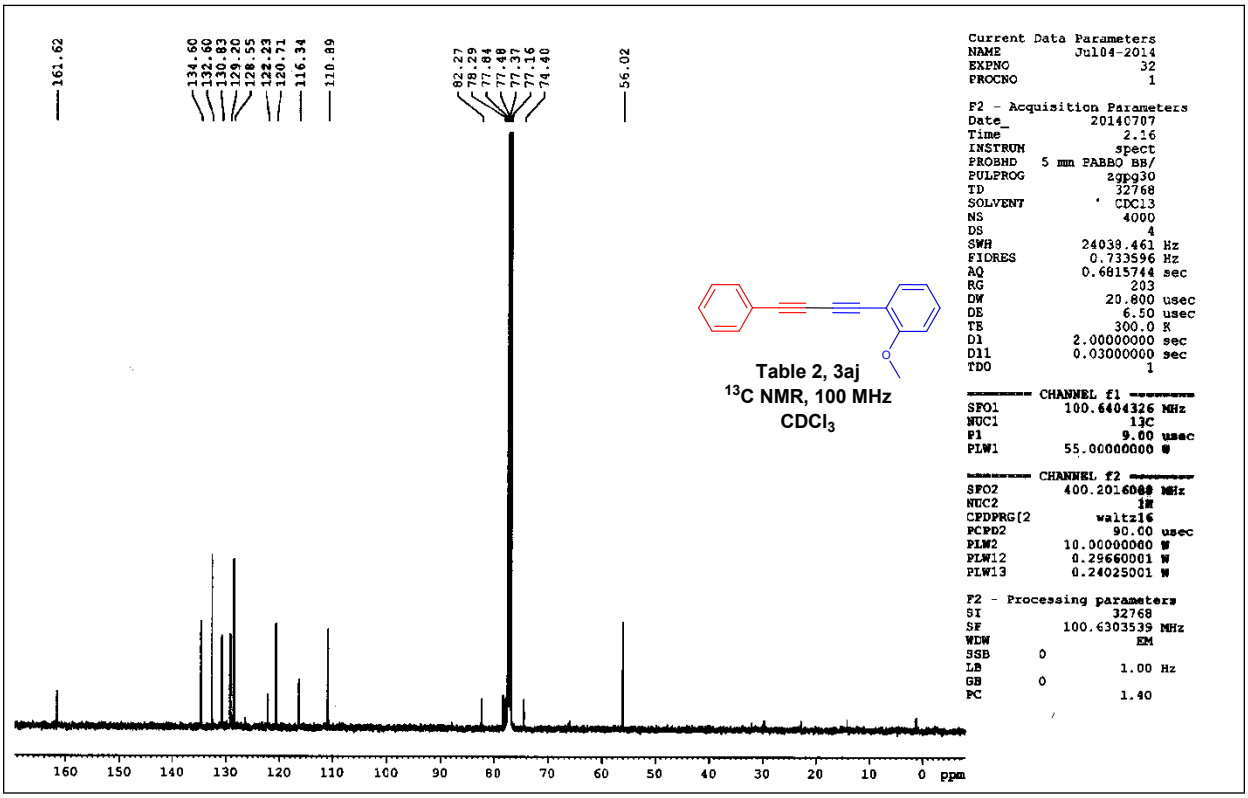


Table 2, 3aj
^{13}C NMR, 100 MHz
$CDCl_3$

```
Current Data Parameters
NAME                  Jul04-2014
EXPNO                         32
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20140707
Time                        2.16
INSTRUM                    spect
PROBHD     5 mm PABBO BB/
PULPROG                 zgpg30
TD                         32768
SOLVENT                  ' CDCl3
NS                          4000
DS                             4
SWH                    24038.461 Hz
FIDRES                 0.733596 Hz
AQ                     0.6815744 sec
RG                           203
DW                        20.800 usec
DE                         6.50 usec
TE                        300.0 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
SFO1           100.6404326 MHz
NUC1                      13C
P1                       9.00 usec
PLW1          55.00000000 W

======== CHANNEL f2 ========
SFO2           400.2016080 MHz
NUC2                       1H
CPDPRG[2               waltz16
PCPD2                   90.00 usec
PLW2          10.00000000 W
PLW12          0.29660001 W
PLW13          0.24025001 W

F2 - Processing parameters
SI                         32768
SF             100.6303539 MHz
WDW                           EM
SSB                    0
LB                         1.00 Hz
GB                     0
PC                         1.40
```

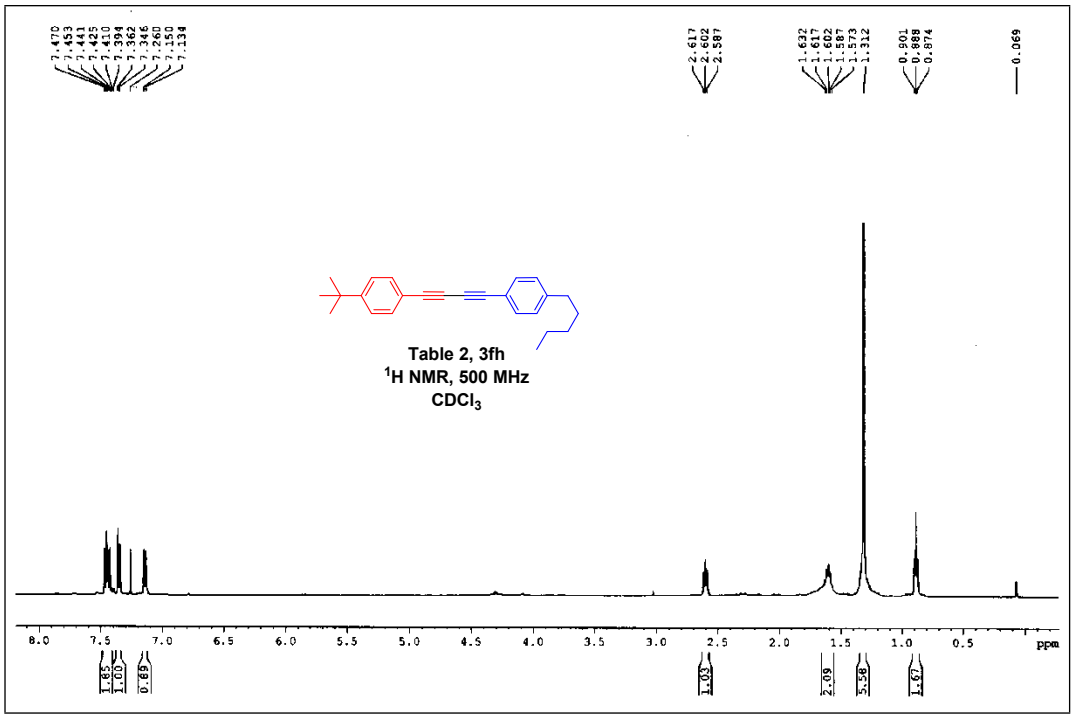


Table 2, 3fh
^{1}H NMR, 500 MHz
$CDCl_3$
ppm

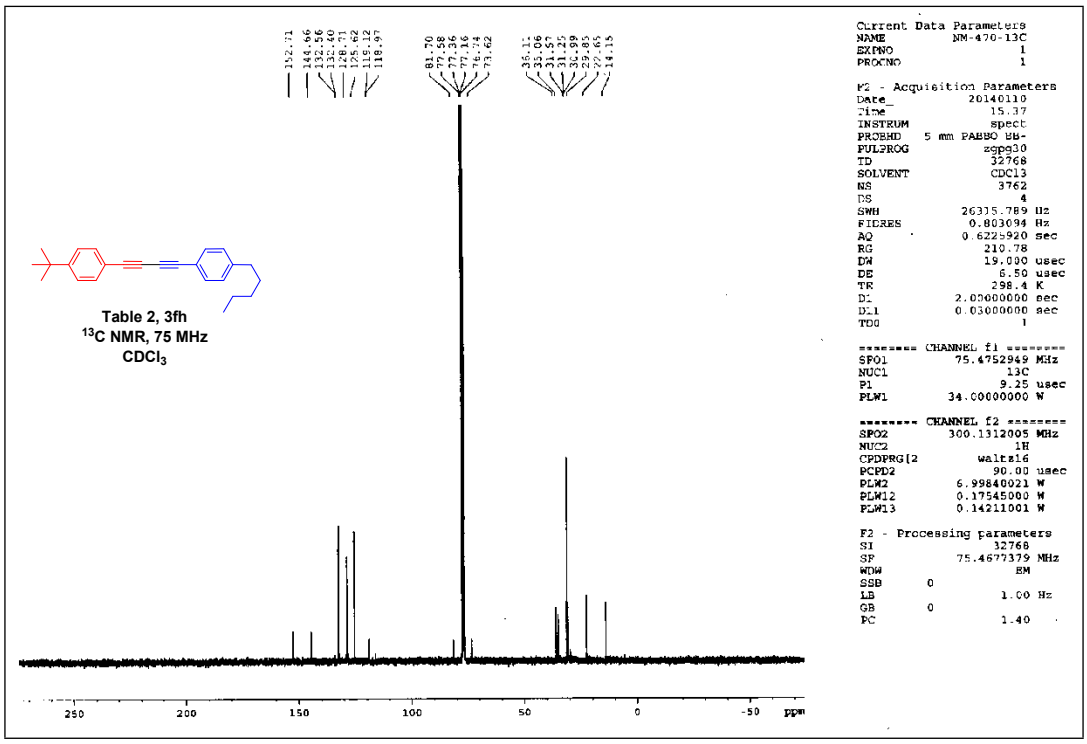
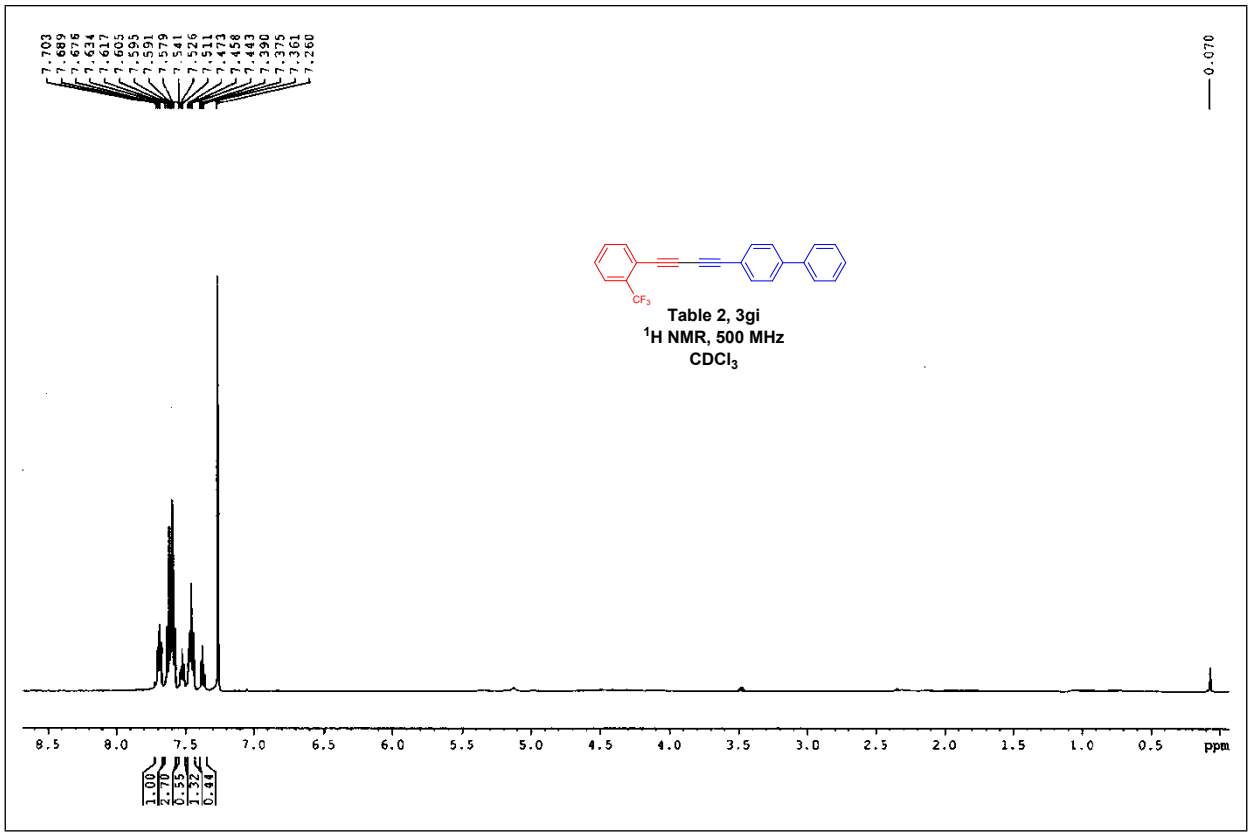
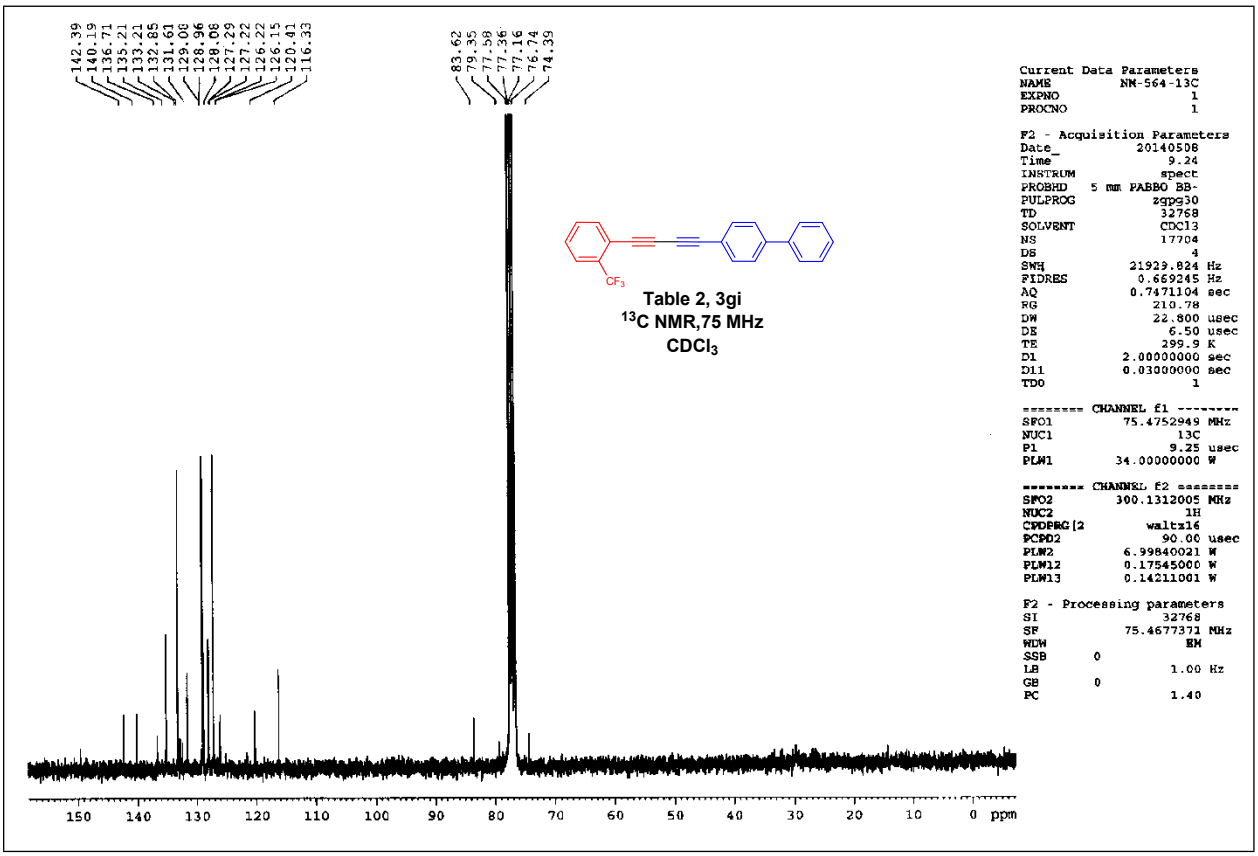
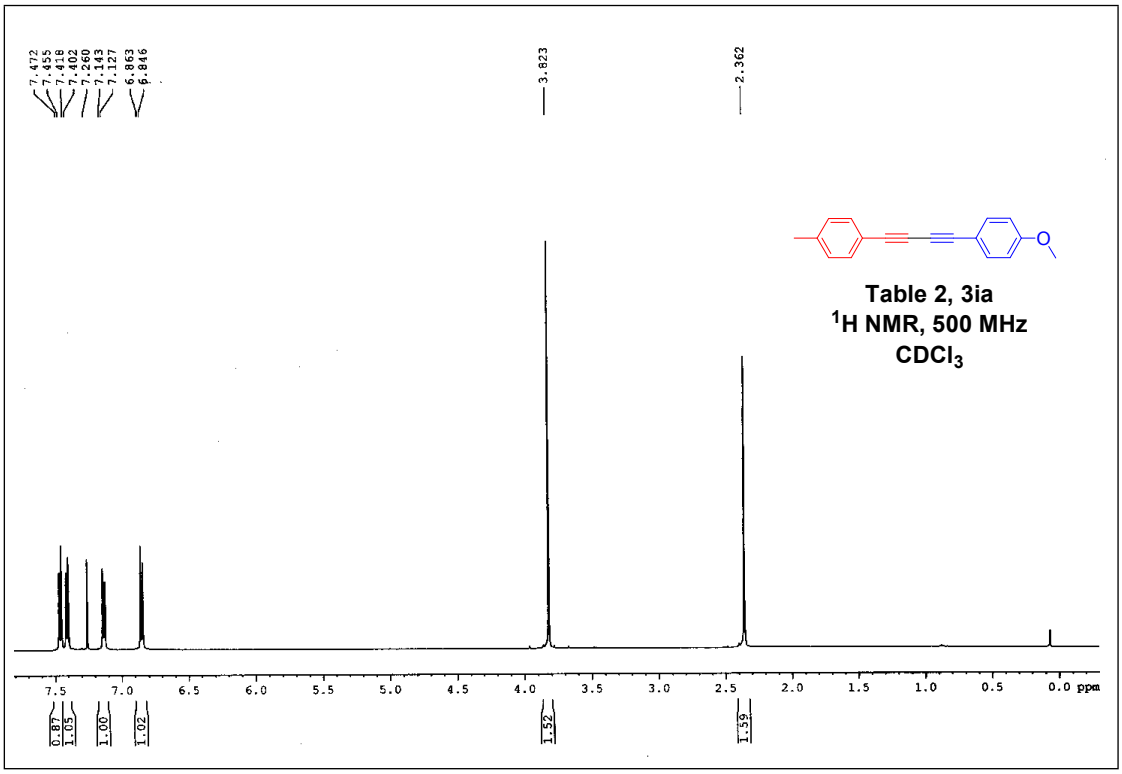
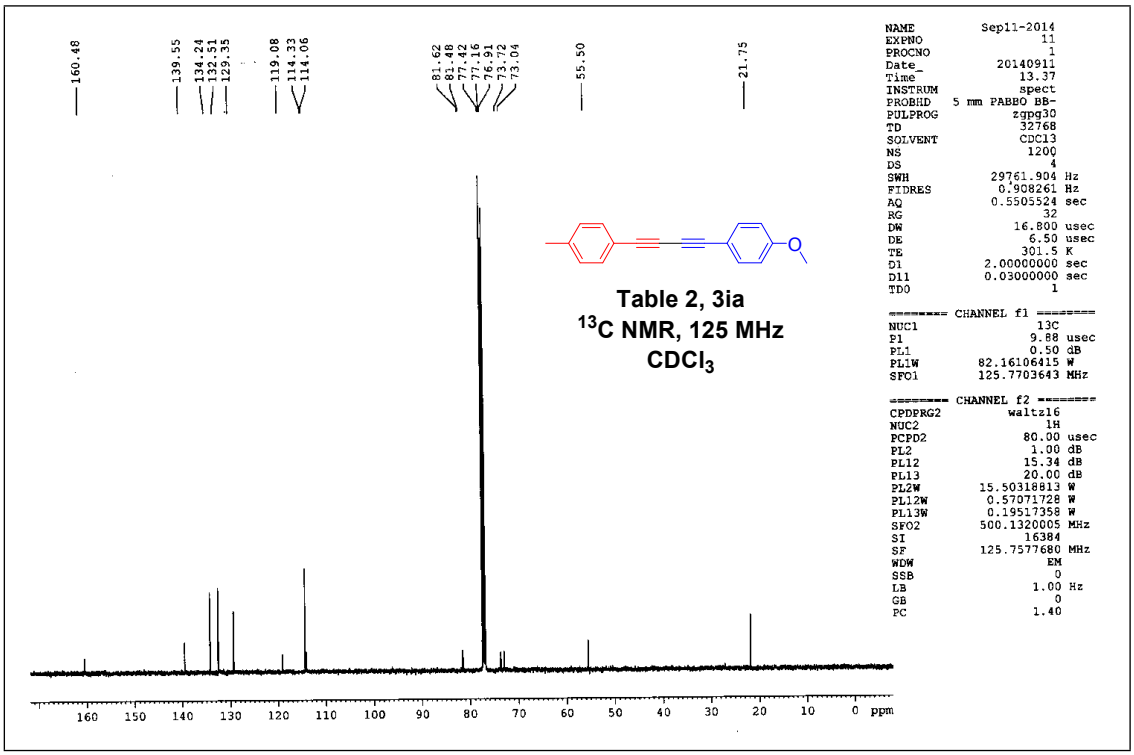


Table 2, 3fh
^{13}C NMR, 75 MHz
$CDCl_3$
ppm
Current Data Parameters
NAME NM-476-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140110
Time 15.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 3762
DS 4
SWH 26315.789 Hz
FIDRES 0.803094 Hz
AQ 0.6225920 sec
RG 210.78
DW 19.000 usec
DE 6.50 usec
TE 298.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 75.4752949 MHz
NUC1 13C
P1 9.25 usec
PLW1 34.00000000 W
======== CHANNEL f2 ========
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 6.99840021 W
PLW12 0.17545000 W
PLW13 0.14211001 W
F2 - Processing parameters
SI 32768
SF 75.4677379 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


7.703
7.689
7.676
7.634
7.617
7.605
7.595
7.591
7.579
7.541
7.526
7.511
7.473
7.458
7.443
7.390
7.375
7.361
7.260
0.070
CF3
Table 2, 3gi
1H NMR, 500 MHz
CDCl3
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 ppm
1.00
2.70
0.55
1.32
0.44


142.39
140.19
136.71
135.21
133.21
132.85
131.61
129.06
128.96
128.06
127.29
127.22
126.22
126.15
120.41
116.33
83.62
79.35
77.58
77.36
77.16
76.74
74.39
CF3
Table 2, 3gi
13C NMR,75 MHz
CDCl3
Current Data Parameters
NAME NM-564-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140508
Time 9.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 17704
DS 4
SWH 21929.824 Hz
FIDRES 0.669245 Hz
AQ 0.7471104 sec
RG 210.78
DW 22.800 usec
DE 6.50 usec
TE 299.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 75.4752949 MHz
NUC1 13C
P1 9.25 usec
PLW1 34.00000000 W
======== CHANNEL f2 ========
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 6.99840021 W
PLW12 0.17545000 W
PLW13 0.14211001 W
F2 - Processing parameters
SI 32768
SF 75.4677371 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm





NAME	Sep11-2014
EXPNO	11
PROCNO	1
Date_	20140911
Time	13.37
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	1200
DS	4
SWH	29761.904 Hz
FIDRES	0.908261 Hz
AQ	0.5505524 sec
RG	32
DW	16.800 usec
DE	6.50 usec
TE	301.5 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.88 usec
PL1	0.50 dB
PL1W	82.16106415 W
SFO1	125.7703643 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	1.00 dB
PL12	15.34 dB
PL13	20.00 dB
PL2W	15.50318813 W
PL12W	0.57071728 W
PL13W	0.19517358 W
SFO2	500.1320005 MHz
SI	16384
SF	125.7577680 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

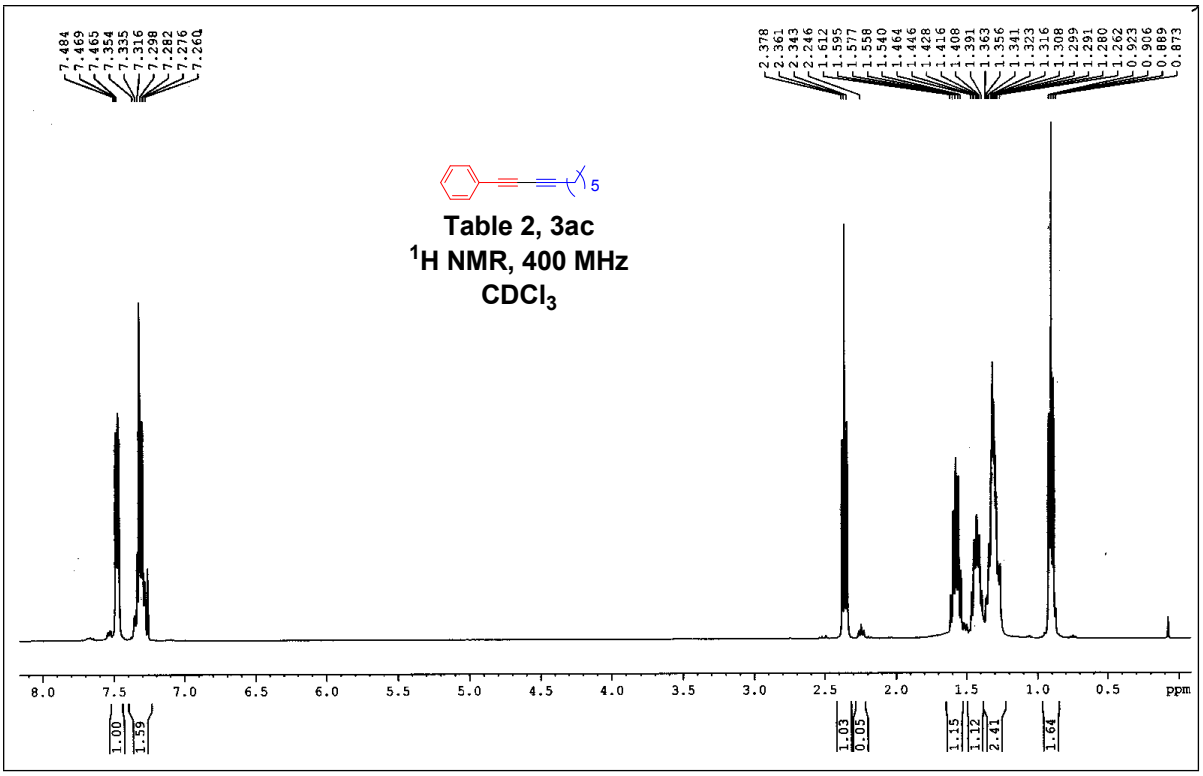


Table 2, 3ac
1H NMR, 400 MHz
CDCl3
ppm

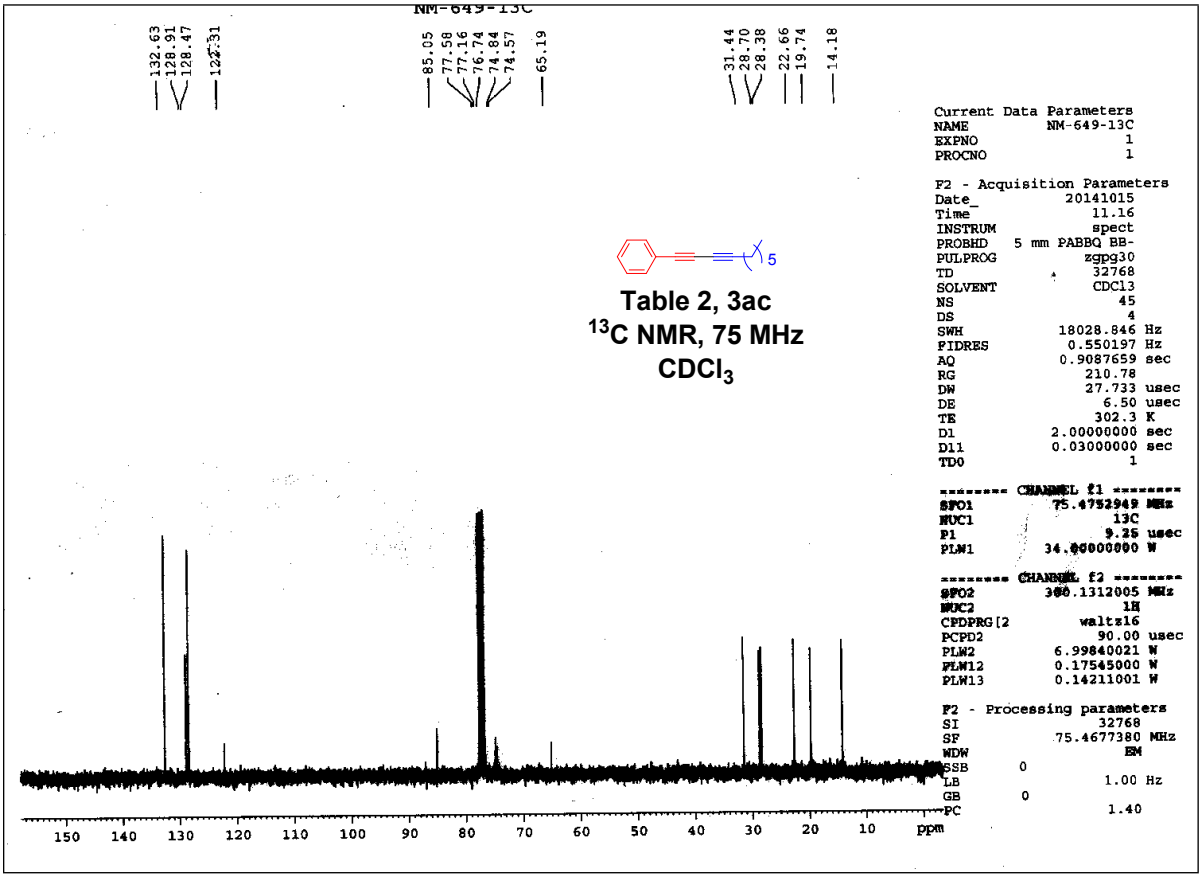
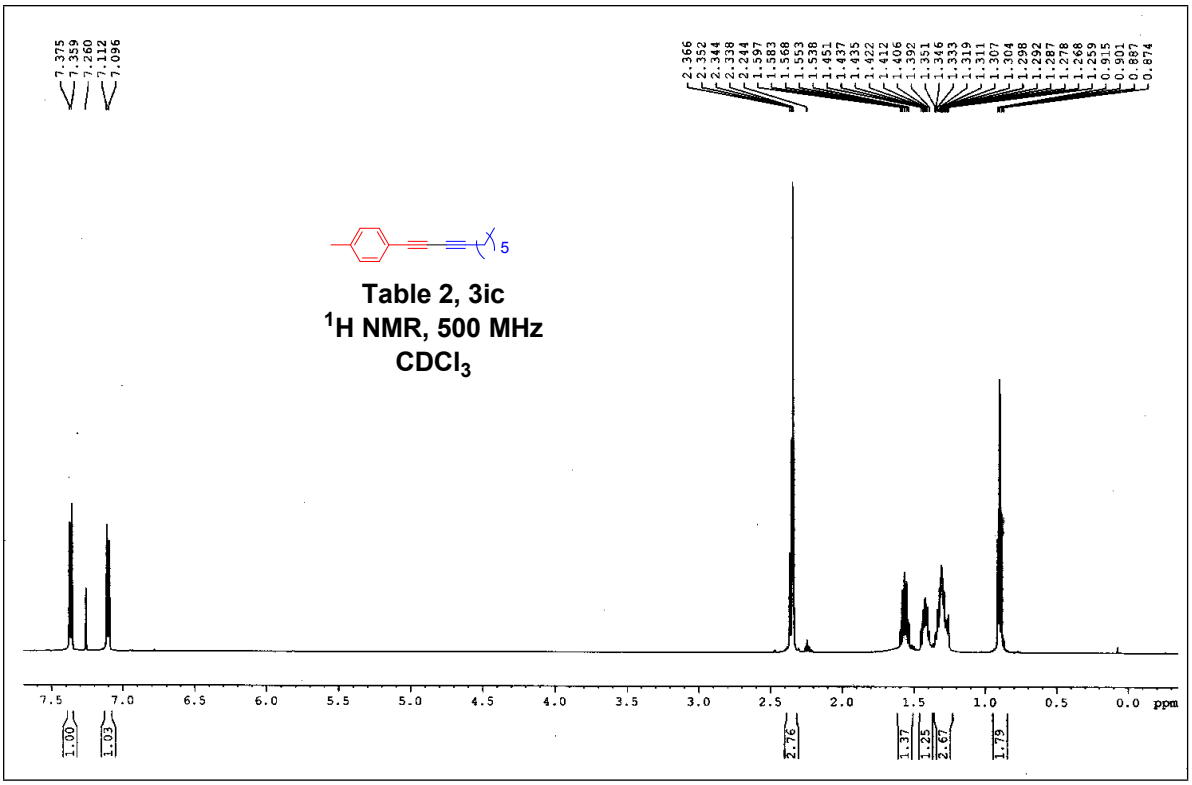
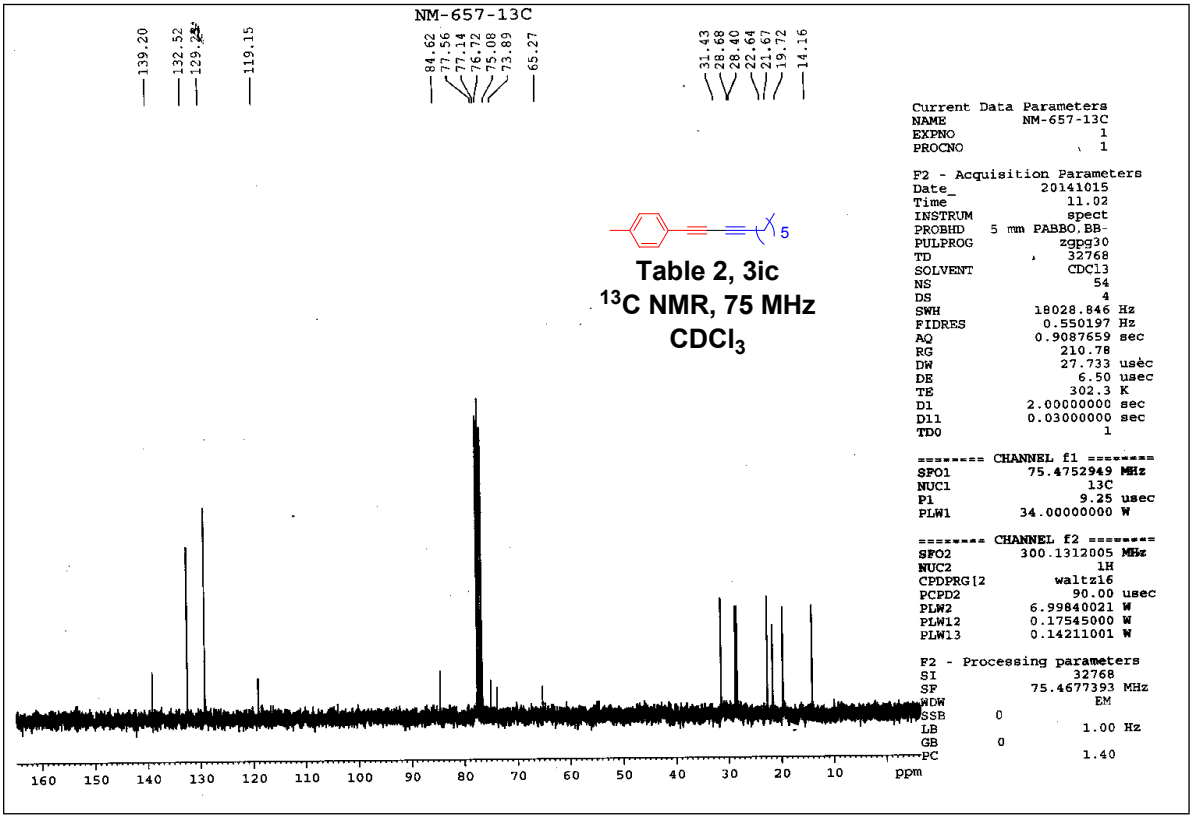
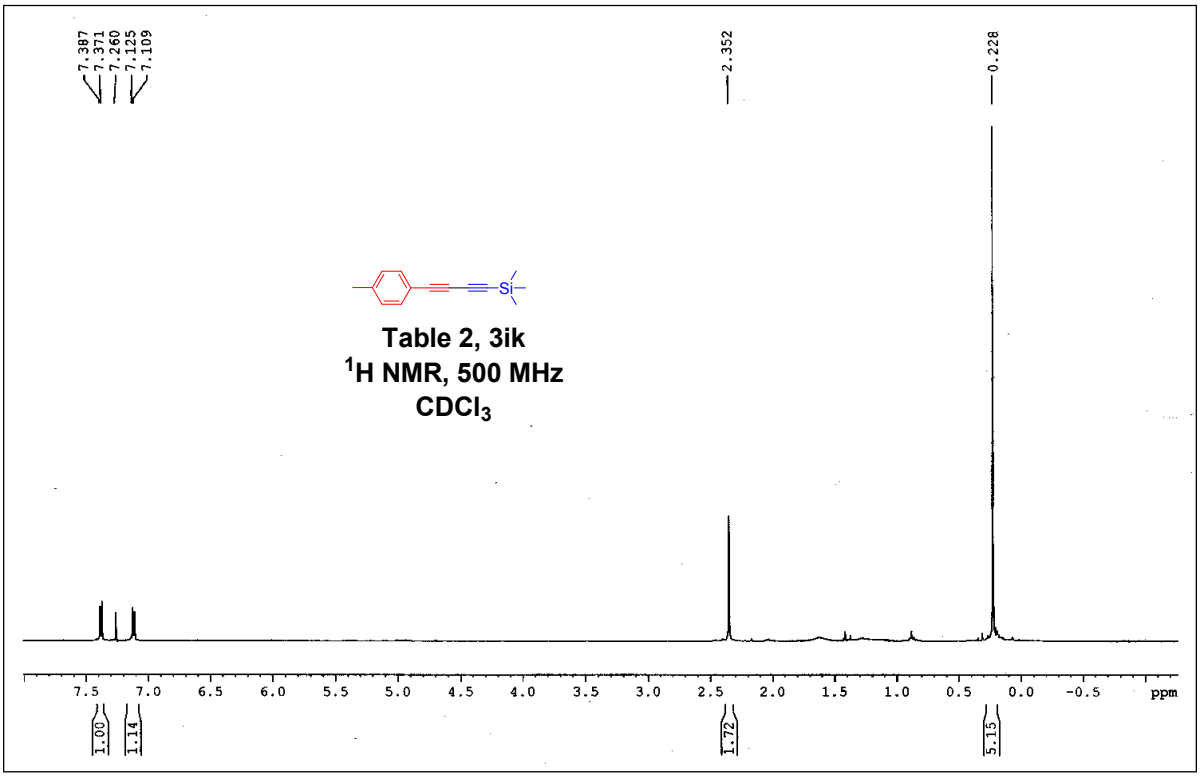
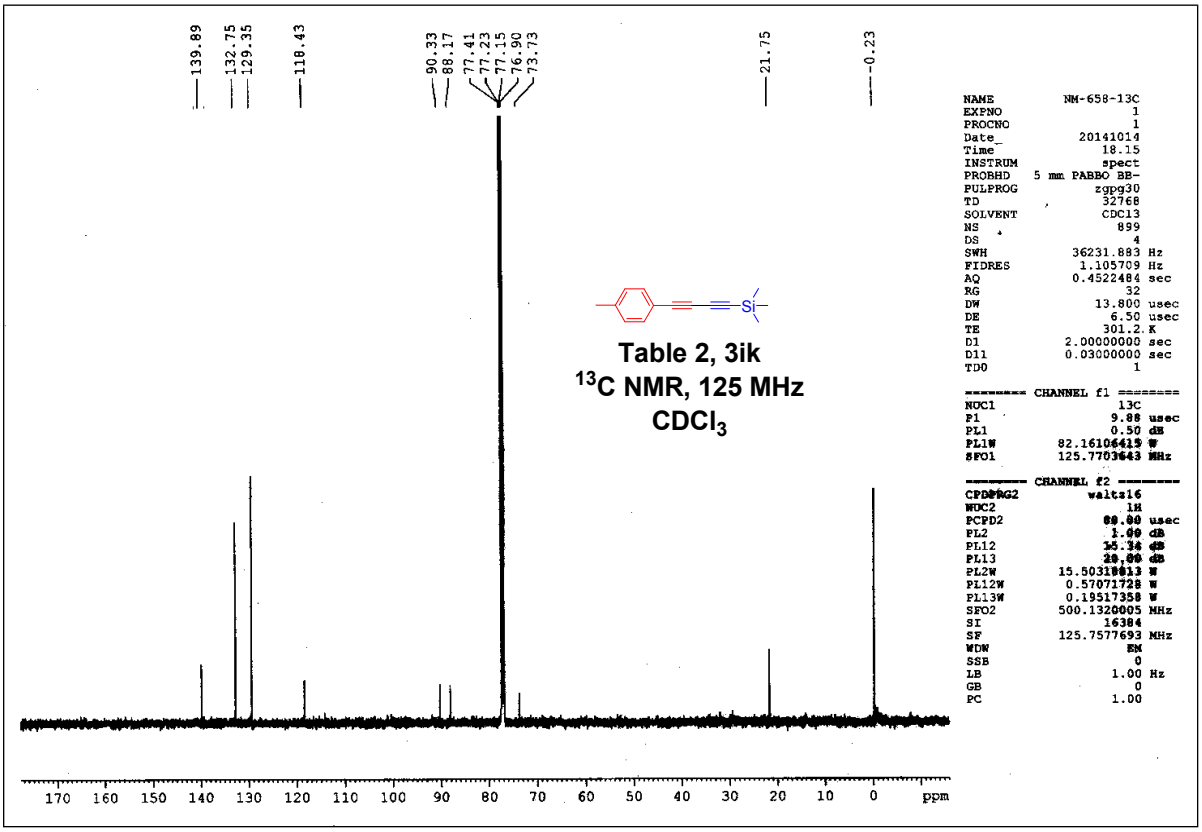


Table 2, 3ac
13C NMR, 75 MHz
CDCl3
ppm


7.375
7.359
7.260
7.112
7.096
2.366
2.352
2.344
2.338
2.244
1.597
1.583
1.568
1.553
1.538
1.451
1.437
1.435
1.422
1.412
1.406
1.392
1.351
1.346
1.333
1.319
1.311
1.307
1.304
1.298
1.292
1.287
1.278
1.268
1.259
0.915
0.901
0.887
0.874
5
Table 2, 3ic
1H NMR, 500 MHz
CDCl3
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
ppm
1.00
1.03
2.76
1.37
1.25
2.67
1.79


NM-657-13C
139.20
132.52
129.25
119.15
84.62
77.56
77.14
76.72
75.08
73.89
65.27
31.43
28.68
28.40
22.64
21.67
19.72
14.16
5
Table 2, 3ic
13C NMR, 75 MHz
CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
Current Data Parameters
NAME NM-657-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20141015
Time 11.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 54
DS 4
SWH 18028.846 Hz
FIDRES 0.550197 Hz
AQ 0.9087659 sec
RG 210.78
DW 27.733 usec
DE 6.50 usec
TE 302.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 75.4752949 MHz
NUC1 13C
P1 9.25 usec
PLW1 34.00000000 W
======== CHANNEL f2 ========
SFO2 300.1312005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 6.99840021 W
PLW12 0.17545000 W
PLW13 0.14211001 W
F2 - Processing parameters
SI 32768
SF 75.4677393 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


7.387
7.371
7.260
7.125
7.109
2.352
0.228
Si
Table 2, 3ik
1H NMR, 500 MHz
CDCl3
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 ppm
1.00
1.14
1.72
5.15


139.89
132.75
129.35
118.43
90.33
88.17
77.41
77.23
77.15
76.90
73.73
21.75
-0.23
Si
Table 2, 3ik
13C NMR, 125 MHz
CDCl3
NAME NM-658-13C
EXPNO 1
PROCNO 1
Date_ 20141014
Time 18.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 899
DS 4
SWH 36231.883 Hz
FIDRES 1.105709 Hz
AQ 0.4522484 sec
RG 32
DW 13.800 usec
DE 6.50 usec
TE 301.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.88 usec
PL1 0.50 dB
PL1W 82.16106415 W
SFO1 125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 15.34 dB
PL13 20.00 dB
PL2W 15.50319813 W
PL12W 0.57071728 W
PL13W 0.19517358 W
SFO2 500.1320005 MHz
SI 16384
SF 125.7577693 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

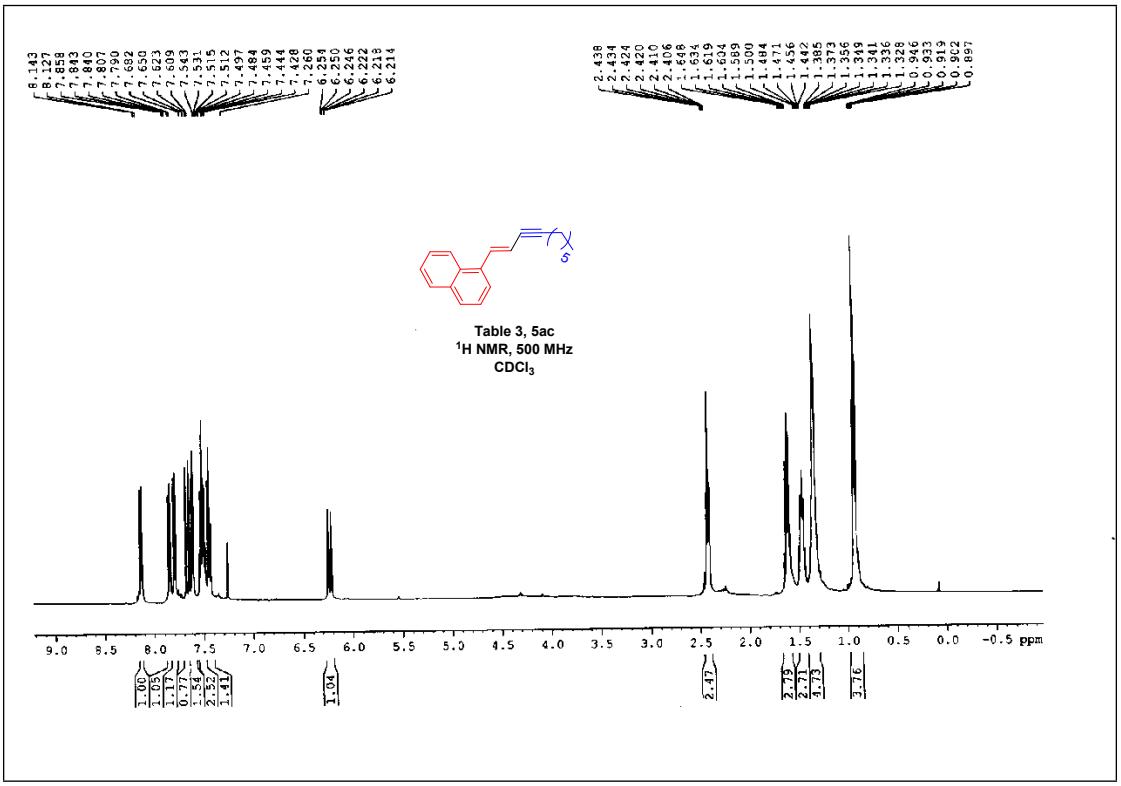


Table 3, 5ac
^{1}H NMR, 500 MHz
$CDCl_3$

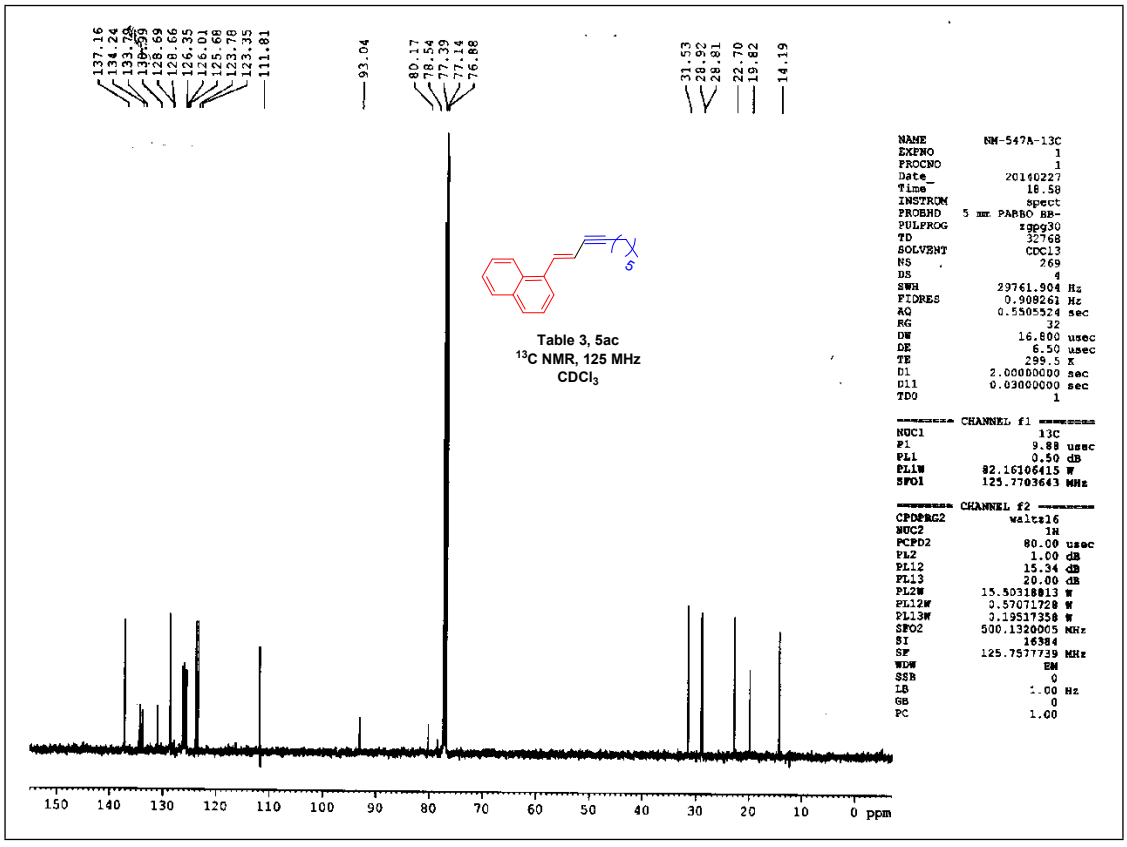


Table 3, 5ac
^{13}C NMR, 125 MHz
$CDCl_3$

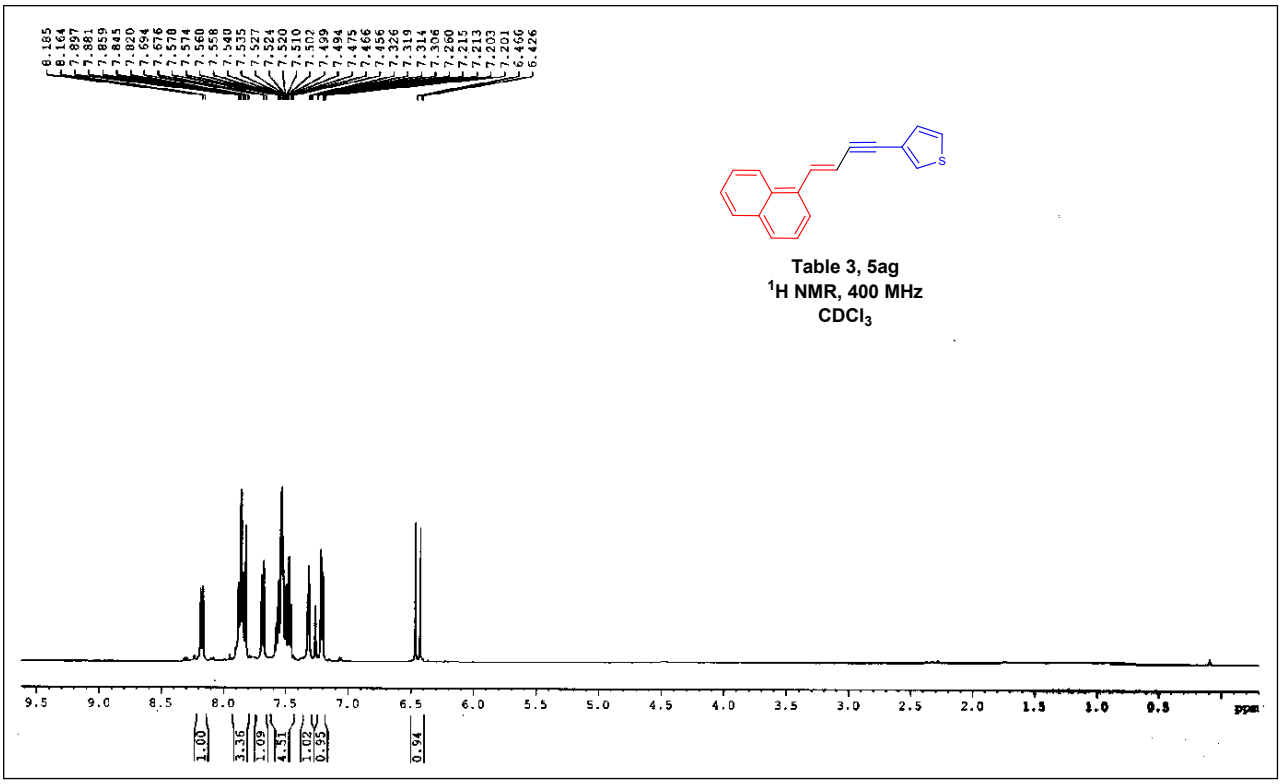


Table 3, 5ag
^{1}H NMR, 400 MHz
$CDCl_3$

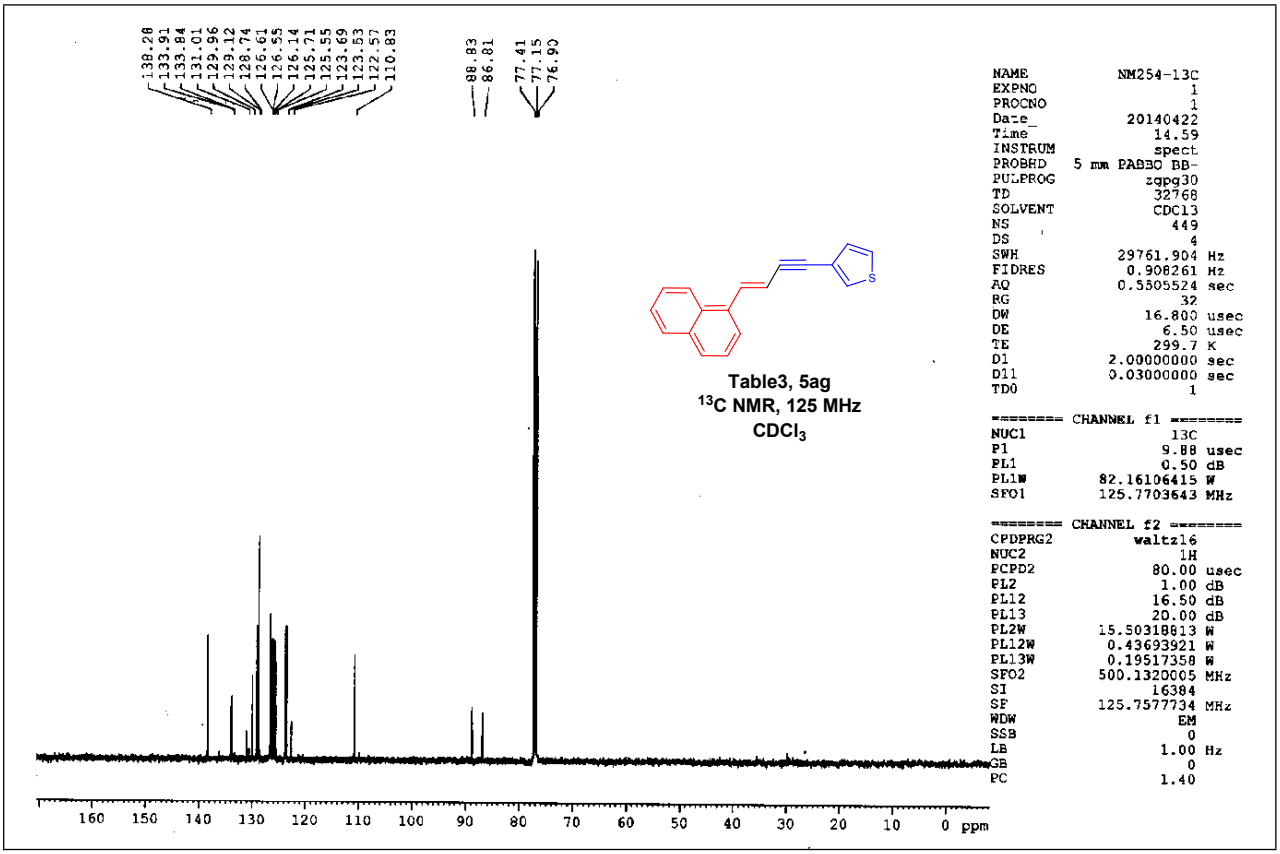
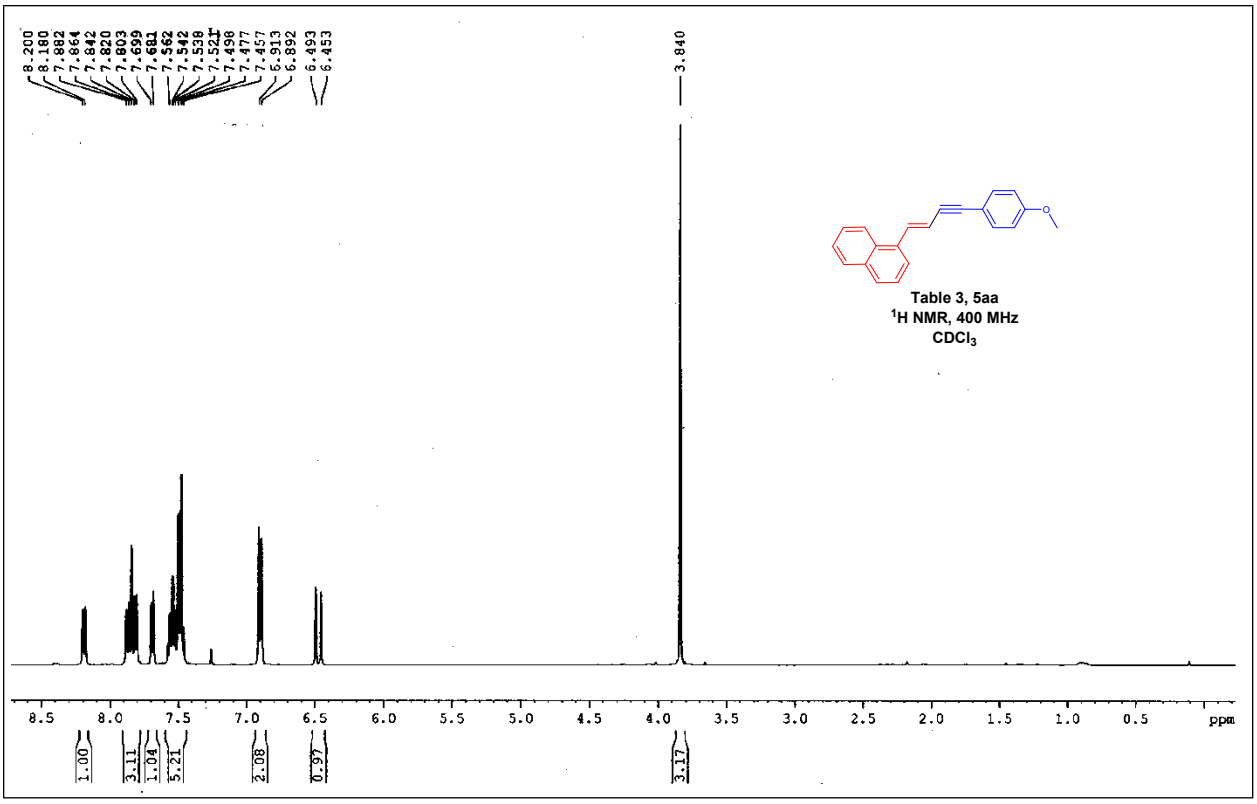
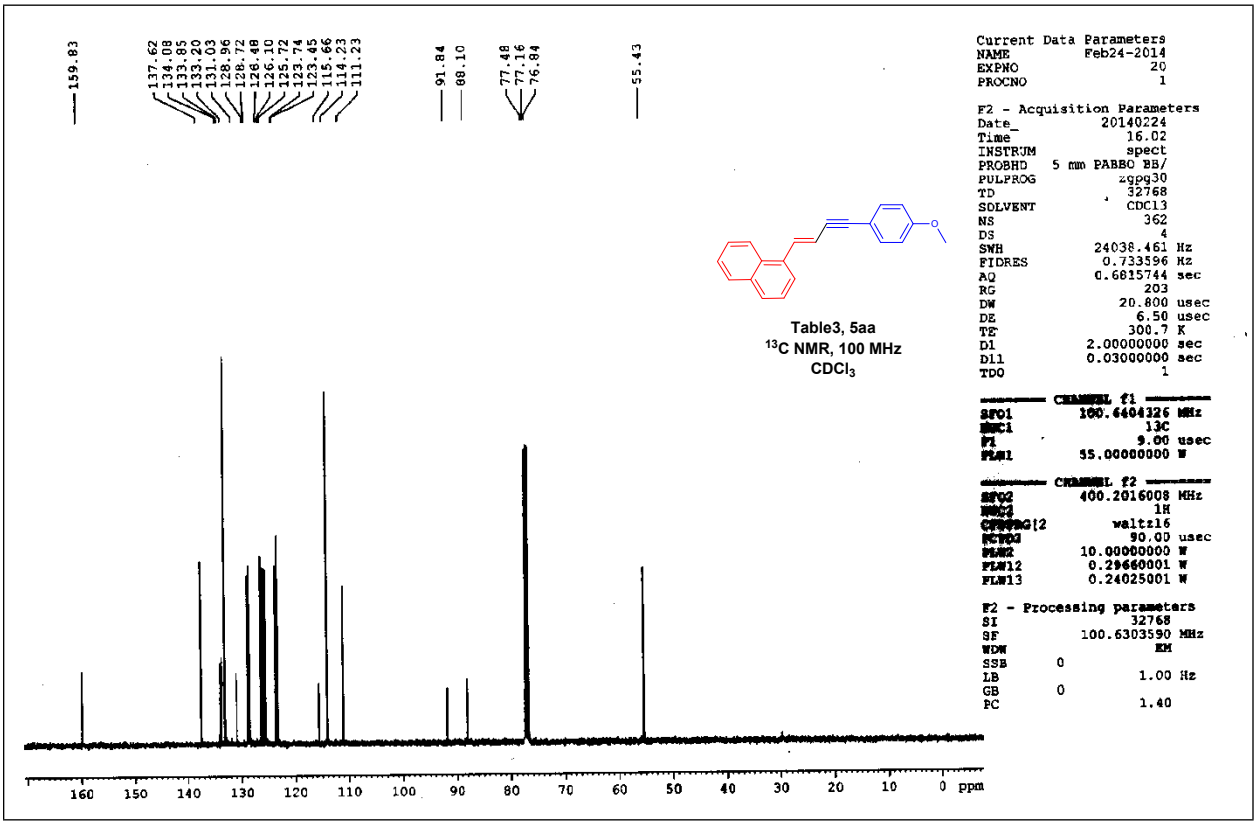
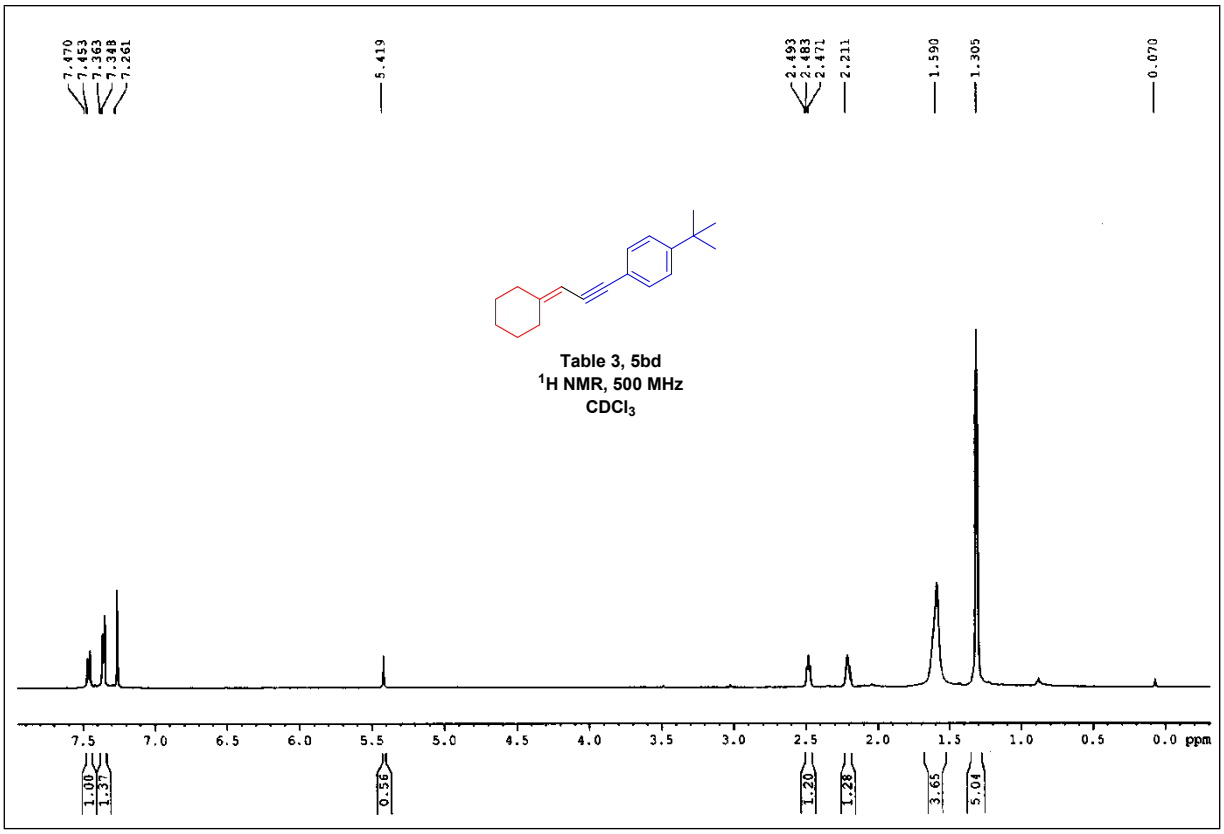
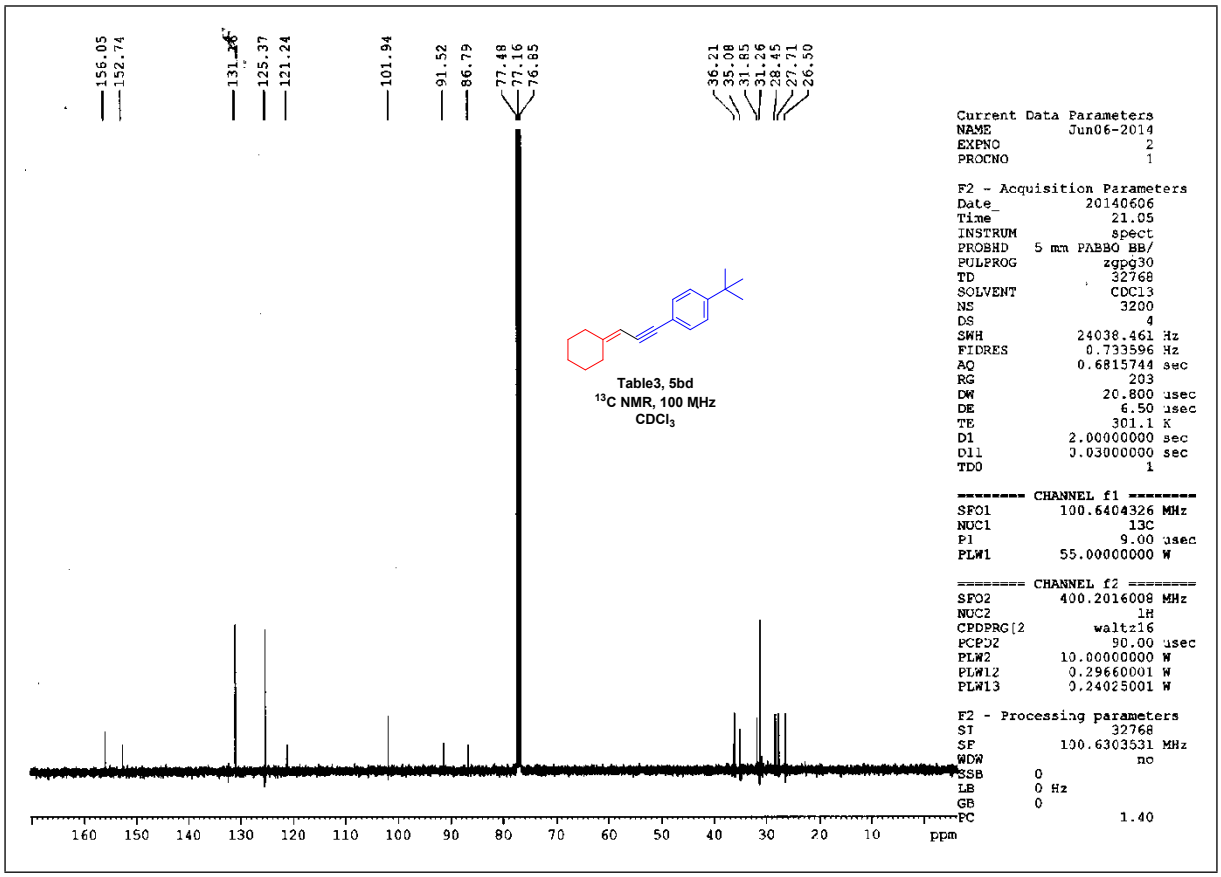


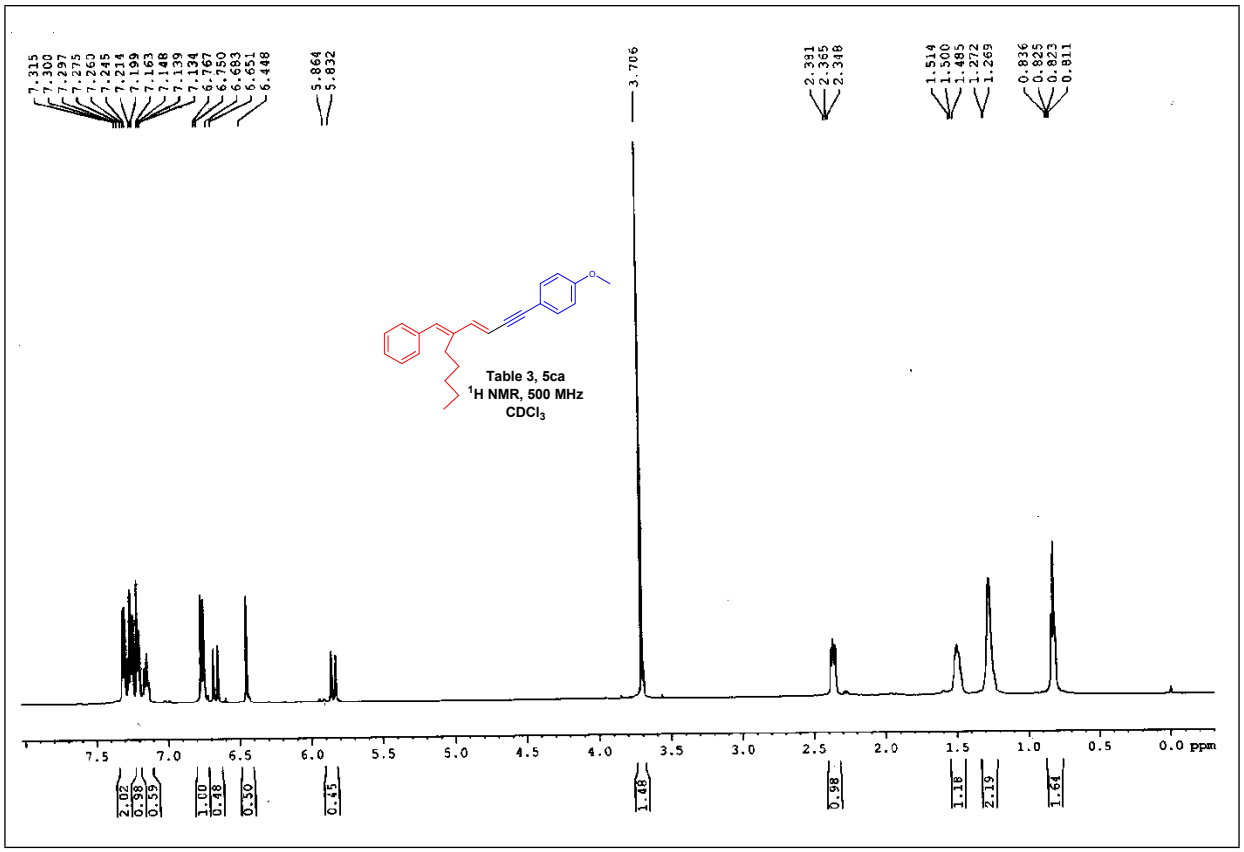
Table3, 5ag
^{13}C NMR, 125 MHz
$CDCl_3$

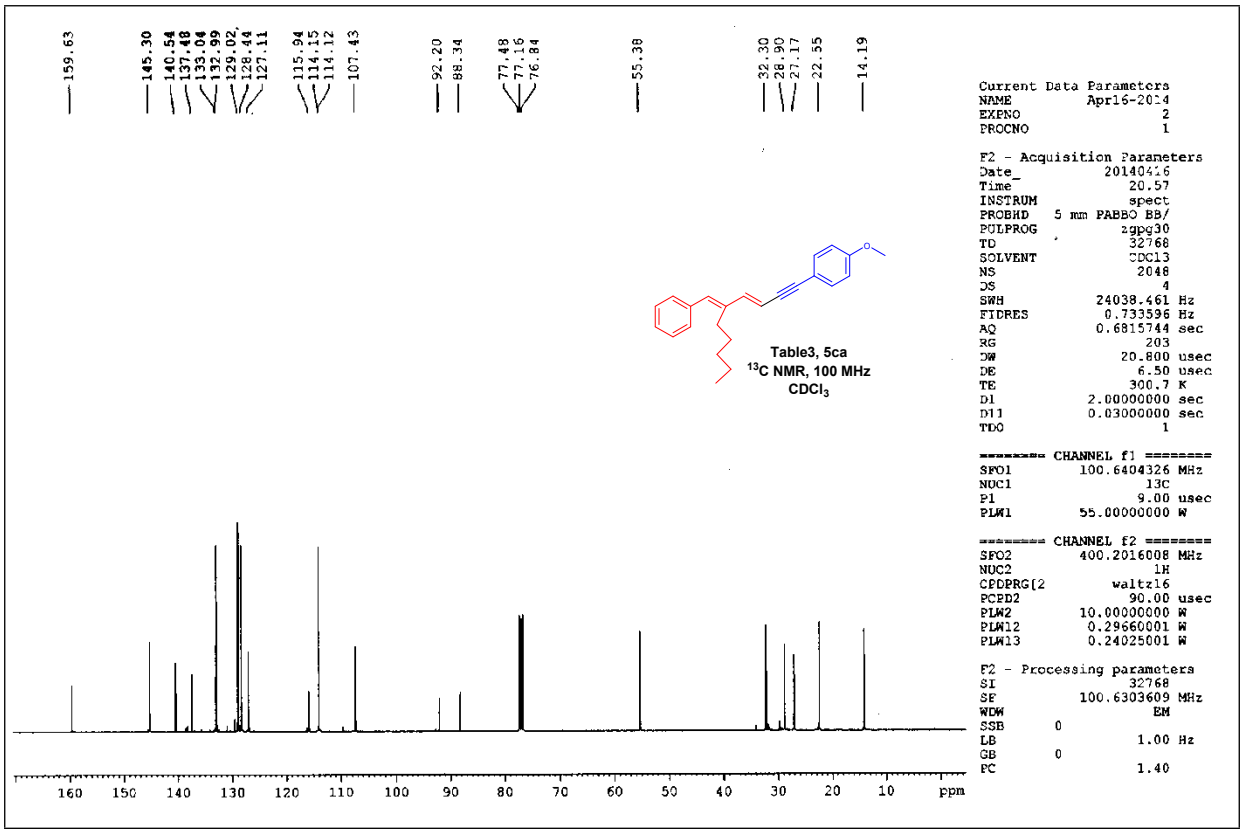

8.200
8.180
7.882
7.864
7.842
7.820
7.803
7.699
7.681
7.562
7.542
7.538
7.521
7.496
7.477
7.457
6.913
6.892
6.493
6.453
3.840
Table 3, 5aa
1H NMR, 400 MHz
CDCl3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
3.11
1.04
5.21
2.08
0.97
3.17

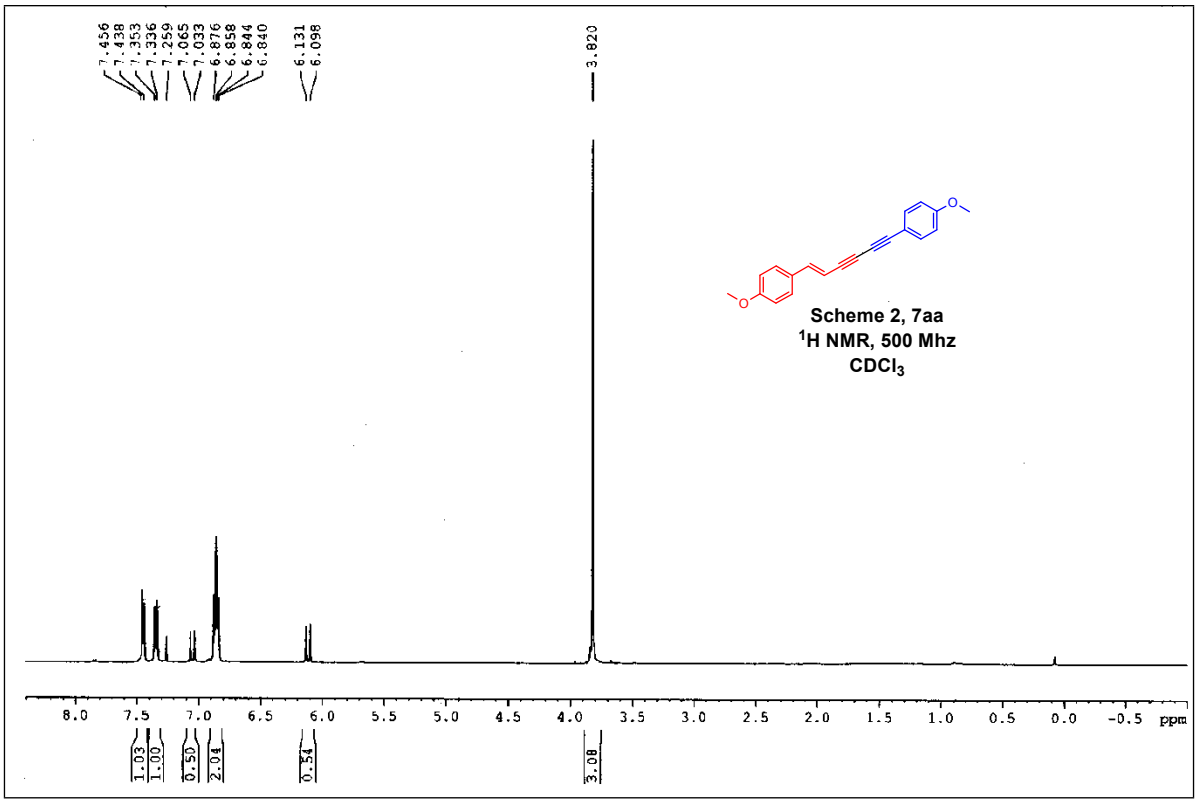

159.83
137.62
134.08
133.85
133.20
131.03
128.96
128.72
126.48
126.10
125.72
123.74
123.45
115.66
114.23
111.23
91.84
88.10
77.48
77.16
76.84
55.43
Table3, 5aa
13C NMR, 100 MHz
CDCl3
Current Data Parameters
NAME Feb24-2014
EXPNO 20
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140224
Time 16.02
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 362
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
SFO1 100.6404326 MHz
NUC1 13C
P1 9.00 usec
PLW1 55.00000000 W
CHANNEL f2
SFO2 400.2016008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 10.00000000 W
PLW12 0.29660001 W
PLW13 0.24025001 W
F2 - Processing parameters
SI 32768
SF 100.6303590 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

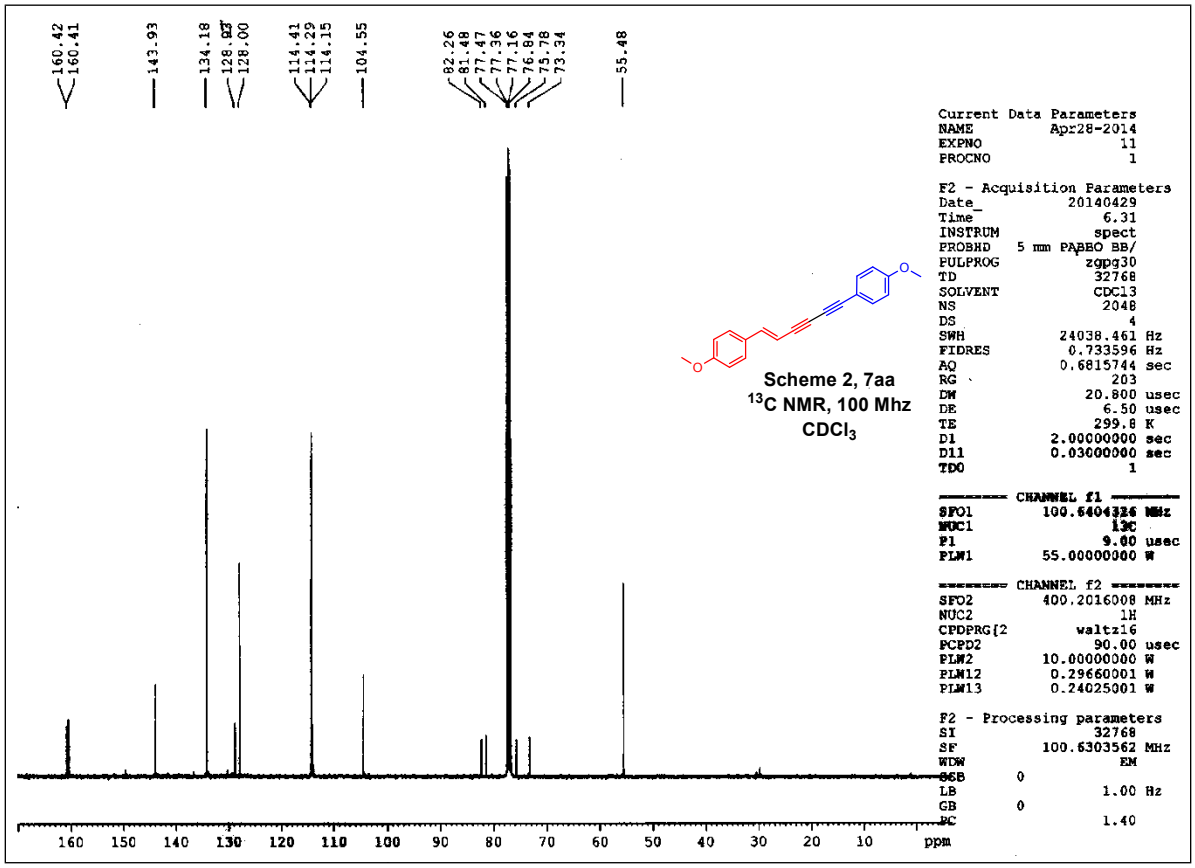

7.470
7.453
7.363
7.348
7.261
5.419
2.493
2.483
2.471
2.211
1.590
1.305
0.070
Table 3, 5bd
1H NMR, 500 MHz
CDCl3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
1.00
1.37
0.56
1.20
1.28
3.65
5.04

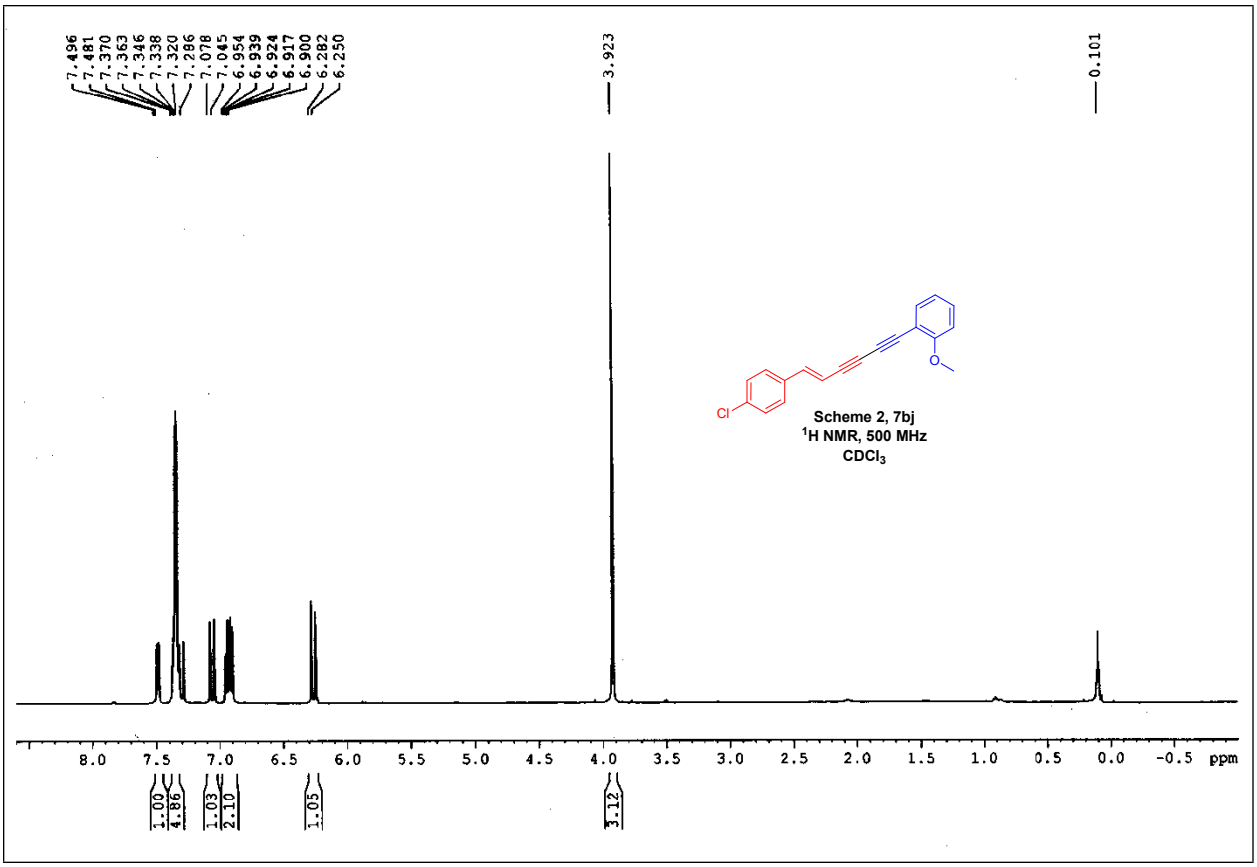

156.05
152.74
131.26
125.37
121.24
101.94
91.52
86.79
77.48
77.16
76.85
36.21
35.08
31.85
31.26
28.45
27.71
26.50
Table3, 5bd
13C NMR, 100 MHz
CDCl3
Current Data Parameters
NAME Jun06-2014
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140606
Time 21.05
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 3200
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 301.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6404326 MHz
NUC1 13C
P1 9.00 usec
PLW1 55.00000000 W
======== CHANNEL f2 ========
SFO2 400.2016008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 10.00000000 W
PLW12 0.29660001 W
PLW13 0.24025001 W
F2 - Processing parameters
SI 32768
SF 100.6303531 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.40
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

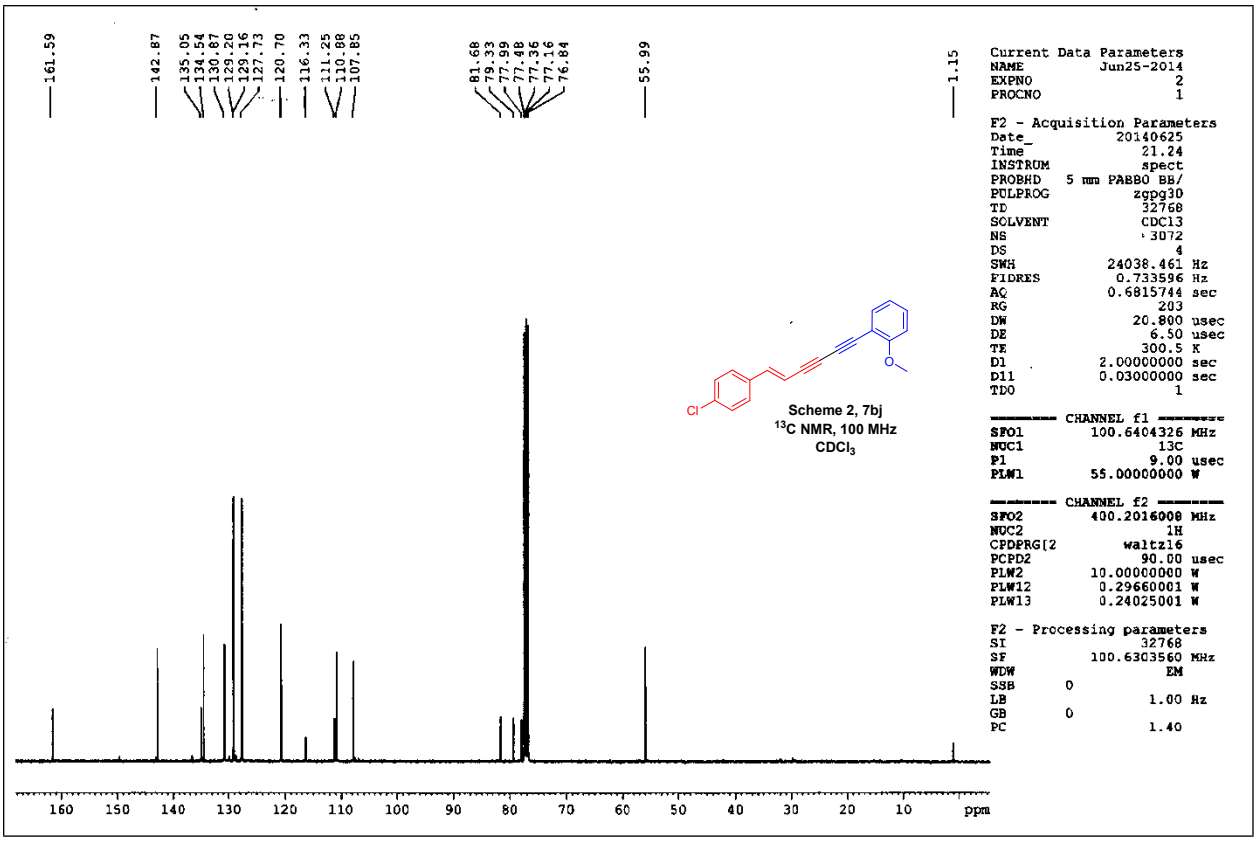

7.315
7.300
7.297
7.275
7.260
7.245
7.214
7.199
7.163
7.148
7.139
7.134
6.767
6.750
6.683
6.651
6.448
5.864
5.832
3.706
2.381
2.365
2.348
1.514
1.500
1.485
1.272
1.269
0.836
0.825
0.823
0.811
Table 3, 5ca
^{1}H NMR, 500 MHz
$CDCl_3$
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm
2.02
0.98
0.59
1.00
0.48
0.50
0.45
1.48
0.98
1.18
2.19
1.64

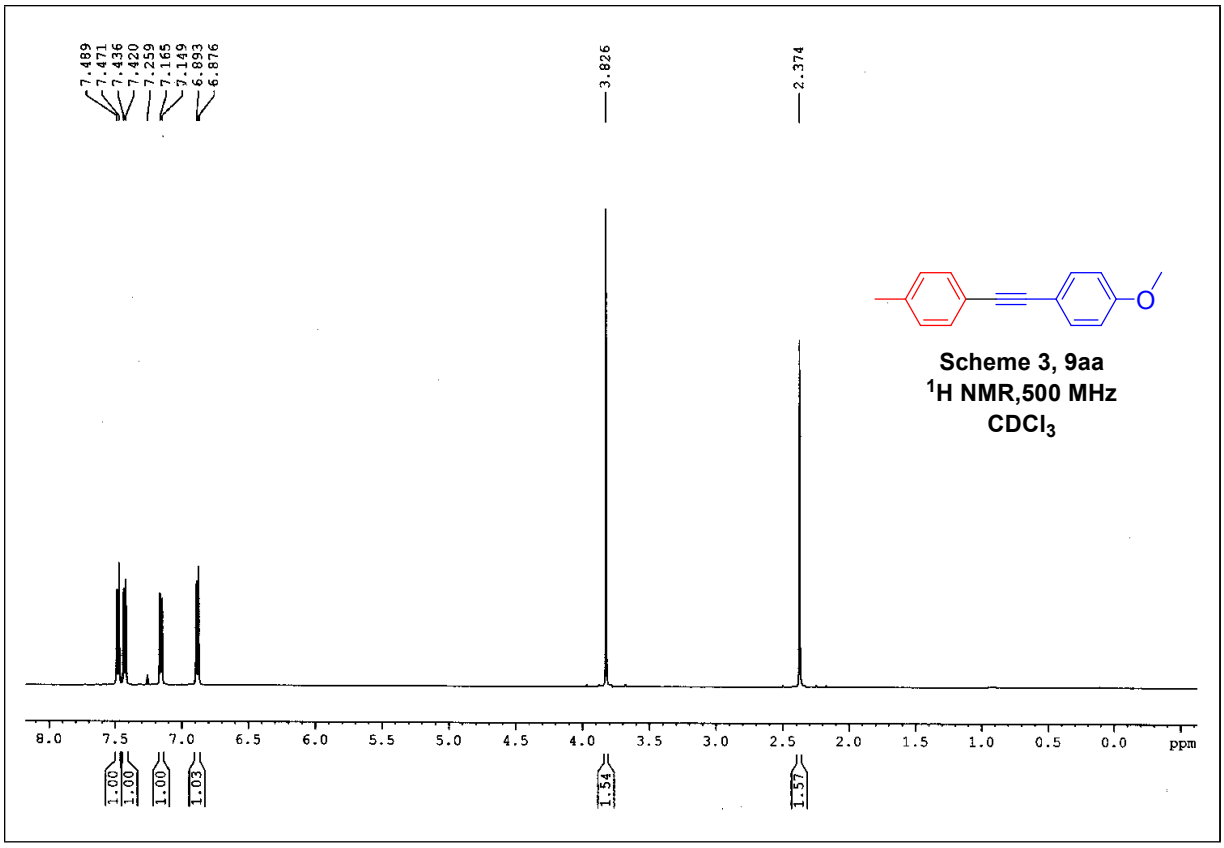

159.63
145.30
140.54
137.48
133.04
132.99
129.02
128.44
127.11
115.94
114.15
114.12
107.43
92.20
88.34
77.48
77.16
76.84
55.38
32.30
28.90
27.17
22.55
14.19
Table3, 5ca
^{13}C NMR, 100 MHz
$CDCl_3$
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
Current Data Parameters
NAME Apr16-2014
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140416
Time 20.57
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 2048
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6404326 MHz
NUC1 13C
P1 9.00 usec
PLW1 55.00000000 W
======== CHANNEL f2 ========
SFO2 400.2016008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 10.00000000 W
PLW12 0.29660001 W
PLW13 0.24025001 W
F2 - Processing parameters
SI 32768
SF 100.6303609 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

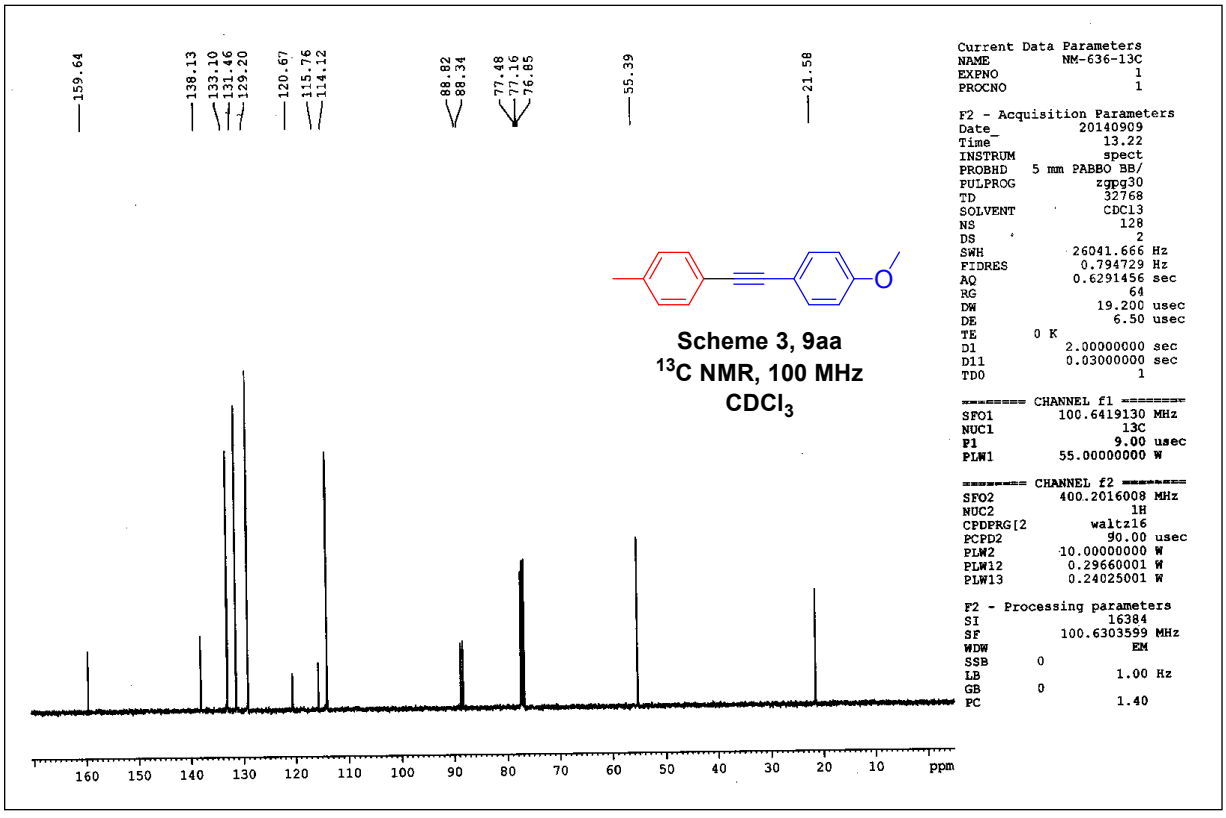

7.456
7.438
7.353
7.336
7.259
7.065
7.033
6.876
6.858
6.844
6.840
6.131
6.098
3.820
Scheme 2, 7aa
1H NMR, 500 Mhz
CDCl3
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.03
1.00
0.50
2.04
0.54
3.08

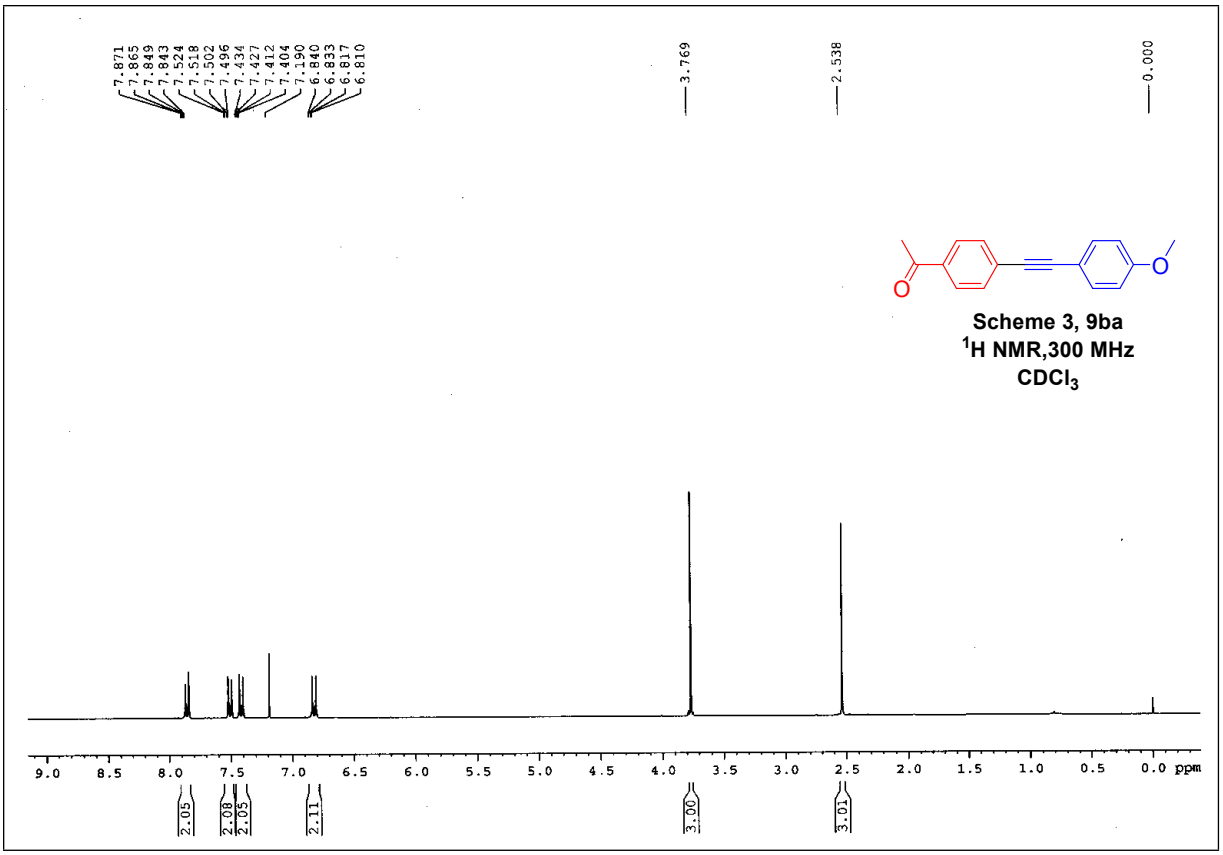

160.42
160.41
143.93
134.18
128.00
114.41
114.29
114.15
104.55
82.26
81.48
77.47
77.36
77.16
76.84
75.78
73.34
55.48
Scheme 2, 7aa
13C NMR, 100 Mhz
CDCl3
Current Data Parameters
NAME Apr28-2014
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140429
Time 6.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 2048
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 299.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
SFO1 100.6404326 MHz
NUC1 13C
P1 9.00 usec
PLW1 55.00000000 W
CHANNEL f2
SFO2 400.2016008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 10.00000000 W
PLW12 0.29660001 W
PLW13 0.24025001 W
F2 - Processing parameters
SI 32768
SF 100.6303562 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.496
7.481
7.370
7.363
7.346
7.338
7.320
7.286
7.078
7.045
6.954
6.939
6.924
6.917
6.900
6.282
6.250
3.923
0.101
Cl
O
Scheme 2, 7bj
1H NMR, 500 MHz
CDCl3
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
ppm
1.00
4.86
1.03
2.10
1.05
3.12

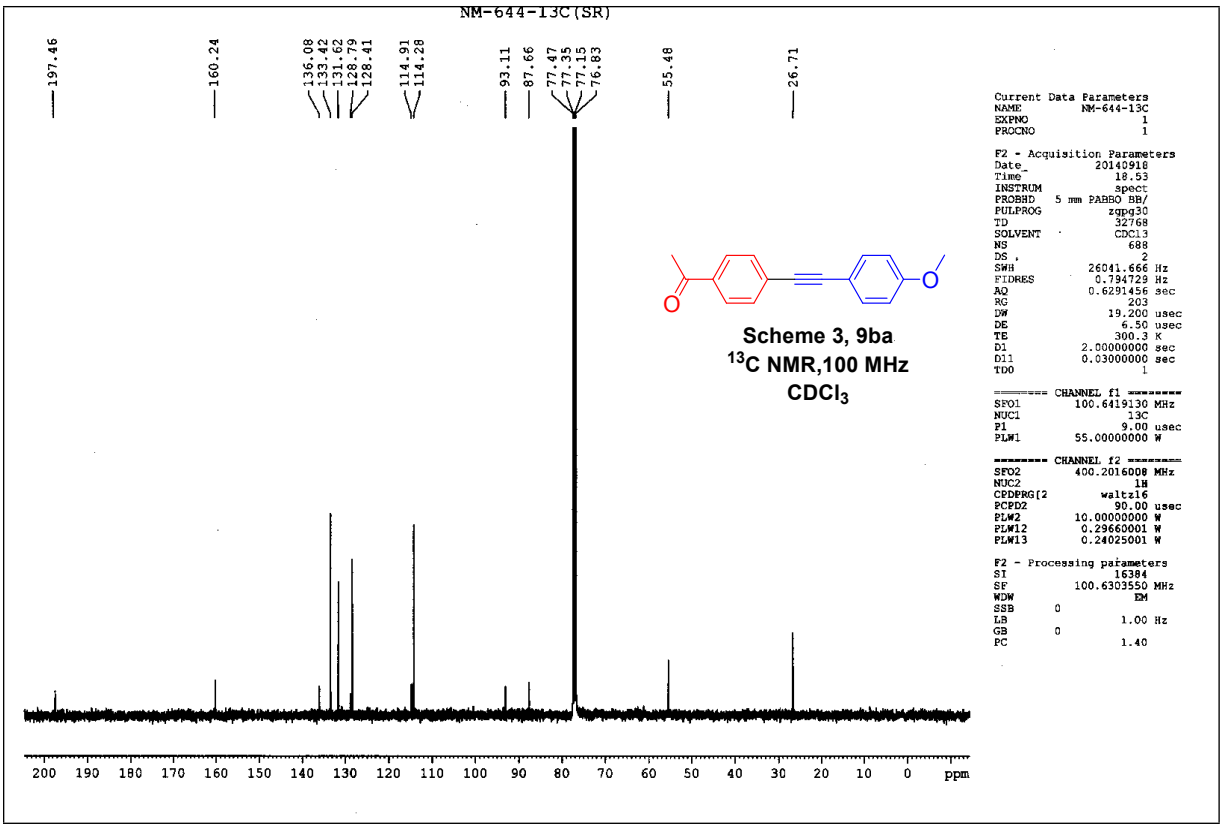

161.59
142.87
135.05
134.54
130.87
129.20
129.16
127.73
120.70
116.33
111.25
110.88
107.85
81.68
79.33
77.99
77.48
77.36
77.16
76.84
55.99
1.15
Cl
O
Scheme 2, 7bj
13C NMR, 100 MHz
CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
Current Data Parameters
NAME Jun25-2014
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140625
Time 21.24
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 3072
DS 4
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
SFO1 100.6404326 MHz
NUC1 13C
P1 9.00 usec
PLW1 55.00000000 W
CHANNEL f2
SFO2 400.2016008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 10.00000000 W
PLW12 0.29660001 W
PLW13 0.24025001 W
F2 - Processing parameters
SI 32768
SF 100.6303560 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


7.489
7.471
7.436
7.420
7.259
7.165
7.149
6.893
6.876
3.826
2.374
O
Scheme 3, 9aa
1H NMR,500 MHz
CDCl3
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
ppm
1.00
1.00
1.00
1.03
1.54
1.57

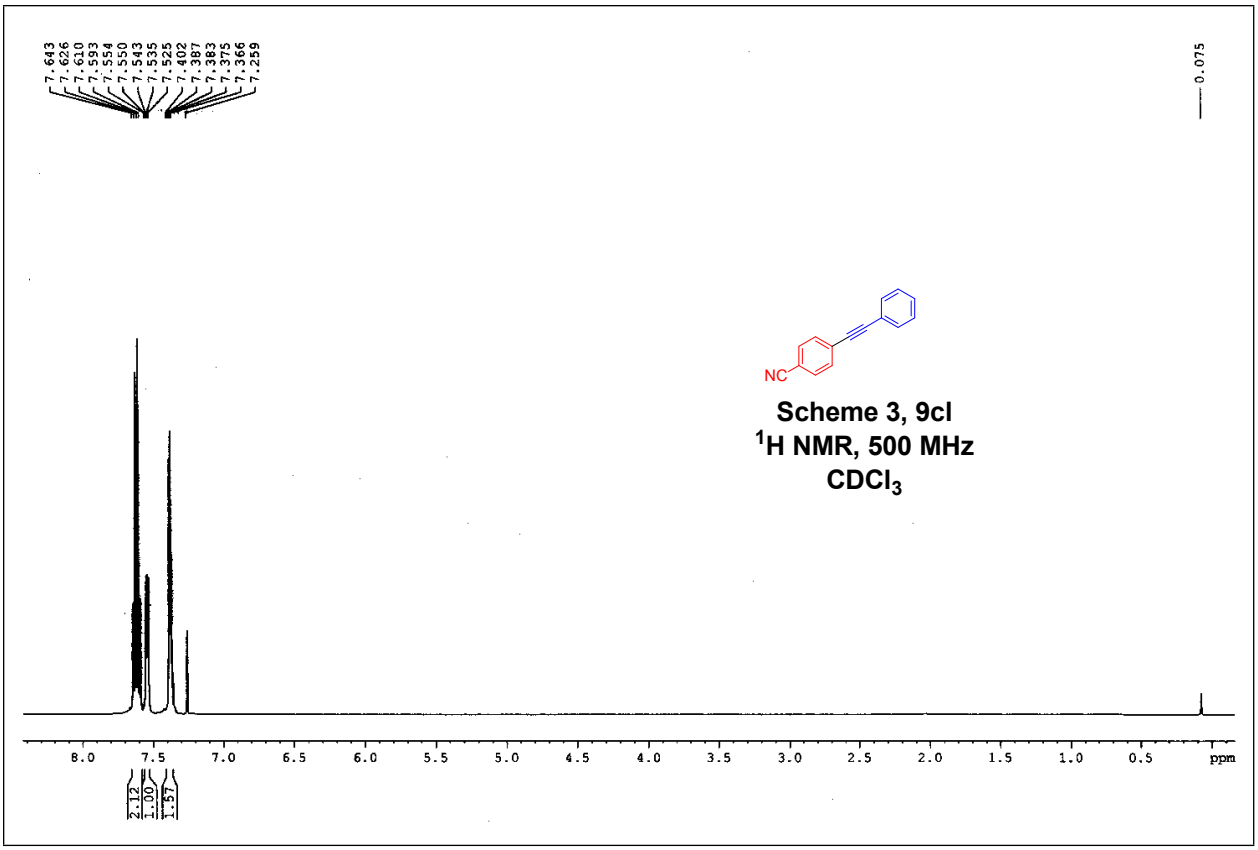

159.64
138.13
133.10
131.46
129.20
120.67
115.76
114.12
88.82
88.34
77.48
77.16
76.85
55.39
21.58
O
Scheme 3, 9aa
13C NMR, 100 MHz
CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
Current Data Parameters
NAME NM-636-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140909
Time 13.22
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 128
DS 2
SWH 26041.666 Hz
FIDRES 0.794729 Hz
AQ 0.6291456 sec
RG 64
DW 19.200 usec
DE 6.50 usec
TE 0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6419130 MHz
NUC1 13C
P1 9.00 usec
PLW1 55.00000000 W
======== CHANNEL f2 ========
SFO2 400.2016008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 10.00000000 W
PLW12 0.29660001 W
PLW13 0.24025001 W
F2 - Processing parameters
SI 16384
SF 100.6303599 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

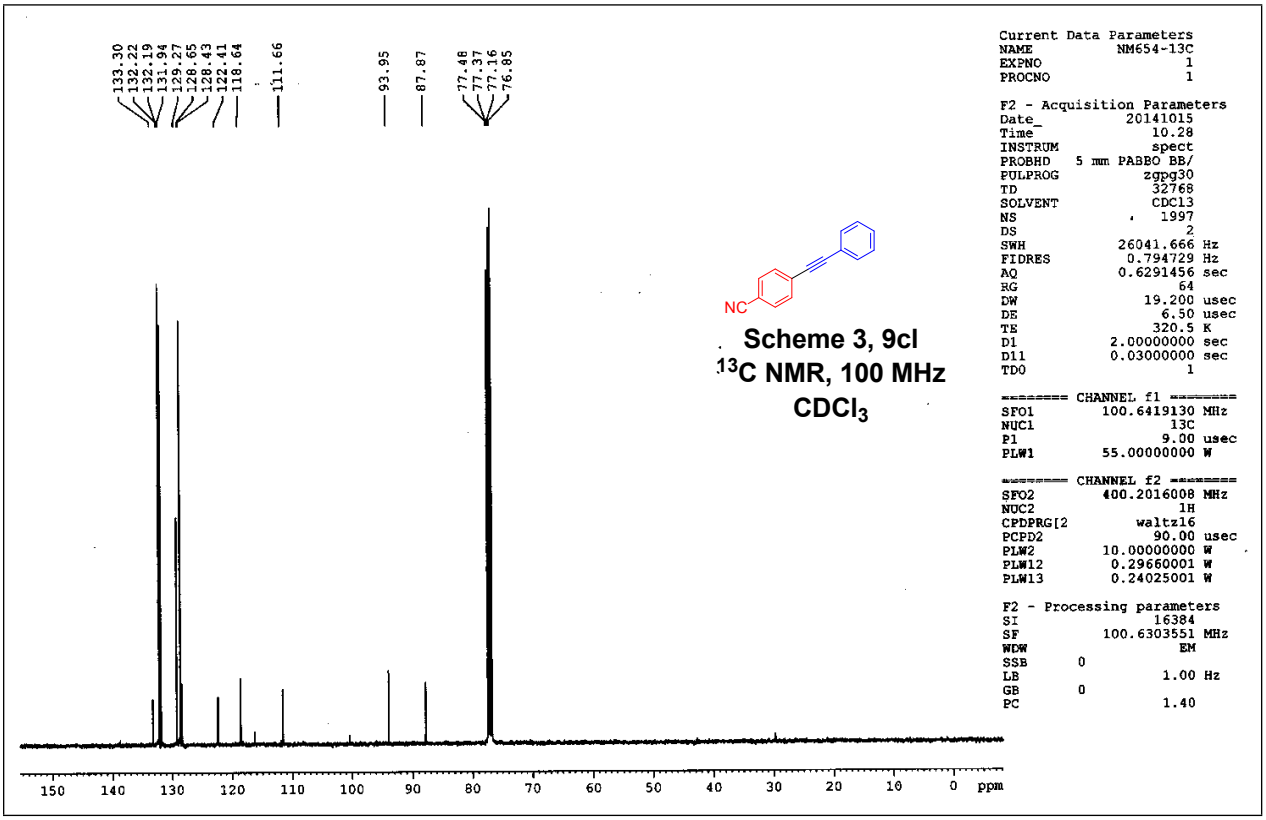


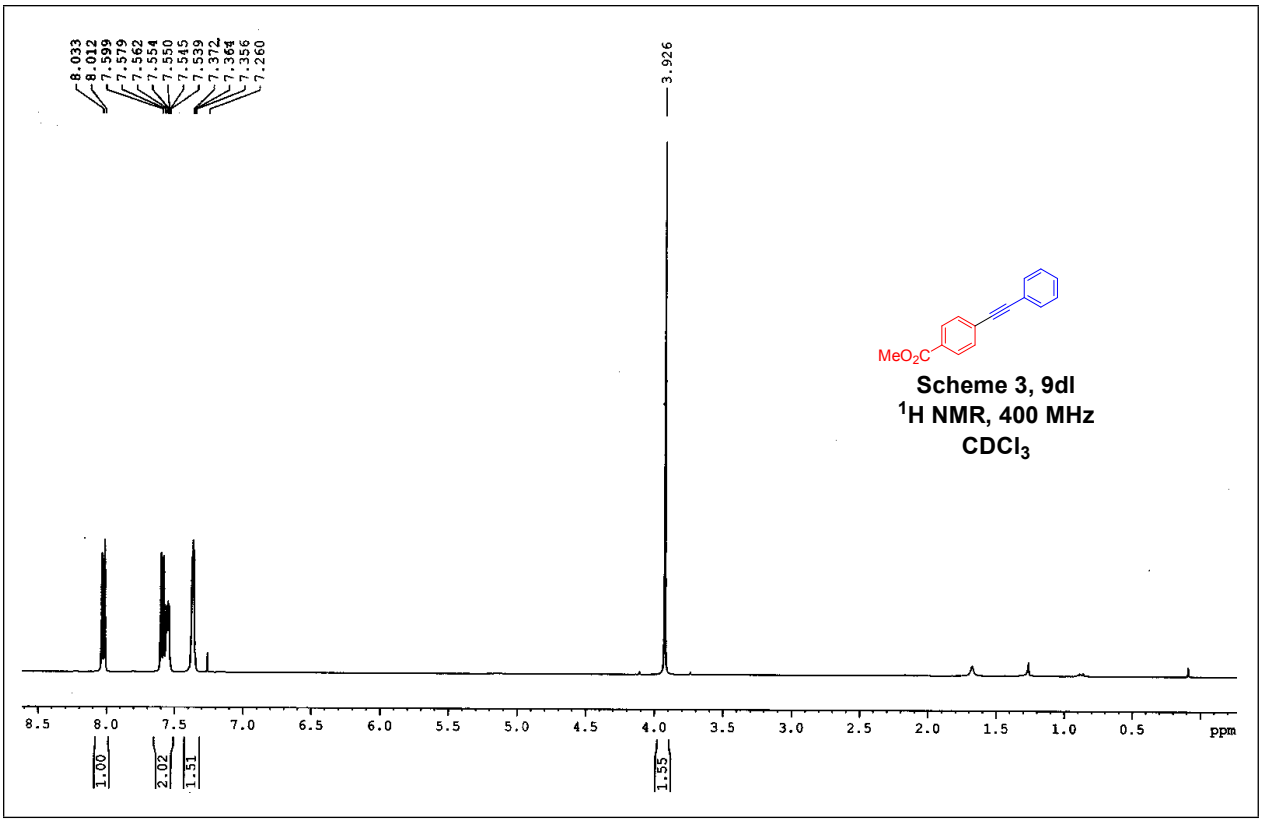
Scheme 3, 9ba
^{1}H NMR,300 MHz
$CDCl_3$

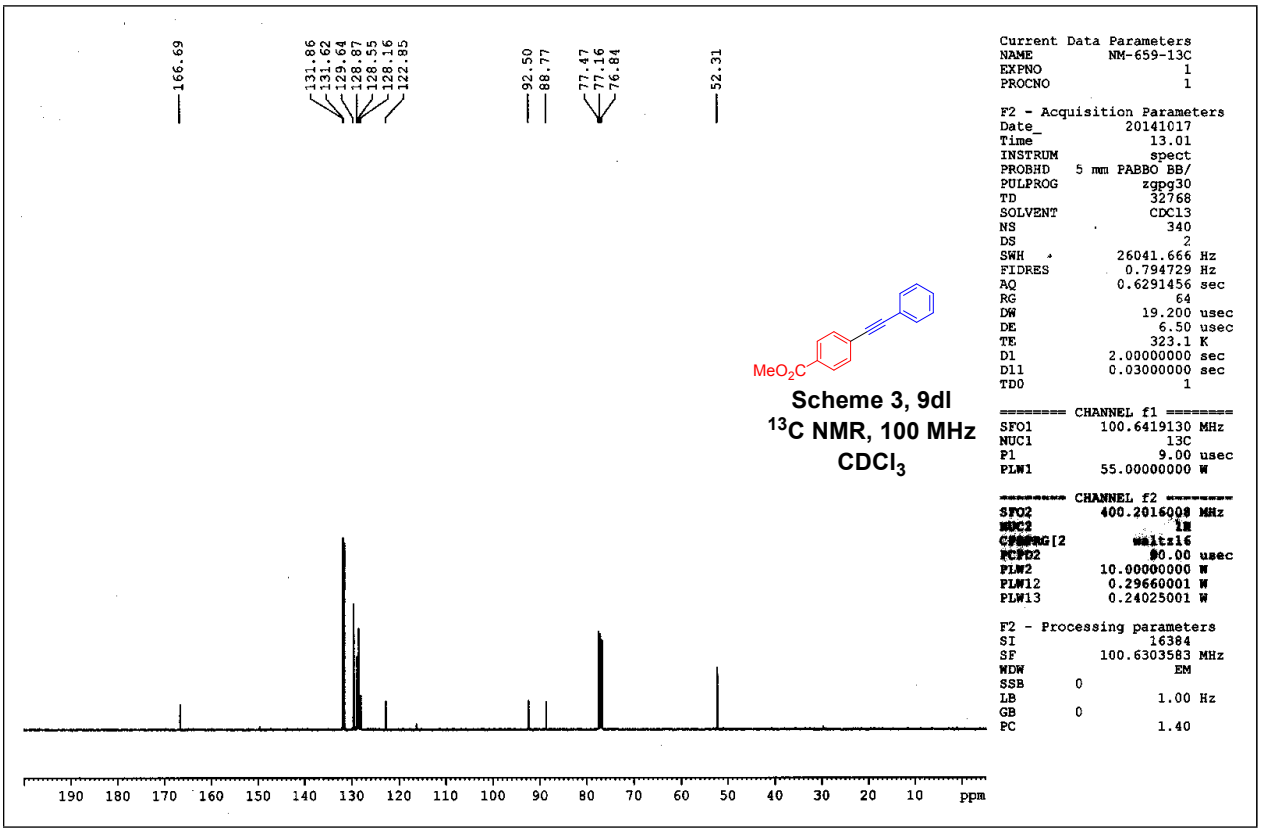


Scheme 3, 9ba
^{13}C NMR,100 MHz
$CDCl_3$


7.643
7.626
7.610
7.593
7.554
7.550
7.543
7.535
7.525
7.402
7.387
7.383
7.375
7.366
7.259
0.075
NC
Scheme 3, 9cl
1H NMR, 500 MHz
CDCl3
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
ppm
2.12
1.00
1.57


133.30
132.22
132.19
131.94
129.27
128.65
128.43
122.41
118.64
111.66
93.95
87.87
77.48
77.37
77.16
76.85
NC
Scheme 3, 9cl
13C NMR, 100 MHz
CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
Current Data Parameters
NAME NM654-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20141015
Time 10.28
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 1997
DS 2
SWH 26041.666 Hz
FIDRES 0.794729 Hz
AQ 0.6291456 sec
RG 64
DW 19.200 usec
DE 6.50 usec
TE 320.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 100.6419130 MHz
NUC1 13C
P1 9.00 usec
PLW1 55.00000000 W
======== CHANNEL f2 ========
SFO2 400.2016008 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 10.00000000 W
PLW12 0.29660001 W
PLW13 0.24025001 W
F2 - Processing parameters
SI 16384
SF 100.6303551 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40





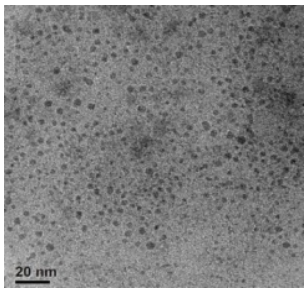

```
Current Data Parameters
NAME          NM-659-13C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20141017
Time              13.01
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD              32768
SOLVENT           CDCl3
NS                  340
DS                    2
SWH           26041.666 Hz
FIDRES         0.794729 Hz
AQ             0.6291456 sec
RG                   64
DW                19.200 usec
DE                 6.50 usec
TE                323.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6419130 MHz
NUC1                13C
P1                 9.00 usec
PLW1         55.00000000 W

======== CHANNEL f2 ========
SFO2        400.2016008 MHz
NUC2                1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2         10.00000000 W
PLW12         0.29660001 W
PLW13         0.24025001 W

F2 - Processing parameters
SI                  16384
SF          100.6303583 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

(a) 

(b)

Figure 2 (a) TEM image of Ni(0) nanoparticles. (b) Ni(0) nanopaticles fringe calculation from HRTEM image.

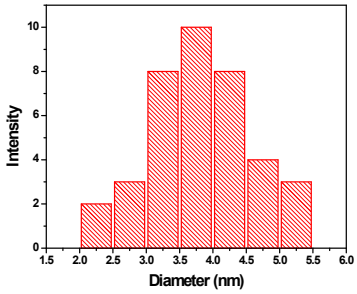


Figure 3. Histogram of the size of Ni(0) nanoparticles obtained from the TEM image.

UV-experiment for the observation of the progress of the reaction

The progress of the reaction was clearly tracked by UV study. The characteristic peak of the reactant **1d** was obtained at 269 nm while the same for product **3dc** (Figure 4(a)) was found at 283 and 301 nm. Thus the formation of **3dc** was chosen as model experiment and the cross coupling between **1d** (0.10 M) and **2c** (0.10 M) at 100 ^{o}C in NMP was monitored in situ by UV. The diminution of **1d** and creation of **3dc** were clearly shown by shifting of the peak position from 270 nm and evolution of two new peaks at 283 nm and 300 nm (Figure 4 (b)). Increase in the concentration of the product was observed with time.

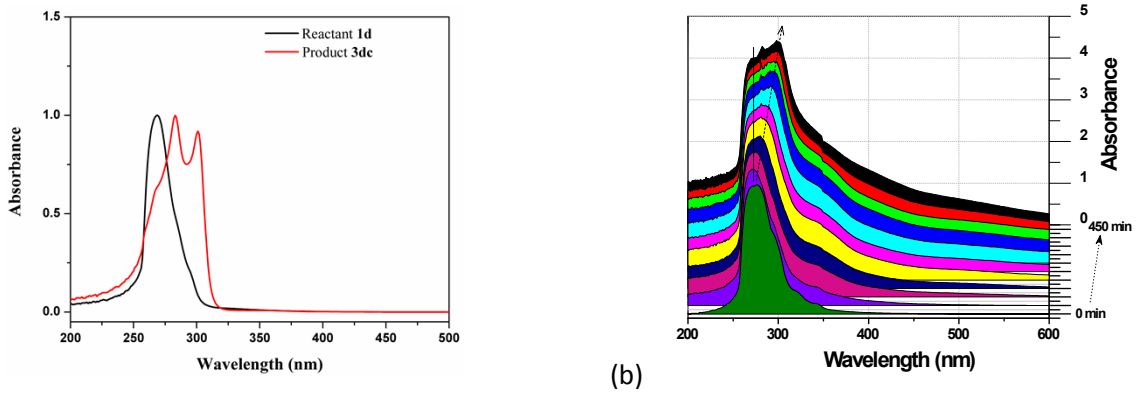


Figure 4. (a) UV-spectra of reactant **1d**, and product **3dc.** (b) *In situ* UV-spectra for the reaction of 1-(2-bromoethynyl)-4-methoxybenzene and 1-octyne in the standardized reaction conditions