Cleavage of Carbon-Carbon Triple Bond: Direct Transformation of Alkynes to Nitriles

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Supporting Information

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General. ^{1}H NMR and ^{13}C NMR spectra were recorded on 600 MHz spectrometer. Chemical Shifts are reported in δ (ppm) from tetramethylsilane as an internal standard. Data are reported as follows: chemical shifts, relative integration value, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz). Infrared spectra were obtained using an FT spectrometer. Analytical thin layer chromatography was performed on Merck silica gel 60 F254 TLC plates.

General procedure for the preparation of Internal alkynes 1

Alkyne **1a**,[S1] **1c**,[S2] **1e**,[S3] **1f**,[S4] **1h**,[S5] **1i**,[S6] **1j**,[S7] **1k**,[S5] **1l**,[S8] **1m**,[S9] **1n**,[S6] **1o**,[S1] **1p**,[S10] **1q**,[S11] **1z**,[S12] **1aa**[S13] and **1bb**[S14] are all known compounds. Diphenylacetylene (**1d**) and 4-Ethynylanisole (**1s**) were purchased from Aldrich and used as received.

To a solution of aryl iodide (1 mmol) in Et_3N (5 mL) was added $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), PPh_3 (26 mg, 0.1 mmol), CuI (9.5 mg, 0.05 mmol) and alkyne (1.3 mmol) and stirred at room temperature under nitrogen. The reaction was monitored by TLC to establish completion. Saturated aqueous NH_4Cl solution was added to the reaction mixture and extracted with AcOEt (three times). The combined organic solution was washed with brine, dried over anhydrous $MgSO_4$, and concentrated at the reduced pressure. Column chromatography on silica gel using hexanes/ethyl acetate as an eluent afforded **1** (Table S1).

Table S1. Synthesis of Internal Alkyne 1

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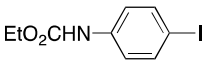
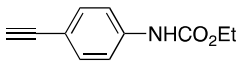
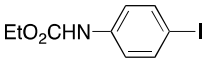
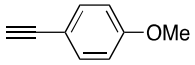
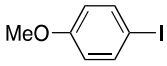
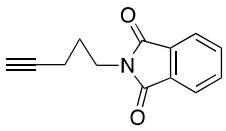
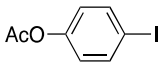
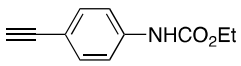
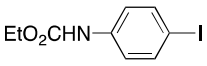
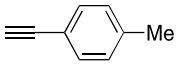
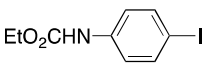
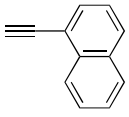
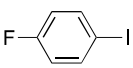
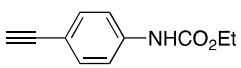
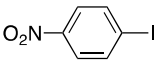
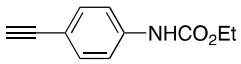
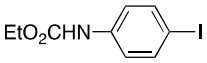
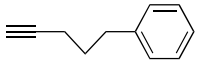
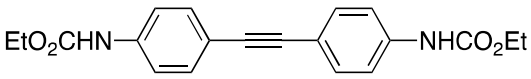
1b			82
1g			85
1r			quant.
1t			85
1u			97
1v			80
1w			89

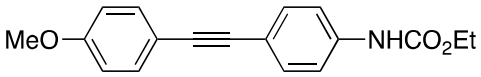
1x			86
1y			82



1b

Diethyl (ethyne-1,2-diylbis(4,1-phenylene))dicarbamate: 1b.

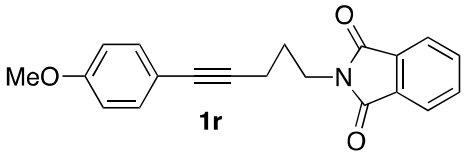
Colorless needles; mp 224–225 °C. ^{1}H-NMR (DMSO-d_6) δ 9.85 (2H, br s), 7.50 (4H, d, J = 8.6 Hz), 7.45 (4H, d, J = 8.6 Hz), 4.14 (4H, q, J = 7.0 Hz), 1.26 (6H, t, J = 7.0 Hz). ^{13}C-NMR (DMSO-d_6) δ 153.9, 139.8, 132.3, 118.5, 116.4, 88.9, 60.9, 14.8. IR ($CHCl_3$, cm^{-1}) 3433, 3036, 3009, 1734, 1516, 1197, 810. MS (EI): *m/z* = 352 (M^+). HRMS (EI): *m/z* calcd for $C_{20}H_{20}N_2O_4$: 352.1423; found: 352.1425.



1g

Ethyl (4-(4-methoxyphenylethynyl)phenyl)carbamate: 1g.

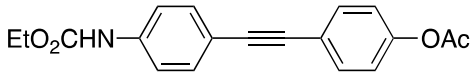
Colorless prisms; mp 149–150.5 °C. ^{1}H-NMR ($CDCl_3$) δ 7.45 (4H, d, J = 8.9 Hz), 7.37 (2H, d, J = 8.2 Hz), 6.87 (2H, d, J = 8.9 Hz), 6.67 (1H, br s), 4.23 (2H, q, J = 7.0 Hz), 3.82 (3H, s), 1.31 (3H, t, J = 7.0 Hz). ^{13}C-NMR ($CDCl_3$) δ 159.5, 153.3, 137.7, 133.0, 132.3, 118.3, 118.2, 115.5, 114.0, 88.7, 87.8, 61.4, 55.3, 14.5. IR ($CHCl_3$, cm^{-1}) 3434, 3037, 3008, 2839, 1734, 1611, 1584, 1528, 1517, 1502, 1466, 1409, 1316, 1287, 1252, 1244, 1196, 1181, 1174, 1140, 1064, 1032, 835. MS (EI): *m/z* = 295 (M^+). HRMS (EI): *m/z* calcd for $C_{18}H_{17}NO_3$: 295.1208; found: 295.1204.



1r

2-(5-(4-Methoxyphenyl)pent-4-yn-1-yl)isoindoline-1,3-dione: 1r.

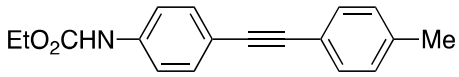
Yellow powder; mp 86–88 °C. ^{1}H-NMR ($CDCl_3$) δ 7.82 (2H, dd, J = 2.9, 1.5 Hz), 7.67 (2H, dd, J = 2.9, 1.5 Hz), 7.22 (2H, d, J = 8.9 Hz), 6.75 (2H, d, J = 8.9 Hz), 3.86 (2H, t, J = 7.2 Hz), 3.78 (3H, s), 2.48 (2H, t, J = 6.9 Hz), 2.03–1.98 (2H, m). ^{13}C-NMR ($CDCl_3$) δ 168.4, 159.0, 133.9, 132.8, 132.1, 123.2, 115.8, 113.7, 87.1, 81.0, 55.2, 37.4, 27.5, 17.30. IR ($CHCl_3$, cm^{-1}) 3019, 2955, 2939, 2911, 1771, 1712, 1608, 1510, 1469, 1441, 1397, 1374, 1289, 1246, 1173, 1117, 1029, 884, 833. MS (EI): *m/z* = 319 (M^+). HRMS (EI): *m/z* calcd for $C_{20}H_{17}NO_3$: 319.1208; found: 319.1209.



1t

4-(4-(Ethoxycarbonyl)aminophenylethynyl)phenyl acetate: 1t.

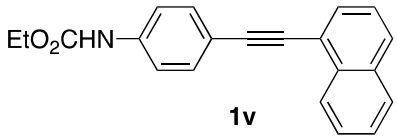
Colorless needles; mp 199–200 °C. ^{1}H-NMR ($CDCl_3$) δ7.52 (2H, d, J = 8.2 Hz), 7.47 (2H, d, J = 8.2 Hz), 7.38 (2H, d, J = 7.6 Hz), 7.08 (2H, d, J = 8.2 Hz), 6.64 (1H, br s), 4.24 (2H, q, J = 7.2 Hz), 2.31 (3H, s), 1.32 (3H, t, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$) δ 169.2, 153.2, 150.3, 138.1, 132.6, 132.5, 121.7, 121.1, 118.1, 117.7, 89.2, 87.9, 61.4, 21.2, 14.5. IR ($CHCl_3$, cm^{-1}) 3434, 3037, 3009, 1765, 1735, 1610, 1584, 1525, 1518, 1498, 1409, 1370, 1311, 1254, 1239, 1190, 1165, 1064, 1017, 1097, 1017, 839. MS (EI): *m/z* = 323 (M^+). HRMS (EI): *m/z* calcd for $C_{19}H_{17}NO_4$: 323.1158; found: 323.1156.



1u

Ethyl (4-(*p*-tolylethynyl)phenyl)carbamate: 1u.

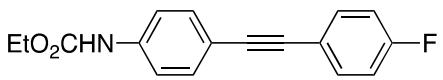
Colorless plates; mp 120–122 °C. ^{1}H-NMR ($CDCl_3$) δ 7.46 (2H, d, J = 8.9 Hz), 7.41 (2H, d, J = 8.2 Hz), 7.37 (2H, d, J = 8.2 Hz), 7.14 (2H, d, J = 7.6 Hz), 6.69 (1H, br s), 4.23 (2H, q, J = 7.1 Hz), 2.36 (3H, s), 1.31 (3H, t, J = 6.9 Hz). ^{13}C-NMR ($CDCl_3$) δ 153.3, 138.2, 137.8, 132.4, 131.4, 129.1, 120.2, 118.1, 118.1, 88.9, 88.5, 61.4, 21.5, 14.5. IR ($CHCl_3$, cm^{-1}) 3434, 3026, 3008, 2985, 2924, 1734, 1609, 1584, 1529, 1517, 1501, 1409, 1310, 1289, 1253, 1237, 1196, 1180, 1097, 1065, 838, 818, 810. MS (EI): *m/z* = 279 (M^+). HRMS (EI): *m/z* calcd for $C_{18}H_{17}NO_2$: 279.1259; found: 279.1252.



1v

Ethyl (4-(naphthalen-1-ylethynyl)phenyl)carbamate: 1v.

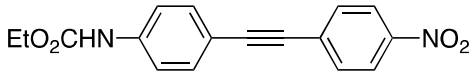
Pale orange powder; mp 110–111 °C. ^{1}H-NMR ($CDCl_3$) δ 8.43 (1H, d, J = 8.2 Hz), 7.86 (1H, d, J = 8.2 Hz), 7.82 (1H, d, J = 8.2 Hz), 7.74 (1H, d, J = 6.9 Hz), 7.60–7.58 (3H, m), 7.53 (1H, td, J = 7.6, 1.4 Hz), 7.45–7.43 (3H, m), 6.71 (1H, s), 4.25 (2H, q, J = 7.2 Hz), 1.32 (3H, t, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$) δ 153.3, 138.1, 133.2, 132.5, 130.2, 128.6, 128.3, 126.7, 126.4, 126.2, 125.3, 121.0, 118.2, 118.0, 94.1, 86.9, 61.4, 14.5. IR ($CHCl_3$, cm^{-1}) 3434, 3009, 1734, 1610, 1585, 1521, 1507, 1504, 1409, 1397, 1314, 1289, 1254, 1197, 1180, 1064, 838, 811. MS (EI): *m/z* = 315 (M^+). HRMS (EI): *m/z* calcd for $C_{21}H_{17}NO_2$: 315.1259; found: 315.1258.



1w

Ethyl (4-(4-fluorophenyl)ethynylphenyl)carbamate: 1w.

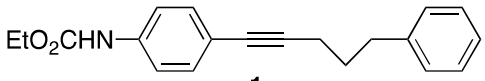
Pale orange powder; mp 133–135 °C. ^{1}H-NMR ($CDCl_3$) δ7.50–7.45 (4H, m), 7.38 (2H, d, *J* = 8.2 Hz), 7.03 (2H, t, *J* = 8.6 Hz), 6.70 (1H, br s), 4.24 (2H, q, *J* = 7.2 Hz), 1.32 (3H, t, *J* = 7.2 Hz). ^{13}C-NMR ($CDCl_3$) δ 163.2, 161.6, 153.3, 138.1, 133.4, 133.3, 132.4, 119.5, 119.5, 118.2, 117.7, 115.7, 115.5, 88.8, 87.7, 61.5, 14.5. IR ($CHCl_3$, cm^{-1}) 3434, 3035, 2985, 1734, 1611, 1584, 1527, 1518, 1500, 1409, 1311, 1254, 1239, 1196, 1182, 1155, 1065, 1017, 838. MS (EI): *m/z* = 283 (M^+). HRMS (EI): *m/z* calcd for $C_{17}H_{14}FNO_2$: 283.1009; found: 283.1007.



1x

Ethyl (4-(4-nitrophenylethynyl)phenyl)carbamate: 1x.

Yellow needles; mp 194–195 °C. ^{1}H-NMR ($CDCl_3$) δ 8.21 (2H, d, *J* = 8.9 Hz), 7.64 (2H, d, *J* = 8.9 Hz), 7.51 (2H, d, *J* = 8.9 Hz), 7.43 (2H, d, *J* = 8.2 Hz), 6.72 (1H, br s), 4.25 (2H, q, *J* = 7.0 Hz), 1.33 (3H, t, *J* = 7.0 Hz). ^{13}C-NMR ($CDCl_3$) δ 153.2, 146.8, 139.0, 132.9, 132.1, 130.4, 123.6, 118.2, 116.5, 94.7, 87.1, 61.5, 14.5. IR ($CHCl_3$, cm^{-1}) 3433, 3035, 2216, 1735, 1592, 1585, 1522, 1410, 1345, 1311, 1255, 1196, 1182, 1108, 1063, 854, 839. MS (EI): *m/z* = 310 (M^+). HRMS (EI): *m/z* calcd for $C_{17}H_{14}N_2O_4$: 310.0954; found: 310.0952.



1y

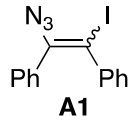
Ethyl (4-(5-phenylpent-1-yn-1-yl)phenyl)carbamate: 1y.

Brown oil. ^{1}H-NMR ($CDCl_3$) δ 7.33–7.30 (6H, m), 7.21–7.20 (3H, m), 6.66 (1H, br s), 4.22 (2H, q, *J* = 7.0 Hz), 2.78 (2H, t, *J* = 7.6 Hz), 2.40 (2H, t, *J* = 6.9 Hz), 1.94–1.89 (2H, m), 1.30 (3H, t, *J* = 7.0 Hz). ^{13}C-NMR ($CDCl_3$) δ 153.3, 141.6, 137.3, 132.3, 128.5, 128.3, 125.9, 118.7, 118.1, 89.0, 80.7, 61.3, 34.8, 30.3, 18.8, 14.5. IR ($CHCl_3$, cm^{-1}) 3435, 3009, 2943, 1733, 1610, 1584, 1521, 1504, 1410, 1312, 1252, 1237, 1197, 1066, 838. MS (EI): *m/z* = 307 (M^+). HRMS (EI): *m/z* calcd for $C_{20}H_{21}NO_2$: 307.1572; found: 307.1578.

General procedure of triple bond cleavage reaction

To a solution of alkyne **1** (0.4 mmol) in 1,2-dichloroethane (1 mL) and MeCN (1 mL) was added NIS (0.96 mmol) and $TMSN_3$ (0.96 mmol). Reaction mixture was stirred at room temperature for 2 h then at 70 °C for 1 h. After the completion of the reaction was confirmed by TLC, 10% $Na_2S_2O_3$ aqueous solution was added for quenching. The aqueous layer was extracted with AcOEt (two times). The combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography to give nitrile **2** and **3**.

Nitrile **2b**[S15] and **3a**[S16] are known compounds. 4-Methoxybenzonitrile (**2a**), *p*-tolunitrile (**2c**), benzonitrile (**2d**), 4-fluorobenzonitrile (**2e**), 3-methoxybenzonitrile (**2f**), 4'-cyanoacetanilide (**2g**), 1-naphthonitrile (**3b**), 4-(trifluoromethyl)benzonitrile (**3c**), 2-(trifluoromethyl)benzonitrile (**3d**), 4-nitrobenzonitrile (**3e**), 4-phenylbutyronitrile (**3f**), 4-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-butyronitrile (**3g**) and 2-methoxybenzonitrile (**3h**) are commercially available reagents.



A1

1-Azide-2-iodo-1,2-diphenylethylene (mixture of *E*-and *Z*-stereoisomers)**: A1.**

Unstable pale yellow prisms. Decomposed at 80 °C. ^{1}H-NMR ($CDCl_3$) δ7.54–7.29 (minor), 7.15–7.06 (major). ^{13}C-NMR ($CDCl_3$) δ 141.9, 141.1, 140.7, 139.1, 136.9, 132.0, 130.3, 129.4, 129.4, 128.9, 128.9, 128.7, 128.7, 128.4, 128.1, 127.8, 127.6, 127.3, 86.0, 85.3. IR ($CHCl_3$, cm^{-1}) 3035, 2110, 1599, 1445, 1294, 1275, 1260, 1237, 808. MS (EI): *m/z* = 347 (M^+). HRMS (EI): *m/z* calcd for $C_{14}H_{10}IN_3$: 346.9919; found: 346.9918.

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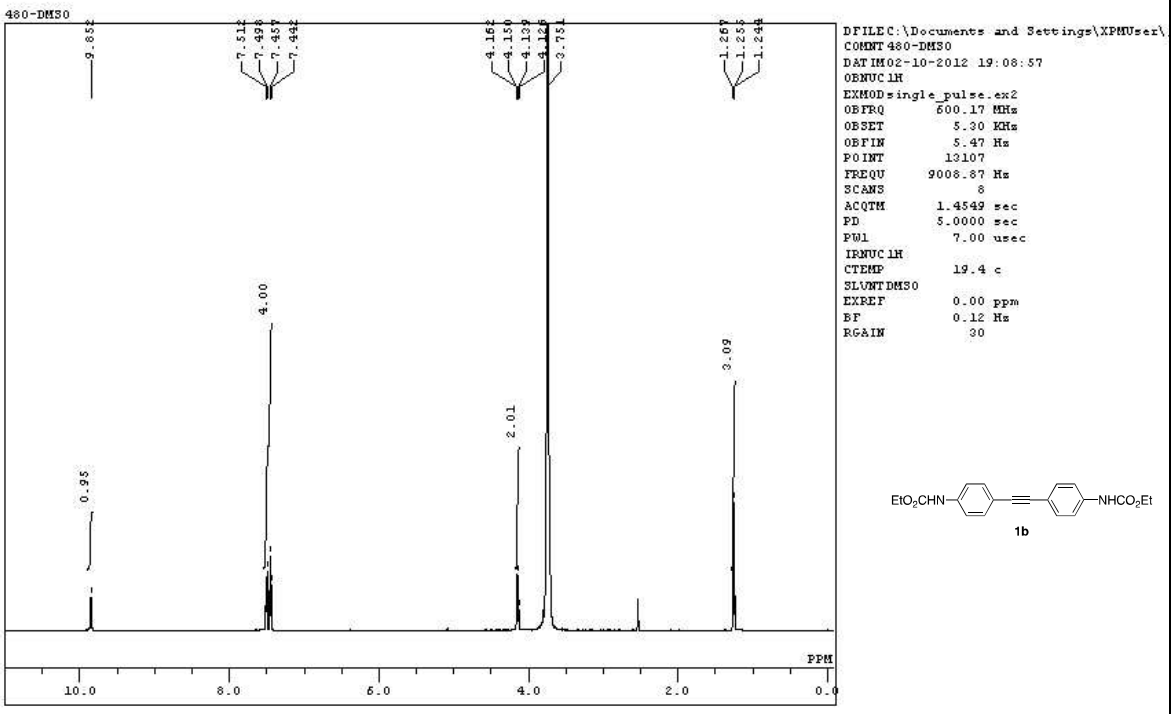
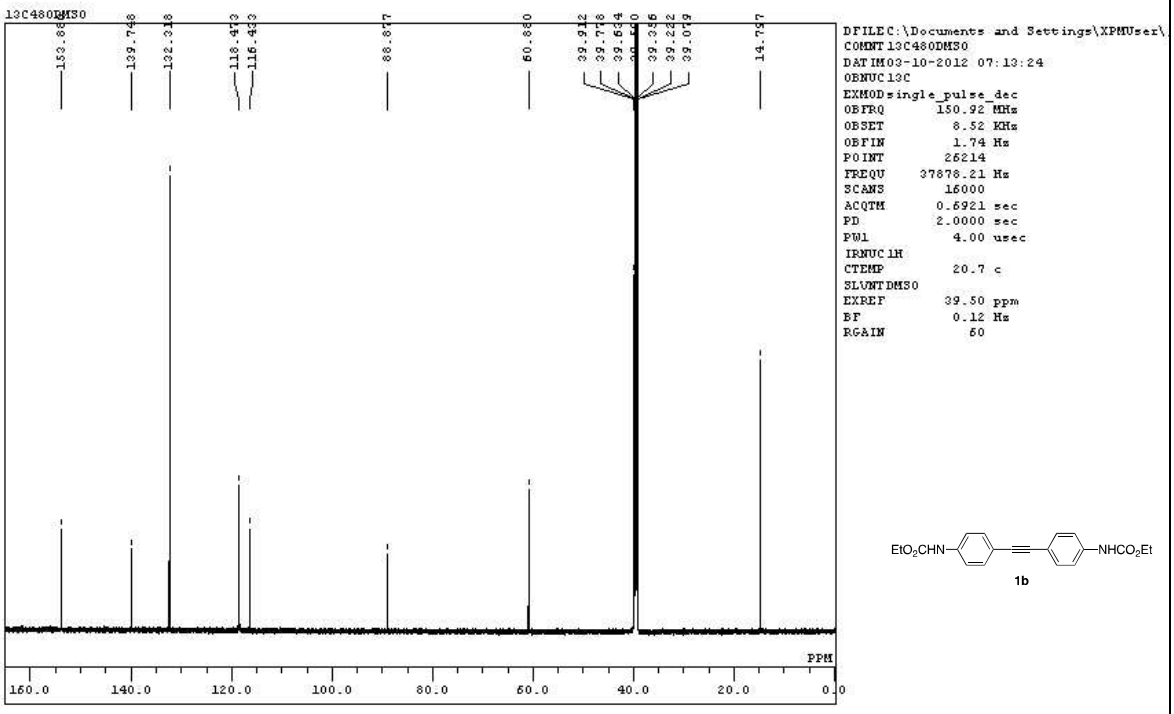
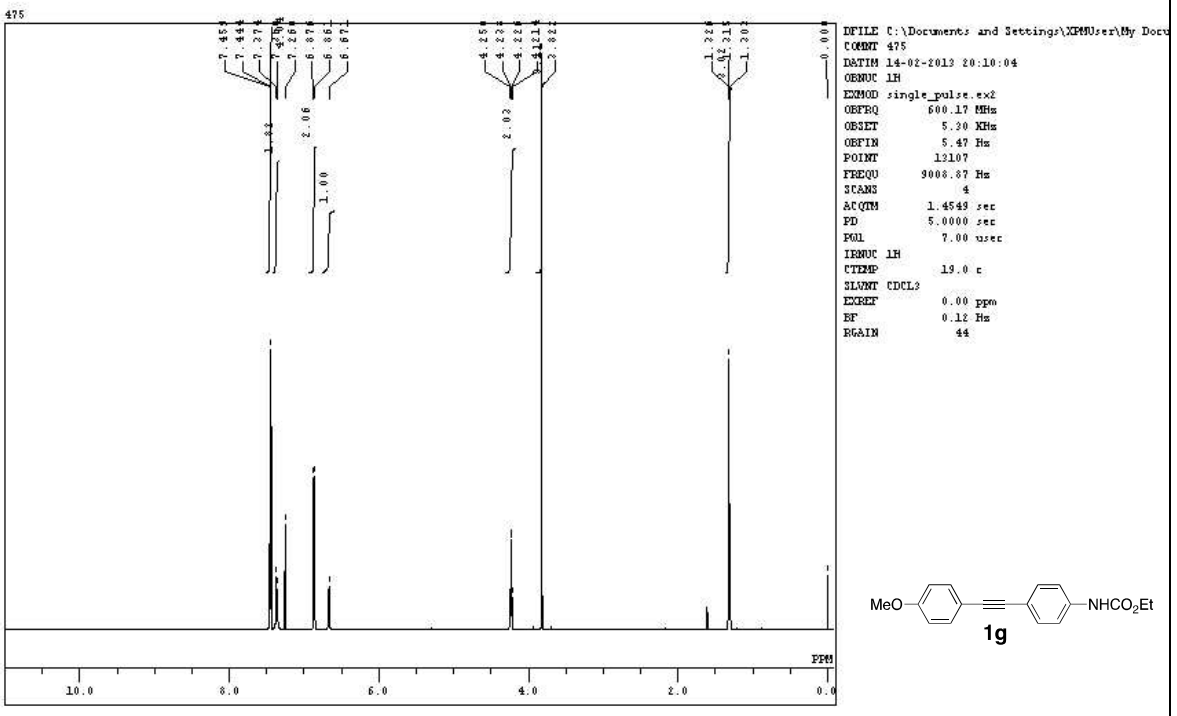
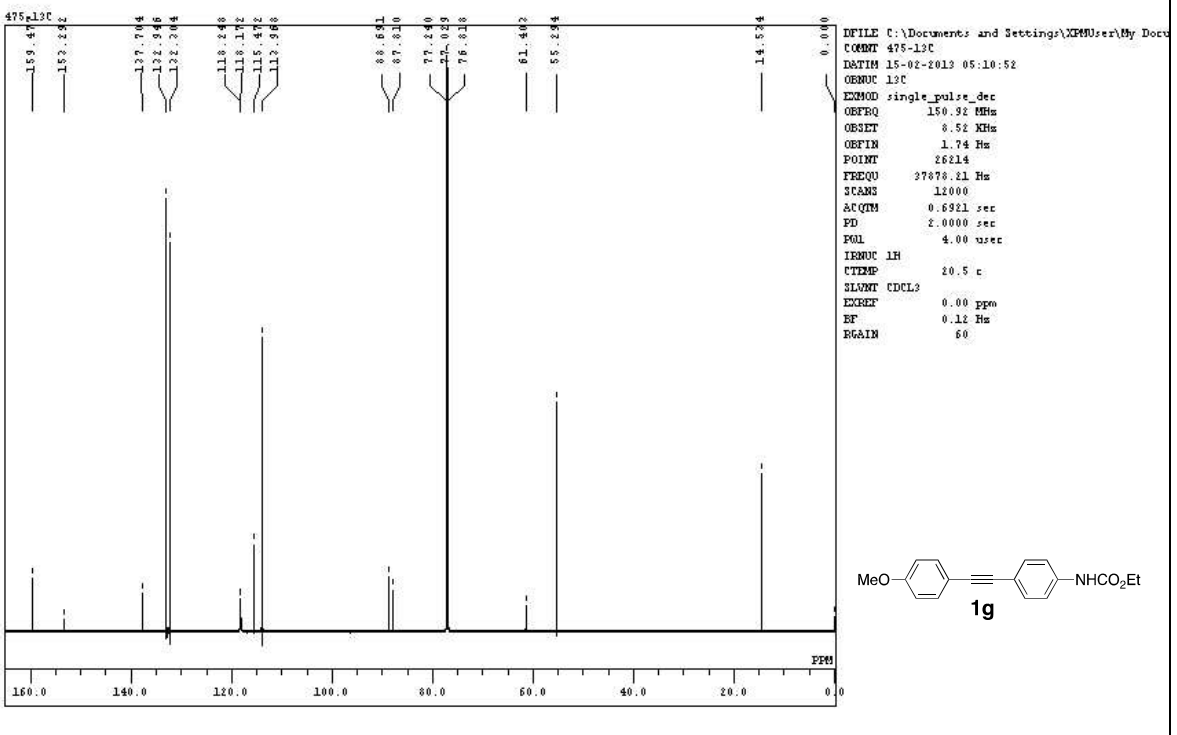
Diethyl (ethyne-1,2-diylbis(4,1-phenylene))dicarbamate (1b)



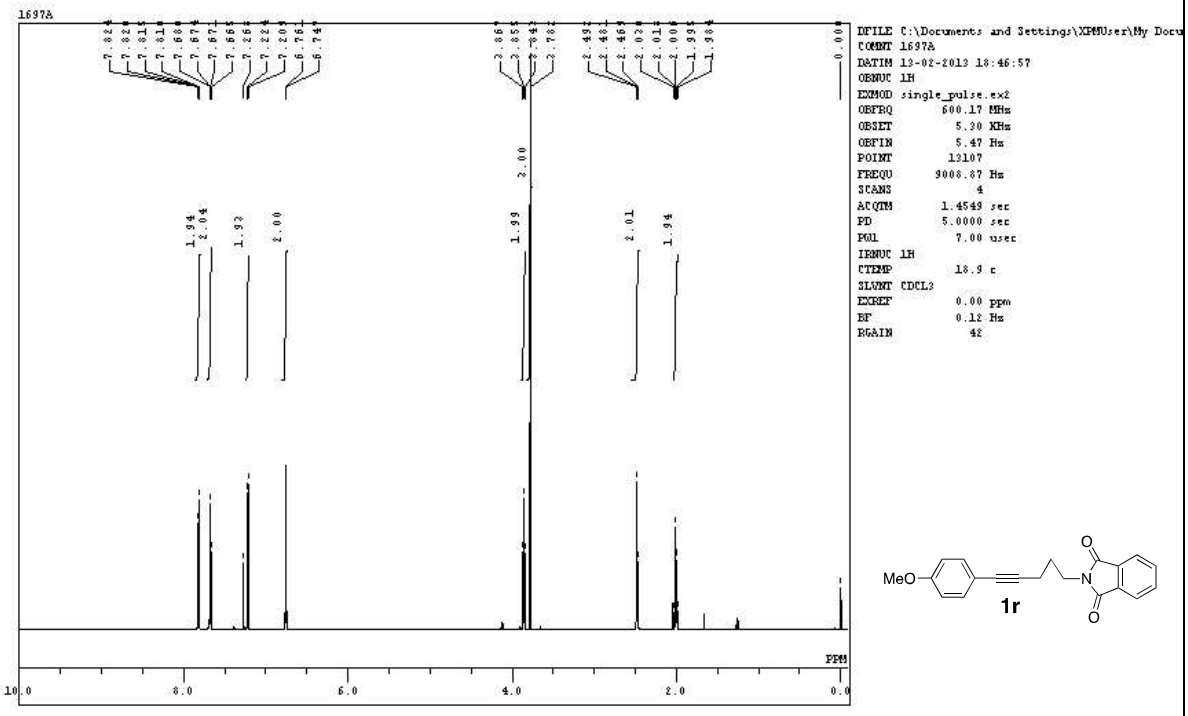


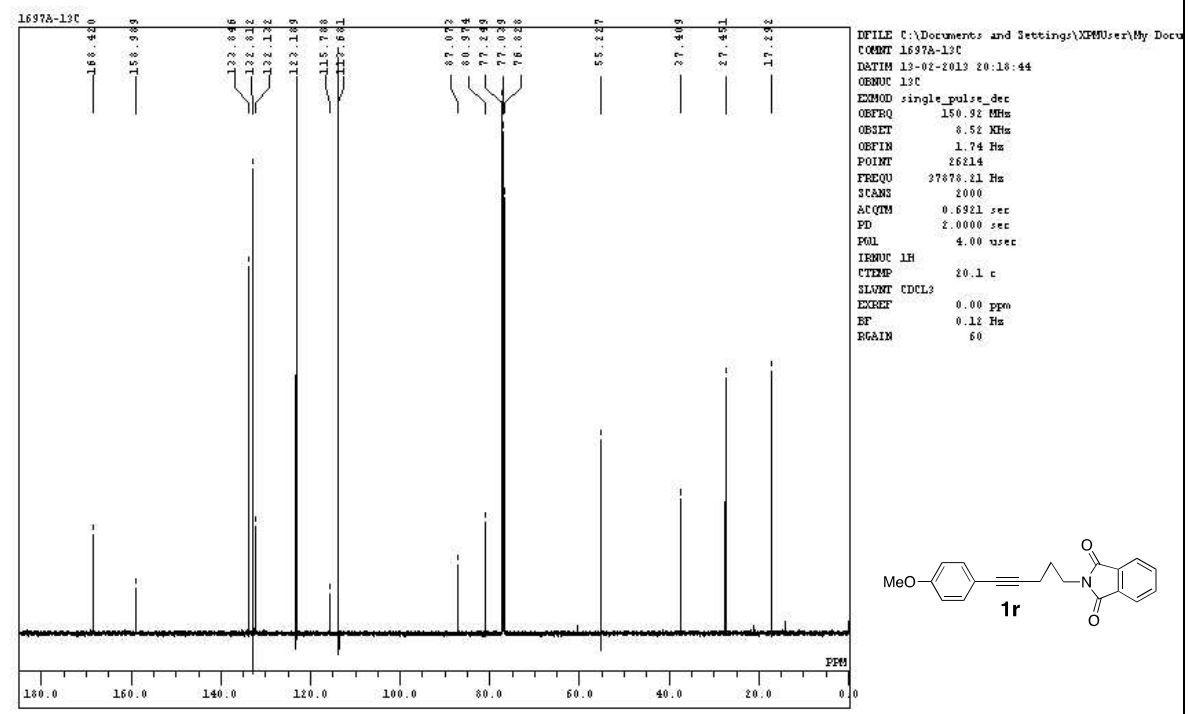
Ethyl (4-(4-methoxyphenylethynyl)phenyl)carbamate (1g)



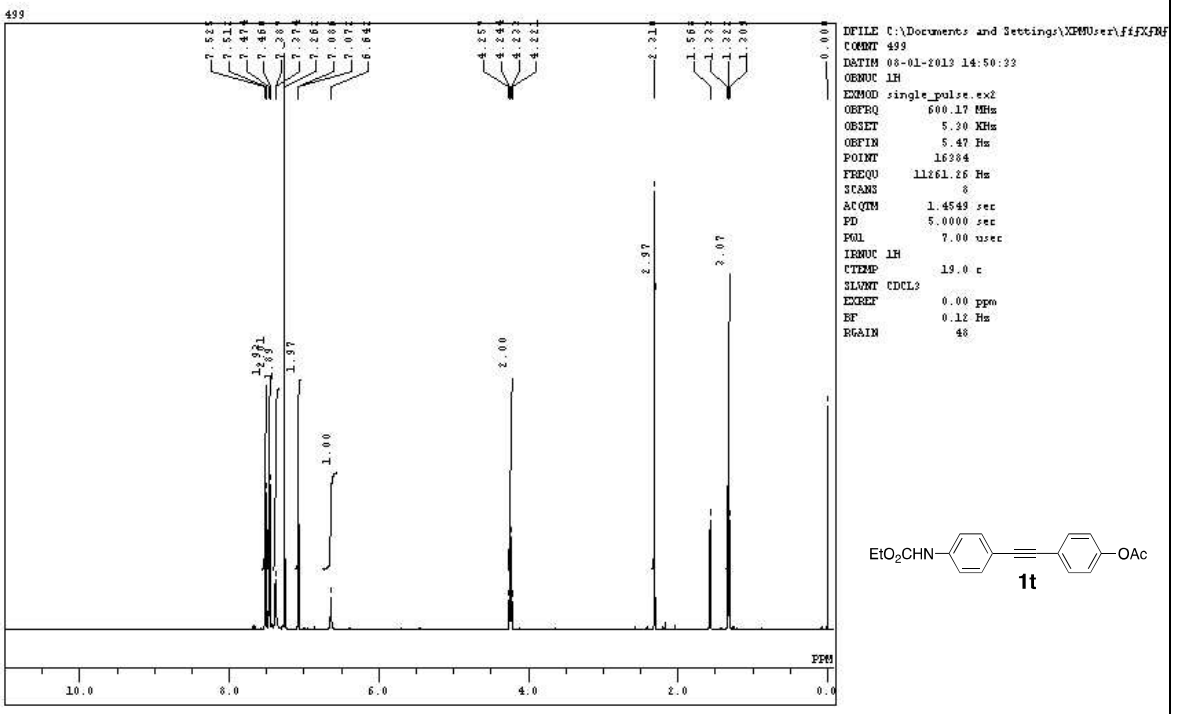


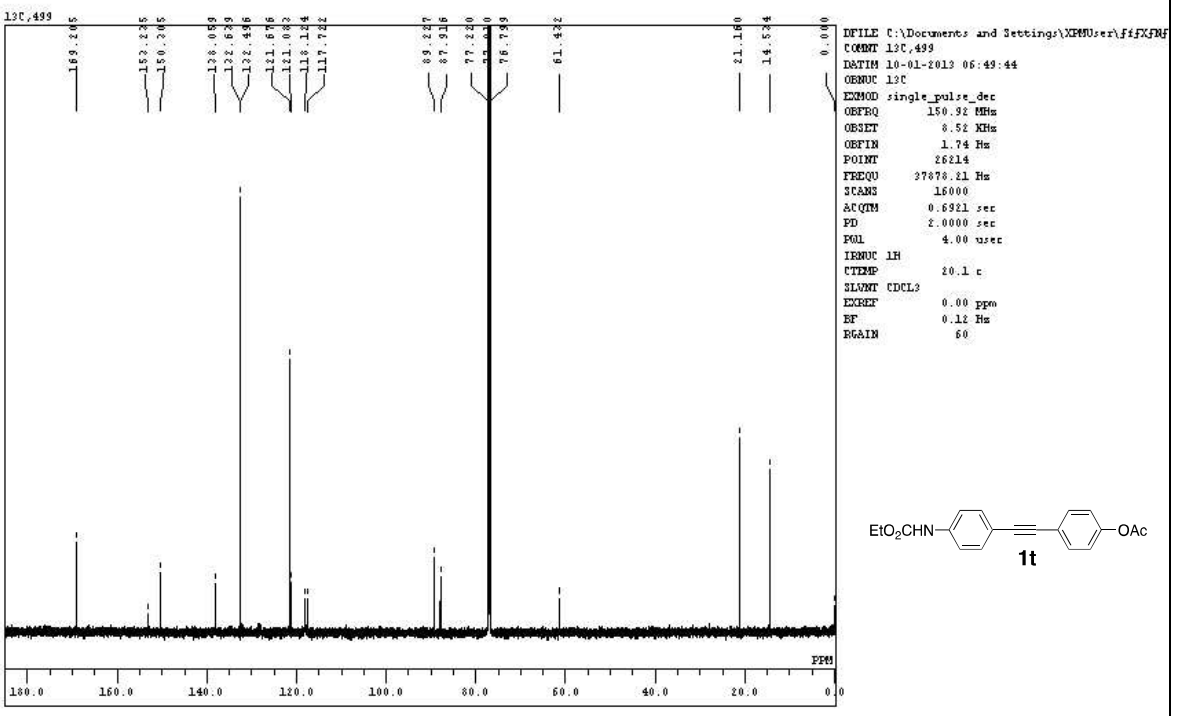
2-(5-(4-Methoxyphenyl)pent-4-yn-1-yl)isoindoline-1,3-dione (1r)





4-(4-(Ethoxycarbonyl)aminophenylethynyl)phenyl acetate (1t)





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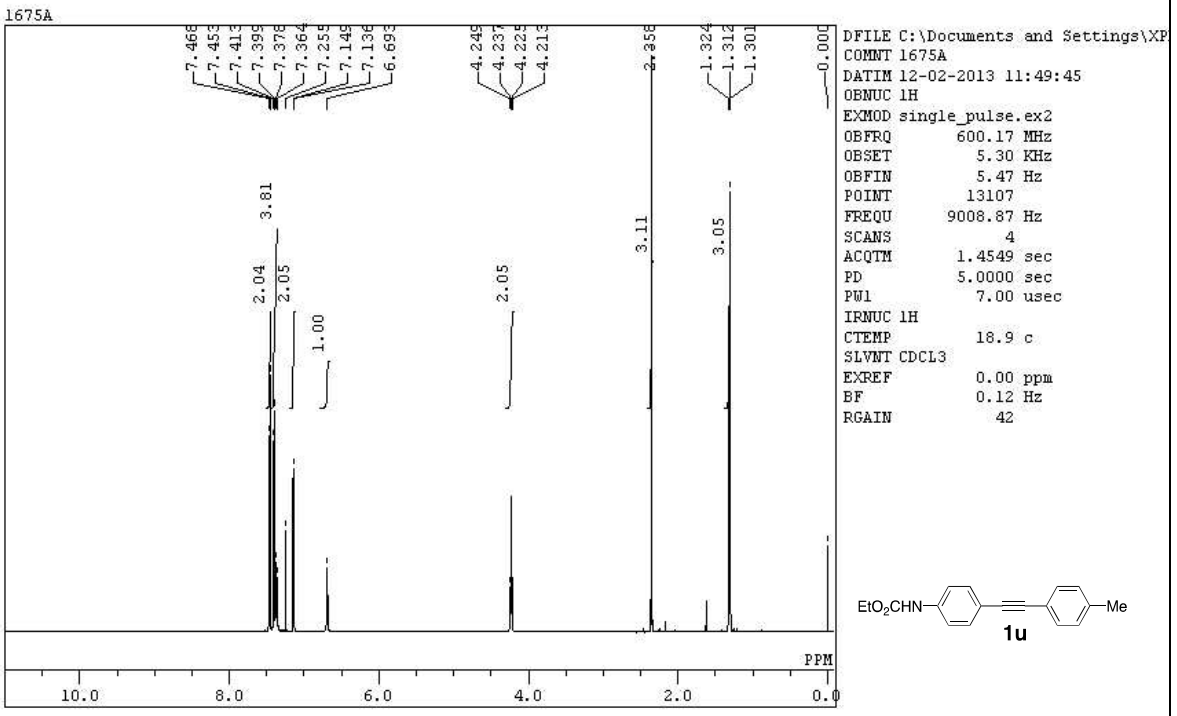
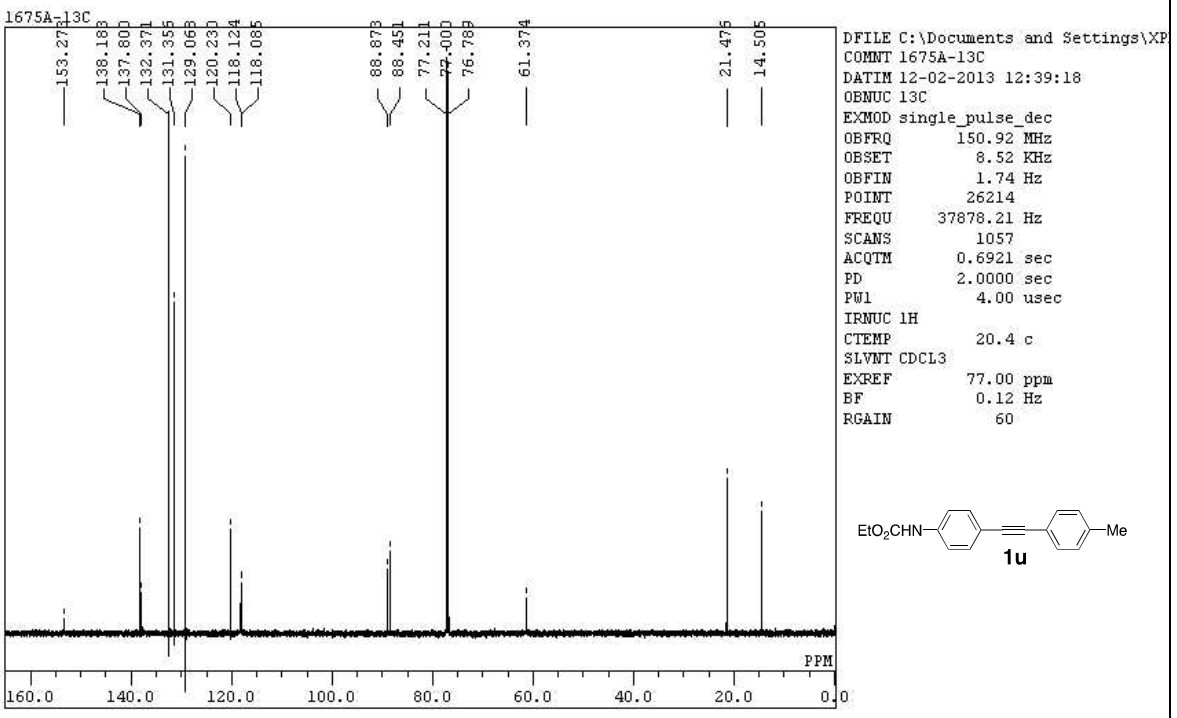
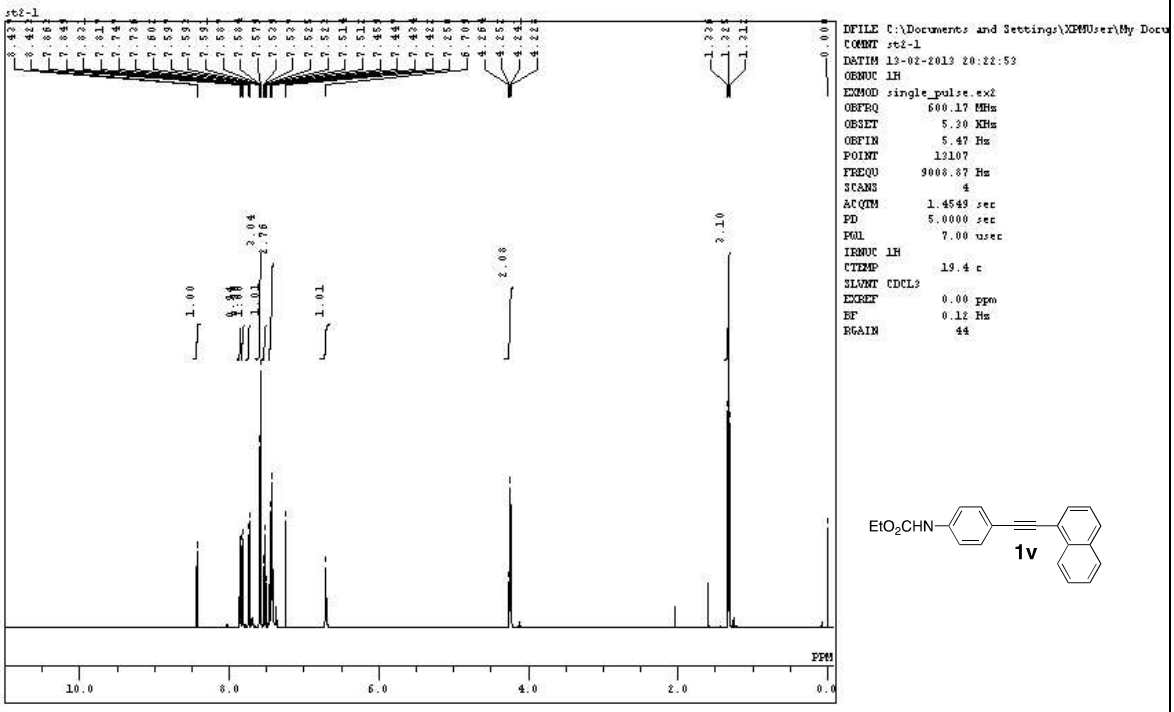
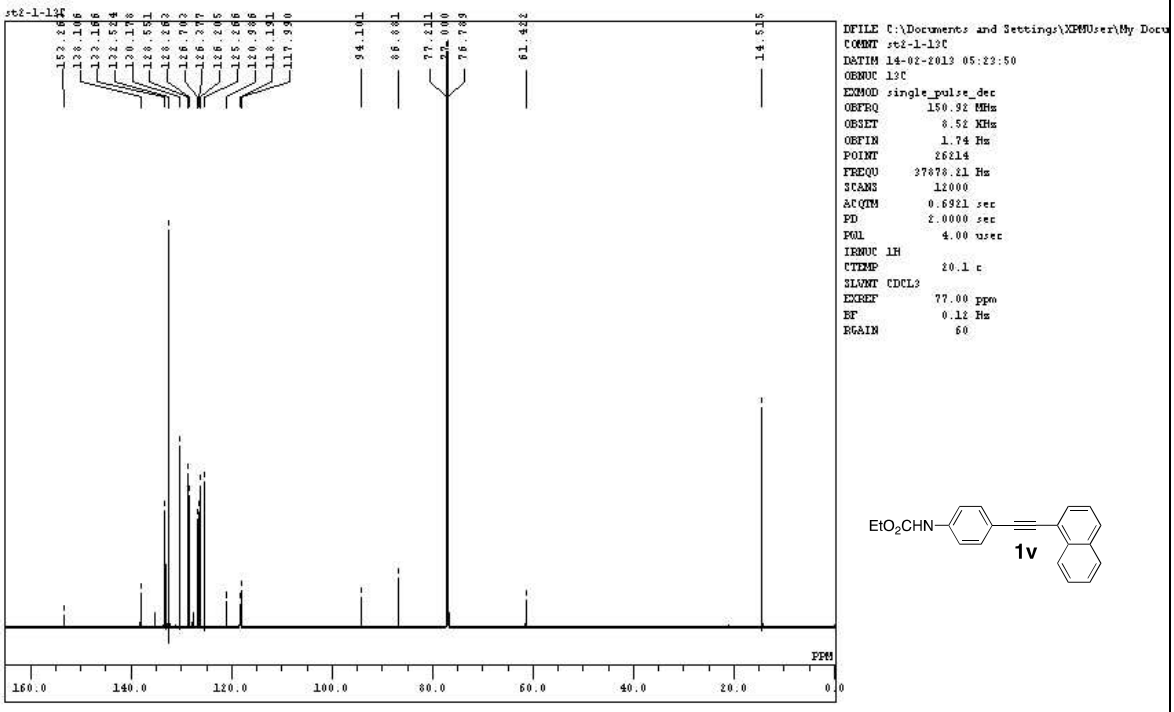


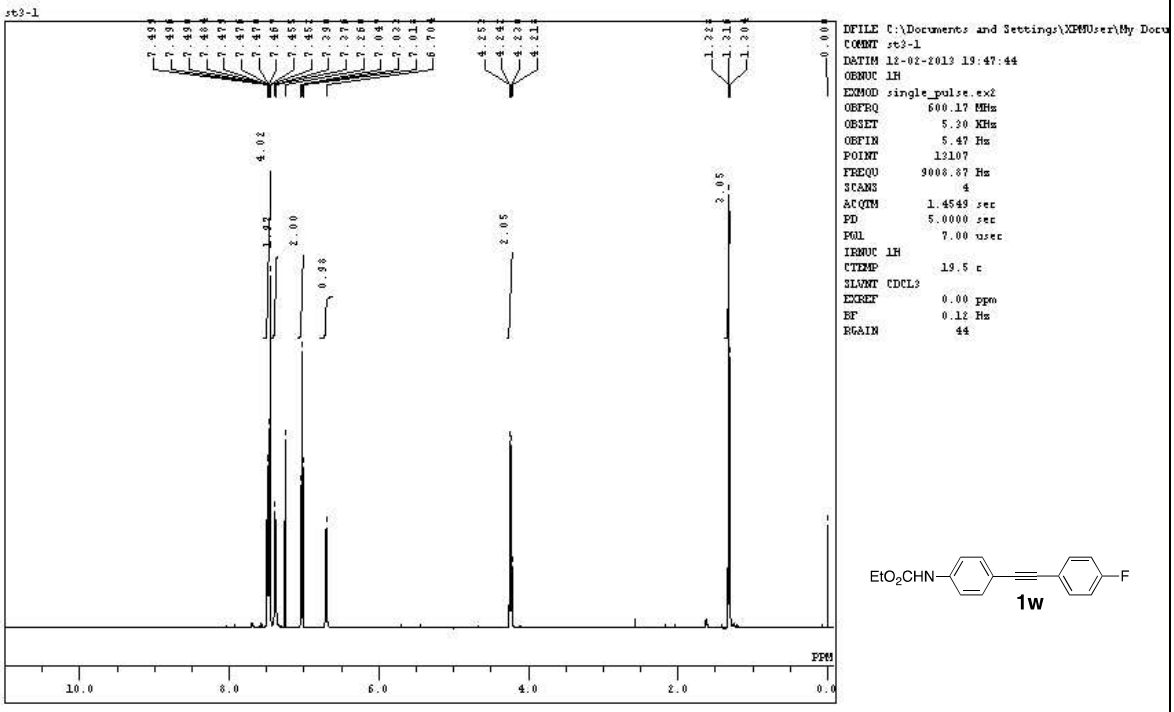


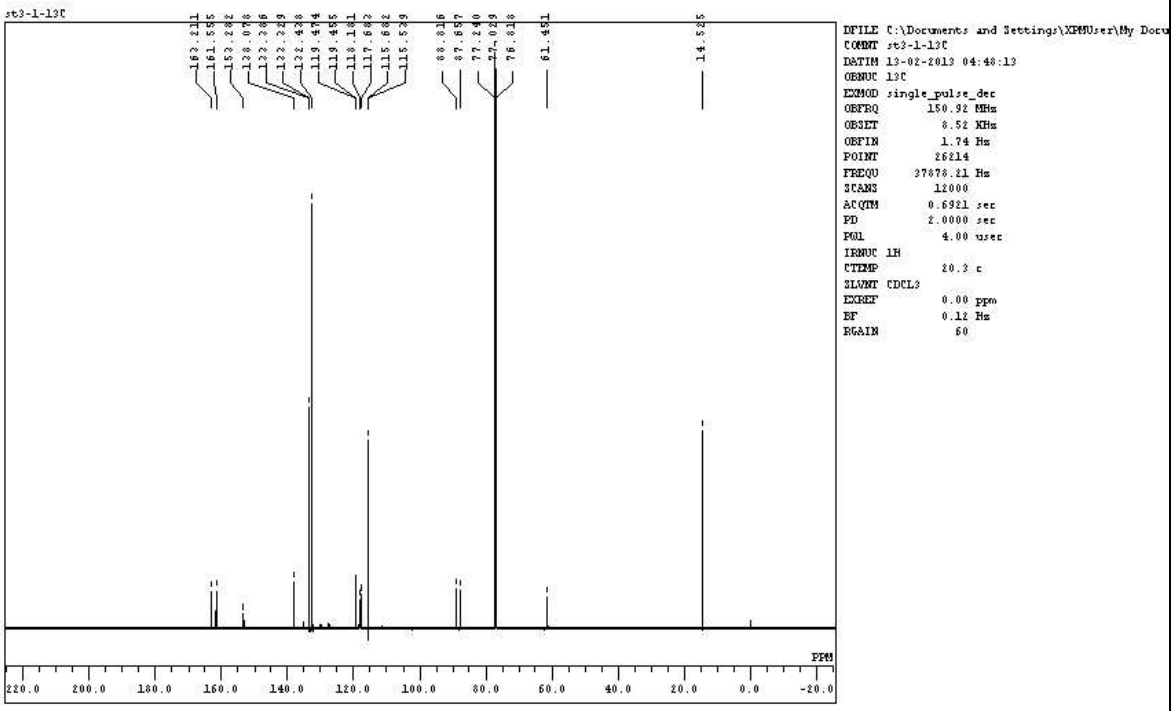
Ethyl (4-(naphthalen-1-ylethynyl)phenyl)carbamate (1v)



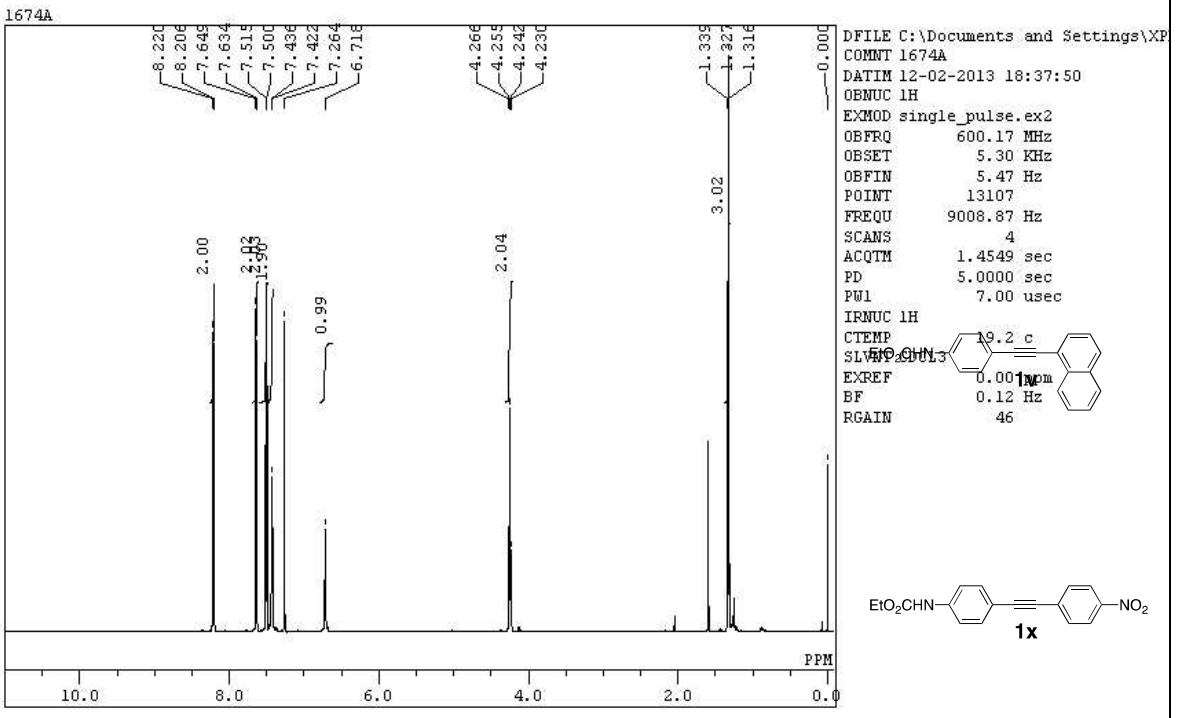


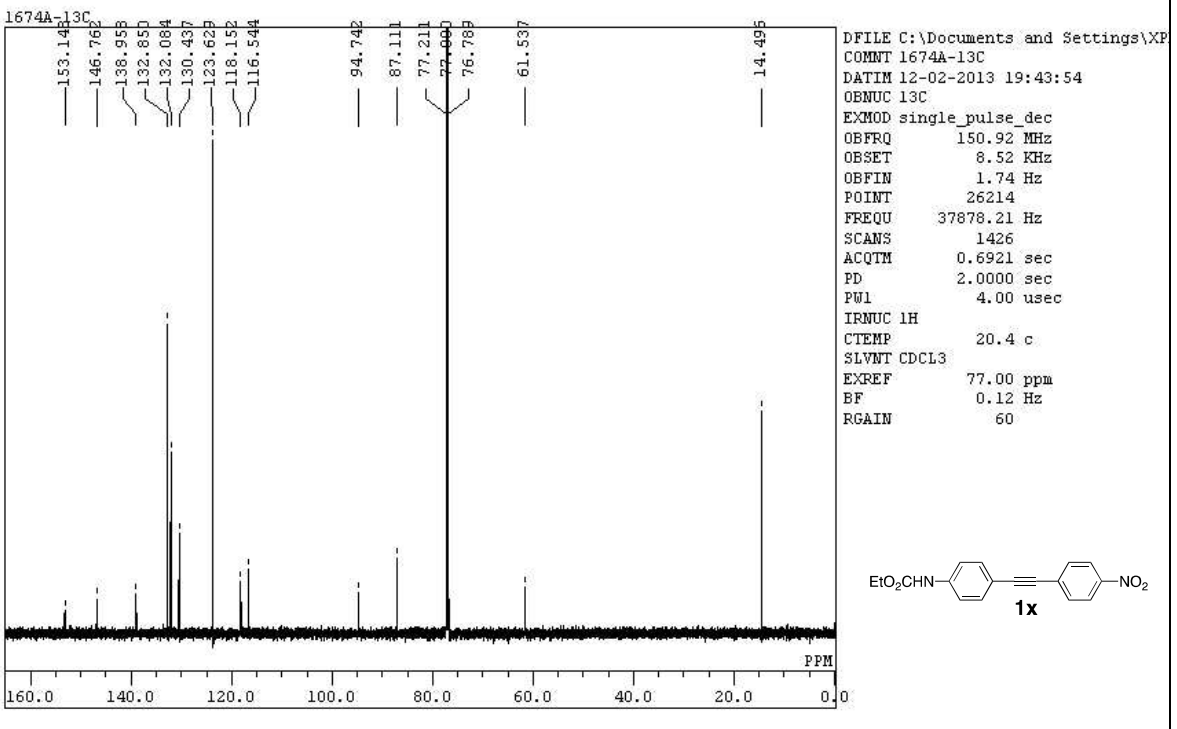
Ethyl (4-(4-fluorophenylethynyl)phenyl)carbamate (1w)



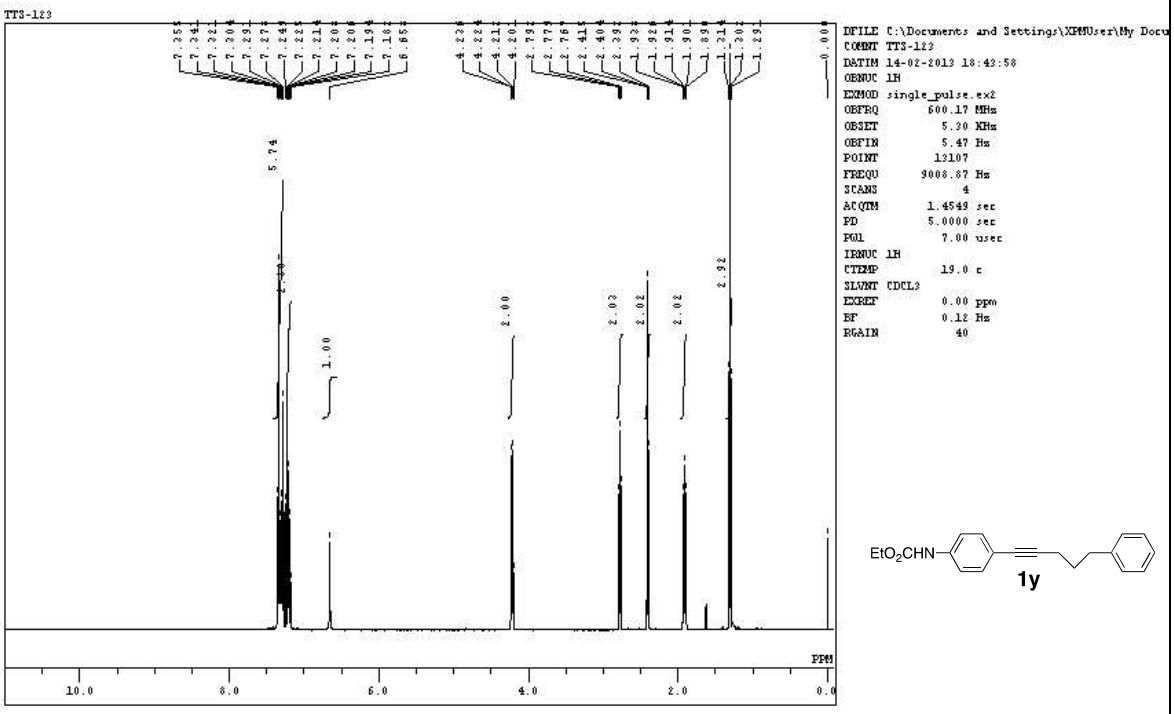


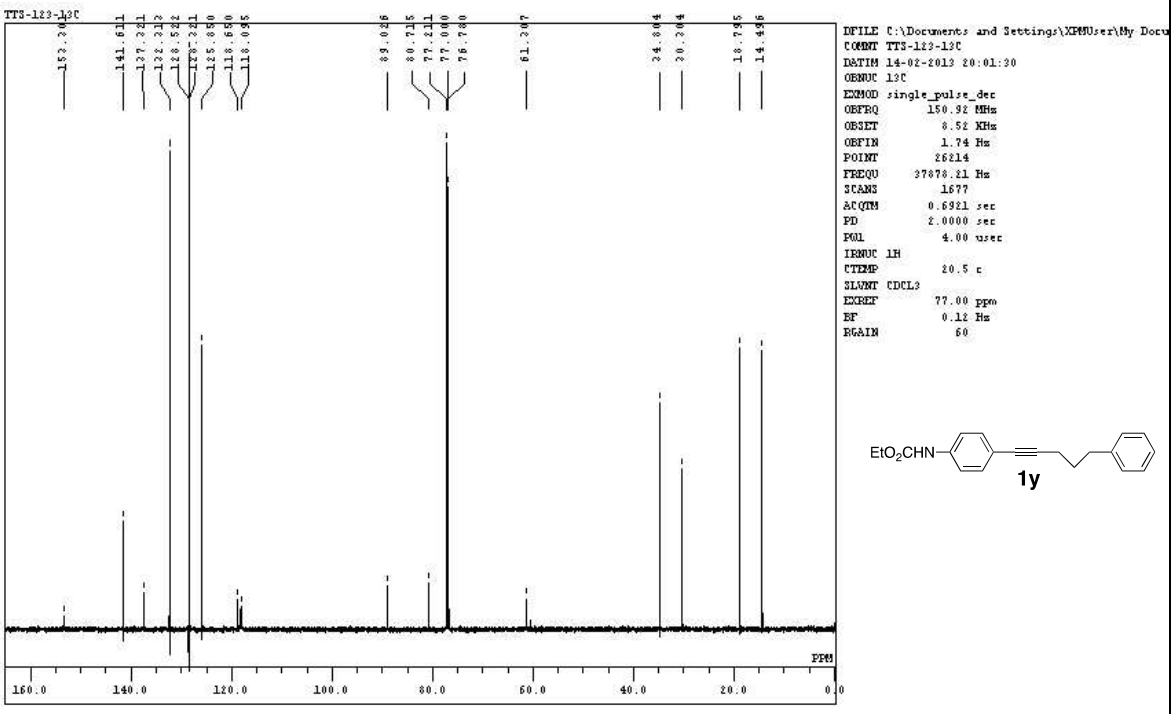
Ethyl (4-(4-nitrophenylethynyl)phenyl)carbamate (1x)



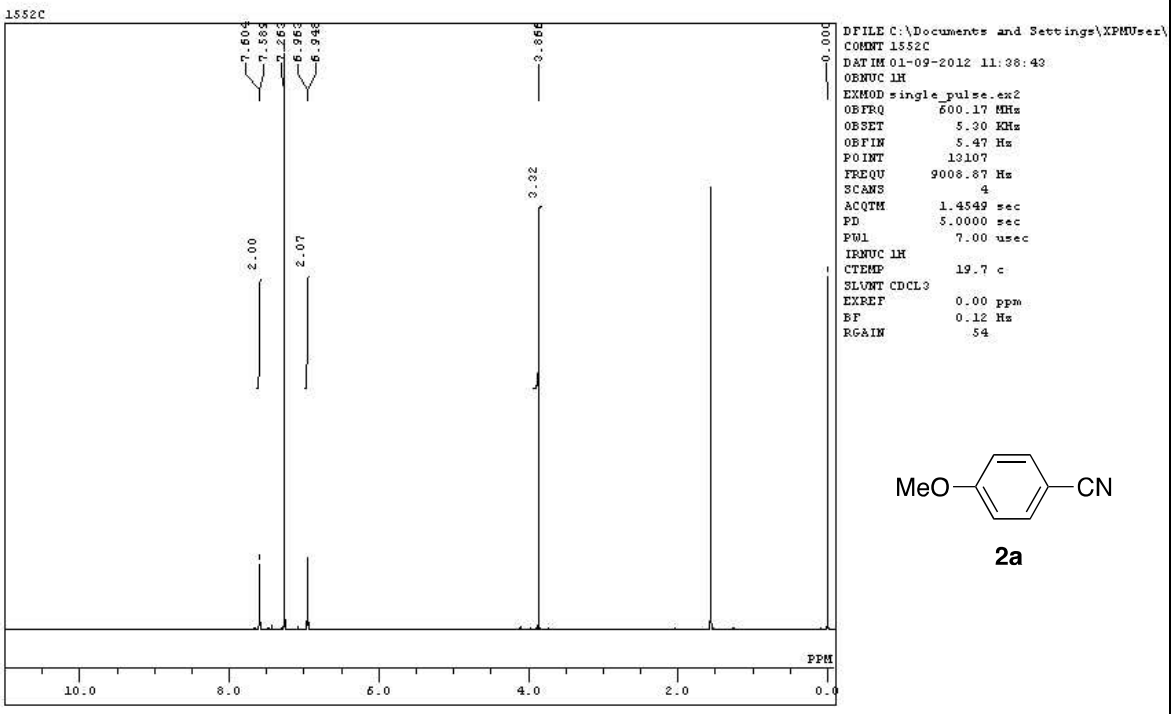


Ethyl (4-(5-phenylpent-1-yn-1-yl)phenyl)carbamate (1y)



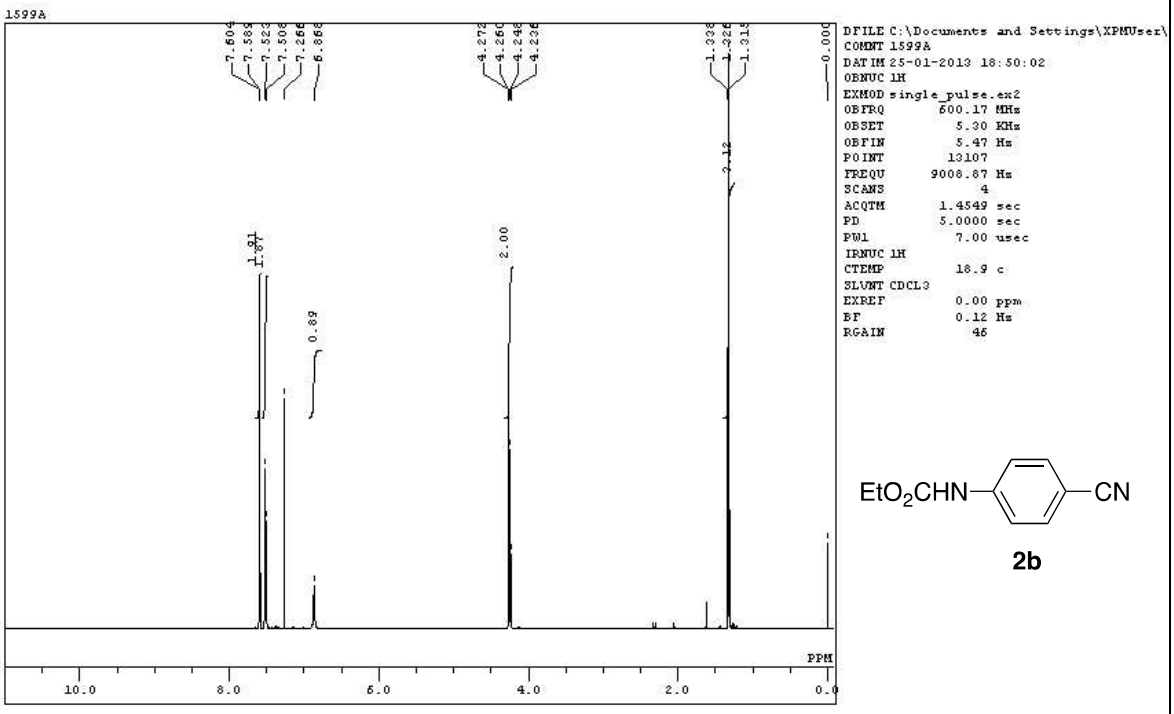


4-Methoxybenzonitrile (2a)



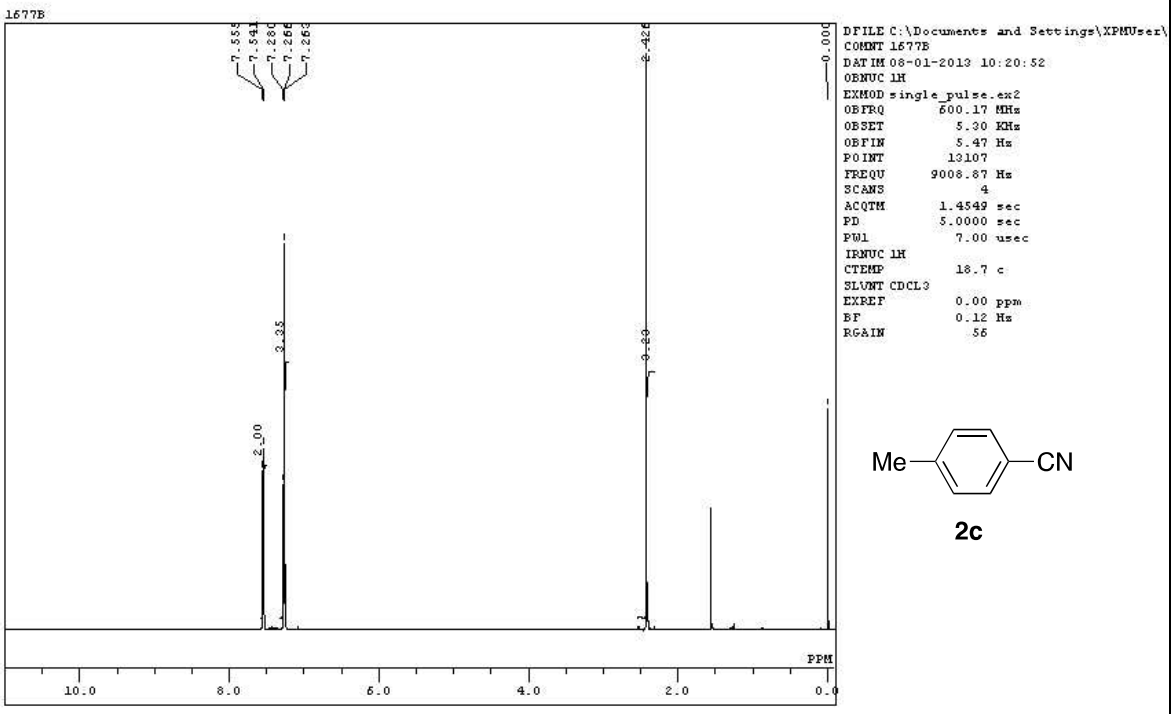
2a

Ethyl (4-cyanophenyl)carbamate (2b)



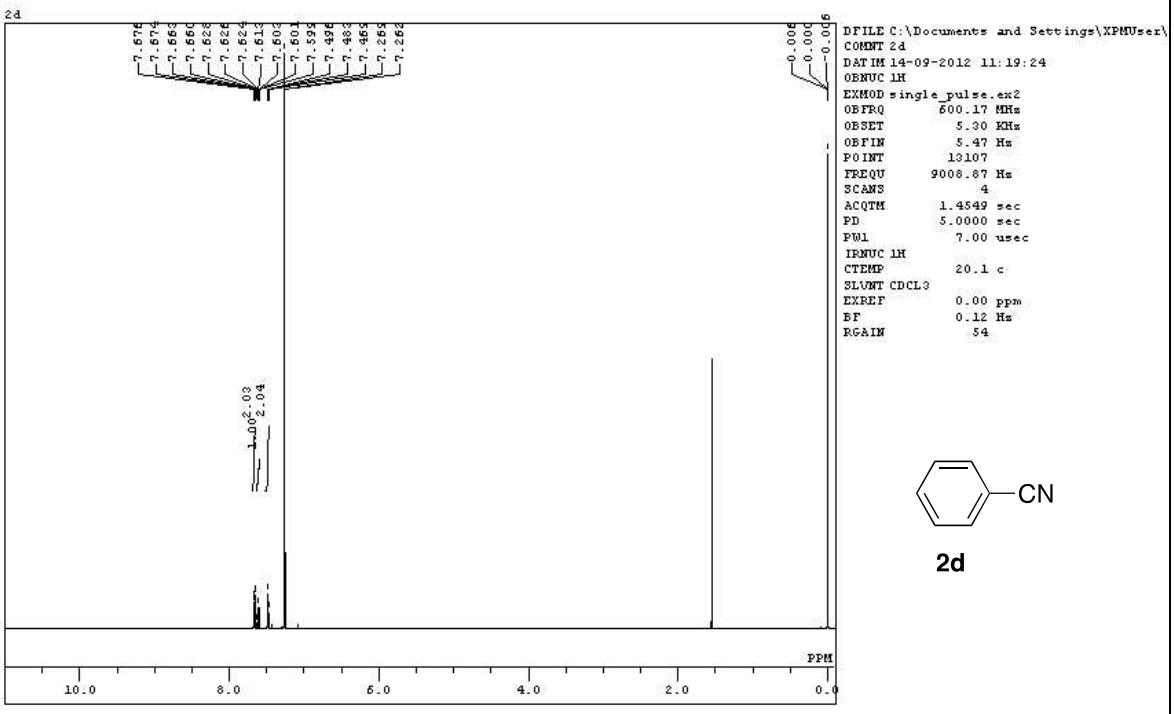
2b

_p_-Tolunitrile (2c)



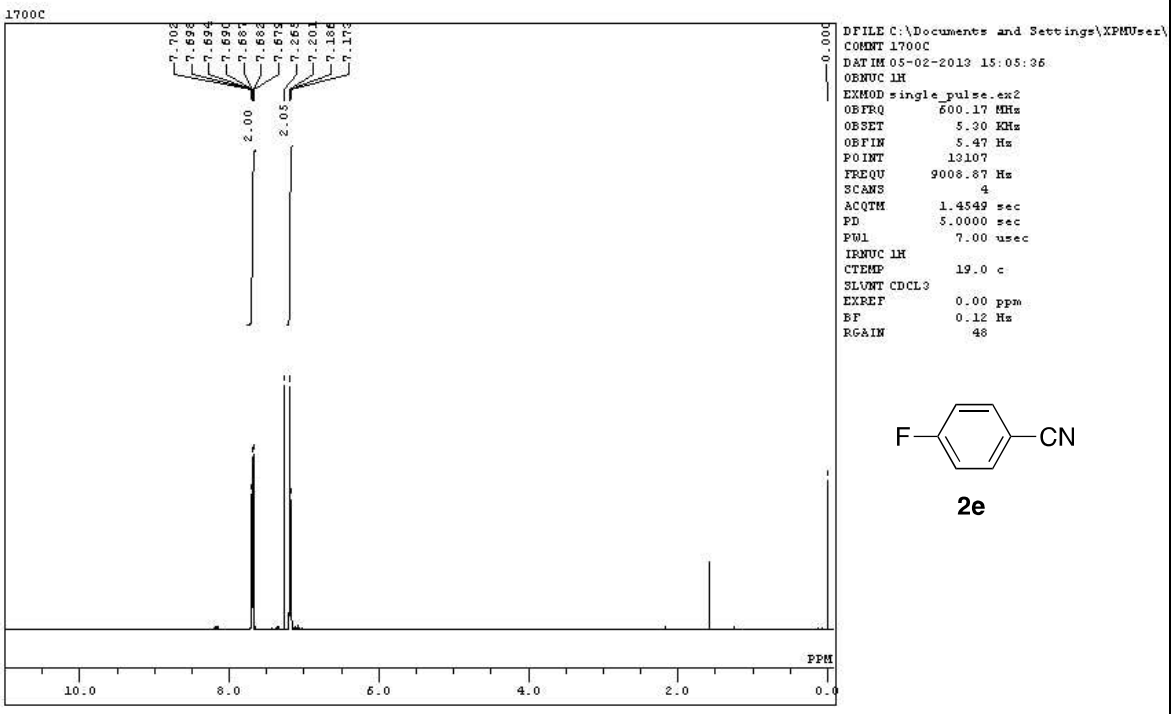
2c

Benzonitrile (2d)



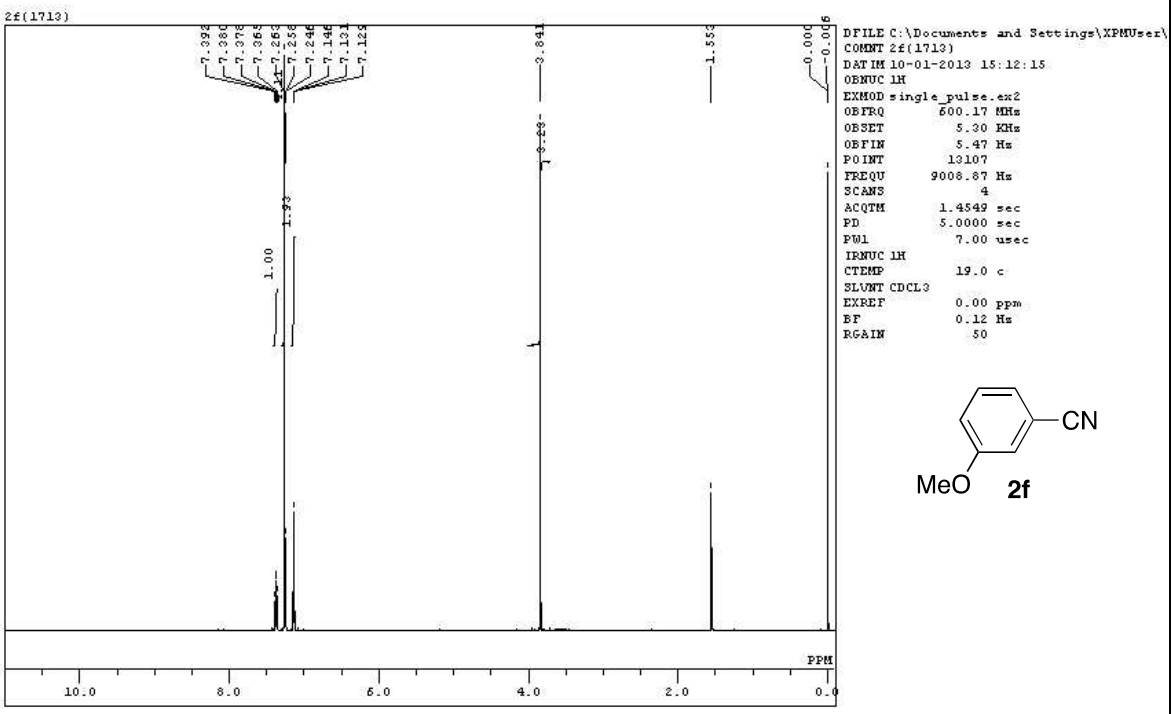
2d

4-Fluorobenzonitrile (2e)



2e

3-Methoxybenzonitrile (2f)



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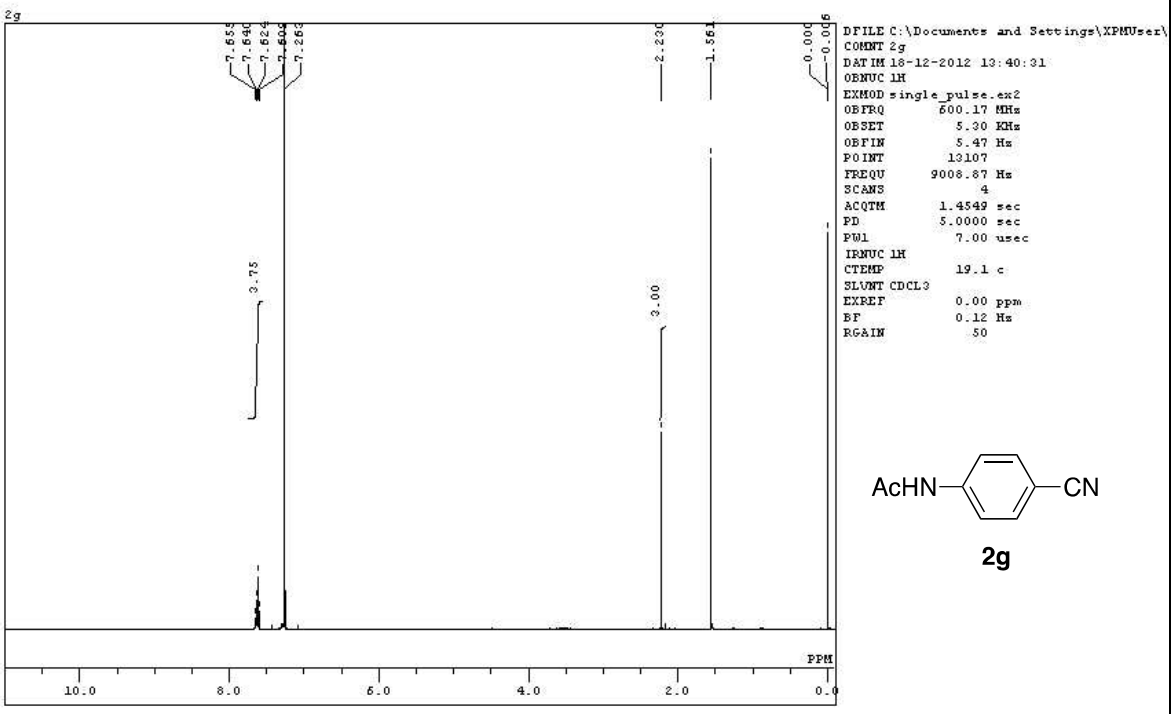
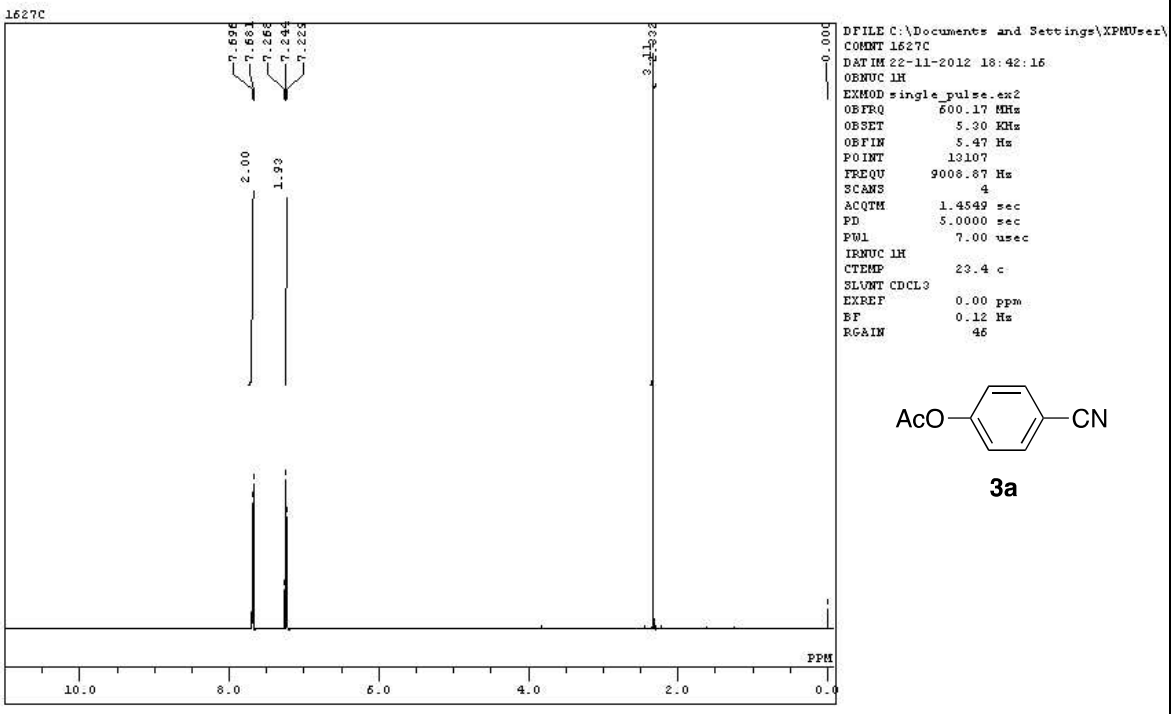
4'-Cyanoacetanilide (2g)



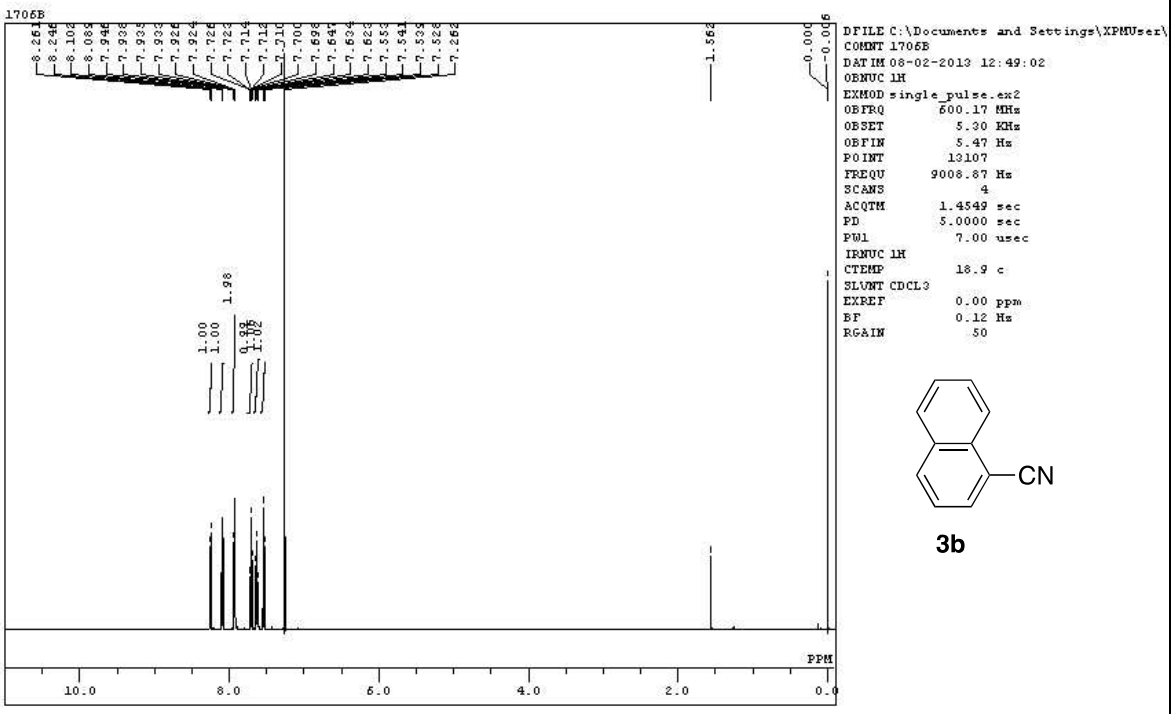
2g

4-Cyanophenyl acetate (3a)

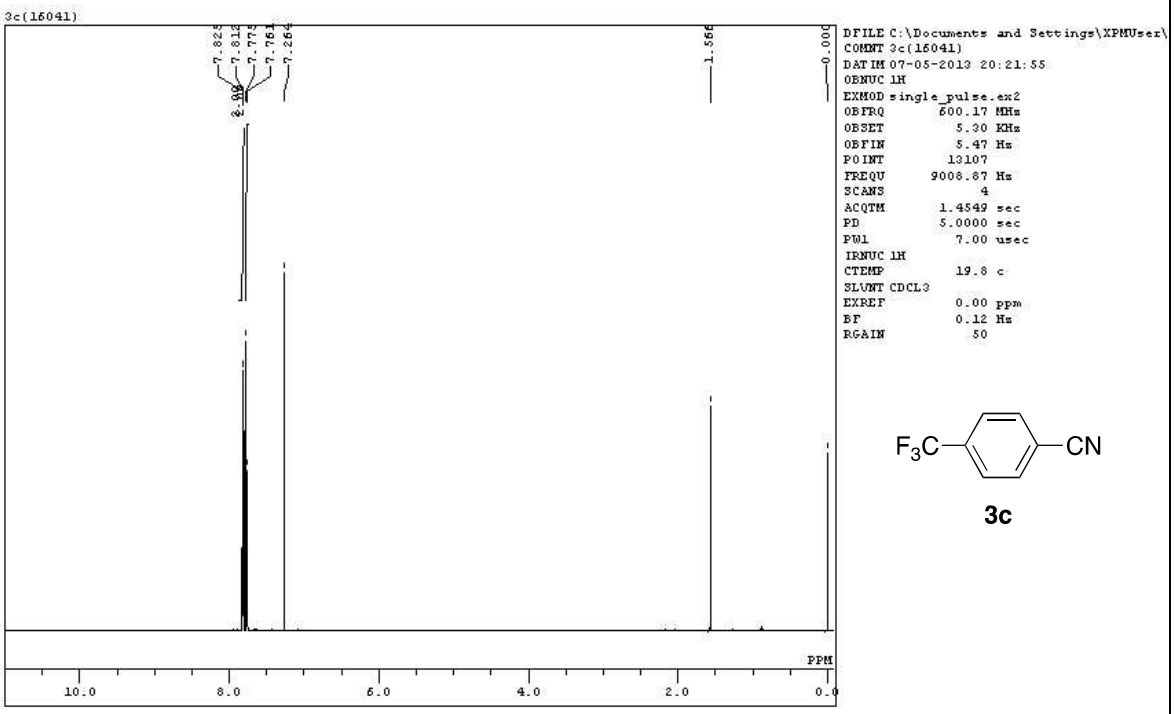


3a

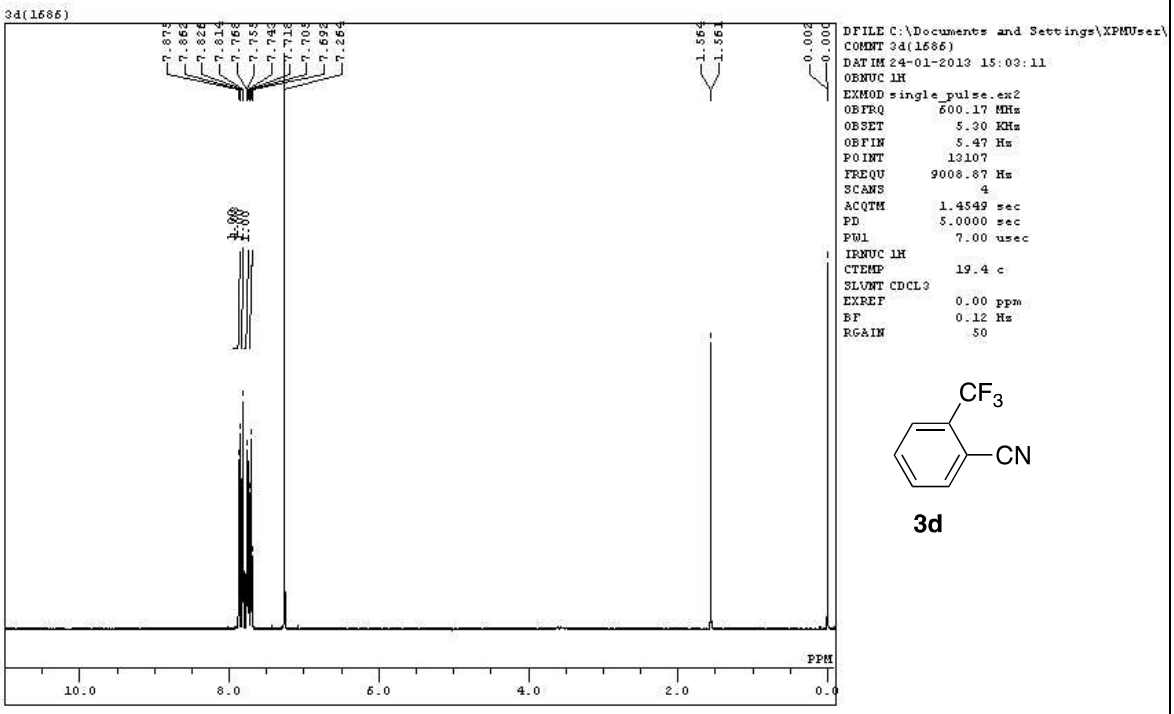
1-Naphthonitrile (3b)



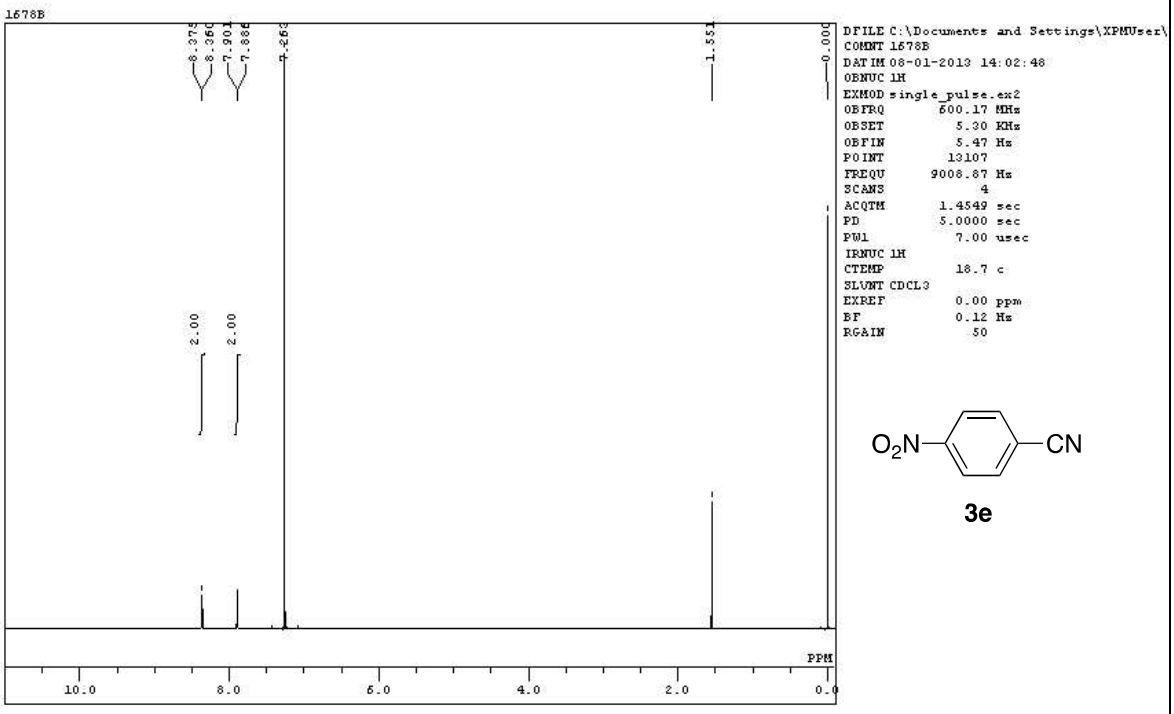
4-(Trifluoromethyl)benzonitrile (3c)



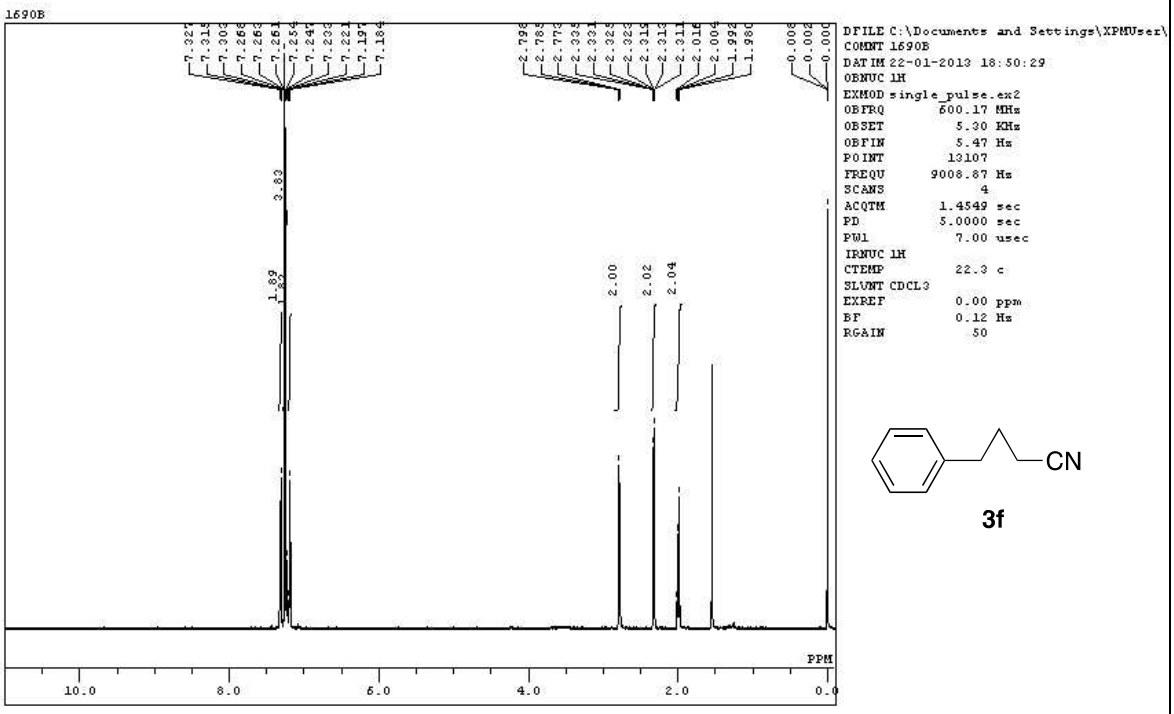
2-(Trifluoromethyl)benzonitrile (3d)



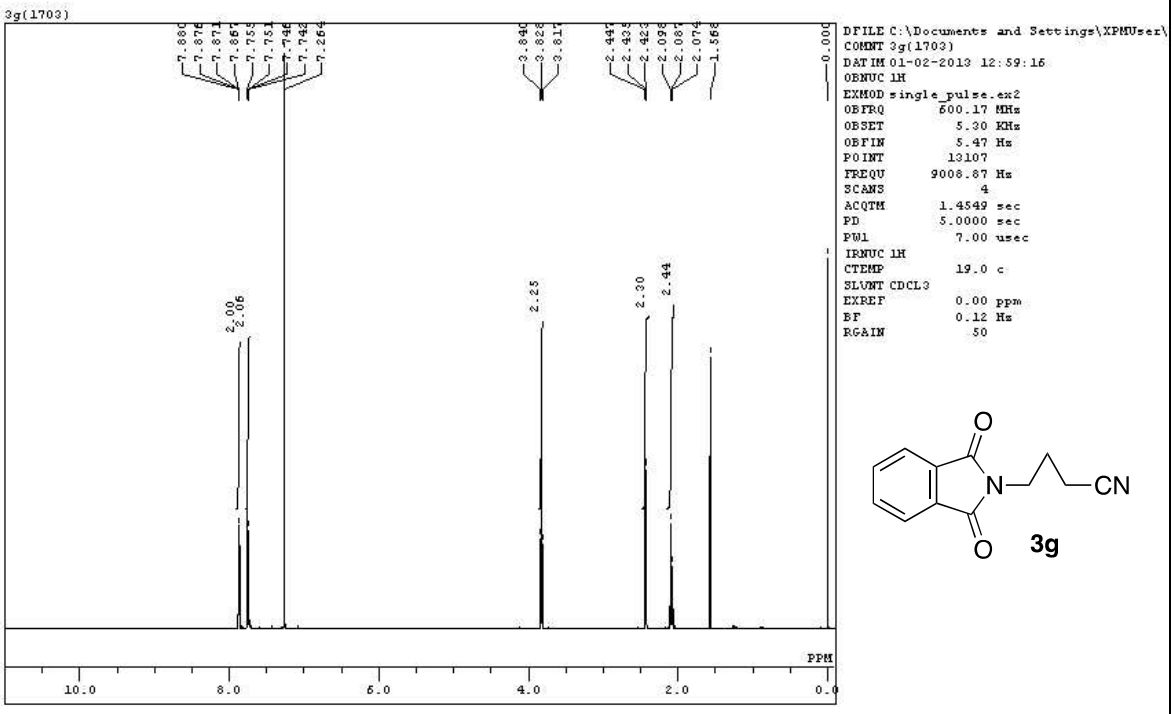
4-Nitrobenzonitrile (3e)



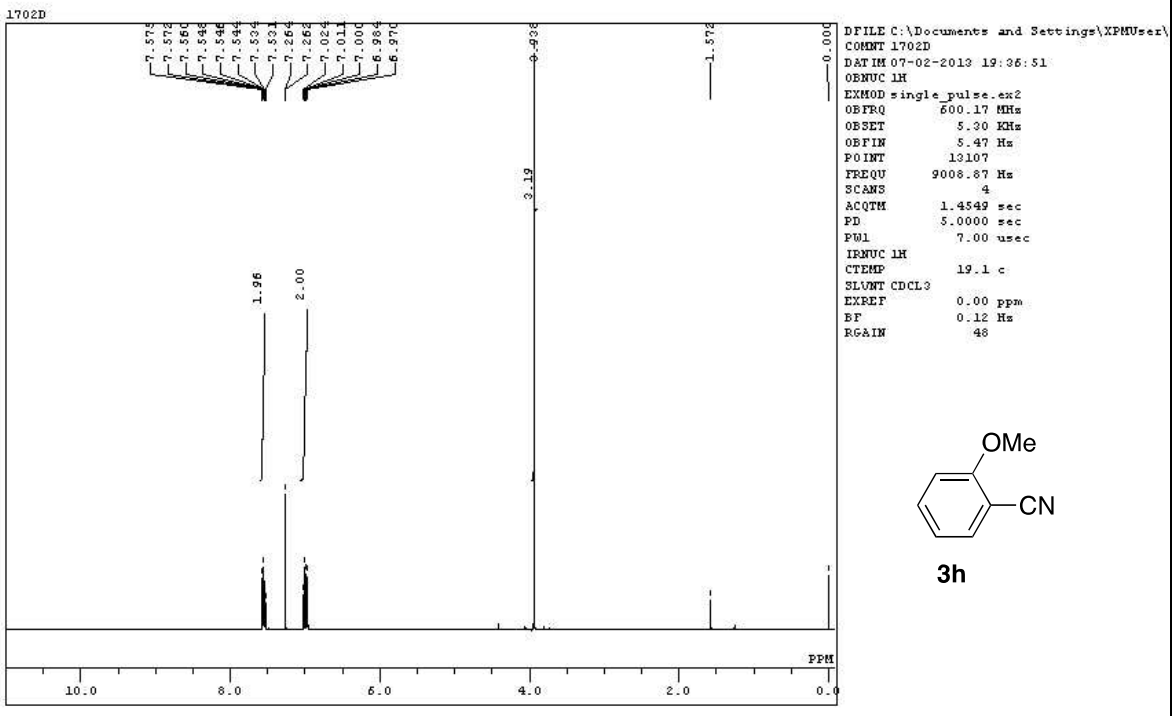
4-Phenylbutyronitrile (3f)



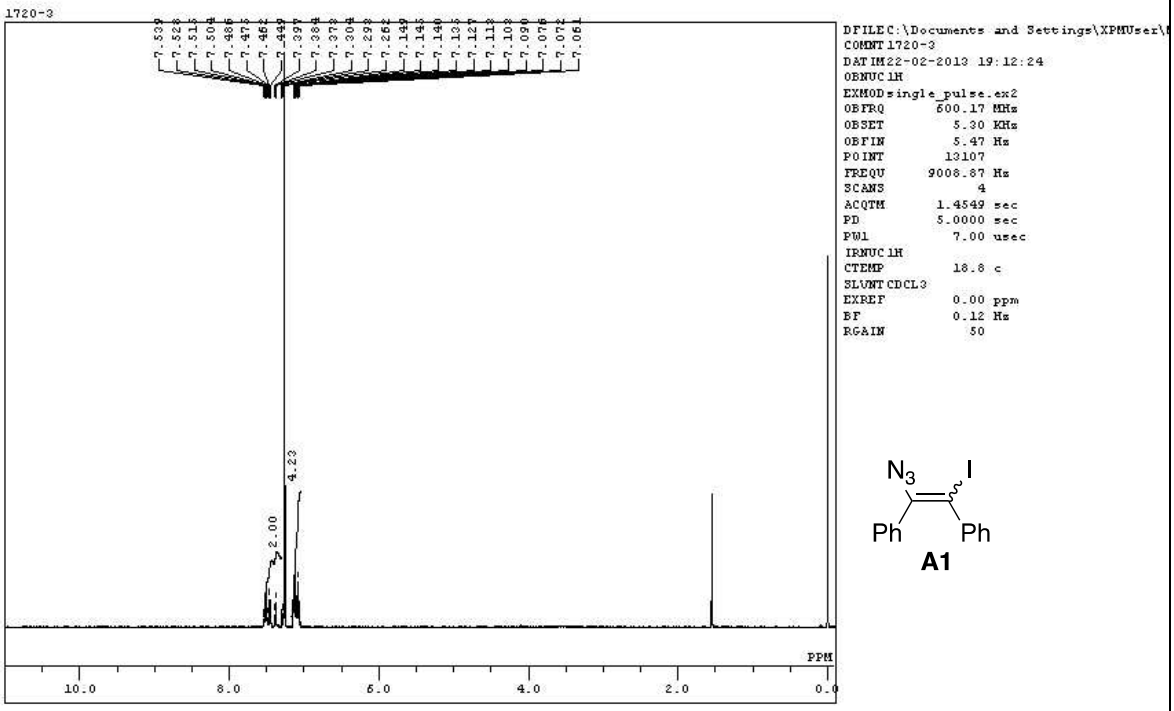
4-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-butyronitrile (3g)



2-Methoxybenzonitrile (3h)



A1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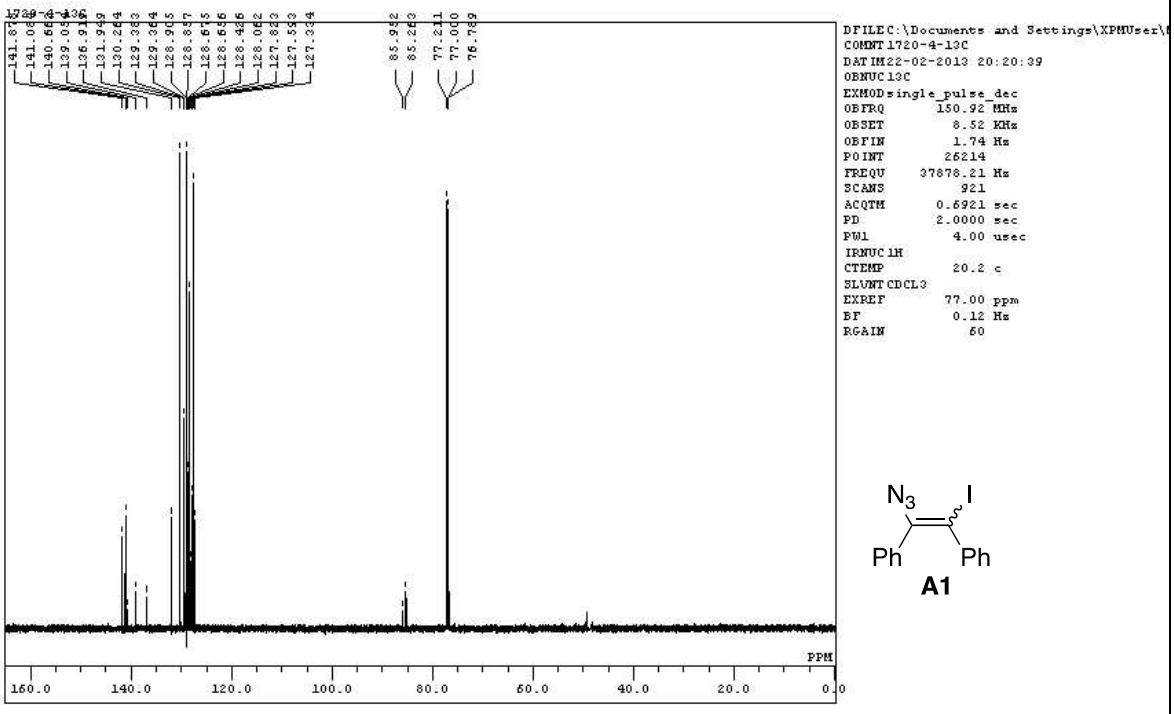
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