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Electronic Supplementary Information

Gallium-Catalysed Bromocyanation of Alkynes: Regio- and Stereoselective Synthesis of *β*-Bromo-*α,β*-unsaturated Nitriles

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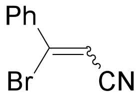
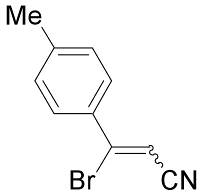
General Methods. Unless otherwise noted, chemicals obtained from commercial suppliers were used without further purification. $ClCH_2CH_2Cl$ was dried by the usual methods, distilled, and bubbled vigorously with a nitrogen gas for 20 min before use. All reactions were carried out under nitrogen atmosphere. NMR spectra were measured for solutions in $CDCl_3$ with tetramethylsilane as an internal standard (^{1}H and ^{13}C): the following abbreviations are used; br s: broad singlet, s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, sext: sextet, m: multiplet. IR spectra were recorded with an FT-IR spectrometer. Melting points (mp) are uncorrected. High-resolution mass spectra (HRMS) was measured with JEOL JMX-SX 102A spectrometer.

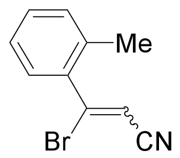
General Procedure of Gallium-catalysed Bromocyanation of Alkynes. A flame dried Schlenk flask was charged with $GaCl_3$ (7.0 mg, 0.040 mmol) and $ClCH_2CH_2Cl$ (1.6 mL), then BrCN (63.6 mg, 0.60 mmol) was added. After stirring at room temperature for 5 min, alkyne (0.40 mmol) was added, and the resulting mixture was stirred at 80 °C. After the time specified in Tables 1-2, the mixture was concentrated in vacuo. The residue was subjected to flash column chromatography on silica gel with hexane/AcOEt (v/v = 10/1–4/1) as eluents to afford the corresponding *β*-bromoacrylonitriles.



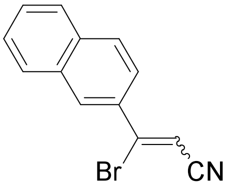
3-Bromo-3-phenylprop-2-enenitrile (1a): A brown oil (*Z*:*E* = 92:8), R_f 0.35 (hexane/AcOEt (v/v = 4/1)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.02 (s, 0.08×1H, C*H*CN for (*E*)-**1a**), 6.30 (s, 0.92×1H, C*H*CN for (*Z*)-**1a**), 7.40-7.50 (m, 3H, Ar*H*), 7.60-7.63 (m, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): (*Z*)-**1a** δ 100.6 (*C*HCN), 116.6(*C*N), 127.8 (*C*H), 128.9 (*C*H), 131.7(*C*H), 136.1 (C^q), 145.6 (*C*=CHCN); (*E*)-**1a** δ 96.0 (*C*HCN), 115.3 (*C*N), 126.6 (*C*H), 128.7 (*C*H), 131.7 (*C*H), 133.7 (C^q), 152.8 (*C*=CHCN). The spectral data match those reported in the literature (*J. Med. Chem.* **2000**, *43*, 4288.).



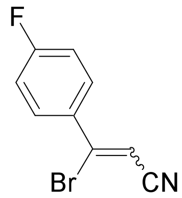
3-Bromo-3-(4-tolyl)prop-2-enenitrile (1b): A brown oil (*Z*:*E* = 95:5), R$_f$ 0.19 (hexane/AcOEt (v/v = 10/1)). IR (neat): 822, 890, 1250, 1277, 1363, 1456, 1612, 1678, 2219 (CN), 3042 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.40 (s, 6H, C*H*$_3$), 5.98 (s, 0.05×1H, C*H*CN for (*E*)-**1b**), 6.26 (s, 0.95×1H, C*H*CN for (*Z*)-**1b**), 7.23 (d, 0.95×2H, *J* = 8.8 Hz, Ar*H* for (*Z*)-**1b**), 7.24 (d, 0.05×2H, *J* = 8.8 Hz, Ar*H* for (*E*)-**1b**), 7.51 (d, 0.95×2H, *J* = 8.8 Hz, Ar*H* for (*Z*)-**1b**), 7.55 (d, 0.95×2H, *J* = 8.8 Hz, Ar*H* for (*E*)-**1b**). ^{13}C NMR (100 MHz, CDCl$_3$): (*Z*)-**1b** δ 21.3 (*C*H$_3$), 99.5 (*C*HCN), 116.8 (*C*N), 127.7 (*C*H), 129.5 (*C*H), 133.2 (C^q), 142.5 (C^q), 145.7 (*C*=CHCN); (*E*)-**1b** δ 21.4 (*C*H$_3$), 95.0 (*C*HCN), 115.6 (*C*N), 126.8 (*C*H), 129.6 (*C*H), 133.4 (C^q), 142.7 (C^q), 153.3 (*C*=CHCN). HRMS (FAB) calcd for M+H$^+$ of C$_{10}$H$_8$BrN 221.9918, found 221.9928.



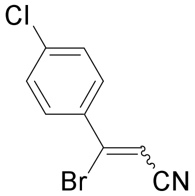
3-Bromo-3-(2-tolyl)prop-2-enenitrile (1c): A pale yellow oil (*Z*:*E* = 98:2), R$_f$ 0.31 (hexane/AcOEt (v/v = 10/1)). IR (neat): 818, 890, 1225, 1252, 1288, 1383, 1456, 1485, 1612, 1684,2224 (CN), 3039 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.37 (s, 0.98×3H, C*H*$_3$ for (*Z*)-**1c**), 2.40 (s, 0.02×3H, C*H*$_3$ for (*E*)-**1c**), 5.67 (s, 0.02×1H, C*H*CN for (*E*)-**1c**), 5.99 (s, 0.98×1H, C*H*CN for (*Z*)-**1c**), 7.21-7.34 (m, 4H, Ar*H*). ^{13}C NMR (100 MHz, CDCl$_3$): (*Z*)-**1c** δ 19.8 (*C*H$_3$), 105.1 (*C*HCN), 115.8 (*C*N), 126.1 (*C*H), 128.3 (*C*H), 130.5 (*C*H), 130.9 (*C*H), 135.3 (C^q), 137.7 (C^q), 145.0 (*C*=CHCN). HRMS (FAB) calcd for M+H$^+$ of C$_{10}$H$_8$BrN 221.9918, found 221.9920.



3-Bromo-3-(2-naphtyl)prop-2-enenitrile (1d): A white solid (*Z*:*E* = 95:5), R$_f$ 0.39 (hexane/AcOEt (v/v = 4/1)). mp 39.5-40.2 ^{o}C (from CHCl$_3$/hexane). IR (KBr): 859, 889, 1182, 1273, 1351, 1466, 1505, 1584, 2214 (CN), 3056 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.15 (s, 0.05×1H, C*H*CN for (*E*)-**1d**), 6.43 (s, 0.95 × 1H, C*H*CN for (*Z*)-**1d**), 7.55-7.65 (m, 4H, Ar*H*), 7.84-7.95 (m, 2H, Ar*H*), 8.16 (s, 0.95×1H, Ar*H* for (*Z*)-**1d**), 8.21 (s, 0.05×1H, Ar*H* for (*E*)-**1d**). ^{13}C NMR (100 MHz, $CDCl_3$): (*Z*)-**1d** δ 100.6 (*C*HCN), 116.8 (*C*N), 123.3 (*C*H), 127.4 (*C*H), 127.7 (*C*H), 128.3 (*C*H), 128.7 (*C*H), 129.0 (*C*H), 129.4 (*C*H), 132.6 (C^q), 133.0 (C^q), 134.5 (C^q), 145.6 (*C*=CHCN). HRMS (FAB) calcd for M+H$^+$ of $C_{13}H_8BrN$ 257.9918, found 257.9926.

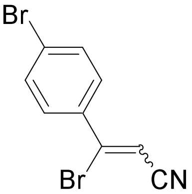


3-Bromo-3-(4-fluorophenyl)prop-2-enenitrile (1e): A white solid (*Z*:*E* = 91:9), R_f 0.19 (hexane/AcOEt (v/v = 10/1)). mp 80.0-80.5 °C (from $CHCl_3$/hexane). IR (KBr): 818, 893, 1164, 1229, 1306, 1409, 1505, 1584, 1599, 2219 (CN), 3042 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.98 (s, 0.09×1H, C*H*CN for (*E*)-**1e**), 6.26 (s, 0.91×1H, C*H*CN for (*Z*)-**1e**), 7.09-7.15 (m, 2H, Ar*H*), 7.61-7.69 (m, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): (*Z*)-**1e** δ 100.6 (*C*HCN), 116.1 (d, *J* = 21.5 Hz, *C*H), 116.3 (*C*N), 130.0 (d, *J* = 9.1 Hz, *C*H), 132.3 (d, *J* = 3.3 Hz, C^q), 144.2 (*C*=CHCN), 164.7 (d, *J* = 253.8 Hz, C^q); (*E*)-**1e** δ 96.1 (*C*HCN), 116.2 (d, *J* = 22.3 Hz, *C*H), 116.5 (*C*N), 129.1 (d, *J* = 9.1 Hz, *C*H), 129.9 (d, *J* = 2.5 Hz, C^q), 152.0 (*C*=CHCN), 164.8 (d, *J* = 254.9 Hz, C^q). HRMS (FAB) calcd for M+H$^+$ of C_9H_5BrFN 225.9668, found 225.9663.

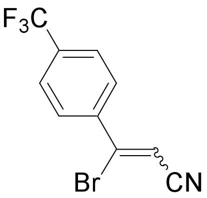


3-Bromo-3-(4-chlorophenyl)prop-2-enenitrile (1f): A white solid (*Z*:*E* = 90:10), R_f 0.26 (hexane/AcOEt (v/v = 10/1)). mp 66.8-67.2 °C (from $CHCl_3$/hexane). IR (KBr): 804, 887, 1012, 1096, 1221, 1401, 1486, 1562, 1586, 2218 (CN), 3041 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.05 (s, 0.10×1H, C*H*CN for (*E*)-**1f**), 6.33 (s, 0.90×1H, C*H*CN for (*Z*)-**1f**), 7.37-7.43 (m, 2H, Ar*H*), 7.54-7.62 (m, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): (*Z*)-**1f** δ 101.0 (*C*HCN), 116.4 (*C*N), 128.9 (*C*H), 129.0 (*C*H), 134.3 (C^q), 137.9 (C^q), 144.0 (*C*=CHCN); (*E*)-**1f** δ 96.6

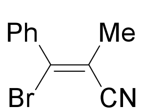
(*C*HCN), 115.1 (*C*N), 128.0 (*C*H), 129.1 (*C*H), 132.4 (C^q), 138.1 (C^q), 151.7 (*C*=CHCN). HRMS (FAB) calcd for M+H$^+$ of C_9H_5BrClN 241.9372, found 241.9370.



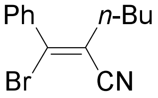
3-Bromo-3-(4-bromophenyl)prop-2-enenitrile (1g): A white solid (*Z*:*E* = 91:9), R_f 0.24 (hexane/AcOEt (v/v = 10/1)). mp 66.8-67.2 °C (from $CHCl_3$/hexane). IR (KBr): 828, 886, 1008, 1076, 1223, 1396, 1482, 1582, 2216 (CN), 3035 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.04 (s, 0.09×1H, C*H*CN for (*E*)-**1g**), 6.32 (s, 0.91×1H, C*H*CN for (*Z*)-**1g**), 7.46-7.52 (m, 2H, Ar*H*), 7.53-7.61 (m, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): (*Z*)-**1g** δ 101.1 (*C*HCN), 116.4 (*C*N), 126.5, 129.1, 132.1, 134.9, 144.2 (*C*=CHCN); (*E*)-**1g** δ 96.7 (*C*HCN), 115.1 (*C*N), 126.8, 128.3, 132.2, 136.0, 152.1 (*C*=CHCN). HRMS (FAB) calcd for M+H$^+$ of $C_9H_5Br_2N$ 285.8867, found 285.8855.



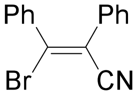
3-Bromo-3-(4-trifluoromethylphenyl)prop-2-enenitrile (1h): A pale yellow oil (*Z*:*E* = 92:8). IR (neat): 848, 890, 1015, 1069, 1131, 1172, 1325, 1409, 1599, 2224 (CN), 2925, 3047 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.12 (s, 0.08H, C*H*CN for (*E*)-**1h**), 6.39 (s, 0.92H, C*H*CN for (*Z*)-**1h**), 7.69-7.80 (m, 4H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): (*Z*)-**1h** δ 102.9 (*C*HCN), 116.0 (*C*N), 123.3 (q, J = 271.9 Hz, CF_3), 125.9 (q, J = 3.8 Hz, *C*H), 128.2 (*C*H), 133.3 (q, J = 33.2 Hz, C^q), 139.4, 143.7; (*E*)-**1h** δ 98.5 (*C*HCN), 114.8 (*C*N), 123.3 (q, J = 271.9 Hz, CF_3), 126.0 (q, J = 3.8 Hz, *C*H), 127.3 (*C*H), 133.5 (q, J = 33.2 Hz, C^q), 137.5, 151.6.



3-Bromo-2-methyl-3-phenylprop-2-enenitrile (1i): A pale yellow crystal (*Z*:*E* = 95:5), R_f 0.24 (hexane/AcOEt (v/v = 10/1)). mp 37.5-37.8 °C (from $CHCl_3$/hexane). IR (KBr): 883, 1019, 1235, 1443, 1489, 1614, 1686, 2218 (CN), 3060 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.94 (s, 0.95×3H, CH_3 for (*Z*)-**1i**), 2.01 (s, 0.05×3H, C*H*$_3$ for (*E*)-**1i**), 7.31-7.34 (m, 2H, Ar*H*), 7.39-7.42 (m, 3H, Ar*H*). ^{13}C NMR (100 MHz, CDCl$_3$): (*Z*)-**1i** δ 19.4 (*C*H$_3$), 112.6 (*C*CN), 118.9 (*C*N), 128.4 (*C*H), 128.5 (*C*H), 130.0 (*C*H), 135.9, 136.7. HRMS (FAB) calcd for M+H$^+$ of $C_{10}H_8BrN$ 221.9918, found 221.9916.

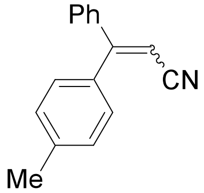


3-Bromo-2-buthyl-3-phenylprop-2-enenitrile (1j): A colorless oil (*Z*:*E* = 91:9), R$_f$ 0.51 (hexane/AcOEt (v/v = 4/1)). IR (KBr): 883, 1231, 1444, 1489, 1594, 1685, 2217 (CN), 2862, 2930, 2959, 3060 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.83 (t, *J* = 7.3 Hz, 0.91×3H, C*H*$_3$ for (*Z*)-**1j**), 0.91 (t, *J* = 7.3 Hz, 0.09×3H, C*H*$_3$ for (*E*)-**1j**), 1.26 (sext, *J* = 7.3 Hz, 0.91×2H, CH$_3$C*H*$_2$ for (*Z*)-**1j**), 1.37 (sext, *J* = 7.3 Hz, 0.09×2H, CH$_3$C*H*$_2$ for (*E*)-**1j**), 1.57 (quint, *J* = 7.3 Hz, 0.91×2H, CH$_3$CH$_2$C*H*$_2$ for (*Z*)-**1j**), 1.74 (quint, *J* = 7.3 Hz, 0.09×2H, CH$_3$CH$_2$C*H*$_2$ for (*E*)-**1j**), 2.22 (t, *J* = 7.3 Hz, 0.91×2H, CH$_3$CH$_2$CH$_2$C*H*$_2$ for (*Z*)-**1j**), 2.96 (t, *J* = 7.3 Hz, 0.09×2H, CH$_3$CH$_2$CH$_2$C*H*$_2$ for (*E*)-**1j**), 7.28-7.31 (m, 2H, Ar*H*), 7.40-7.42 (m, 3H, Ar*H*). ^{13}C NMR (100 MHz, CDCl$_3$): (*Z*)-**1j** δ 13.5 (*C*H$_3$), 21.8 (CH$_3$*C*H$_2$), 30.3 (CH$_3$CH$_2$*C*H$_2$), 32.4 (CH$_3$CH$_2$CH$_2$*C*H$_2$), 118.2, 118.8, 128.2, 128.6, 130.0, 135.6, 137.2; (*E*)-**1j** δ 13.9 (*C*H$_3$), 22.5 (CH$_3$*C*H$_2$), 31.5 (CH$_3$CH$_2$*C*H$_2$), 38.6 (CH$_3$CH$_2$CH$_2$*C*H$_2$), 118.1, 118.7, 128.0, 128.5, 132.8, 133.6, 137.1. HRMS (FAB) calcd for M+H$^+$ of $C_{13}H_{14}BrN$ 264.0388, found 264.0394.

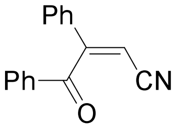


(*Z*)-3-Bromo-2,3-diphenylprop-2-enenitrile (1k): A pale yellow solid, R$_f$ 0.37 (hexane/AcOEt (v/v = 10/1)). mp 77.2-77.9 °C (from CHCl$_3$/hexane). IR (KBr): 883, 919, 1081, 1266, 1444, 1488, 1584, 1597, 2214 (CN), 3062 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.14-7.31 (m, 10H, Ar*H*). ^{13}C NMR (100 MHz, CDCl$_3$): δ 117.9, 118.7, 128.5, 128.7, 129.0, 129.1, 129.5, 130.2, 133.2, 137.2, 138.4. HRMS (FAB) calcd for M+H$^+$ of $C_{15}H_{10}BrN$ 284.0075, found 284.0071.

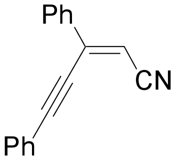
Synthetic Application of *β*-Bromocinnamonitrile 1a



Palladium-catalysed Cross-coupling Reaction of 1a with Tributhyl-4-tolylstannane. A flame dried Schlenk flask was charged with $Pd(PPh_3)_4$ (9.2 mg, 0.0080 mmol), CuI (3.0 mg, 0.016 mmol), **1a** (82.9 mg, 0.40 mmol), tributhyl-4-tolylstannane (183 mg, 0.48 mmol), and dioxane (1.6 mL). The mixture was stirred at 100 °C for 8 h, and then diluted with Et_2O (5 mL). The resulting mixture was treated with a 10 mol% KF aqueous solution (2 mL) for 30 min, and the insoluble materials were filtered through a Celite pad. The organic layer was washed with water and brine, and then dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to flash column chromatography on silica gel with hexane/AcOEt (v/v = 7/1) as eluents to afford 3-(4-methylphenyl)-3-phenyl-2-propenenitrile **2** (83.0 mg, 0.38 mmol) as a white solid (*Z*:*E* = 94:6). R_f 0.43 (hexane/AcOEt (v/v = 4/1)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 0.96×3H, C*H*$_3$ for (*Z*)-**2**), 2.36 (s, 0.04×1H, C*H*$_3$ for (*E*)-**2**), 5.67 (s, 0.96×1H, C*H*CN for (*Z*)-**2**), 5.70 (s, 0.04×1H, C*H*CN for (*E*)-**2**), 7.23-7.44 (m, 9H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): (*Z*)-**2** δ 21.4 (*C*H$_3$), 94.2 (*C*HCN), 118.1 (*C*N), 128.4 (*C*H), 128.5 (*C*H), 129.2 (*C*H), 129.5 (*C*H), 130.3 (*C*H), 134.1 (C^q), 139.2 (C^q), 140.3 (C^q), 163.1 (*C*=CHCN); (*E*)-**2** δ 21.2 (*C*H$_3$), 94.0 (*C*HCN), 117.8 (*C*N), 128.4 (*C*H), 128.5 (*C*H), 129.0 (*C*H), 129.3 (*C*H), 129.8 (*C*H), 135.5 (C^q), 137.2 (C^q), 140.7 (C^q), 162.9 (*C*=CHCN). The spectral data match those reported in the literature (*Synthesis* **2002**, 1903.).

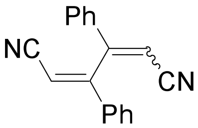


Palladium-catalysed Cross-coupling Reaction of 1a with Benzoyltributhylstannane. A flame dried Schlenk flask was charged with $Pd(OAc)_2$ (9.2 mg, 0.040 mmol), PPh_3 (21.0 mg, 0.080 mmol), **1a** (82.9 mg, 0.40 mmol), benzoyltributhylstannane (316 mg, 0.80 mmol), and dioxane (1.6 mL). The mixture was stirred at 100 °C for 12 h, and then diluted with Et_2O (5 mL). The resulting mixture was treated with a 10 mol% KF aqueous solution (2 mL) for 30 min, and the insoluble materials were filtered through a short silica gel pad with Et_2O as an eluent. The organic layer was washed with water and brine, and then dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to flash column chromatography on silica gel with hexane/AcOEt (v/v = 4/1) as eluents to afford (2*Z*)-4-oxo-3,4-diphenylbut-2-en-carbonitrile **3** (53.6 mg, 0.23 mmol, 57% yield) as a colorless oil. R_f 0.24 (hexane/AcOEt (v/v = 4/1)). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.03 (s, 1H, C*H*CN), 7.39-7.50 (m, 7H, Ar*H*), 7.63 (t, *J* = 6.8 Hz, 1H, Ar*H*), 7.94 (d, *J* = 7.8 Hz, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 96.1 (*C*HCN), 115.5 (*C*N), 126.6 (*C*H), 129.1 (*C*H), 129.4 (*C*H), 129.9 (*C*H), 131.4 (*C*H), 133.2 (*C*H), 134.7 (C^q), 134.8 (C^q), 161.0 (*C*=CHCN), 194.0 (*C*=O). The spectral data match those reported in the literature (*J. Org. Chem.* **2008**, *73*, 2396.).

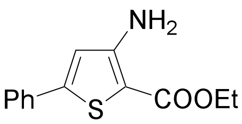


Palladium-catalysed Cross-coupling Reaction of 1a with Phenylacetylene. A flame dried Schlenk flask was charged with **1a** (82.9 mg, 0.40 mmol) and phenylacetylene (44.9 mg, 0.44 mmol) in THF (1.6 mL) was degassed by three freeze-thaw cycles. To this were added $Pd(PPh_3)_4$ (4.6 mg, 0.0040 mmol), CuI (1.5 mg, 0.0080 mmol), and Et_3N (44.5 mg, 0.44 mmol), and then the mixture was stirred at rt for 5 h. The reaction mixture was washed with water and brine, and then dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to flash column chromatography on silica gel with hexane/AcOEt (v/v = 10/1) as eluents to afford (2*Z*)-3,5-diphenylpent-2-en-4-ynenitrile **4** as a pale yellow oil (88.0 mg, 0.38 mmol, 96% yield). R_f 0.49 (hexane/AcOEt (v/v = 4/1)). IR (neat): 919, 1069, 1213, 1257, 1362, 1444, 1489, 1556, 2191, 2217 (CN), 2362, 3060 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.98 (s, 1H, C*H*CN), 7.33-7.45 (m, 6H, Ar*H*), 7.63 (dd, *J* = 2.0, 7.8 Hz, 2H, Ar*H*), 7.71 (dd, *J* = 2.0, 7.8 Hz, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$):

δ 85.2 ($C\equiv$C), 100.0 ($C\equiv$C), 101.9 (CHCN), 117.4 (CN), 121.3 (CH), 126.6 (CH), 128.4 (CH), 128.8 (CH), 129.8 (CH), 130.9 (CH), 132.2 (C^q), 134.2 (C^q), 142.9 (C=CHCN). HRMS (FAB) calcd for M+H$^+$ of $C_{17}H_{11}N$ 230.0970, found 230.0977.

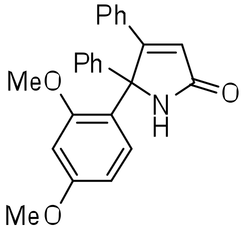


Palladium-catalysed Homo-coupling Reaction of 1a. A flame dried Schlenk flask was charged with $NiBr_2(PPh_3)_2$ (6.7 mg, 0.0090 mmol), PPh_3 (4.7 mg, 0.018 mmol), zinc powder (19.6 mg, 0.30 mmol), and dioxane (1.2 mL). The solution was stirred at room temperature for 10 min, and then **1a** (62.2 mg, 0.30 mmol) was added dropwise. The mixture was stirred at 80 °C for 6 h, and then diluted with Et_2O (5 mL). The reaction mixture was washed with water and brine, and then dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to flash column chromatography on silica gel with hexane/AcOEt (v/v = 10/1) as eluents to afford 3,4-diphenylhexa-2,4-hexadiene-1,6-dinitrile **5** (28.5 mg, 0.11 mmol, 74% yield) as a white solid **(***Z*:*E* = 96:4). R_f 0.21 (hexane/AcOEt (v/v = 4/1**)**). mp 183.8-184.6 °C (from $CHCl_3$/hexane). IR (KBr): 1031, 1372, 1445, 1493, 1604, 2215 (CN), 2922, 3057 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.77 (s, 0.04×1H, C*H*CN for (4*E*)-**5**), 5.95 (s, 0.04×1H, C*H*CN for (4*E*)-**5**), 6.20 (s, 0.96×2H, C*H*CN for (4*Z*)-**5**), 7.36-7.46 (m, 10H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): (4*Z*)-**5** δ 99.2 (CHCN), 115.9 (CN), 126.8 (CH), 129.4 (CH), 131.4 (CH), 134.0 (C^q), 157.8 (C=CHCN). HRMS (FAB) calcd for M+H$^+$ of $C_{18}H_{12}N_2$ 257.1079, found 257.1078.



Synthesis of Ethyl 3-Amino-5-phenylthiophene-2-carboxylate 6. To a stirred solution of **1a** (82.9 mg, 0.40 mmol) and ethyl thioglycolate (57.7 mg, 0.48 mmol) in EtOH (2 mL) was added sodium ethoxide (32.7 mg, 0.48 mmol) at rt. After stirring at 70 °C for 12 h, the solvent was removed. The residue was dissolved in Et_2O, washed with water, and then dried over

$MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to flash column chromatography on silica gel with hexane/AcOEt (v/v = 4/1) as eluents to afford ethyl 3-amino-5-phenylthiophene-2-carboxylate **6** as a white solid (84.0 mg, 0.34 mmol, 86% yield). R_f 0.30 (hexane/AcOEt (v/v = 4/1)). mp 92.1-92.7 ^{o}C. IR (KBr): 768, 1039, 1094, 1129, 1294, 1368, 1467, 1553, 1607, 1673, 3309, 3389 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (t, J = 7.3 Hz, 3H, CH_3), 4.30 (q, J = 7.3 Hz, 2H, CH_2CH_3), 5.47 (br, 2H, NH_2), 6.75 (s, 1H, 4-thienyl C*H*), 7.30-7.40 (m, 3H, Ar*H*), 7.55-7.59 (m, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5 (CH_3), 58.2 (CH_3CH_2), 100.8 (C^q), 115.5 (*C*H), 125.9 (*C*H), 128.8 (*C*H), 128.9 (*C*H), 133.3 (C^q), 148.9 (C^q), 154.1 (C^q), 164.6 (*C*=O). HRMS (FAB) calcd for $M+H^+$ of $C_{13}H_{13}NO_2S$ 248.0745, found 248.0744.



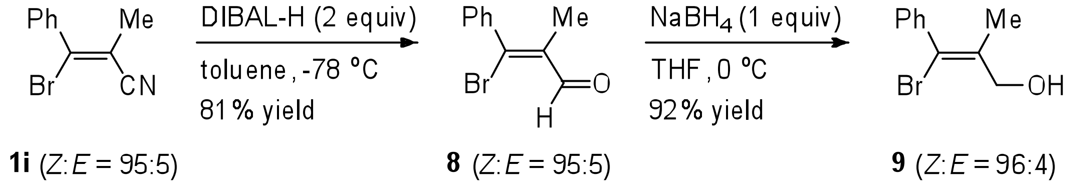
Copper-catalysed Reaction of Carbonyl-ene-nitrile Compound 3. A flame dried Schlenk flask was charged with $Cu(OTf)_2$ (7.2 mg, 0.020 mmol), **3** (46.6 mg, 0.20 mmol), 1,3-dimethoxybenzene (138.2 mg, 1.0 mmol), and $ClCH_2CH_2Cl$ (2.0 mL). After stirring at 80 ^{o}C for 15 h, the mixture was diluted with Et_2O and filtered through a short silica gel pad. Filtrate was concentrated under reduced pressure and the residue was subjected to flash column chromatography on with hexane/AcOEt (v/v = 7/1-3/1) as eluents to afford 4,5-diphenyl-5-(2,4-dimethoxyphenyl)-3-pyrrolin-2-one **7** (52.1 mg, 0.14 mmol, 70% yield) as a white solid. R_f 0.18 (hexane/AcOEt (v/v = 2/1)). mp 210.3-210.8 ^{o}C. IR (KBr): 794, 832, 868, 922, 1038, 1211, 1262, 1353, 1378, 1418, 1447, 1586, 1612, 1693 (C=O), 2838, 2942, 3017, 3276 (N-H) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.57 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 6.22 (s, 1H, C*H*C=O), 6.48 (s, 1H, Ar*H*), 6.48-6.49 (m, 1H, Ar*H*), 7.07-7.23 (m, 5H, Ar*H*), 7.31 (d, J = 7.8 Hz, 2H, Ar*H*), 7.32-7.39 (m, 2H, Ar*H*), 7.41 (br s, 1H, N*H*) , 7.83 (d, J = 7.8 Hz, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3

(O*C*H_3), 55.4 (O*C*H_3), 67.8 (C^q), 100.8, 104.27, 122.4, 125.6, 127.1, 127.2, 128.1, 128.2, 128.3, 128.5, 131.0, 132.8, 141.0, 146.1, 158.0, 162.8, 171.8 (*C*=O). HRMS (FAB) calcd for M+H^+ of $C_{24}H_{21}NO_3$ 372.1602, found 372.1600.

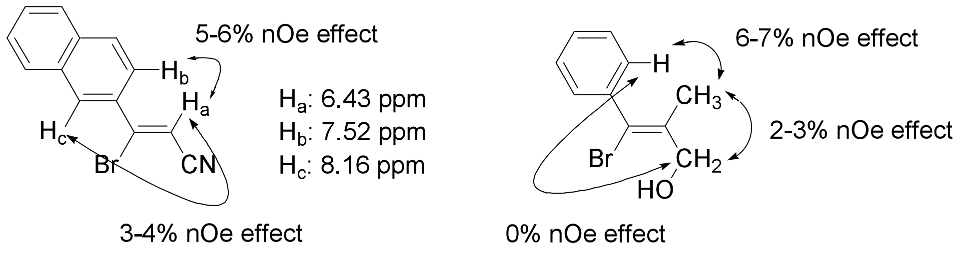
NMR Studies on Bromocyantion of 1-Phenyl-1-hexyne. In a globe box, BrCN (15.9 mg, 0.15 mmol) was added to a solution of $GaCl_3$ (26.4 mg, 0.15 mmol) in $CDCl_3$ (0.6 mL) placed in a vial. After stirring at room temperature for 5 min, 1-phenyl-1-hexyne (23.7 mg, 0.15 mmol) was added, and the resulting mixture was further stirred at room temperature for 6 h. The progress of the reaction was monitored by ^{13}C NMR spectroscopic analysis. Reaction yield and *Z*:*E* ratio of the product were determined on the basis of the ^{1}H NMR measurement using dioxane as an internal standard.

Determination of Products Structures. The structures of known compounds **1a**, **2**, and **3** were determined on the basis of NMR spectrum in literatures. The regio- and stereochemistry of other bromocyanation adducts derived from terminal acetylenes, such as **1b**-**1h** were determined by comparing their chemical shift values of analogous vinyl protons with that of **1a**. The stereochemistry of **1i** was determined by nOe analysis of the corresponding 3-bromo-2-propen-1-ol **9**, which was derived from subsequent reduction of **1i** with DIBAL-H and $NaBH_4$ (Scheme S1). The stereochemistry of other products was also confirmed by nOe experiments of ^{1}H NMR. Selected results are shown below (Figure S1). The structure of major product of **1e** was unambiguously determined by

Scheme S1



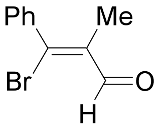
X-ray crystallographic analysis (Figure S2).



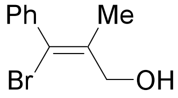
1d (major)

3 (major)

Figure S1. Determination of stereochemistry of the products.



Reduction of 1h with DIBAL-H. To a solution of **1i** (222 mg, 1.0 mmol) in toluene (4 mL) was added a 1.5 M solution of DIBAL-H in toluene (1.0 mL, 1.5 mmol) at -78 °C, and the resulting mixture was stirred at the same temperature for 1 h. The reaction was quenched with MeOH (0.5 mL) at -78 °C and was warmed at room temperature. The mixture was filtered through a short silica gel pad with Et_2O as an eluent, and concentrated in vacuo. The residue was subjected to flash column chromatography on silica gel with hexane/AcOEt (v/v = 10/1) as eluents to give 3-bromo-2-methyl-3-phenylprop-2-enen-1-al **8** (112 mg, 0.81 mmol, 81% yield) as a colorless oil (*Z*:*E* = 95:5). R_f 0.63 (hexane/AcOEt (v/v = 4/1)). IR (neat): 865, 1022, 1261, 1443, 1490, 1591, 1604, 1681 (C=O), 1717, 2863, 3057 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.79 (s, 0.95×3H, CH_3 for (*Z*)-**8**), 1.85 (s, 0.05×3H, CH_3 for (*E*)-**8**), 7.25-7.45 (m, 5H, Ar*H*), 10.2 (s, 0.95×1H, C*H*O for (*Z*)-**8**), 10.4 (s, 0.05×1H, C*H*O for (*E*)-**8**). ^{13}C NMR (100 MHz, $CDCl_3$): (*Z*)-**8** δ 14.8 (CH_3), 128.4 (*C*H), 128.5 (*C*H), 129.7 (*C*H), 134.6 (C^q), 139.3 (C^q), 139.4 (C^q), 194.3 (*C*=O). HRMS (FAB) calcd for $M+H^+$ of $C_{10}H_9BrO$ 224.9915, found 224.9912.



Reduction of 2 by $NaBH_4$. To a suspension of $NaBH_4$ (15.1 mg, 0.40 mmol) in THF (2.0 mL) was added a solution of **8** (90 mg, 0.40 mmol) in THF (1.0 mL) at 0 °C, and the resulting mixture was stirred for 30 min. The reaction was quenched with 10% HCl aqueous solution at 0 °C, and the resulting mixture was extracted with Et_2O (10 mL × 3). The combined organic layers were washed with a sat. $NaHCO_3$ aqueous solution and brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was subjected to flash column chromatography on silica gel with hexane/AcOEt (v/v = 3/1) as eluents to give 3-bromo-2-methyl-3-phenyl-2-propen-1-ol **9** (83.5 mg, 0.37 mmol, 92% yield) as a colorless oil (*Z*:*E* = 96:4). R_f 0.19 (hexane/AcOEt (v/v = 4/1)). IR (neat): 867, 1012, 1263, 1442, 1490, 1704, 2857, 2917, 3336 (OH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.81 (s, 0.96×3H, CH_3 for (*Z*)-**9**), 1.85 (s, 0.04×3H, CH_3 for (*E*)-**9**), 4.45 (s, 0.96×2H, CH_2OH for (*Z*)-**9**), 4.47 (s, 0.04×2H, CH_2OH for (*E*)-**9**), 7.25-7.32 (m, 2H, Ar*H*), 7.33-7.38 (m, 3H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): (*Z*)-**9** δ 18.3 (CH_3), 67.4 (CH_2), 118.4, 128.1, 128.2, 129.1, 136.2, 140.3. HRMS (FAB) calcd for $M+H^+$ of $C_{10}H_{11}BrO$ 227.0072, found 227.0072.

X-ray Crystallographic Studies of 1e. Colorless crystals of (*Z*)-**1e** suitable for X-ray analysis were obtained by recrystallization from $CHCl_3$ /hexane. The single crystal was sealed in a Pyrex glass capillary under N_2 atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-Kα radiation. Details of crystal and data collection parameters are summarized in Table S1. The positions of non-hydrogen atoms were determined by direct methods (SIR92) and subsequent Fourier syntheses (DIRDIF PATTY). An ORTEP drawing of (*Z*)-**1e** is shown in Figure S2.

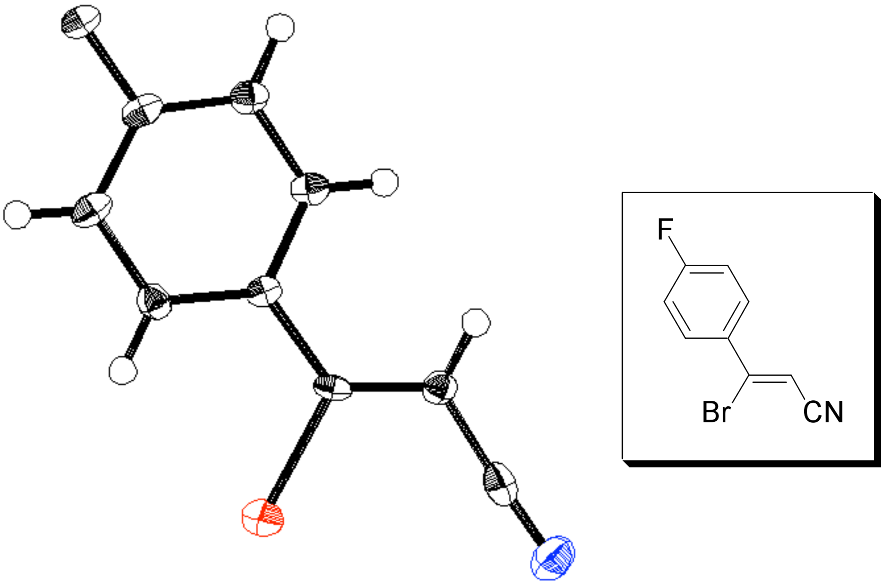


Figure S2. ORTEP drawing of (*Z*)-**1e**.

Table S1. Summary of Crystallographic Data of (*Z*)-**1e**

Empirical formula: C_9H_6BrFN
Formula weight: 227.06
Crystal system: triclinic
Space group: P-1 (#2)
Crystal color: colorless
Lattice parameters:
a (Å) = 7.460(4), b (Å) = 9.197(5), c (Å) = 12.279(7)
V (Å^3) = 822.2(8), α = 83.7518(18)°, β = 86.002(16)°
γ = 79.445(15)°
Z = 4
D_{calc} (g cm^{-3}): 1.834
μ (Mo Kα) (cm^{-1}): 49.662
Goodness of fit (GOF) = 1.002
F(000): 444
Diffractometer: Rigaku RAXIS-RAPID
Radiation: MoKα (λ = 0.71070Å), Graphite Monochromated
Temp (°C): -150
Scan type: $\omega - 2\theta$
Max. 2θ (°): 54.9
No. of reflections measured total: 5520
No. of observns ($I > 3.00\ \sigma(I)$): 3075
Structure solution: Direct Methods (SIR92)
Refinement: Full-Matrix Least-Squares on F
No. of variables: 217
Reflection/parameter ratio: 14.17
Residuals: R = 0.0634, R_w = 0.0630
Max Shift/Error in Final Cycle: 0.00
Maximum peak in Final Diff Map (e (Å^{-3}): 0.99
Minimum peak in Final Diff Map (e (Å^{-3}): -0.71

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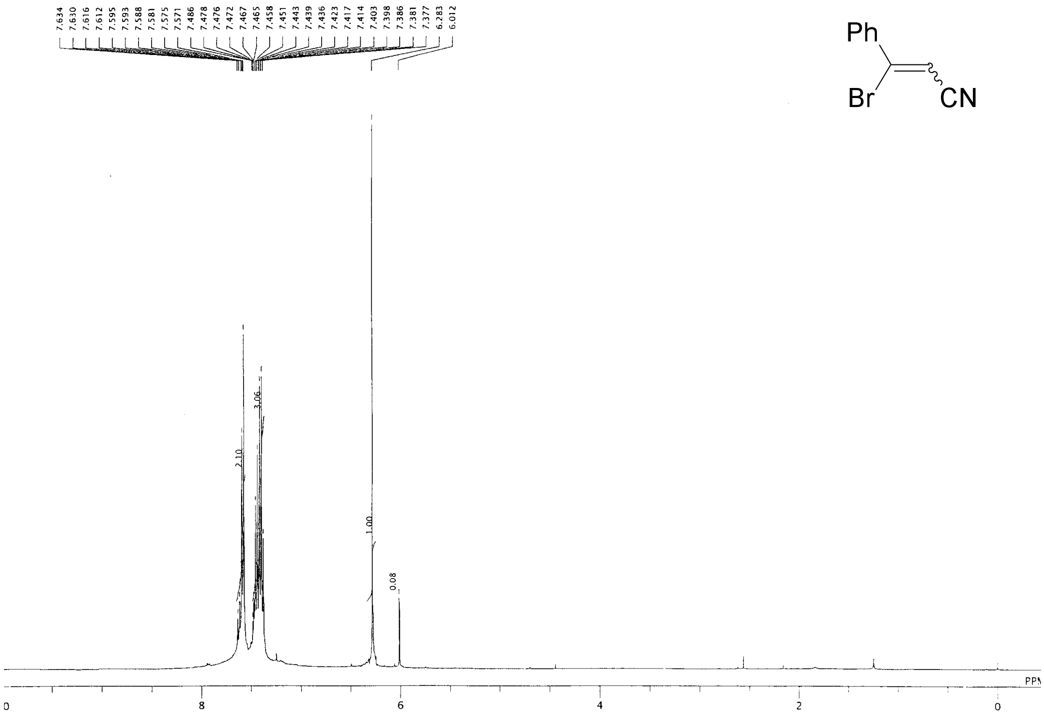
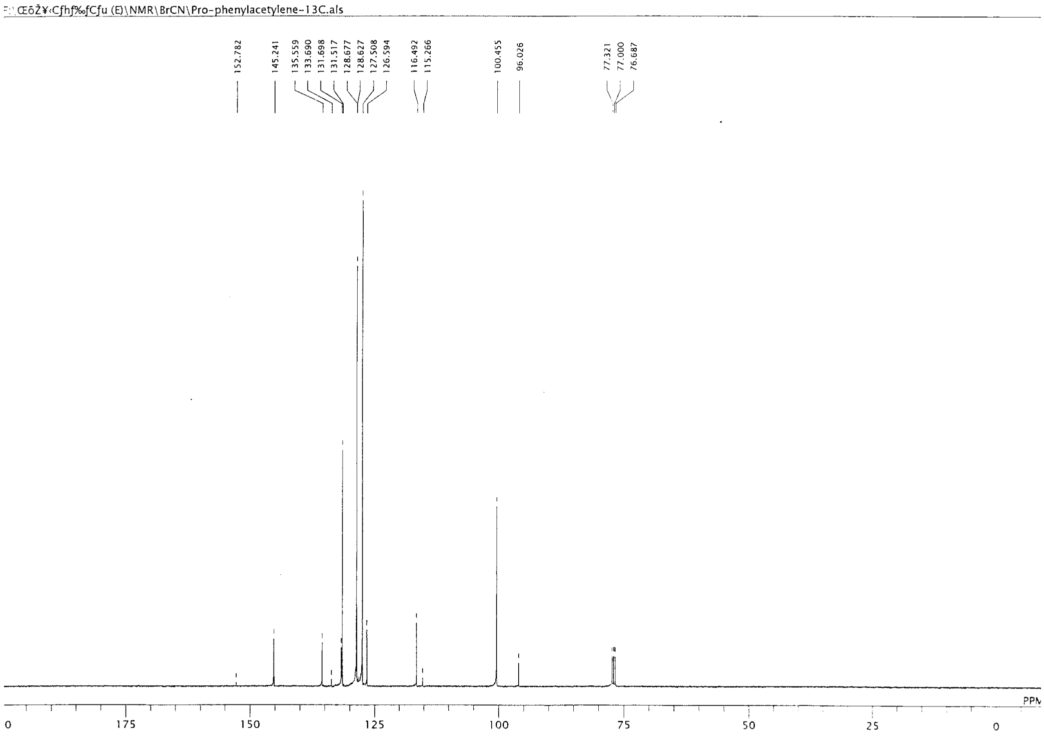
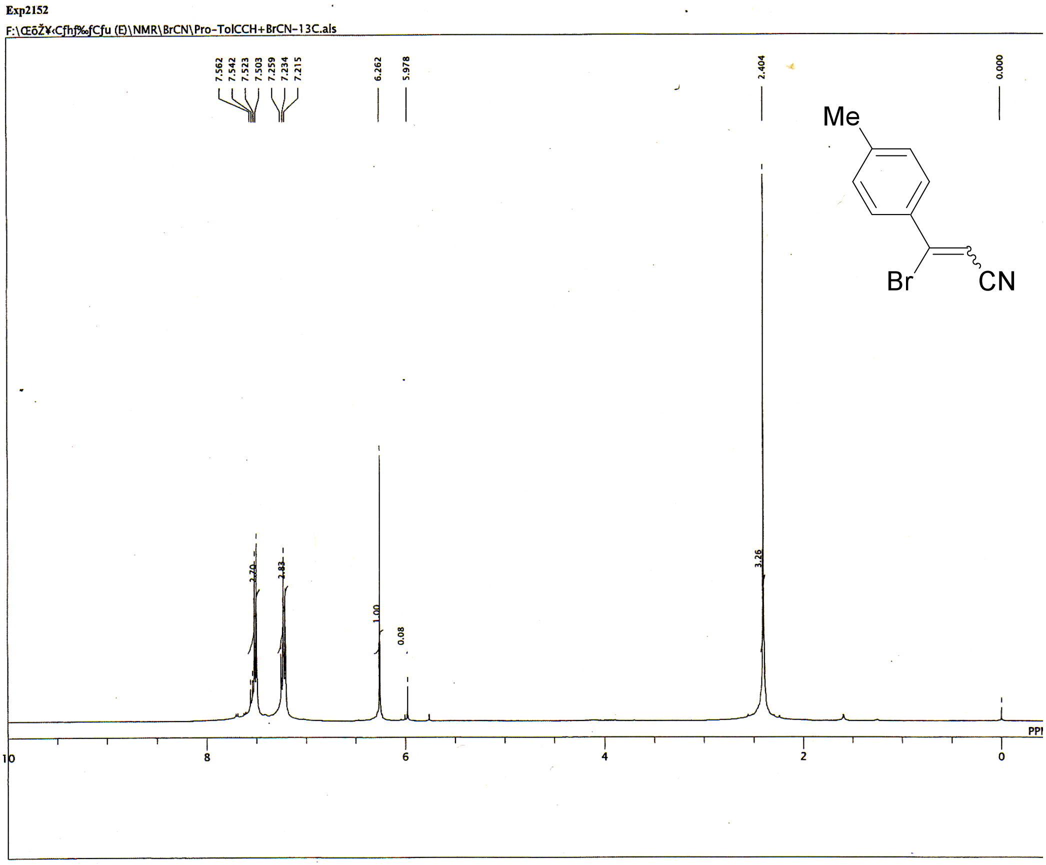
^{1}H NMR and ^{13}C NMR Spectra of Selected Compounds



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7.259
7.234
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6.262
5.978
2.404
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2
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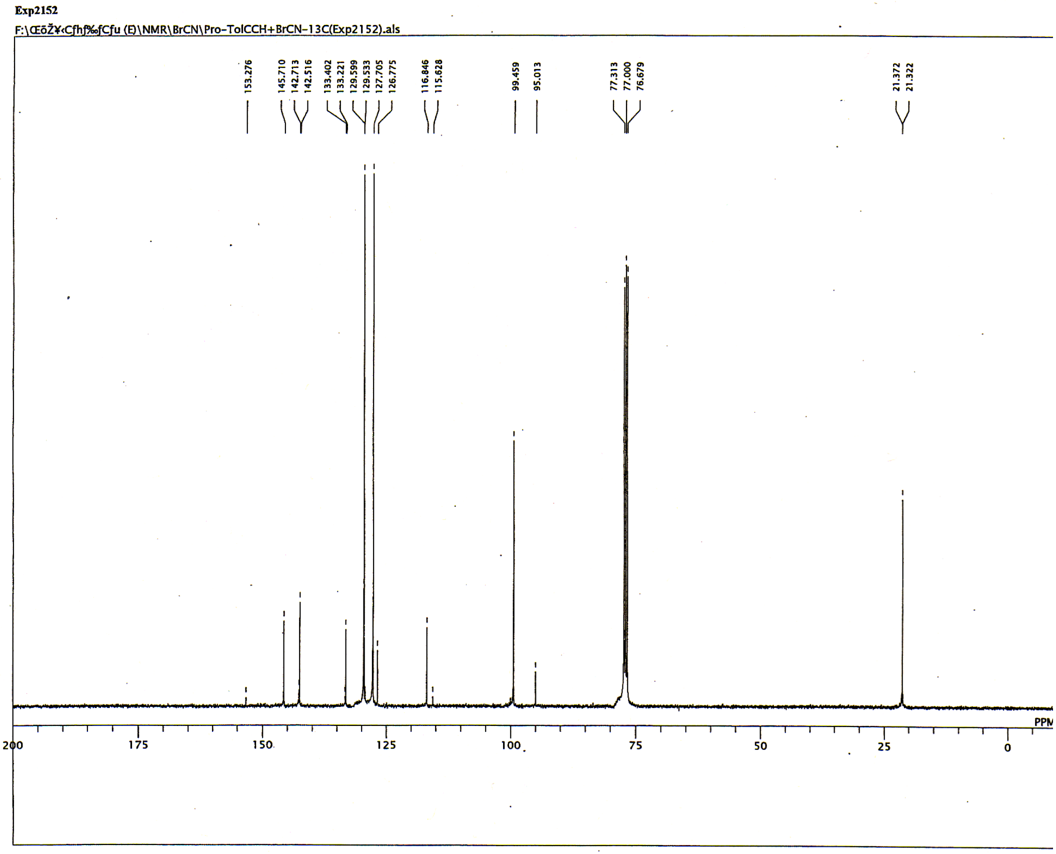
PPM


Exp2152
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116.846
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125
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50
25
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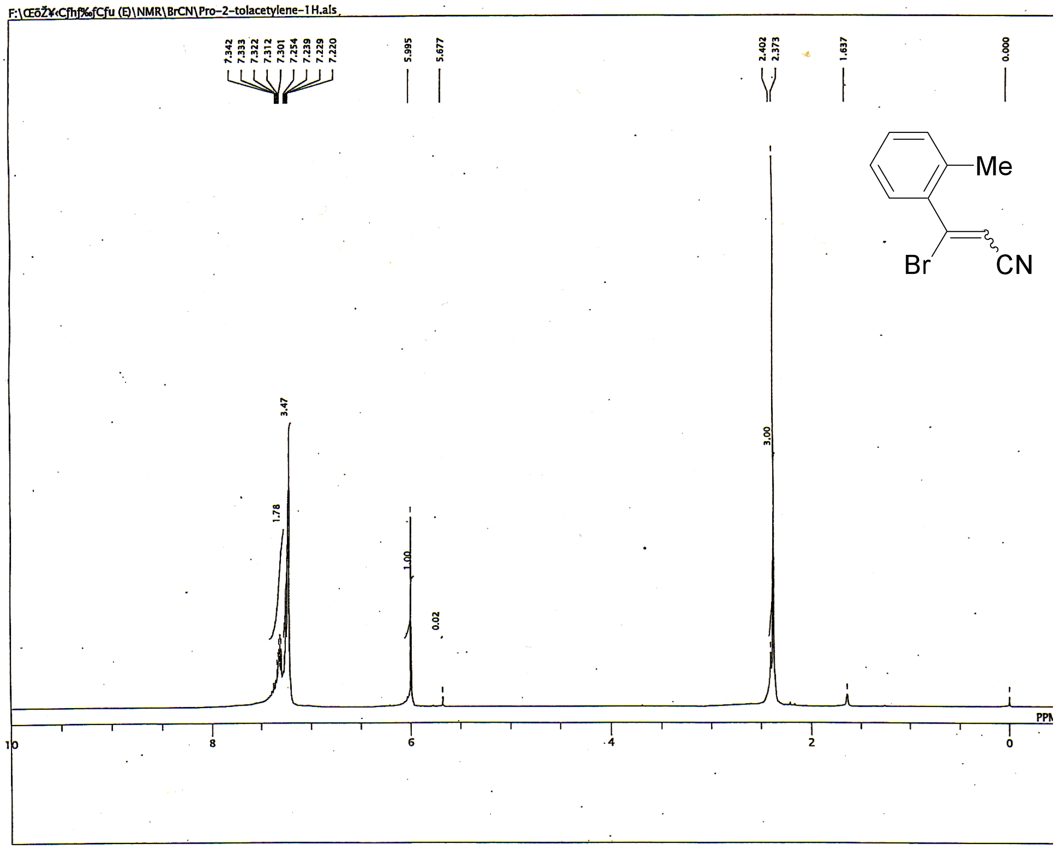
PPM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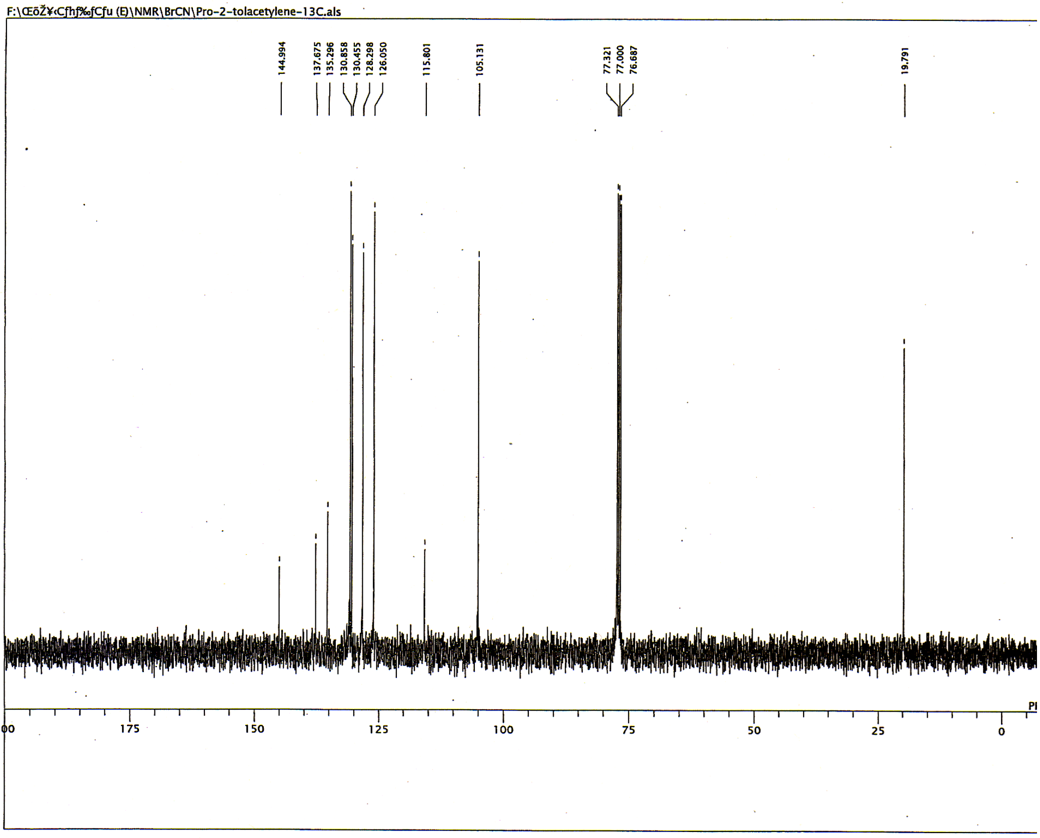
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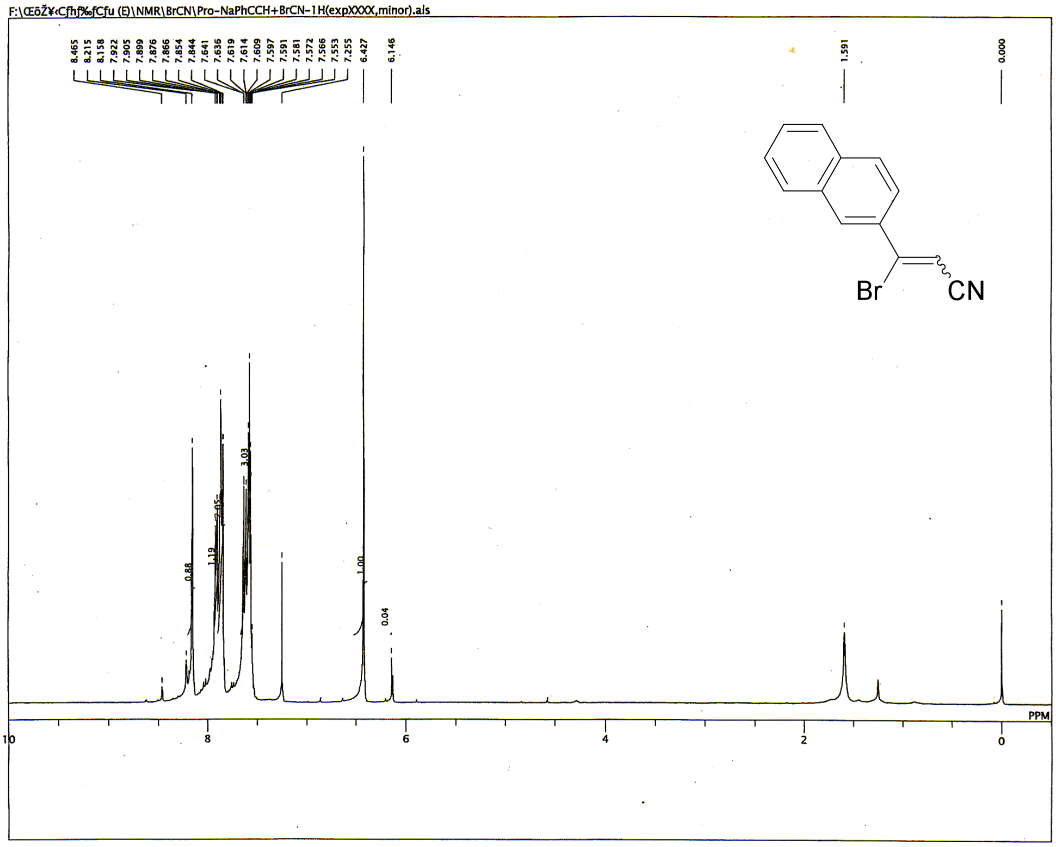
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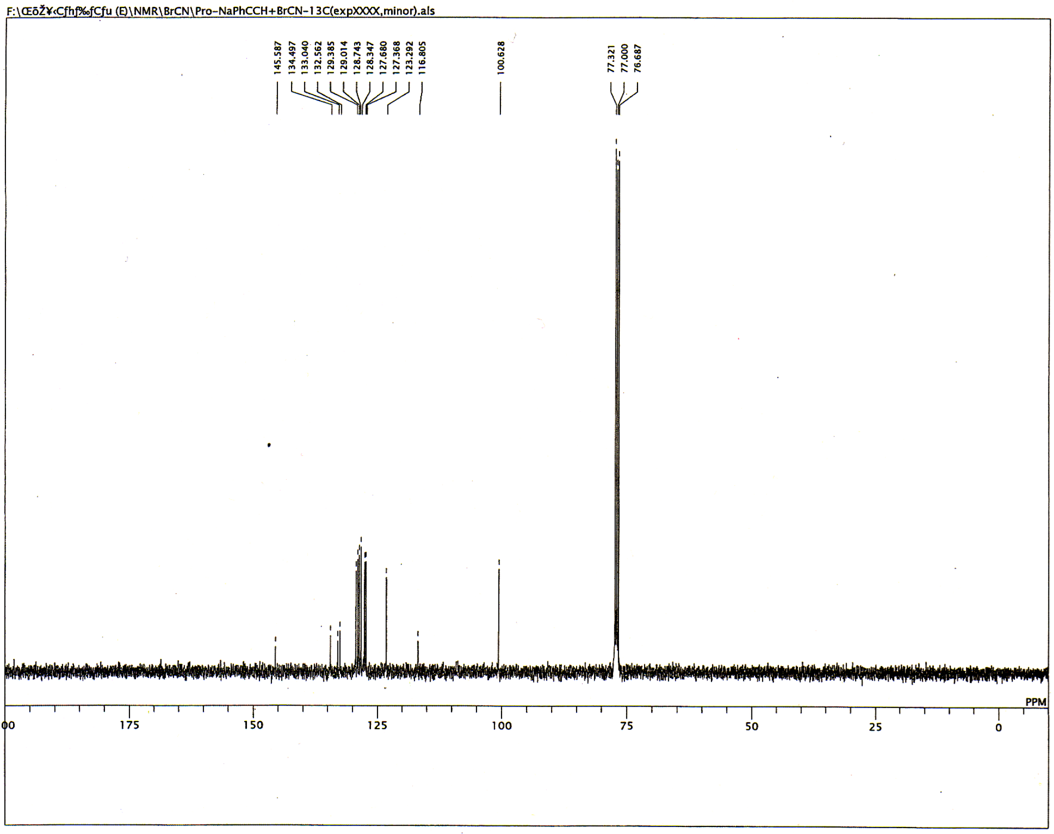
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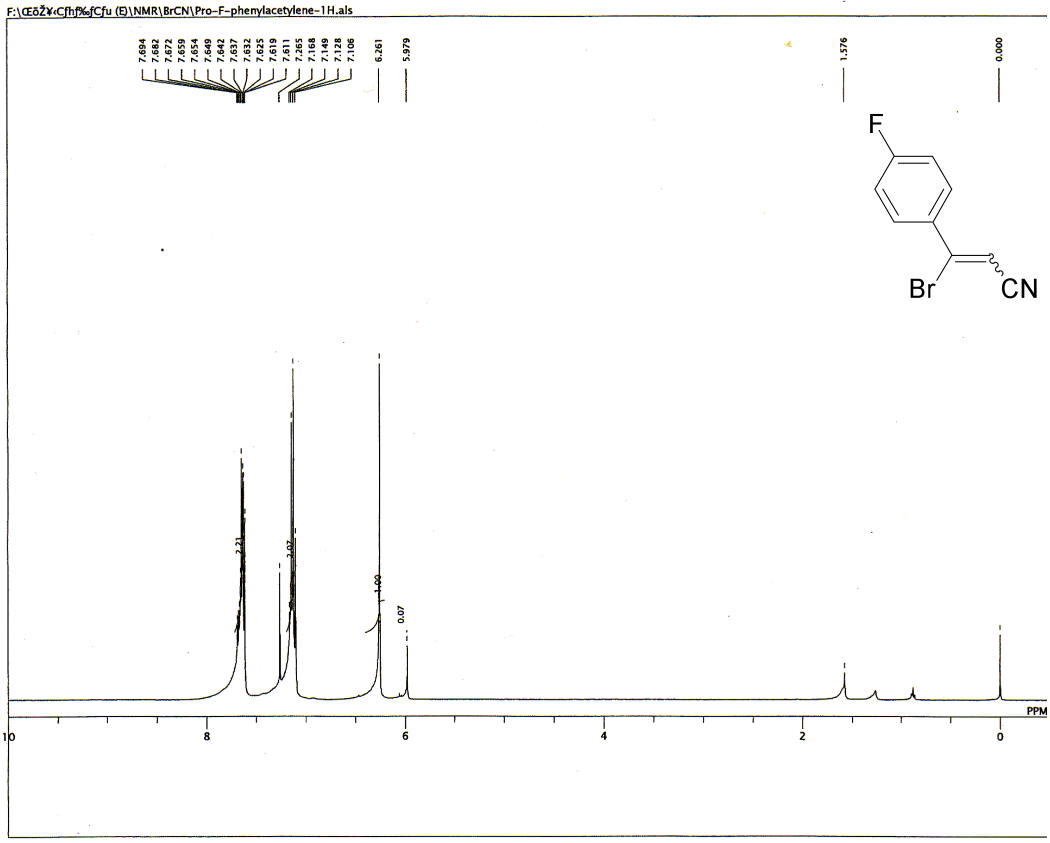
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7.649
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7.625
7.619
7.611
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7.168
7.149
7.128
7.106
6.261
5.979
1.576
0.000
F
Br
CN
2.21
2.07
1.00
0.07
PPM
10
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6
4
2
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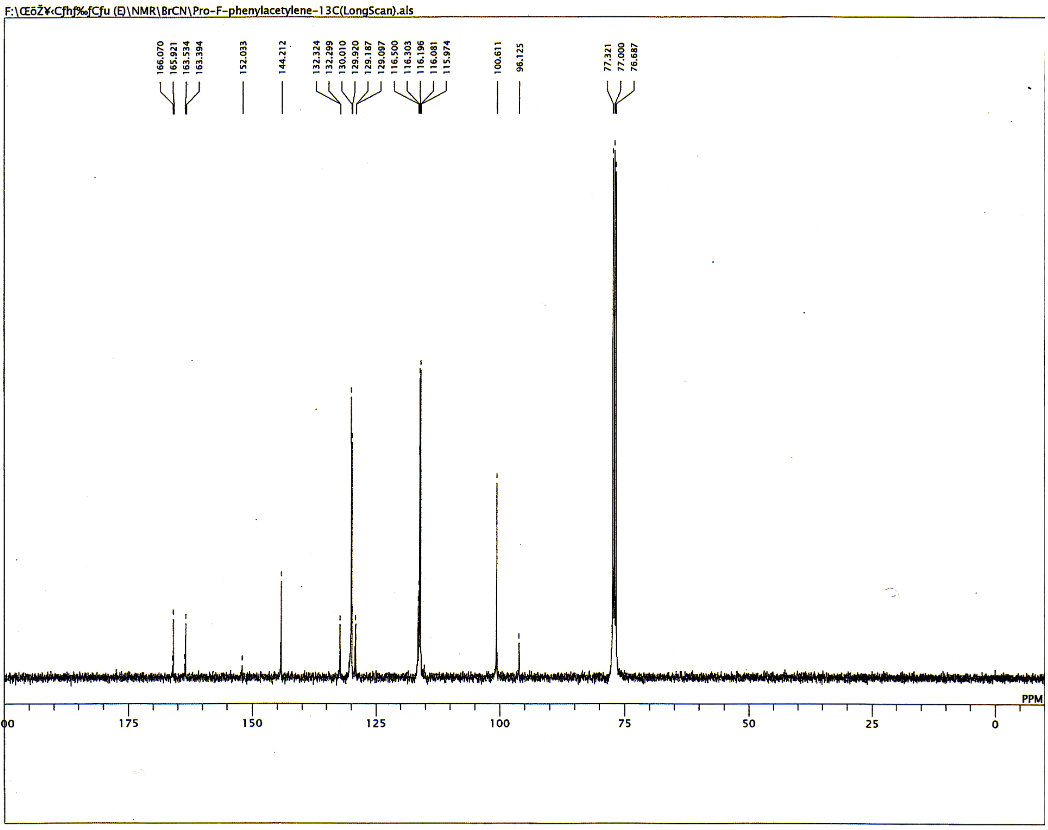
F:\ŒõŽ¥‹Cƒhƒ‰ƒCƒu (E)\NMR\BrCN\Pro-F-phenylacetylene-13C(LongScan).als
166.070
165.921
163.534
163.394
152.033
144.212
132.324
132.299
130.010
129.920
129.187
129.097
116.500
116.303
116.196
116.081
115.974
100.611
96.125
77.321
77.000
76.687
PPM
200
175
150
125
100
75
50
25
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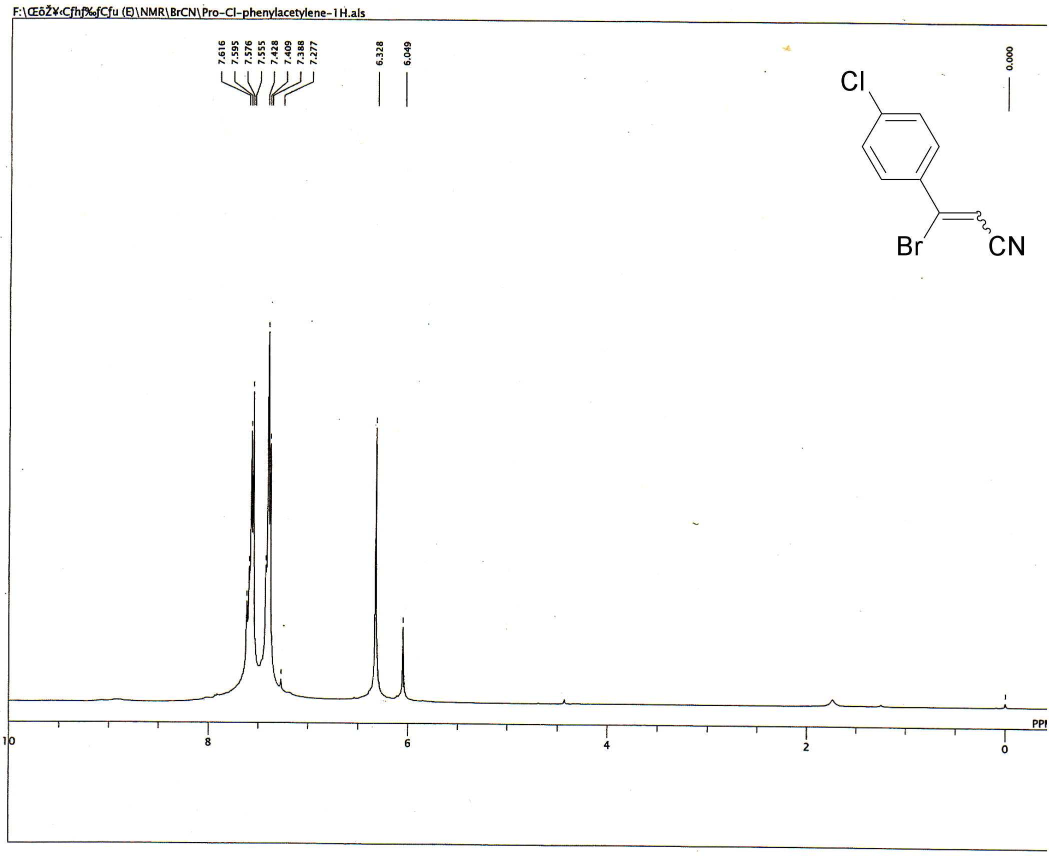
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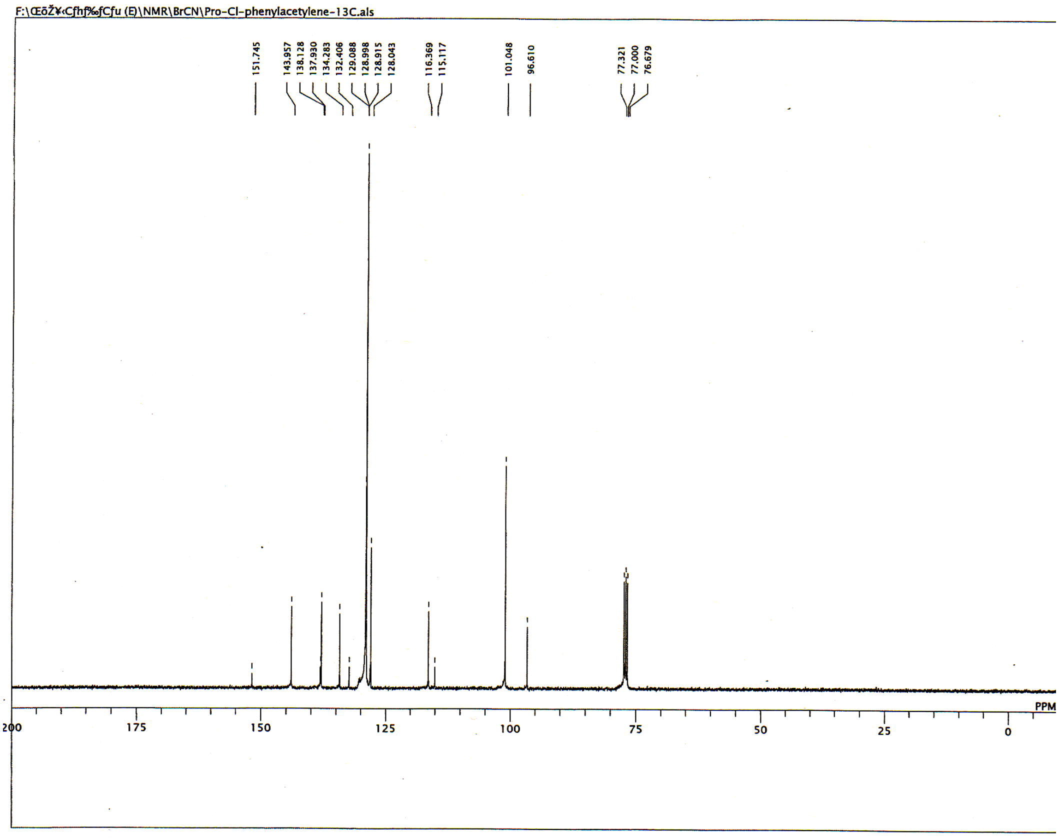
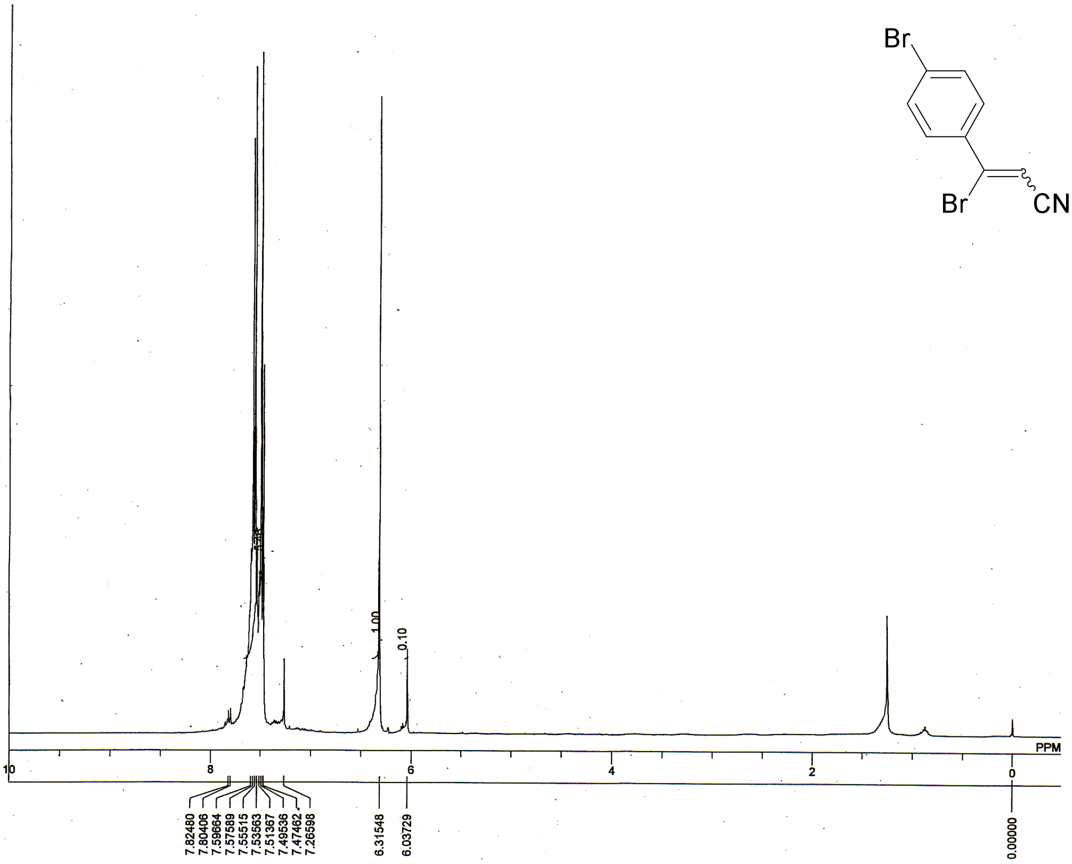
7.616
7.595
7.576
7.555
7.428
7.409
7.388
7.277
6.328
6.049
0.000
Cl
Br
CN
10
8
6
4
2
0
PPM


F:\ŒõŽ¥‹Cƒhƒ‰ƒCƒu (E)\NMR\BrCN\Pro-Cl-phenylacetylene-13C.als
151.745
143.957
138.128
137.930
134.283
132.406
129.088
128.998
128.915
128.043
116.369
115.117
101.048
96.610
77.321
77.000
76.679
200
175
150
125
100
75
50
25
0
PPM


Br
Br
CN
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0.10
PPM
10
8
6
4
2
0
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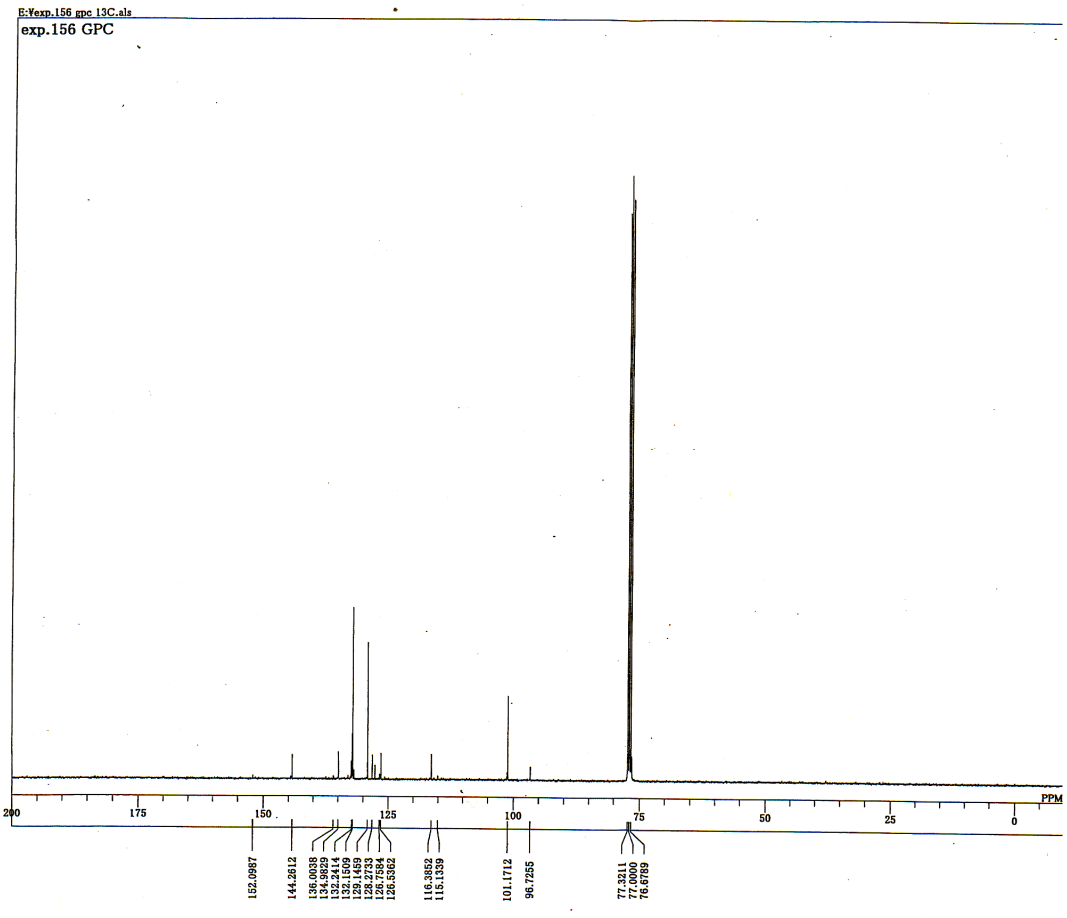
7.53563
7.51367
7.49536
7.47462
7.26598
6.31548
6.03729
0.00000


E:¥exp.156 gpc 13C.als
exp.156 GPC
PPM
200
175
150
125
100
75
50
25
0
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144.2612
136.0038
134.9829
132.2414
132.1509
129.1459
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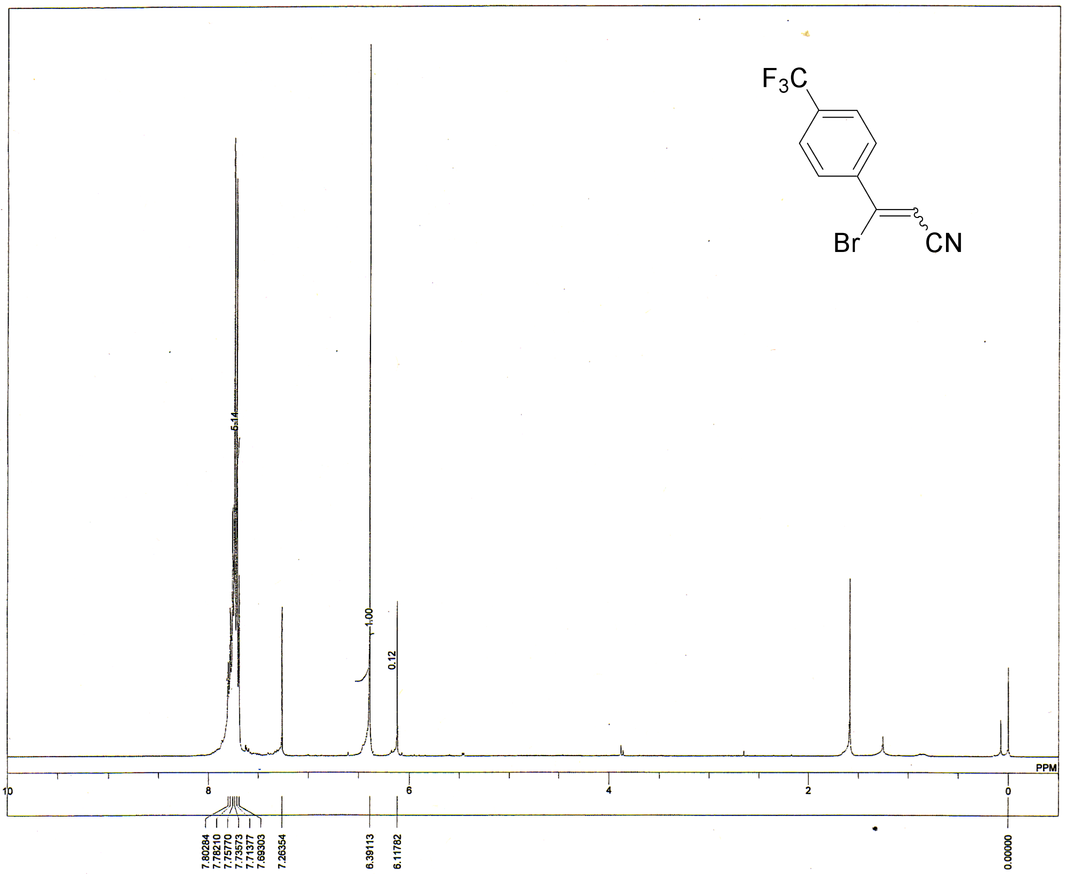
126.5362
116.3852
115.1339
101.1712
96.7255
77.3211
77.0000
76.6789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Br
CN
5.14
1.00
0.12
PPM
10
8
6
4
2
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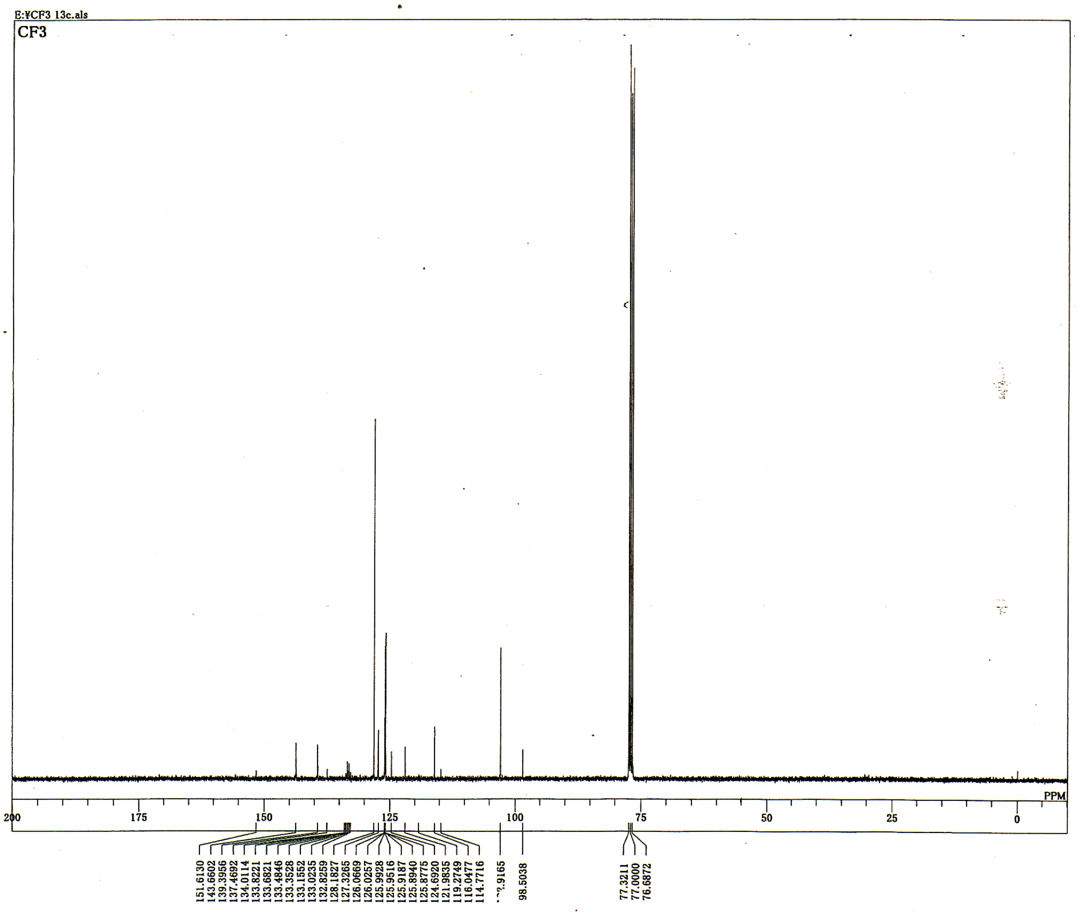
7.75770
7.73573
7.71377
7.69303
7.26354
6.39113
6.11782
0.00000


E:¥CF3 13c.als
CF3
PPM
200
175
150
125
100
75
50
25
0
151.6130
143.6602
139.3956
137.4692
134.0114
133.8221
133.6821
133.4846
133.3528
133.1552
133.0235
132.8259
128.1827
127.3265
126.0669
126.0257
125.9928
125.9516
125.9187
125.8940
125.8775
124.6920
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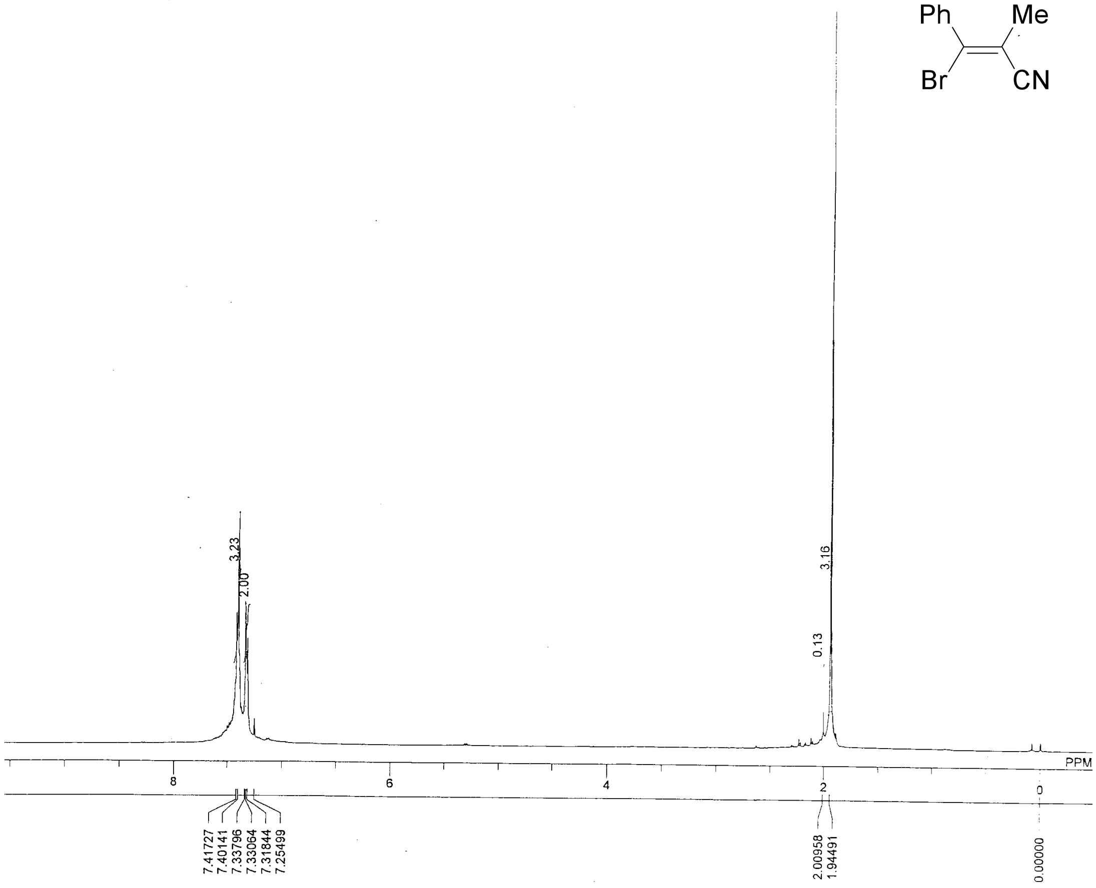
119.2749
116.0477
114.7716
2.9165
98.5038
77.3211
77.0000
76.6872


Ph
Me
Br
CN
3.23
2.00
3.16
0.13
8
6
4
2
0
PPM
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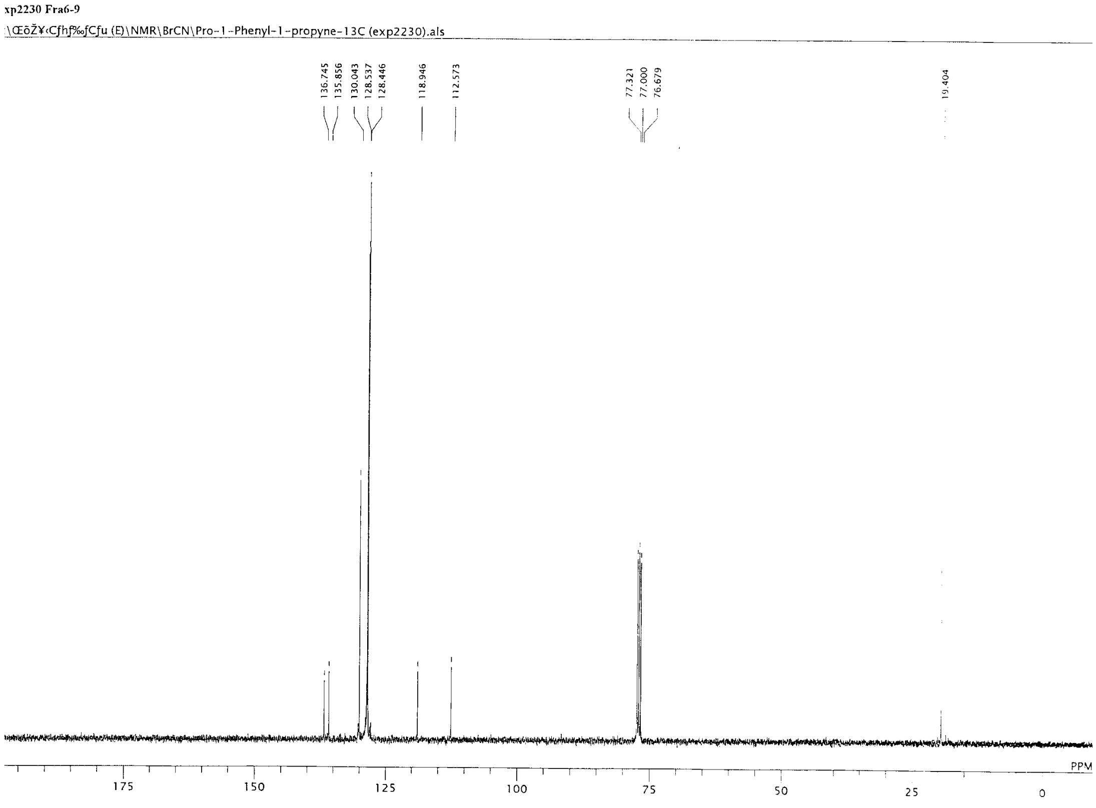
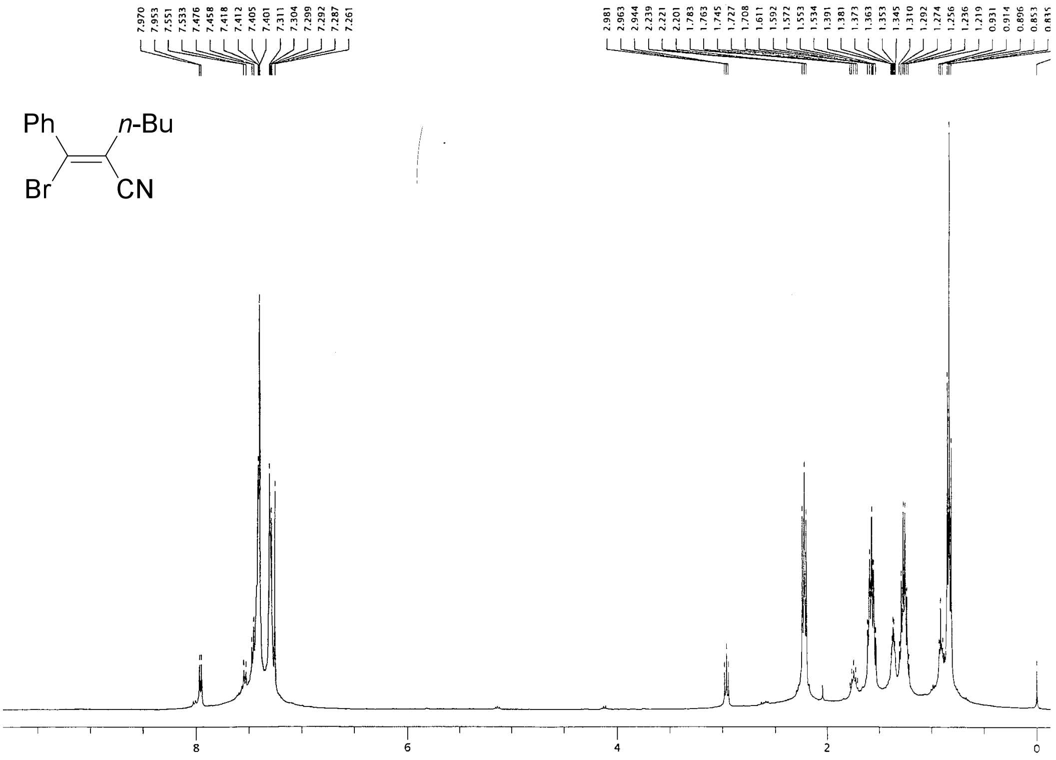
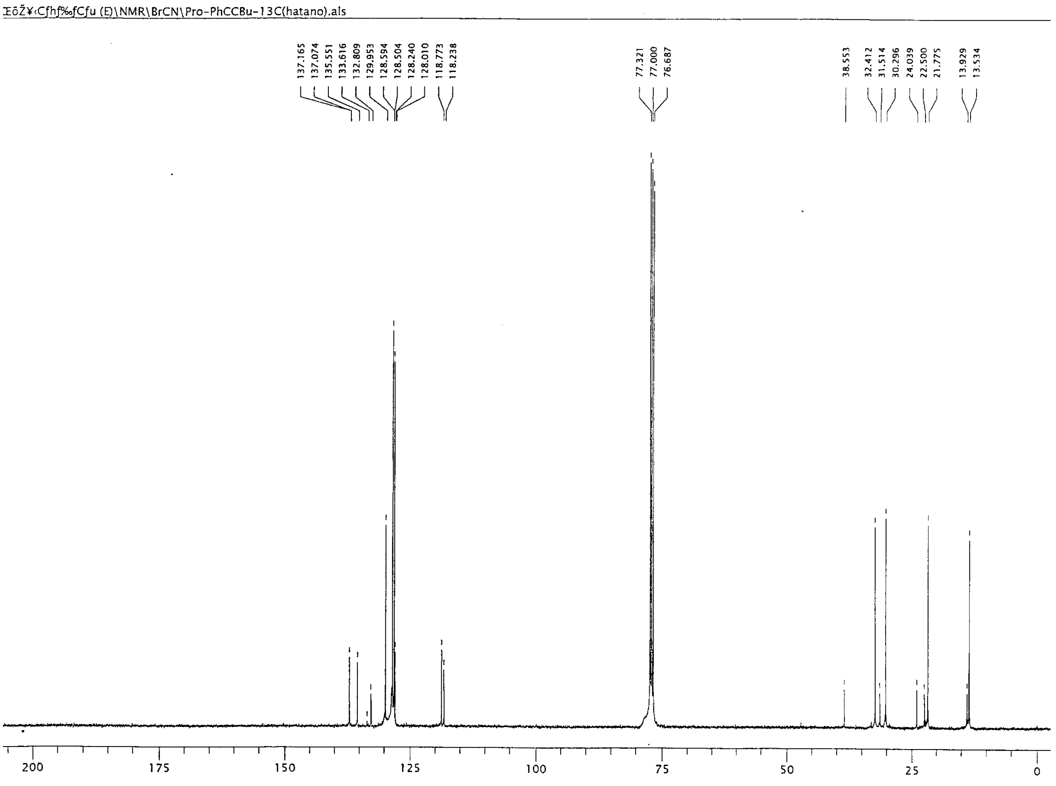
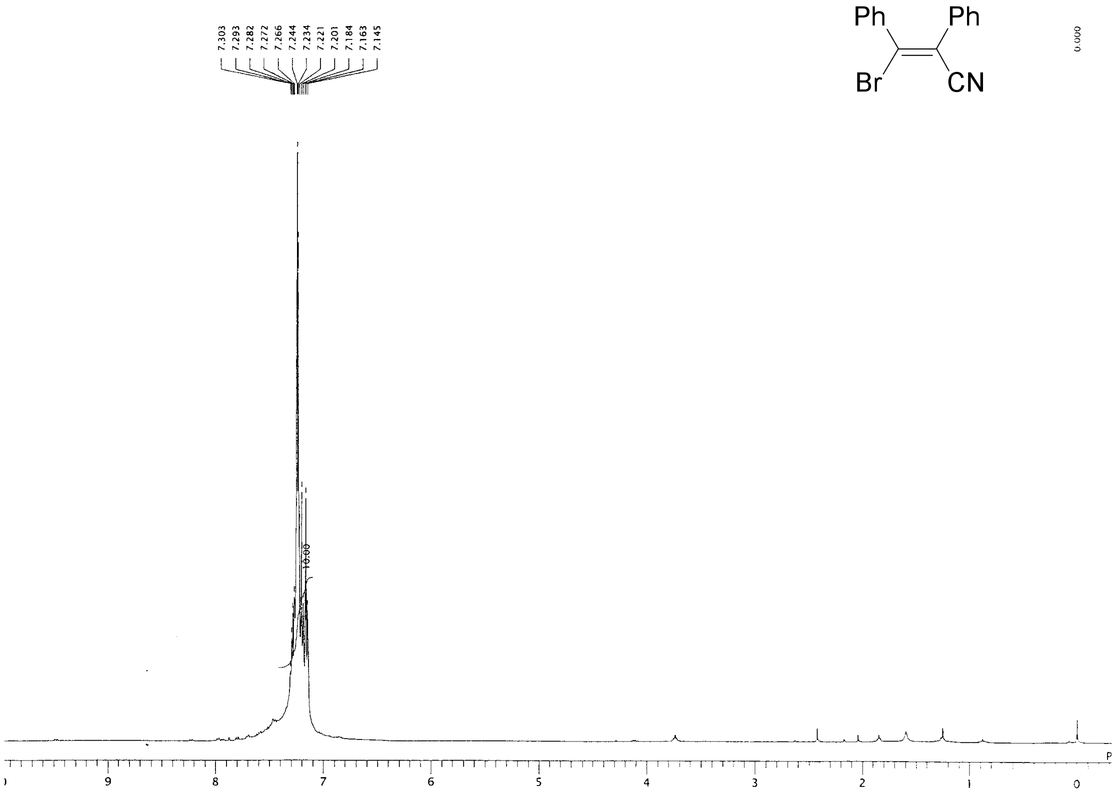
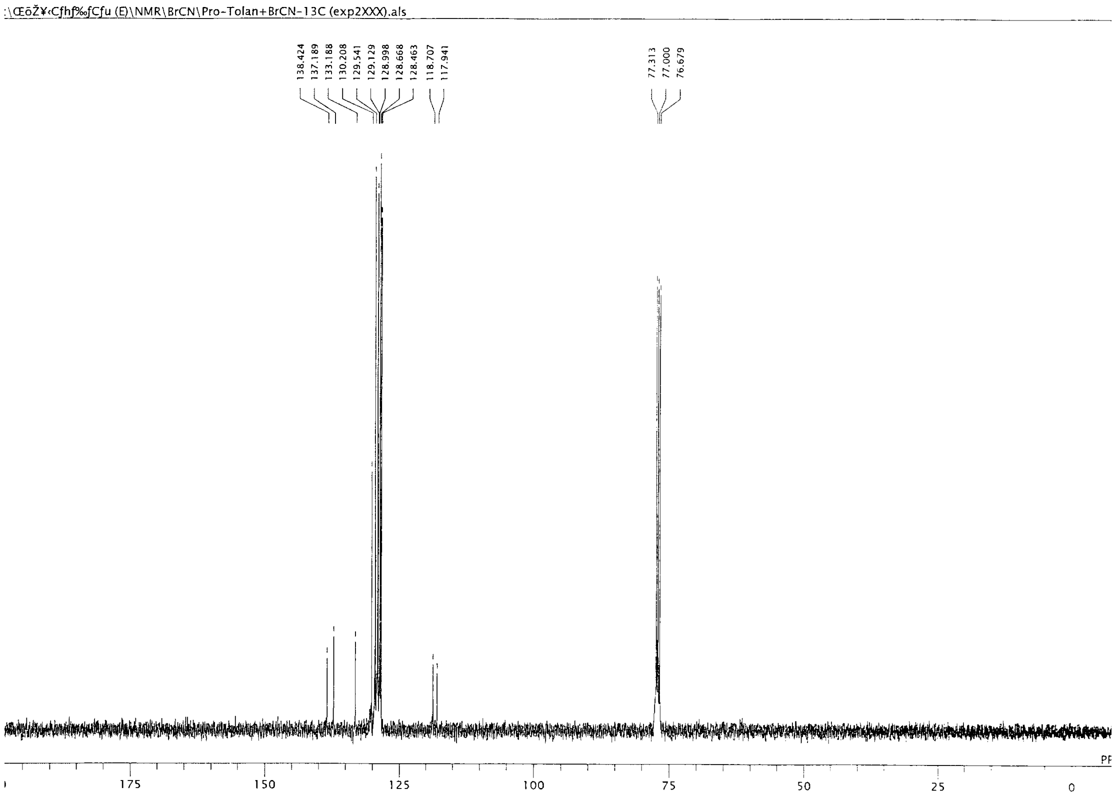
7.40141
7.33796
7.33064
7.31844
7.25499
2.00958
1.94491
0.00000

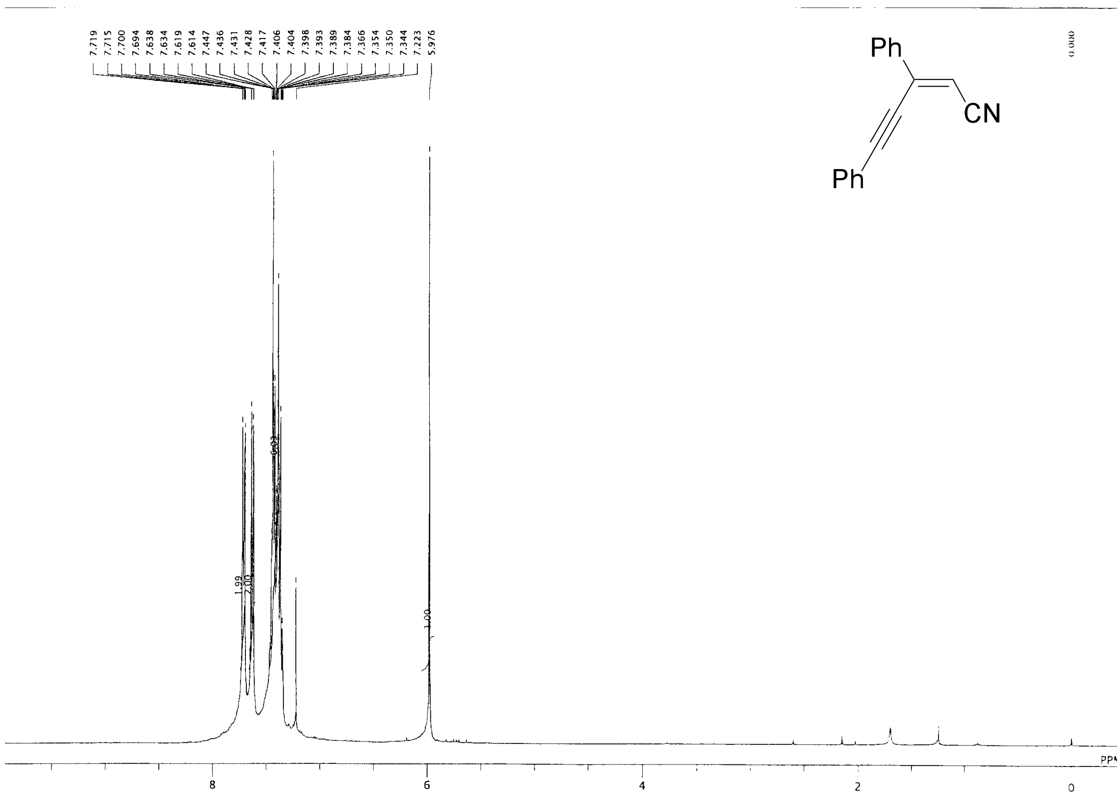

xp2230 Fra6-9
\ŒõŽ¥‹Cƒhƒ‰ƒCƒu (E)\NMR\BrCN\Pro-1-Phenyl-1-propyne-13C (exp2230).als
136.745
135.856
130.043
128.537
128.446
118.946
112.573
77.321
77.000
76.679
19.404
175
150
125
100
75
50
25
0
PPM

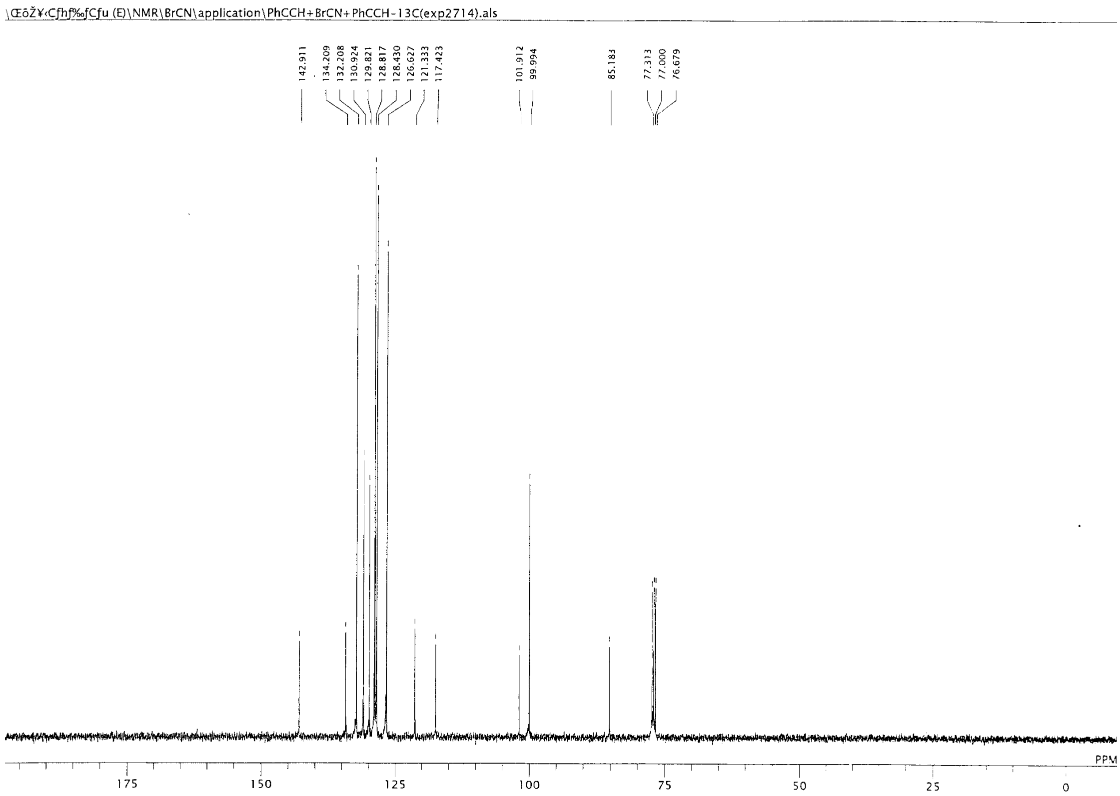

7.970
7.953
7.551
7.533
7.476
7.458
7.418
7.412
7.405
7.401
7.311
7.304
7.299
7.292
7.287
7.261
2.981
2.963
2.944
2.239
2.221
2.201
1.783
1.763
1.745
1.727
1.708
1.611
1.592
1.572
1.553
1.534
1.391
1.381
1.373
1.363
1.353
1.345
1.310
1.292
1.274
1.256
1.236
1.219
0.931
0.914
0.896
0.853
0.83
Ph
n-Bu
Br
CN
8
6
4
2
0

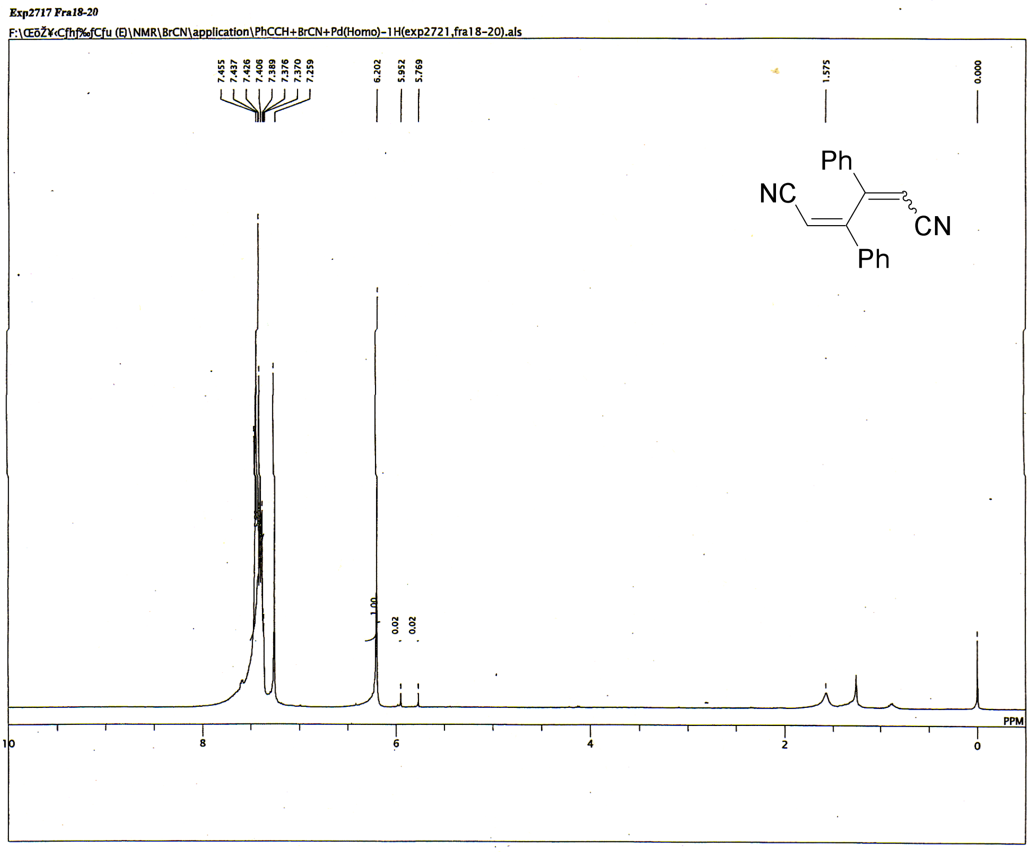

ŒõŽ¥‹Cƒhƒ‰ƒCƒu (E)\NMR\BrCN\Pro-PhCCBu-13C(hatano).als
137.165
137.074
135.551
133.616
132.809
129.953
128.594
128.504
128.240
128.010
118.773
118.238
77.321
77.000
76.687
38.553
32.412
31.514
30.296
24.039
22.500
21.775
13.929
13.534
200
175
150
125
100
75
50
25
0

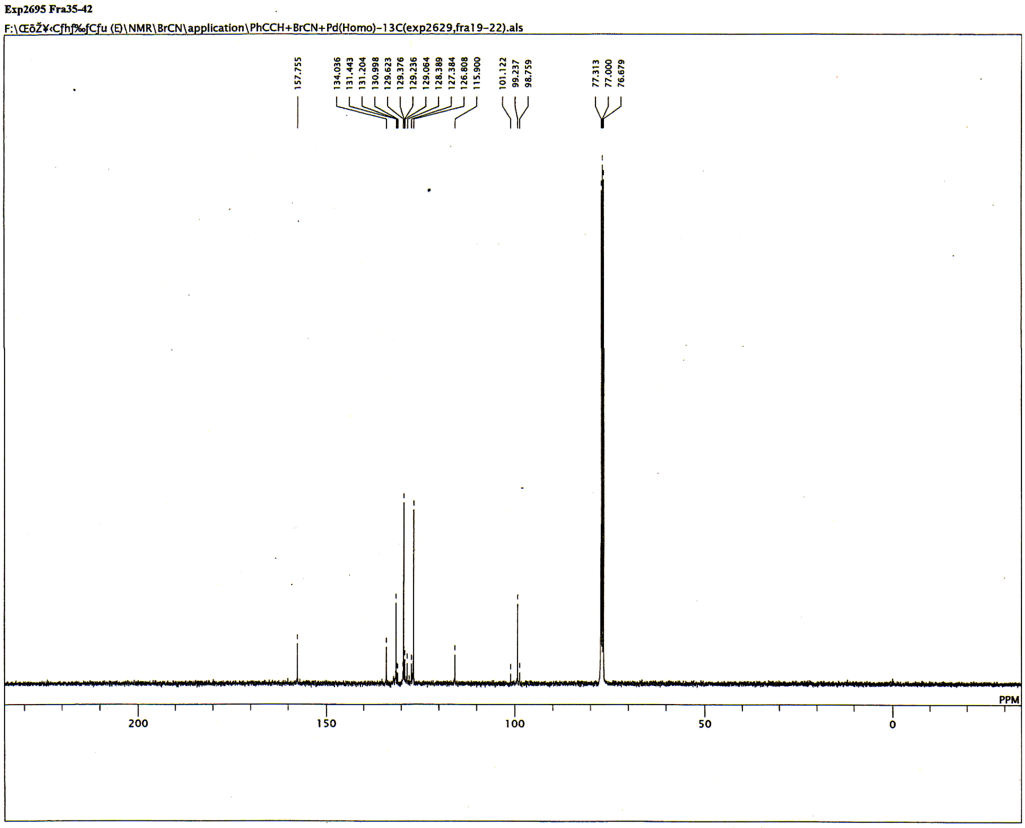

7.303
7.293
7.282
7.272
7.266
7.244
7.234
7.221
7.201
7.184
7.163
7.145
0.000
10.00
Ph
Ph
Br
CN
9
8
7
6
5
4
3
2
1
0

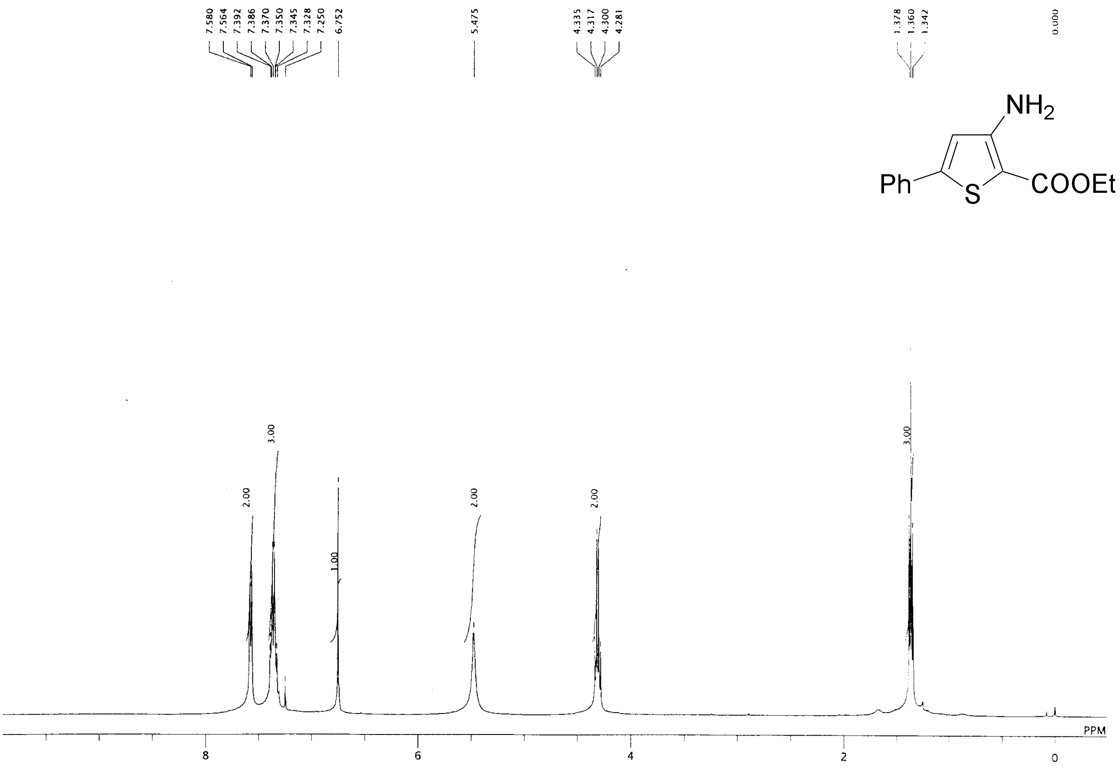

:\ŒõŽ¥‹Cfhƒ‰ƒCfu (E)\NMR\BrCN\Pro-Tolan+BrCN-13C (exp2XXX).als
138.424
137.189
133.188
130.208
129.541
129.129
128.998
128.668
128.463
118.707
117.941
77.313
77.000
76.679
175
150
125
100
75
50
25
0


7.719
7.715
7.700
7.694
7.638
7.634
7.619
7.614
7.447
7.436
7.431
7.428
7.417
7.406
7.404
7.398
7.393
7.389
7.384
7.366
7.354
7.350
7.344
7.223
5.976
0.000
Ph
CN
Ph
1.99
2.00
6.02
1.00
PPM
8
6
4
2
0


\ŒõŽ¥‹Cƒhƒ‰ƒCƒu (E)\NMR\BrCN\application\PhCCH+BrCN+PhCCH-13C(exp2714).als
142.911
134.209
132.208
130.924
129.821
128.817
128.430
126.627
121.333
117.423
101.912
99.994
85.183
77.313
77.000
76.679
PPM
175
150
125
100
75
50
25
0


Exp2717 Fra18-20
F:\ŒõŽ¥‹Cƒhƒ‰ƒCƒu (E)\NMR\BrCN\application\PhCCH+BrCN+Pd(Homo)-1H(exp2721,fra18-20).als
7.455
7.437
7.426
7.406
7.389
7.376
7.370
7.259
6.202
5.952
5.769
1.575
0.000
Ph
NC
CN
Ph
1.00
0.02
0.02
PPM
10
8
6
4
2
0


Exp2695 Fra35-42
F:\ŒõŽ¥‹Cƒhƒ‰ƒCƒu (E)\NMR\BrCN\application\PhCCH+BrCN+Pd(Homo)-13C(exp2629,fra19-22).als
157.755
134.036
131.443
131.204
130.998
129.623
129.376
129.236
129.064
128.389
127.384
126.808
115.900
101.122
99.237
98.759
77.313
77.000
76.679
PPM
200
150
100
50
0


7.580
7.564
7.392
7.386
7.370
7.350
7.345
7.328
7.250
6.752
5.475
4.335
4.317
4.300
4.281
1.378
1.360
1.342
0.000
NH2
Ph
S
COOEt
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3.00
1.00
2.00
2.00
3.00
PPM
8
6
4
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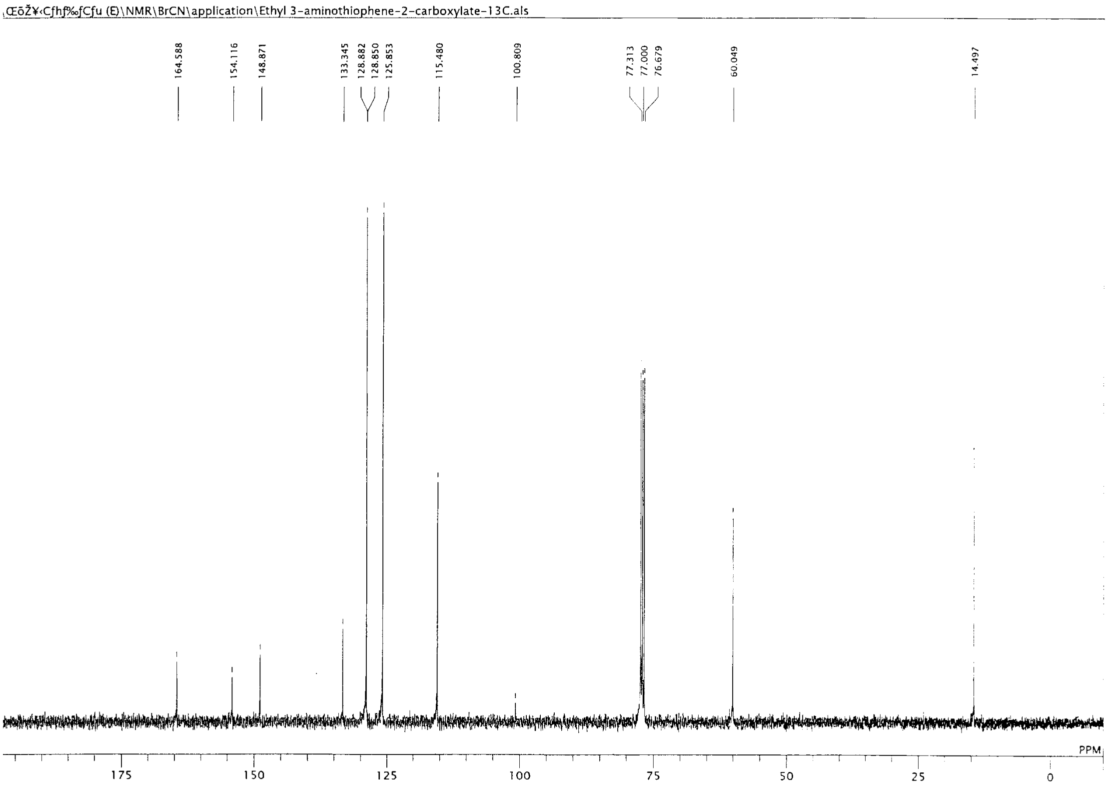
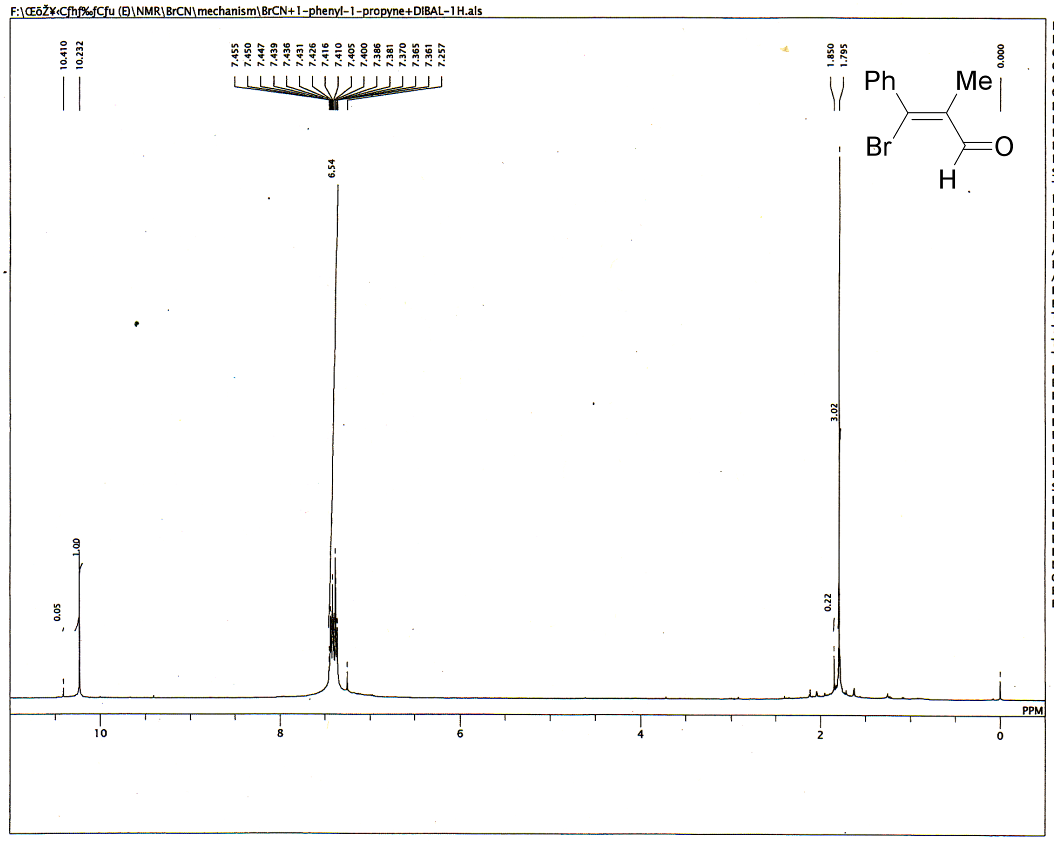
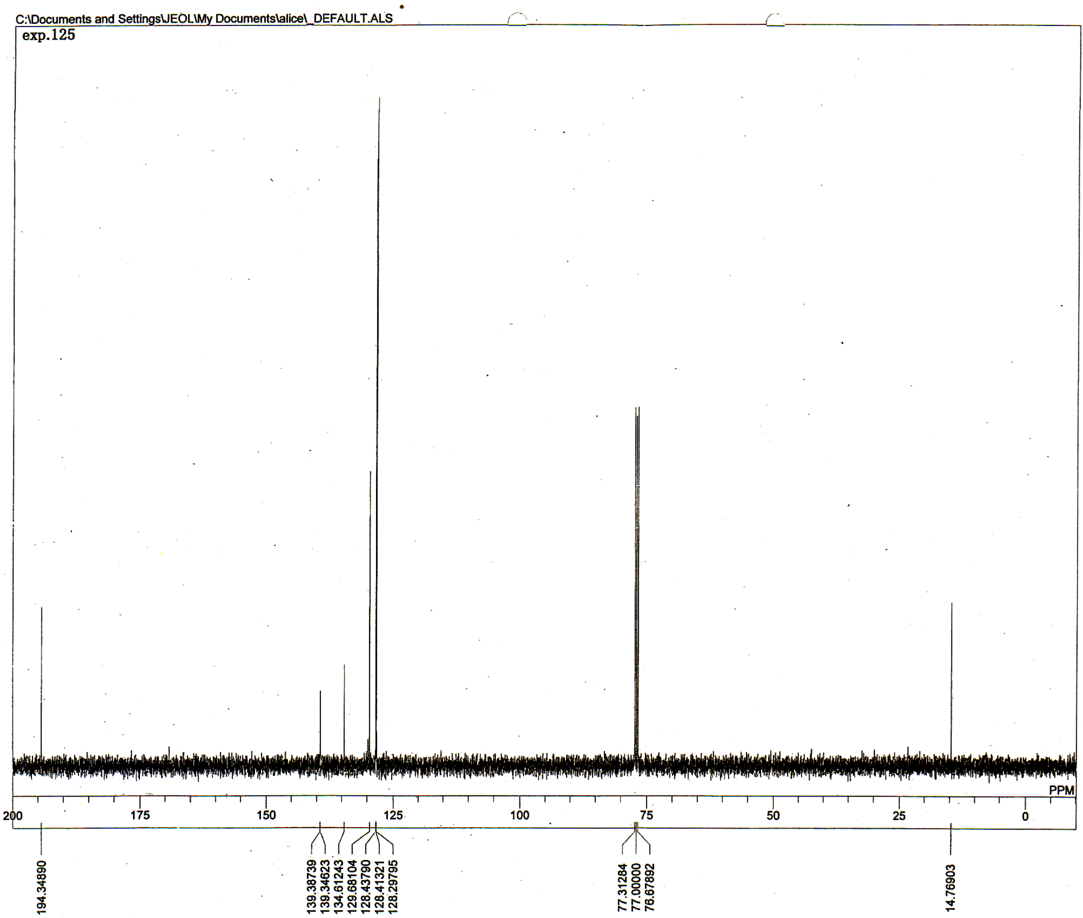

\ŒõŽ¥‹Cƒhƒ‰ƒCƒu (E)\NMR\BrCN\application\Ethyl 3-aminothiophene-2-carboxylate-13C.als
164.588
154.116
148.871
133.345
128.882
128.850
125.853
115.480
100.809
77.313
77.000
76.679
60.049
14.497
PPM
175
150
125
100
75
50
25
0


F:\ŒõŽ¥‹Cƒhƒ‰ƒCƒu (E)\NMR\BrCN\mechanism\BrCN+1-phenyl-1-propyne+DIBAL-1H.als
10.410
10.232
7.455
7.450
7.447
7.439
7.436
7.431
7.426
7.416
7.410
7.405
7.400
7.386
7.381
7.370
7.365
7.361
7.257
1.850
1.795
0.000
Ph
Me
Br
O
H
6.54
3.02
1.00
0.05
0.22
PPM
10
8
6
4
2
0


C:\Documents and Settings\JEOL\My Documents\alice_DEFAULT.ALS
exp.125
PPM
200
175
150
125
100
75
50
25
0
194.34890
139.38739
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128.29795
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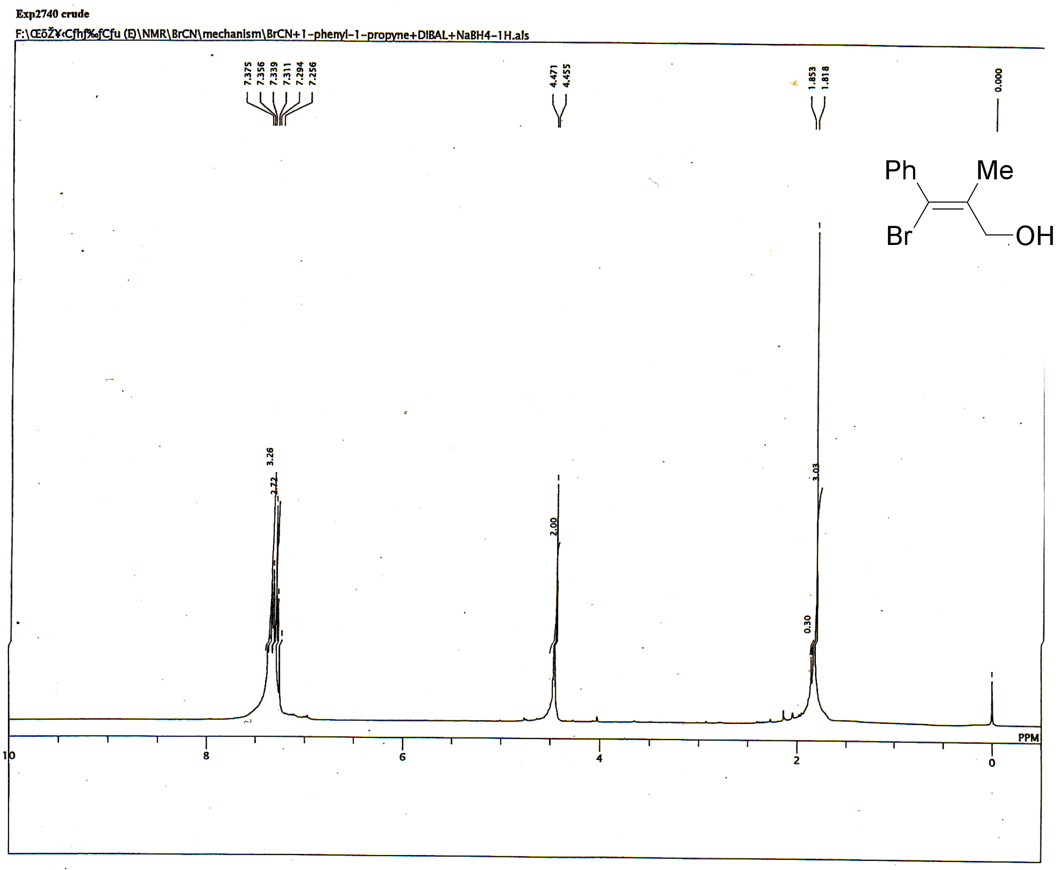
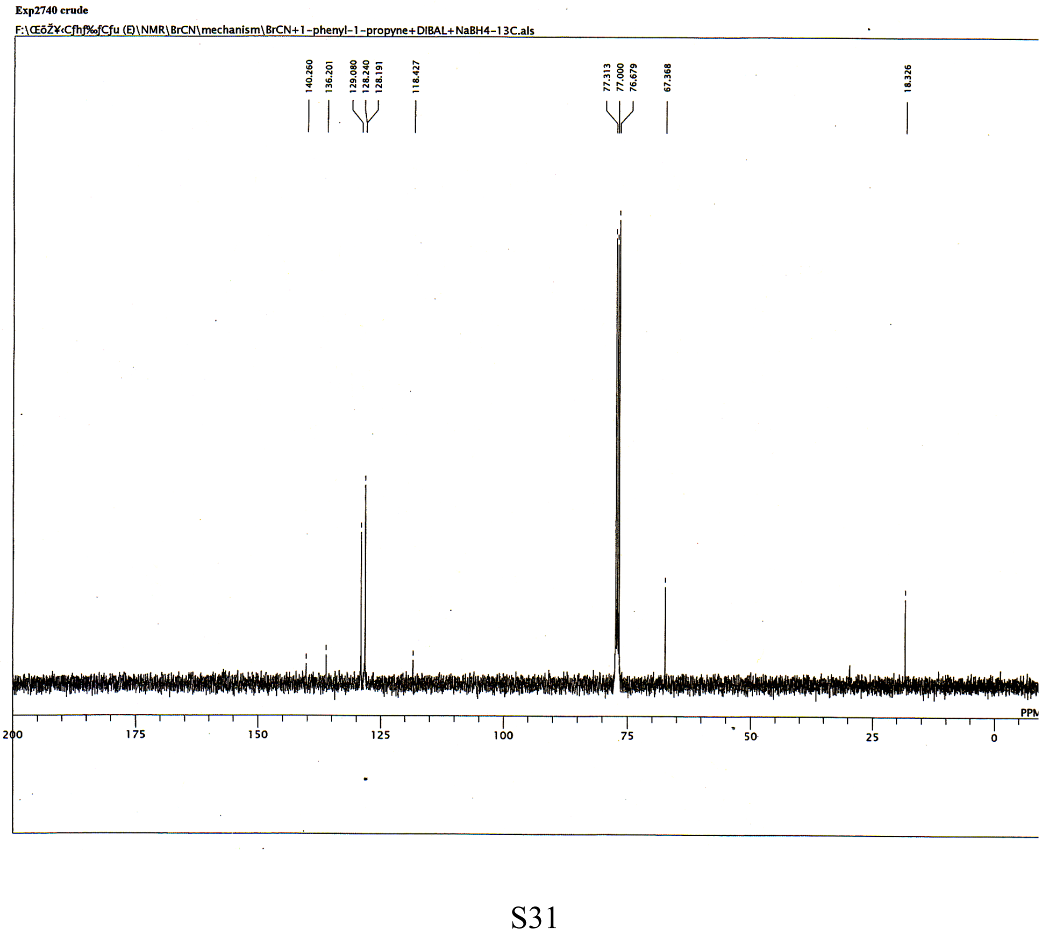
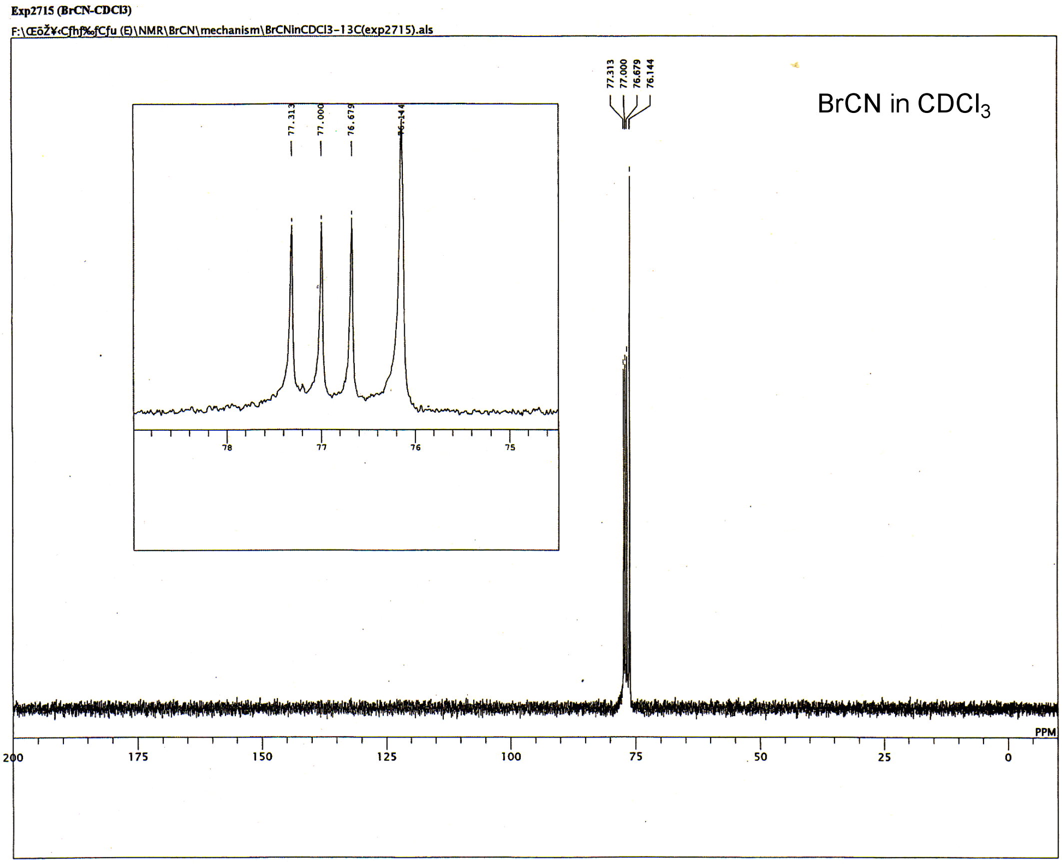
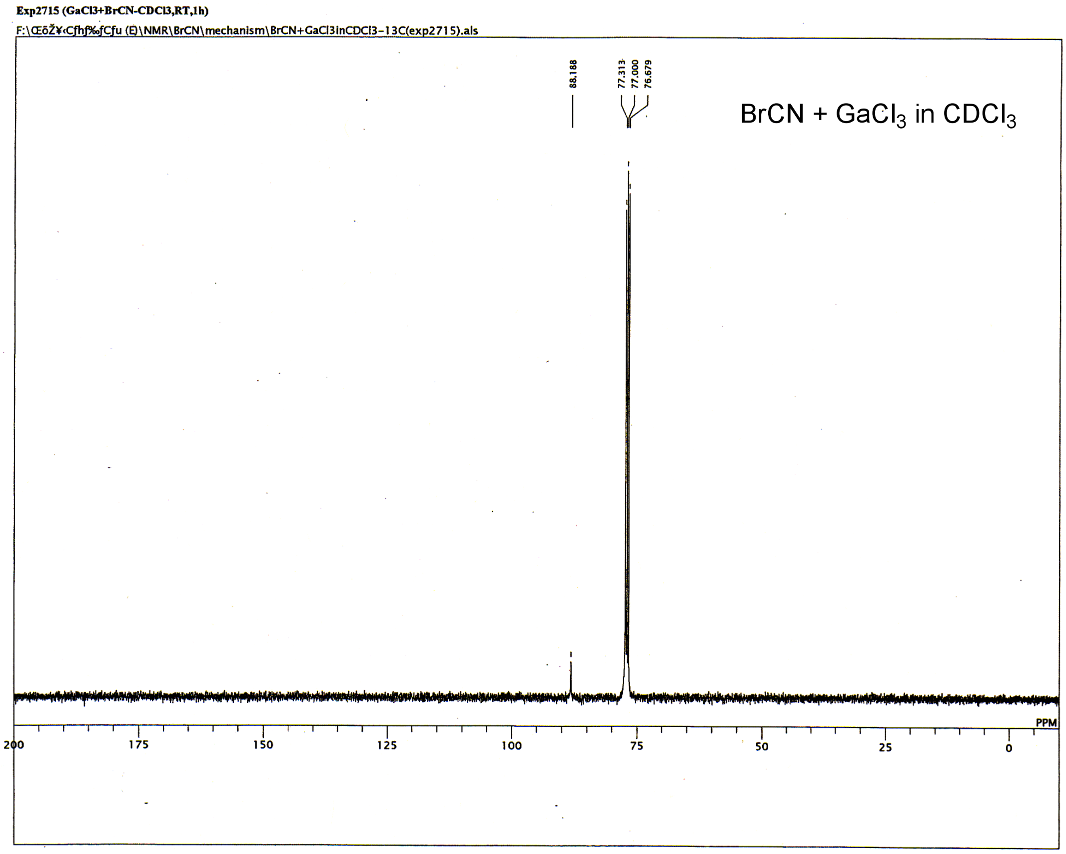

Exp2740 crude
F:\ŒõŽ¥‹Cfhf‰fCfu (E)\NMR\BrCN\mechanism\BrCN+1-phenyl-1-propyne+DIBAL+NaBH4-1H.als
7.375
7.356
7.339
7.311
7.294
7.256
4.471
4.455
1.853
1.818
0.000
Ph
Me
Br
OH
3.26
2.72
2.00
3.03
0.30
10
8
6
4
2
0
PPM


Exp2740 crude
F:\ŒõŽ¥‹Cfhf‰fCfu (E)\NMR\BrCN\mechanism\BrCN+1-phenyl-1-propyne+DIBAL+NaBH4-13C.als
140.260
136.201
129.080
128.240
128.191
118.427
77.313
77.000
76.679
67.368
18.326
200
175
150
125
100
75
50
25
0
PPM


Exp2715 (BrCN-CDCl3)
F:\ŒöŽ¥‹Cƒhƒ‰ƒCƒu (E)\NMR\BrCN\mechanism\BrCNinCDCl3-13C(exp2715).als
BrCN in $CDCl_3$
77.313
77.000
76.679
76.144
78
77
76
75
PPM
200
175
150
125
100
75
50
25
0


Exp2715 (GaCl3+BrCN-CDCl3,RT,1h)
F:\ŒöŽ¥‹Cƒhƒ‰ƒCƒu (E)\NMR\BrCN\mechanism\BrCN+GaCl3inCDCl3-13C(exp2715).als
BrCN + $GaCl_3$ in $CDCl_3$
88.188
77.313
77.000
76.679
PPM
200
175
150
125
100
75
50
25
0