Contents

1 General information

1.1 Synthesis and techniques

When necessary preparations were carried out in oven dried glassware under an atmosphere of inert gas (Argon 5.0, AIR LIQUIDE) employing both SCHLENK line techniques and a GLOVEBOX SYSTEMS inert atmosphere glovebox. For NMR scale experiments Teflon cap sealed J YOUNG NMR tubes were used. Table run experiments where performed in 10 ml headspace vials with PTFE/ butyl rubber crimp caps. Deuterated solvents were vacuum transferred from sodium/benzophenone (benzene-d6, toluene-d8) or CaH_2 ($CDCl_3$, CD_2Cl_2), degassed by 2 freeze-pump-thaw cycles and stored over 3 Å molecular sieves. Toluene, hexane, pentane, THF and Et_2O were distilled from sodium/ benzophenone, dispensed into STRAUS flasks equipped with YOUNG-type Teflon valve stop-cocks and stored over 3 Å molecular sieves. Methanol was purified with a MBRAUN solvent purification system and stored in STRAUS flasks over 3 Å molecular sieves. Molecular sieves were activated at 280 °C under vacuum and stored under inert atmosphere.

1.2 Reagents and materials

All commercially available reagents were purchased from SIGMA ALDRICH, ABCR or TCI CHEMICALS and were used as received without further purification unless stated otherwise. Tris(pentafluorophenyl)borane (**2a**) was purchased from BOULDER SCIENTIFIC COMPANY and used as received. $B(C_6F_2H_3)_3$ (**2c**), $B(C_6F_3H_2)_3$ (**2b**) were prepared as described earlier.[1] Hydrogen 6.0 (AIRLIQUIDE) was purified through a JOHNSON MATTHEY Model HIG 35XL gas purifier.

1.3 Characterization

^1H, ^{13}C, ^{19}F and ^{11}B NMR spectra were recorded on a Bruker AV 300 (300 MHz) or a Bruker AV 500 (500 MHz) spectrometer as solutions in spinning mode. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to the residual solvent signal of C_6D_6 (7.16 ppm for ^1H NMR, 128.06 for ^{13}C NMR), C_7D_8 (2.08 ppm for ^1H NMR, 20.43 ppm for ^{13}C NMR), $CDCl_3$ (7.26 ppm for ^1H NMR, 77.16 ppm for ^{13}C NMR) or CD_2Cl_2 (5.32 ppm for ^1H NMR, 53.84 ppm for ^{13}C NMR). ^{11}B NMR and ^{19}F NMR spectra are referenced to $BF_3{\cdot}OEt_2$ and $CFCl_3$, respectively. All coupling constants (*J*) are absolute values and are expressed in Hertz (Hz). The spectra were analyzed according to first order and the descriptions of the signals include: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, etc. Exact assignments of signals were done under

consideration of $^{1}H,^{1}H$-COSY-, $^{1}H,^{1}H$-NOESY-, $^{1}H,^{13}C$-HSQC-, $^{1}H,^{13}C$-HMBC-, DEPT135- and DEPTQ-spectra. The following abbreviations were used: CH_3 = primary (RCH_3), CH_2 = secondary (R_2CH_2), CH = tertiary (R_3CH), C = quaternary (R_4C), H_{Ar} = aromatic hydrogen, H_{Alk} = alkyl hydrogen.

2 Hydroamination reactions

2.1 General procedure for table run experiments

In a glovebox, the amino alkyne (**1a-k**, 0.5 mmol, 1.00 eq.) and $B(C_6F_5)_3$ (**2a**, 12.8 mg, 0.025 mmol, 0.05 eq.) were dissolved in toluene (2.0 ml). The solution was transferred to a headspace vial with PTFE/ butyl rubber crimp cap and magnetic stirring bar and the sample was heated for given time/ temperature. After cooling to room temperature, a minimum amount of silica was added and the solvent was evaporated to dryness. The powder was subjected to column chromatography.

2.2 General procedure for NMR scale experiments

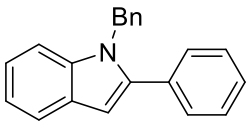
In a glovebox, the amino alkyne (**1a-k**, 0.100 mmol, 1.00 eq.), $B(C_6F_5)_3$ (**2a**, 2.6 mg, 0.005 mmol, 0.05 eq.) and hexamethyl benzene (1.6 mg, 0.010 mmol, 0.1 eq.) were dissolved in deuterated benzene (0.5 ml), transferred to a NMR tube with YOUNG type Teflon tap, heated and analyzed by NMR spectroscopy.

2.3 Hydroamination to indoles

All NMR scale and table run experiments were performed at 70 °C for 4 h unless stated otherwise.

2.3.1 *N*-benzyl-2-phenyl indole (3a)

Cyclohexane, pale white solid, 72%, single crystal for X-ray analysis was grown by condensation of methanol to a saturated solution of **3a** in diethyl ether.

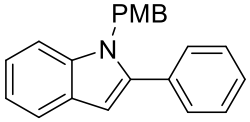


^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.76 – 7.72 (m, 1H, H_{Ar}), 7.41 – 7.35 (m, 2H, H_{Ar}), 7.24 – 7.19 (m, 1H, H_{Ar}), 7.17 – 7.12 (m, 1H, H_{Ar}), 7.08 – 7.02 (m, 4H, H_{Ar}), 6.99 – 6.92 (m, 3H, H_{Ar}), 6.84 – 6.77 (m, 2H, H_{Ar}), 6.71 (d, $^{4}J_{HH}$ = 0.7 Hz, 1H, H_{Olefin}), 4.97 (s, 2H, NC*H*$_2$); **^{13}C-NMR** (126 MHz, C_6D_6, 303 K) δ = 141.96 (C), 138.83 (C), 138.74 (C), 133.43 (C), 129.50 (CH), 129.18 (C), 128.96 (CH), 128.78 (CH),

128.12 (CH), 127.28 (CH), 126.16 (CH), 122.48 (CH), 121.20 (CH), 120.74 (CH), 110.98 (CH), 103.09 (CH), 47.77 (CH_2).

2.3.2 *N-para*-methoxybenzyl-2-phenyl indole (3b)

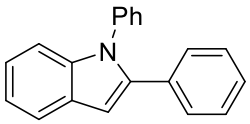
Cyclohexane/ ethyl acetate 50:1, white solid, 63%, single crystal for X-ray analysis was grown by condensation of cyclohexane to a saturated solution of **3b** in dichloromethane.



^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.79 – 7.72 (m, 1H, H_{Ar}), 7.46 – 7.41 (m, 2H, H_{Ar}), 7.25 – 7.17 (m, 2H, H_{Ar}), 7.15 – 7.12 (m, 1H, H_{Ar}), 7.12 – 7.04 (m, 3H, H_{Ar}), 6.75 – 6.72 (m, 2H, H_{Ar}), 6.72 (d, $^{4}J_{HH}$ = 0.7 Hz, 1H, H_{Olefin}), 6.61 – 6.55 (m, 2H, H_{Ar}), 4.98 (s, 2H, NCH_2), 3.21 (s, 3H, OCH_3); **^{13}C-NMR** (126 MHz, C_6D_6, 303 K) δ = 159.30 (C), 141.93 (C), 138.8 3(C), 133.56 (C), 130.55 (C), 129.53 (CH), 129.21 (C), 128.78 (CH), 128.12 (CH), 127.36 (CH), 122.41 (CH), 121.20 (CH), 120.69 (CH), 114.49 (CH), 111.1 (CH), 103.07 (CH), 54.70 (CH_3), 47.28 (CH_2).

2.3.3 *N*-phenyl-2-phenyl indole (3c)

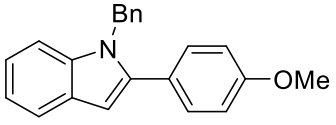
Cyclohexane/ ethyl acetate 50:1, pale yellow oil, 84%



^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.76 – 7.70 (m, 1H, H_{Ar}), 7.30 – 7.26 (m, 3H, H_{Ar}), 7.24 (m, 1H, H_{Ar}), 7.20 – 7.16 (m, 1H, H_{Ar}), 7.03 – 6.98 (m, 2H, H_{Ar}), 6.98 – 6.88 (m, 6H, H_{Ar}), 6.82 (d, $^{4}J_{HH}$ = 0.5 Hz, 1H, H_{Olefin}); **^{13}C-NMR** (126 MHz, C_6D_6, 303 K) δ = 140.90 (C), 139.88 (C), 139.10 (C), 133.29 (C), 129.36 (CH), 129.27 (CH), 129.17 (C), 128.47 (CH), 128.39 (CH), 127.47 (CH), 127.16 (CH), 122.89 (CH), 121.26 (CH), 121.16 (CH), 111.09 (CH), 104.51 (CH).

2.3.4 *N*-benzyl-2-*para*-methoxyphenyl indole (3i)

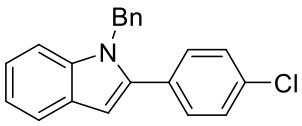
Cyclohexane/ ethyl acetate 50:1, clear oil, 92%



^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.78 – 7.75 (m, 1H, H_{Ar}), 7.33 – 7.29 (m, 2H, H_{Ar}), 7.25 – 7.21 (m, 1H, H_{Ar}), 7.18 – 7.13 (m, 1H, H_{Ar}), 7.10 – 7.05 (m, 1H, H_{Ar}), 7.01 – 6.93 (m, 3H, H_{Ar}), 6.86 – 6.81 (m, 2H, H_{Ar}), 6.71 (d, $^{4}J_{HH}$ = 0.8 Hz, 1H, H_{Olefin}), 6.67 – 6.63 (m, 2H, H_{Ar}), 5.01 (s, 2H, H_{Ar}), 3.25 (s, 3H, CH_3); **^{13}C-NMR** (126 MHz, C_6D_6, 303 K) δ = 160.11 (C), 141.92 (C), 138.94 (C), 138.65 (C), 130.77 (CH), 129.27 (C), 128.97 (C), 127.26 (CH), 126.17 (CH), 125.70 (CH), 122.21 (CH), 121.01 (CH), 120.68 (CH), 114.39 (CH), 110.87 (CH), 102.47 (CH), 54.83 (CH_3), 47.68 (CH_2).

2.3.5 *N*-benzyl-2-*para*-chlorophenyl indole (3j)

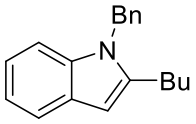
Cyclohexane/ dichloromethane 20:1, clear oil, 71%



^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.76 – 7.69 (m, 1H, H_{Ar}), 7.24 – 7.19 (m, 1H, H_{Ar}), 7.18 – 7.12 (m, 1H, H_{Ar}), 7.08 – 7.02 (m, 3H, H_{Ar}), 6.98 – 6.93 (m, 5H, H_{Ar}), 6.78 – 6.72 (m, 2H, H_{Ar}), 6.59 (d, $^{4}J_{HH}$ = 0.7 Hz, 1H, H_{Olefin}), 4.87 (s, 2H, C*H*$_2$); **^{13}C-NMR** (126 MHz, C_6D_6, 303 K) δ = 140.52 (C), 138.91 (C), 138.50 (C), 134.29 (C), 131.66 (C), 130.60 (CH), 129.02 (CH), 128.99 (C), 128.35 (CH), 127.41 (CH), 126.06 (CH), 122.76 (CH), 121.25 (CH), 120.90 (CH), 110.94 (CH), 103.39 (CH), 47.69 (CH_2).

2.3.6 *N*-benzyl-2-butylindole (3k)

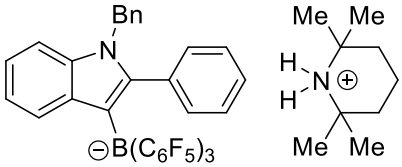
Cyclohexane/ dichloromethane 20:1, clear oil, 4 d, 54%



^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.75 – 7.71 (m, 1H, H_{Ar}), 7.24 – 7.19 (m, 1H, H_{Ar}), 7.18 – 7.14 (m, 1H, H_{Ar}), 7.08 – 7.05 (m, 1H, H_{Ar}), 6.97 – 6.91 (m, 3H, H_{Ar}), 6.75 – 6.71 (m, 2H, H_{Ar}), 6.40 – 6.37 (m, 1H, C*H*), 4.83 (s, 2H, NC*H*$_2$), 2.43 – 2.37 (m, 2H, C*H*$_2$), 1.53 – 1.44 (m, 2H, C*H*$_2$), 1.23 – 1.14 (m, 2H, C*H*$_2$), 0.78 (t, *J* = 7.4 Hz, 3H, C*H*$_3$). **^{13}C-NMR** (126 MHz, C_6D_6, 303 K) δ = 141.07 (C), 138.57 (C), 137.96 (C), 129.05 (C), 128.91 (CH), 128.35 (CH), 127.33 (CH), 126.13 (CH), 121.38 (CH), 120.48 (CH), 120.12 (CH), 109.70 (CH), 100.20 (CH), 46.34 (CH_2), 30.81 (CH_2), 26.63 (CH_2), 22.68 (CH_2), 14.03 (CH_3).

2.4 Isolation of [3a-B(C_6F_5)$_3$][HTMP] (5)

In a glovebox, the amino alkyne (**1a**, 14.2 mg, 0.050 mmol, 1.00 eq), B(C_6F_5)$_3$ (**2a**, 25.6 mg, 0.050 mmol, 1.00 eq) and 2,2,6,6-tetramethylpiperidine (7.1 mg, 0.050 mmol, 1.00 eq) were dissolved in CD_2Cl_2 (0.5 ml), transferred to a NMR tube with YOUNG type teflon tap, heated to 70 °C for 2 h and objected to NMR spectroscopy. Suitable crystals for X-ray single crystal structure analysis were grown by condensation of pentanes into the dichloromethane solution.

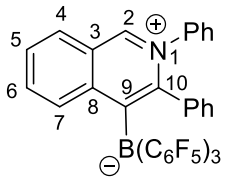


^{1}H-NMR (500 MHz, CD_2Cl_2, 303 K) δ = 7.53 – 7.49 (m, 1H, H_{Ar}), 7.25 (s, 2H, H_{Ar}), 7.17 – 7.07 (m, 6H, H_{Ar}), 7.01 – 6.96 (m, 1H, H_{Ar}), 6.91 – 6.86 (m, 2H, H_{Ar}), 6.74 – 6.70 (m, 2H, H_{Ar}), 5.02 (d, $^{2}J_{HH}$ = 16.8 Hz, 1H, C*H*$_2$), 4.95 (d, $^{2}J_{HH}$ = 16.8 Hz, 1H, C*H*$_2$), 3.74 (s, 2H, N*H*$_2$, TMP), 1.74 – 1.65 (m, 2H, C*H*$_2$, TMP), 1.59 – 1.51 (m, 4H, C*H*$_2$,

TMP), 1.21 (s, 12H, CH_3, TMP); **^{13}C-NMR** (126 MHz, CD_2Cl_2, 303 K) δ = 147.99 (dm, *J* = 240 Hz, CF), 142.28 (C), 139.43 (C), 138.27 (dm, *J* = 242 Hz, CF), 137.86 (C), 136.74 (dm, *J* = 240 Hz, CF), 136.11 (C), 135.32 (C), 131.78 (CH), 131.40 (CH), 131.29 (CH), 128.69 (CH), 127.23 (CH), 127.18 (CH), 127.10 (CH), 126.74 (CH), 126.41 (CH), 123.06 (CH), 119.43 (CH), 118.38 (CH), 110.14 (CH), 60.37 (C, TMP), 47.25 (CH_2, benzyl), 35.84 (CH_2, TMP), 28.32 (CH_3), 16.05 (CH_2, TMP), B-C signal was not observed; **^{11}B-NMR** (160 MHz, CD_2Cl_2, 303 K) δ = −15.56 (s); **^{19}F-NMR** (282 MHz, CD_2Cl_2) δ = -124.63 – -125.13 (m, 1F, F_{ortho}), -127.05 – -127.47 (m, 1F, F_{ortho}), -129.36 – -129.68 (m, 1F, F_{ortho}), -133.17 – -133.76 (m, 2F, F_{ortho}), -135.82 – -136.30 (m, 1F, F_{ortho}), -163.24 – -163.53 (m, 1F, F_{para}), -163.90 – -164.20 (m, 1F, F_{para}), -164.60 – -164.92 (m, 1F, F_{para}), -166.12 – -166.43 (m, 1F, F_{meta}), -166.68 – -167.03 (m, 1F, F_{meta}), -167.37 – -167.95 (m, 3F, F_{meta}), -168.04 – -168.40 (m, 1F, F_{meta}).

2.5 Synthesis of [6b-B(C_6F_5)$_3$] (7)

In a glovebox a screw cap vial equipped with magnetic stirring bar was charged with the amino alkyne (**6b**, 28.3 mg, 0.100 mmol, 1.00 eq.), B(C_6F_5)$_3$ (**2a**, 51.2 mg, 0.100 mmol, 1.00 eq.) and toluene (1.5 ml) and the resulting solution was heated to 90 °C for 2 h. Upon cooling to room temperature the zwitterionic product precipitated as fine white needles and was isolated by filtration (74.8 mg, 0.094 mmol, 94%). Suitable crystals for X-ray single crystal structure analysis were grown by condensation of pentanes into a saturated solution of the zwitterionic product in dichloromethane/ toluene (1:2).

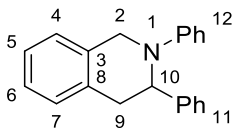


^{1}H-NMR (500 MHz, CD_2Cl_2, 303K) δ = 9.07 (s, 1H, H-2), 8.73 – 8.67 (m, 1H, H-4), 8.09 – 8.04 (m, 1H, H-7), 7.89 – 7.82 (m, 1H, H-5), 7.81 – 7.74 (m, 1H, H-6), 7.39 – 7.31 (br m, 1H, H_{Ph}), 7.32 – 7.28 (m, 1H, H_{Ph}), 7.31 – 7.24 (br m, 1H, H_{Ph}), 7.24 – 7.12 (m, 2H, H_{Ph}), 7.09 – 7.02 (br m, 1H, H_{Ph}), 7.02 – 6.94 (br m, 2H, H_{Ph}), 6.97 – 6.92 (m, 1H, H_{Ph}), 6.81 – 6.70 (br m, 1H, H_{Ph}); **^{1}H-NMR** (500 MHz, CD_2Cl_2, 283 K) δ = 9.08 (s, 1H), 8.71 – 8.66 (m, 1H, H-4), 8.09 – 8.05 (m, 1H, H-7), 7.88 – 7.83 (m, 1H, H-5), 7.80 – 7.75 (m, 1H, H-6), 7.37 – 7.32 (m, 1H, H_{Ph}), 7.32 – 7.25 (m, 2H, H_{Ph}), 7.23 – 7.18 (m, 2H, H_{Ph}), 7.06 – 7.01 (m, 1H, H_{Ph}), 7.01 – 6.96 (m, 2H, H_{Ph}), 6.96 – 6.91 (m, 1H, H_{Ph}), 6.77 – 6.72 (m, 1H, H_{Ph}); **^{13}C-NMR** (126 MHz, CD_2Cl_2, 303 K) δ = 147.98 (C), 147.04 (CH, C-2), 145.70 (C, C-3), 143.75 (C), 135.39 (CH, C-5), 133.70 (C), 133.19 (CH), 131.52 (CH), 130.50 (CH, C-7), 130.28 (CH), 130.15 (CH, C-4), 130.12 (CH, C-6), 129.56 (CH, C_{Ph}), 129.32 (CH, C_{Ph}), 128.80 (CH, C_{Ph}), 127.48 (CH, C_{Ph}), 126.95 (CH, C_{Ph}), 126.89 (CH, C_{Ph}), 126.02 (CH, C_{Ph}), 125.41

(C, C-8), C-B and C-F signals were not observed; **^{1}H/^{15}N-HMBC** (500/51 MHz, CD_2Cl_2, 303 K) δ = 9.07/212.3; **^{11}B-NMR** (160 MHz, CD_2Cl_2, 303 K) δ = −15.56 (s); **^{19}F-NMR** (282 MHz, CD_2Cl_2) δ = -119.37 – -119.97 (m, 1F, F_{ortho}), -128.16 – -128.68 (m, 2F, F_{ortho}), -128.68 – -129.11 (m, 1F, F_{ortho}), -133.05 – -133.53 (m, 1F, F_{ortho}), -136.33 – -136.75 (m, 1F, F_{ortho}), -160.83 – -161.18 (m, 1F, F_{para}), -161.43 – -161.76 (m, 1F, F_{para}), -161.92 – -162.20 (m, 1F, F_{para}), -164.76 – -165.18 (m, 1F, F_{meta}), -165.77 – -166.09 (m, 1F, F_{meta}), -166.51 – -166.85 (m, 2F, F_{meta}), -167.07 – -167.37 (m, 1F, F_{meta}), -167.37 – -167.73 (m, 1F, F_{meta}).

2.6 Synthesis of 2,3-diphenyl-1,2,3,4-tetrahydro-isoquinoline (8)

In a GC-vial equipped with magnetic stirring bar amine **6b** (44.2 mg, 0.16 mmol, 1.00 eq.) and $B(C_6F_5)_3$ (16.4 mg, 0.032 mmol, 0.20 eq.) were dissolved in toluene (0.7 ml). The sample was pressurized with 80 bar H_2 and heated to 100 °C for 24 h. A small part of the sample was transferred to a NMR tube equipped with YOUNG type Teflon tap, the solvent was exchanged to C_6D_6 and the sample was analyzed by NMR spectroscopy showing quantitative yield. The solvent of the combined fractions was evaporated under reduced pressure and the residue was purified by column chromatography (cyclohexane) to yield the product as brown solid (27 mg, 0.095 mmol, 61 %).



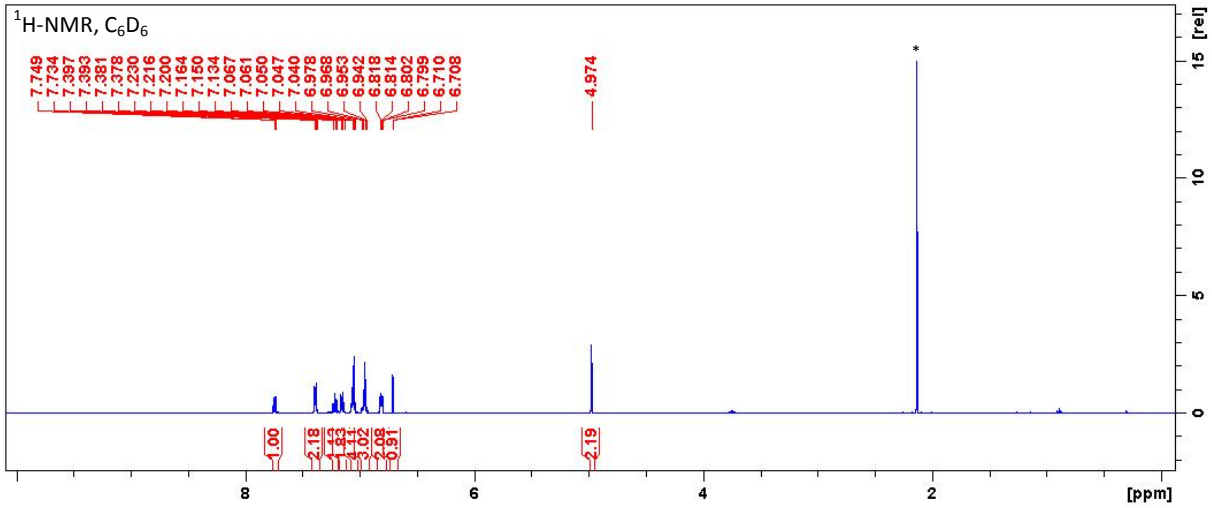
^{1}H-NMR (500 MHz, CD_2Cl_2, 303 K): δ = 7.30 – 7.26 (m, 1H, H-4), 7.24 – 7.21 (m, 2H, H-5 and H_{Ph}), 7.21 – 7.19 (m, 1H, H_{Ph}), 7.19 – 7.15 (m, 2H, H-6 und H_{Ph}), 7.15 – 7.12 (m, 1H, H_{Ph}), 7.12 – 7.09 (m, 2H, H_{Ph}), 7.07-7.03 (m, 1H, H-7), 6.83 – 6.80 (m, 2H, H_{Ph}), 6.75 – 6.70 (m, 1H, H_{Ph}), 5.16 (dd, $^{3}J_{HaHb}$ = 5.6, 3.3 Hz, 1H, H-10), 4.61 (d, $^{2}J_{HaHb}$ = 14.7 Hz, 1H, 1 H-2), 4.56 (d, $^{2}J_{HaHb}$ = 14.7 Hz, 1H, 1 H-2), 3.49 (dd, J_{HaHb} = 15.1, 5.7 Hz, 1H, 1 H-9), 3.16 (dd, J_{HaHb} = 15.2, 3.2 Hz, 1H, 1 H-9).

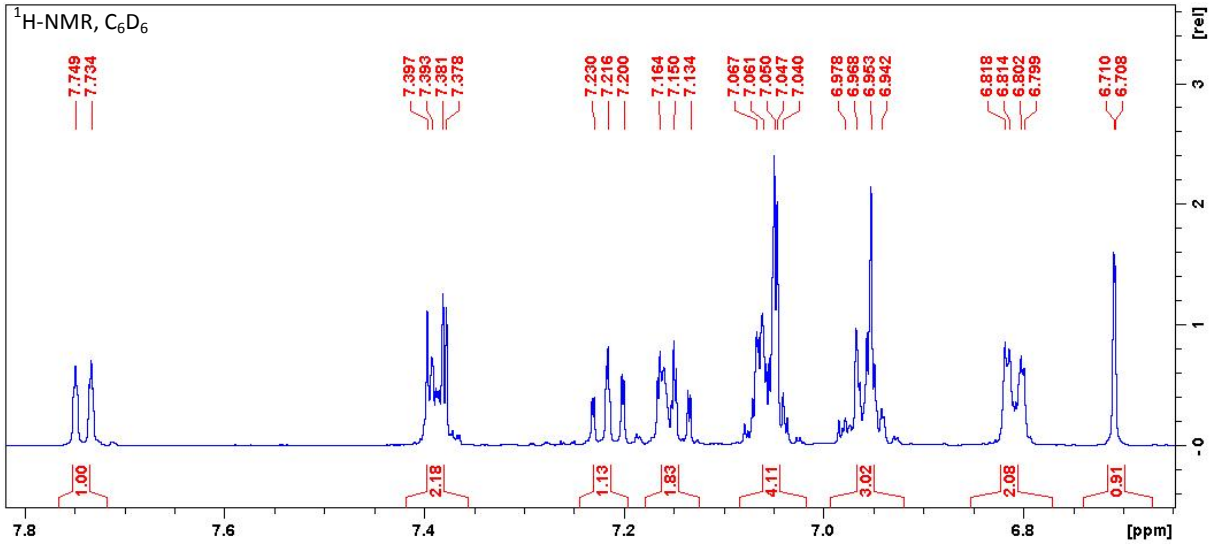
^{13}C-NMR (126 MHz, CD_2Cl_2, 303 K): δ = 149.64 (C-12), 143.97 (C-11), 135.73 (C-3), 134.41 (C-8), 129.49 (2 CH_{Ph}), 128.61 (2 CH_{Ph}), 128.29 (CH-6), 127.29 (CH-7), 127.05 (1 CH_{Ph}), 126.83 (2 CH_{Ph}), 126.78 (CH-5), 126.54 (CH-4), 117.50 (CH_{Ph}), 113.63 (2 CH_{Ph}), 58.60 (CH-10), 48.22 (CH_2-2), 37.32 (CH_2-9).

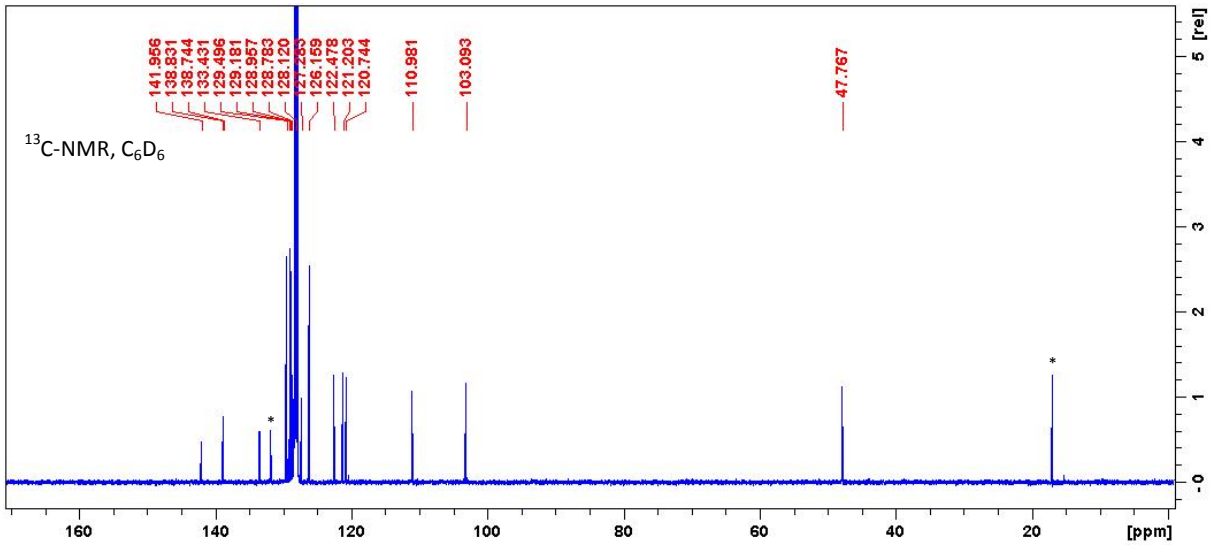
2.7 NMR-spectra of cyclisation products

2.7.1 *N*-benzyl-2-phenyl indole (3a)

* Internal standard: hexamethylbenzene (^{1}H-NMR: 2.13 ppm, ^{13}C-NMR: 16.95 / 131.79 ppm)

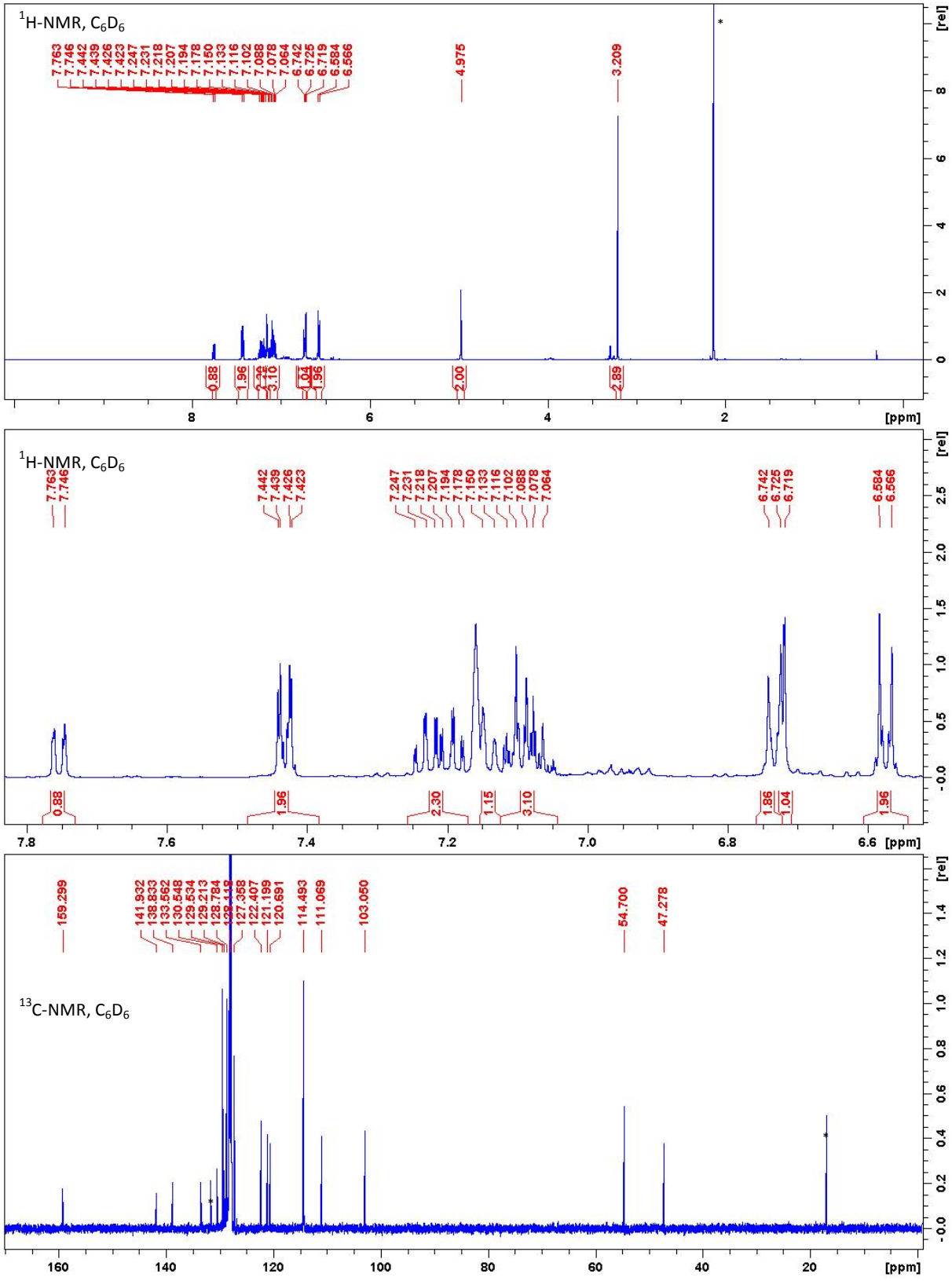




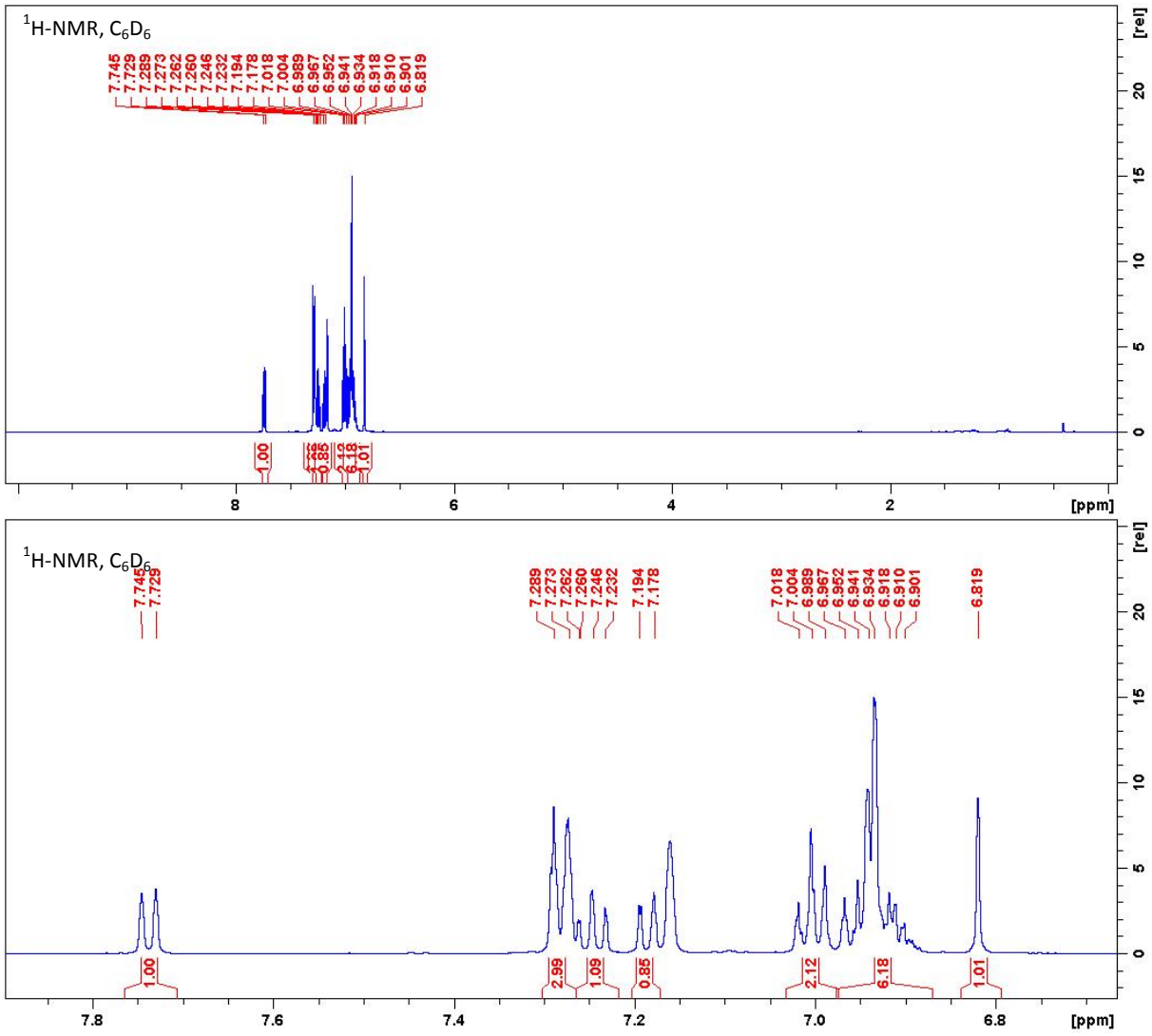


2.7.2 *N-para*-methoxybenzyl-2-phenyl indole (3b)

* Internal standard: hexamethylbenzene (^{1}H-NMR: 2.13 ppm, ^{13}C-NMR: 16.95 / 131.79 ppm)

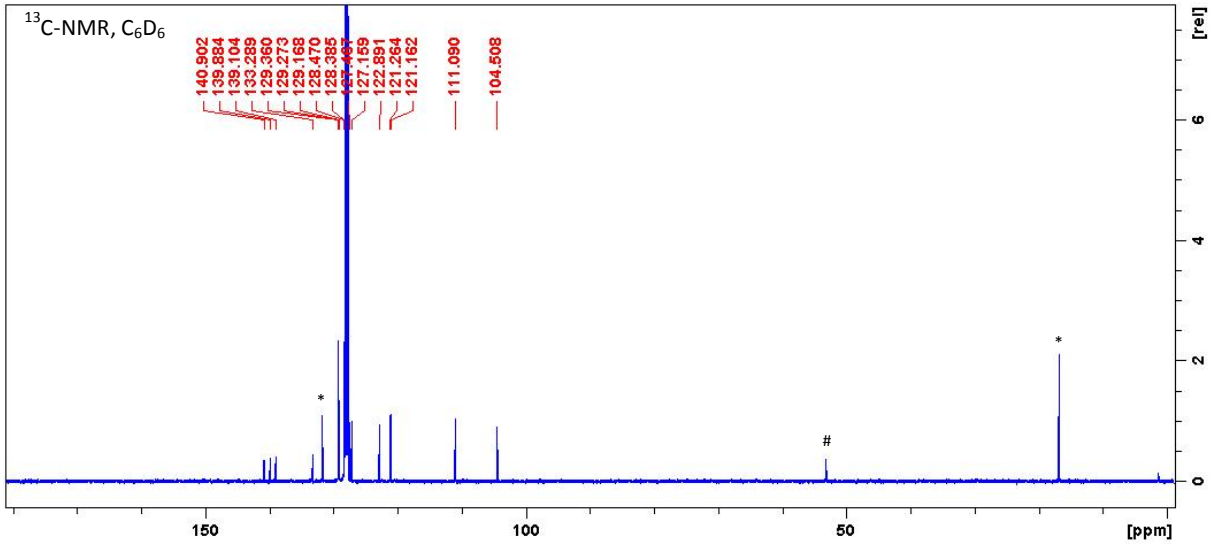


2.7.3 *N*-phenyl-2-phenyl indole (3c)

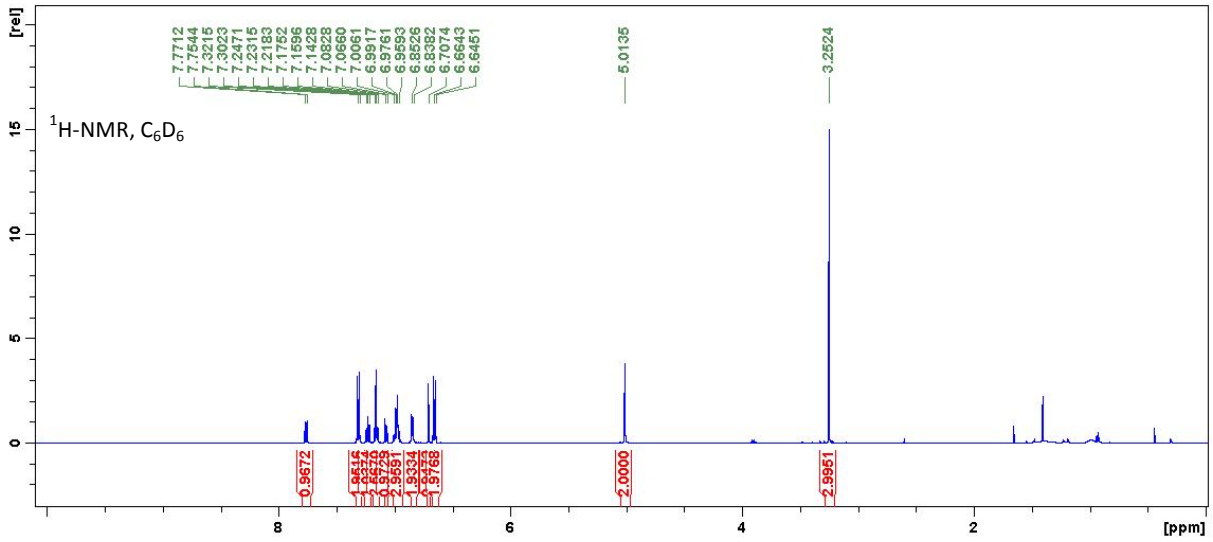


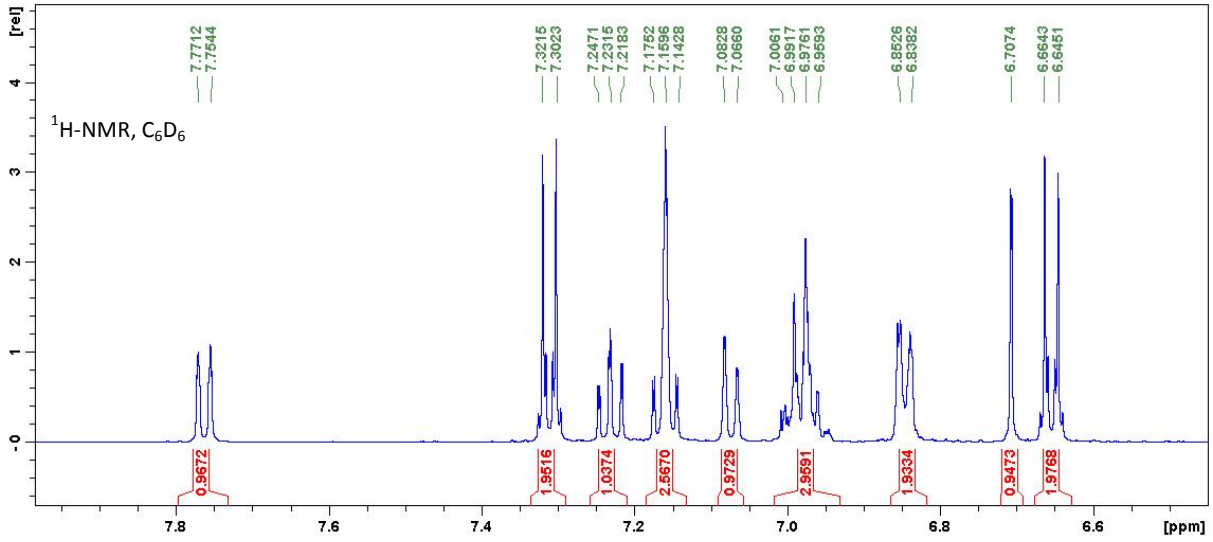
* Internal standard: hexamethylbenzene (^{13}C-NMR: 16.95 / 131.79 ppm)

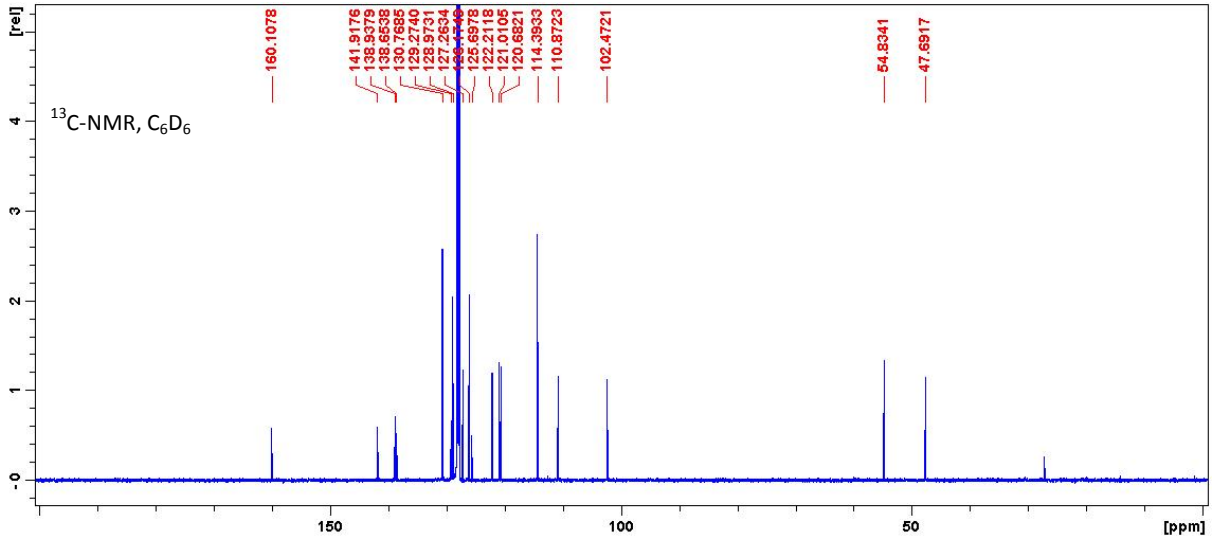
\# Trace amount of dichloromethane (^{13}C-NMR: 53.31 ppm)



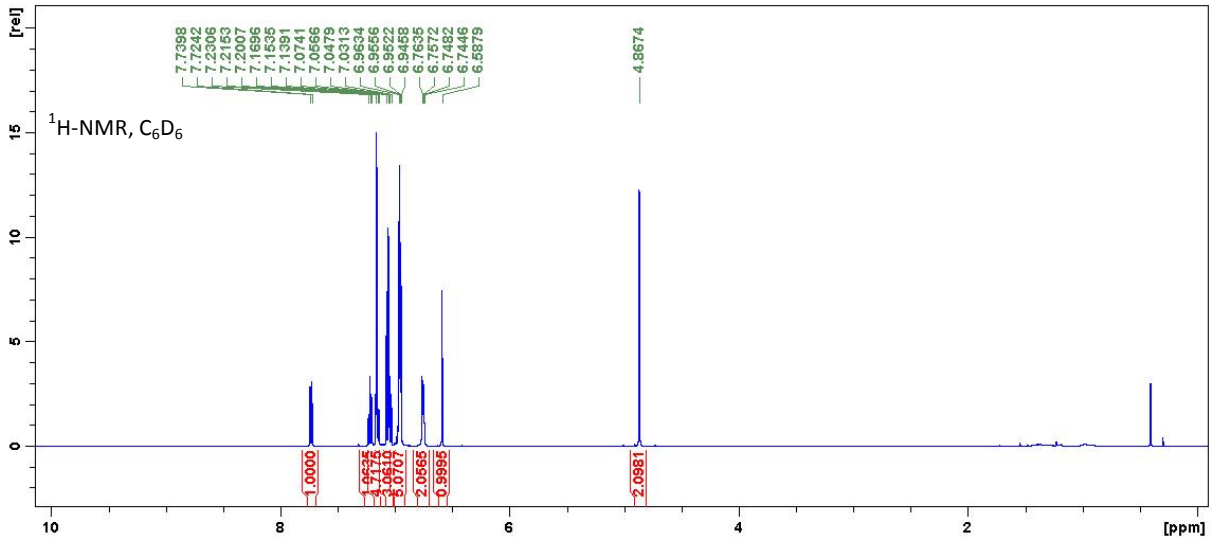
2.7.4 *N*-benzyl-2-*para*-methoxyphenyl indole (3i)

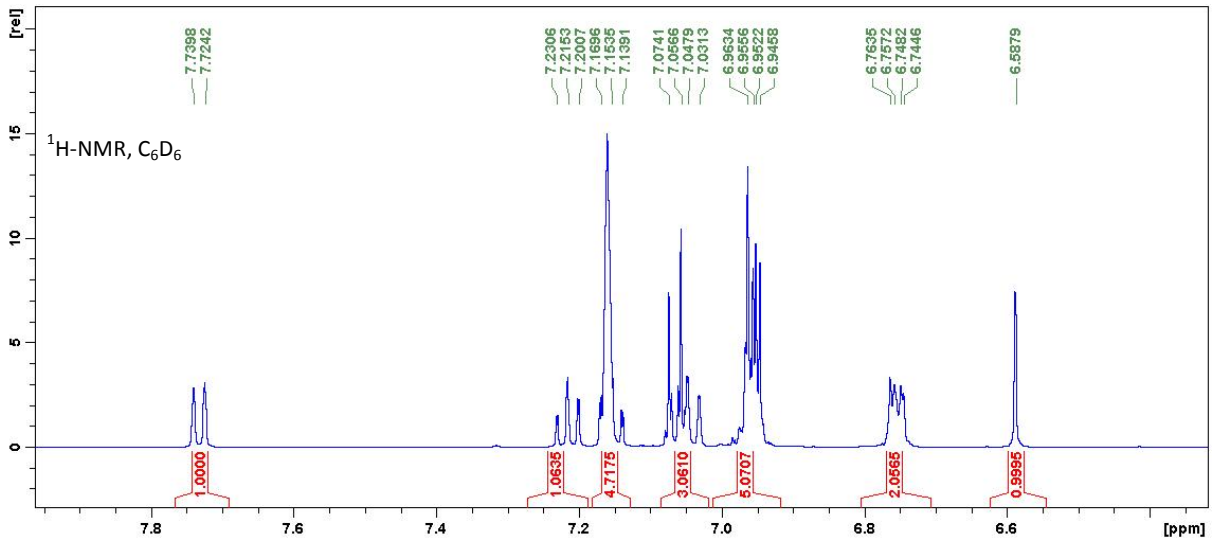


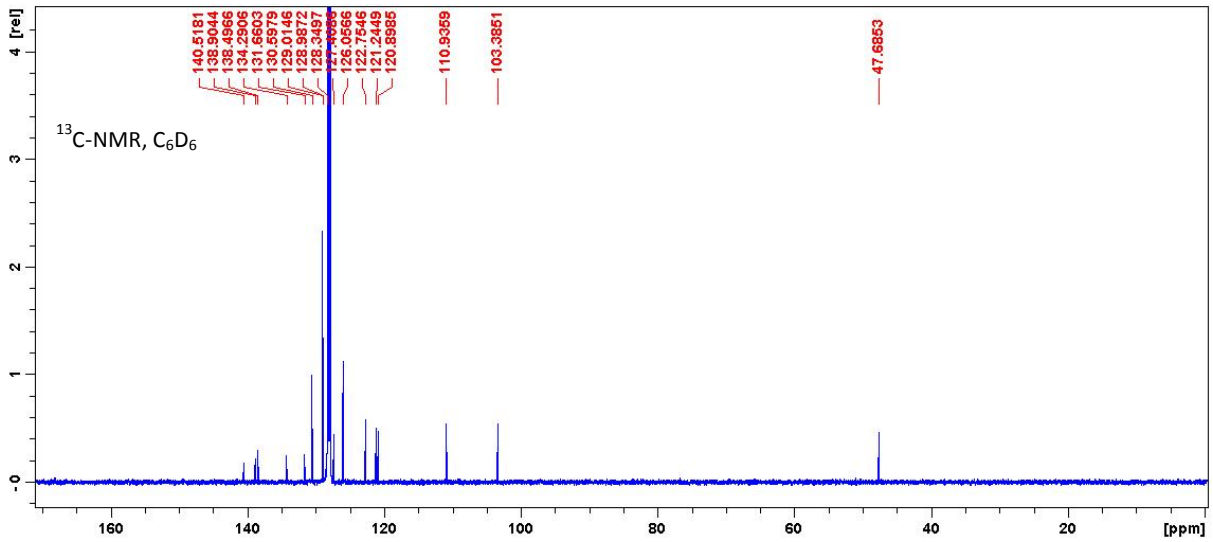




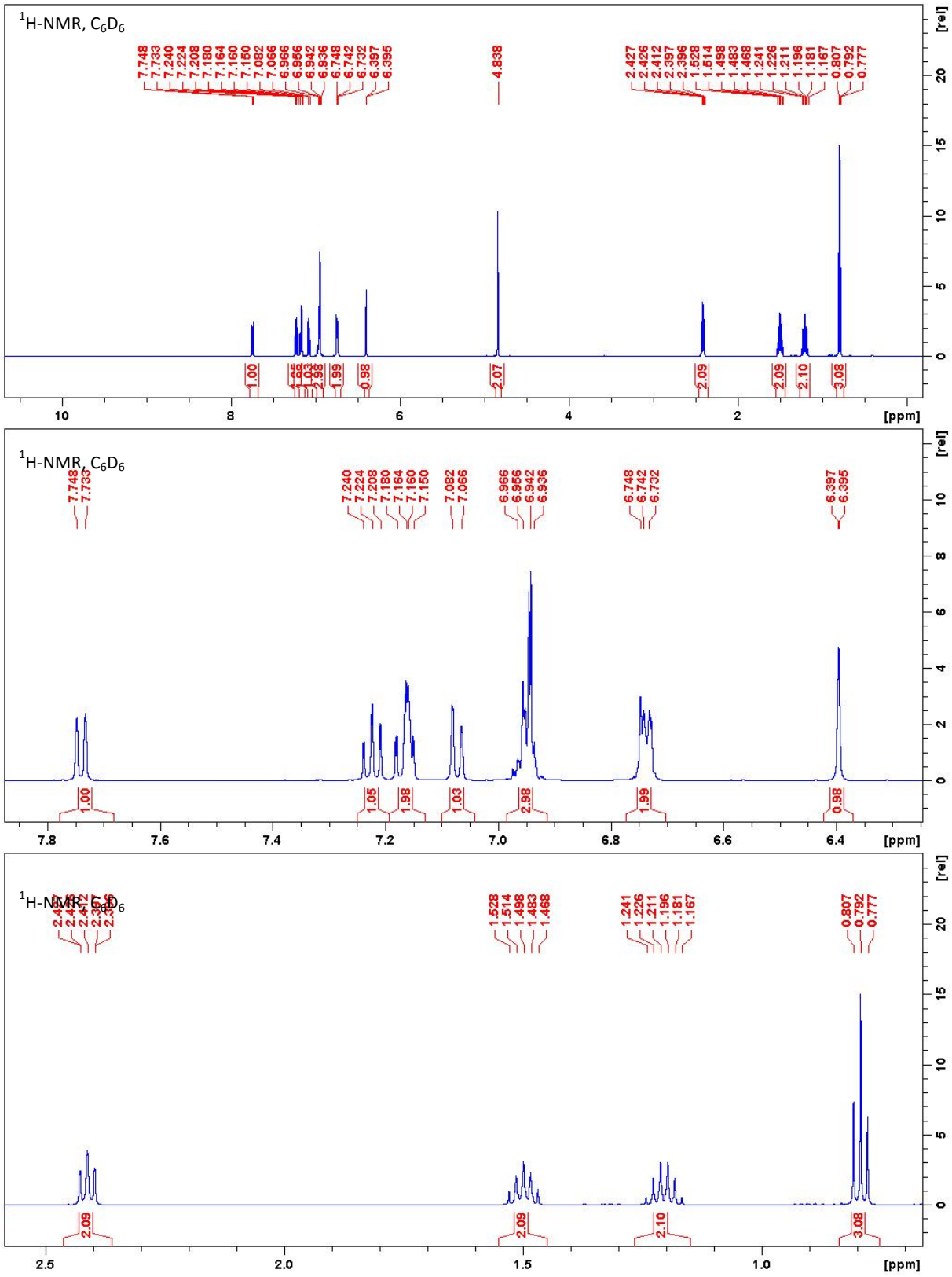
2.7.5 *N*-benzyl-2-*para*-chlorophenyl indole (3j)

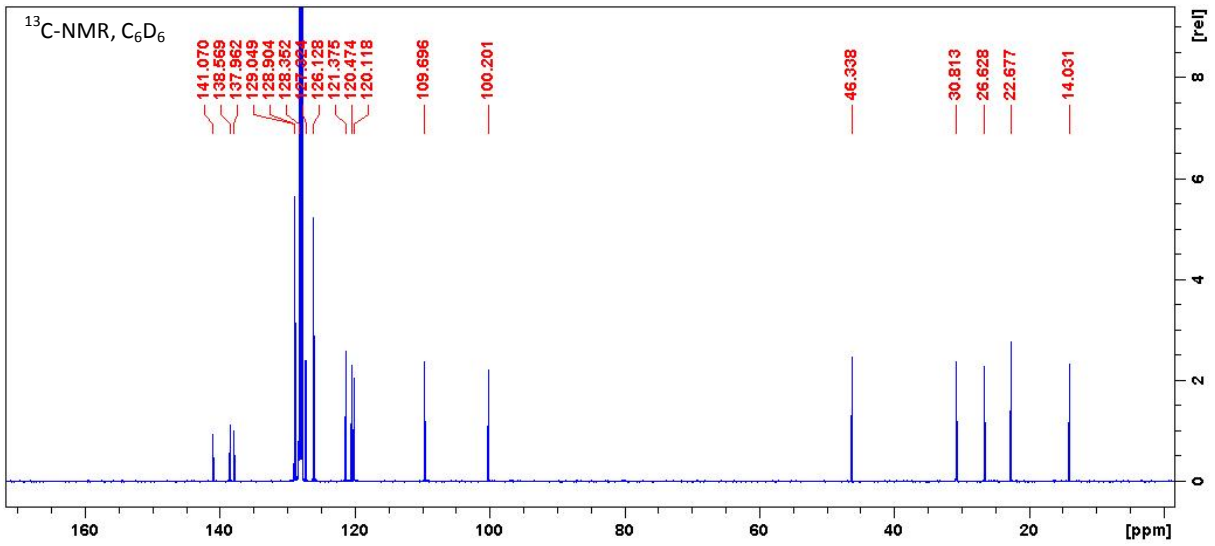




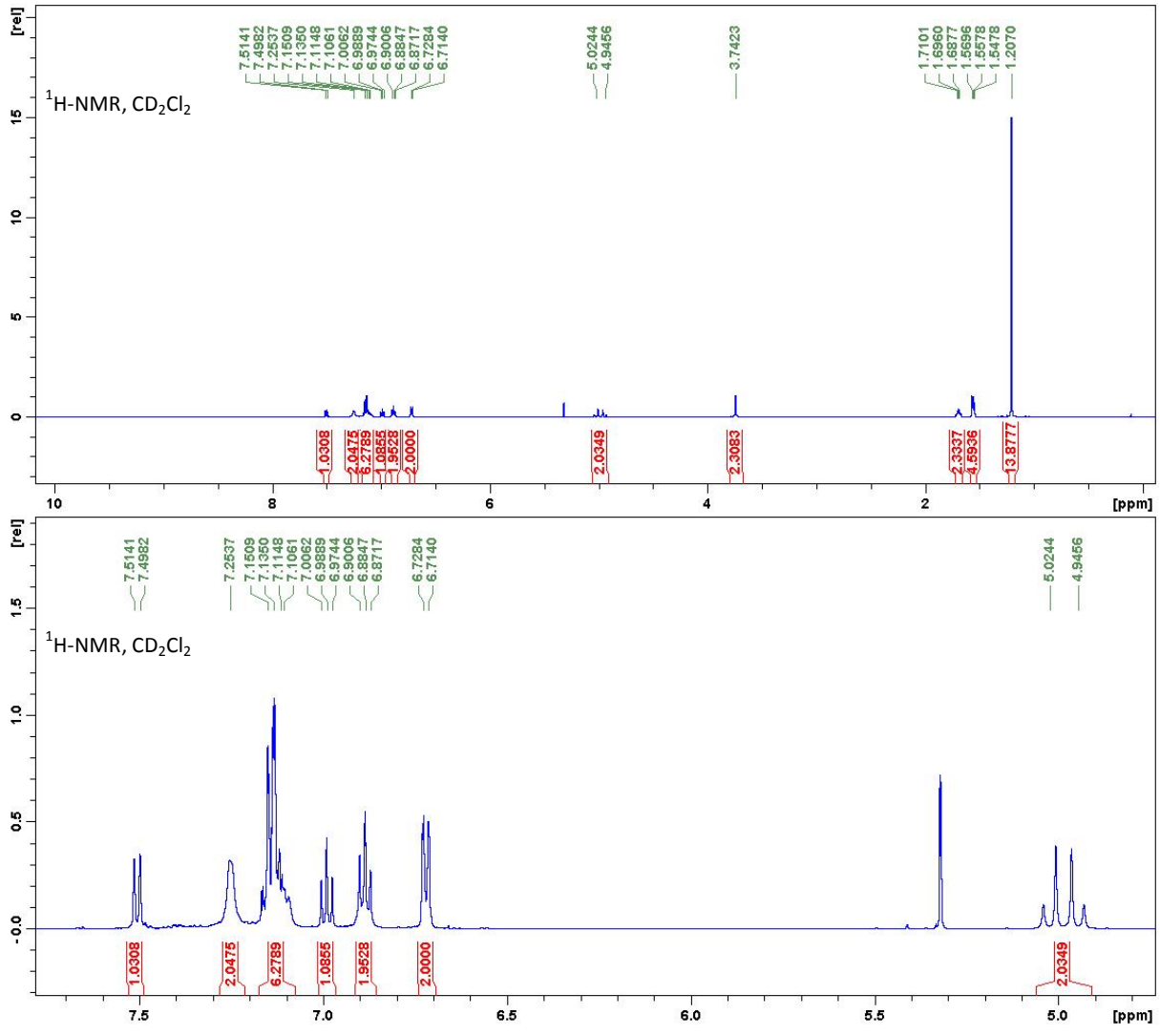


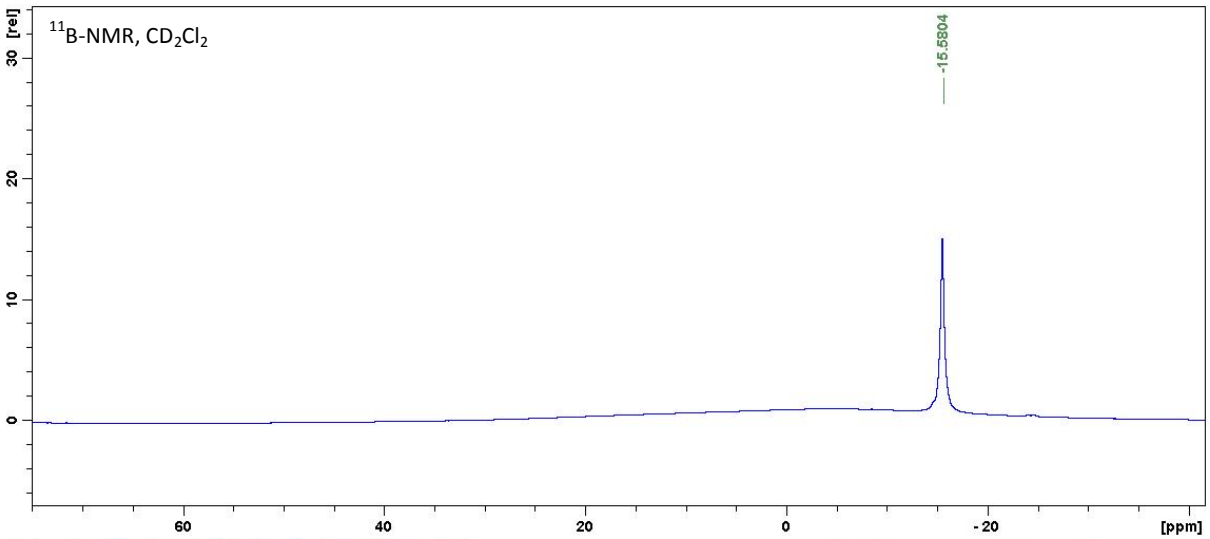
2.7.6 *N*-benzyl-2-butylindole (3k)

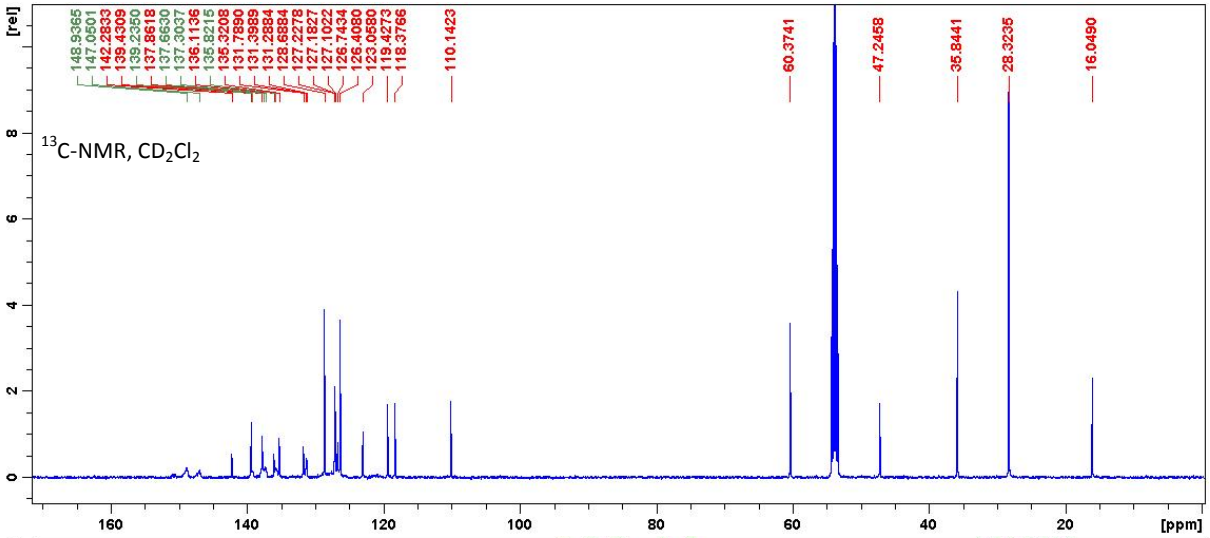


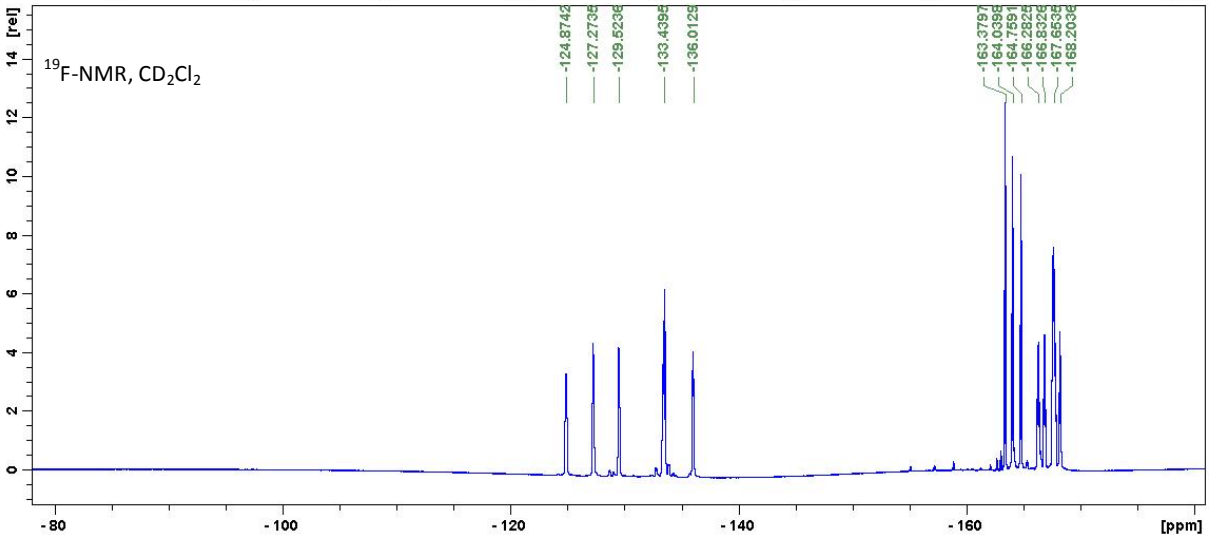


2.7.7 [3a-B(C_6F_5)$_3$][HTMP] (5)

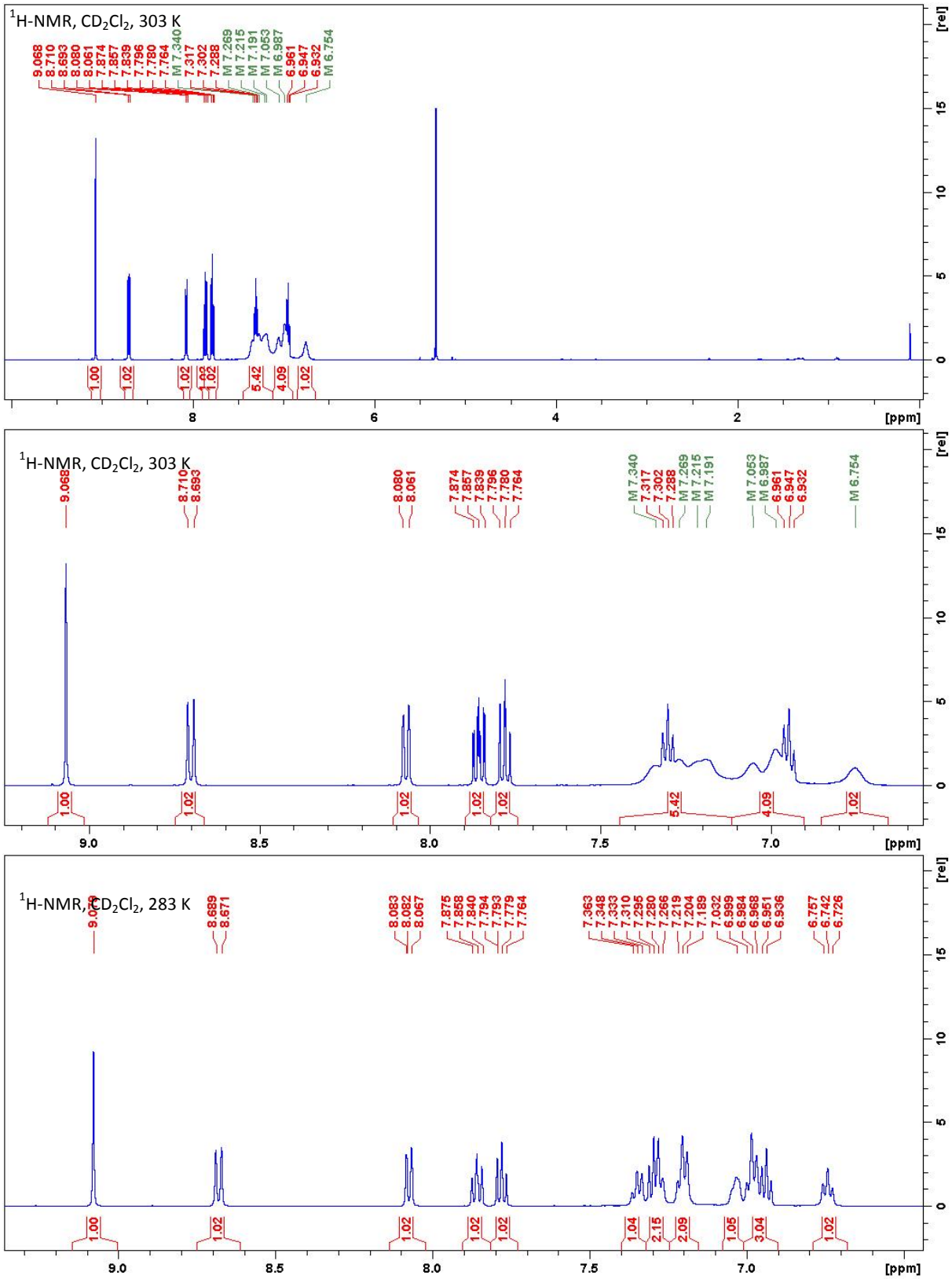


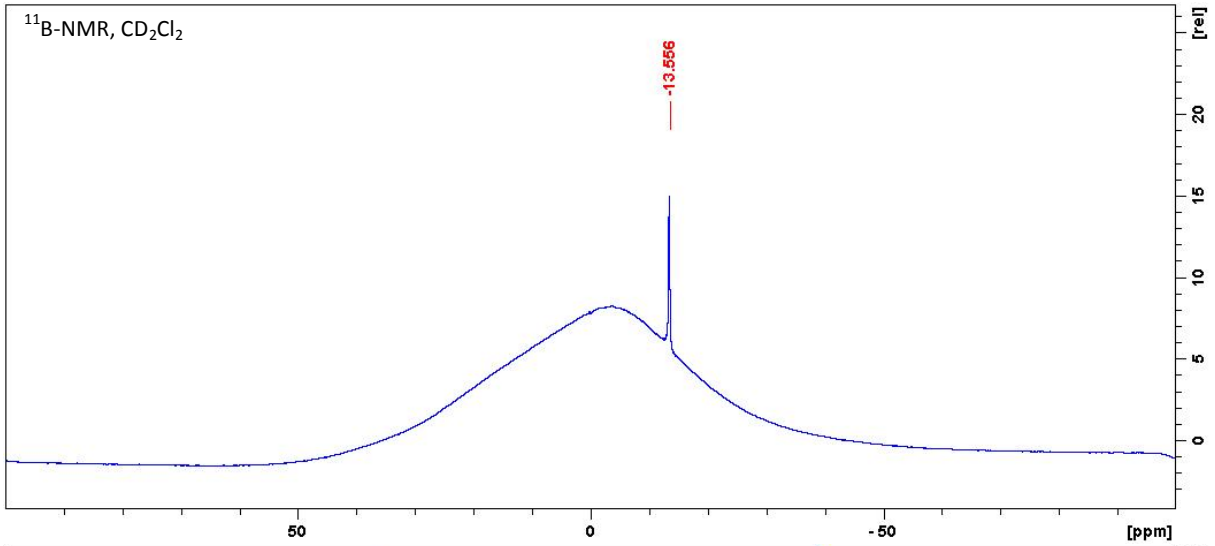

^{11}B-NMR, CD_2Cl_2
-15.5804
[rel]
[ppm]

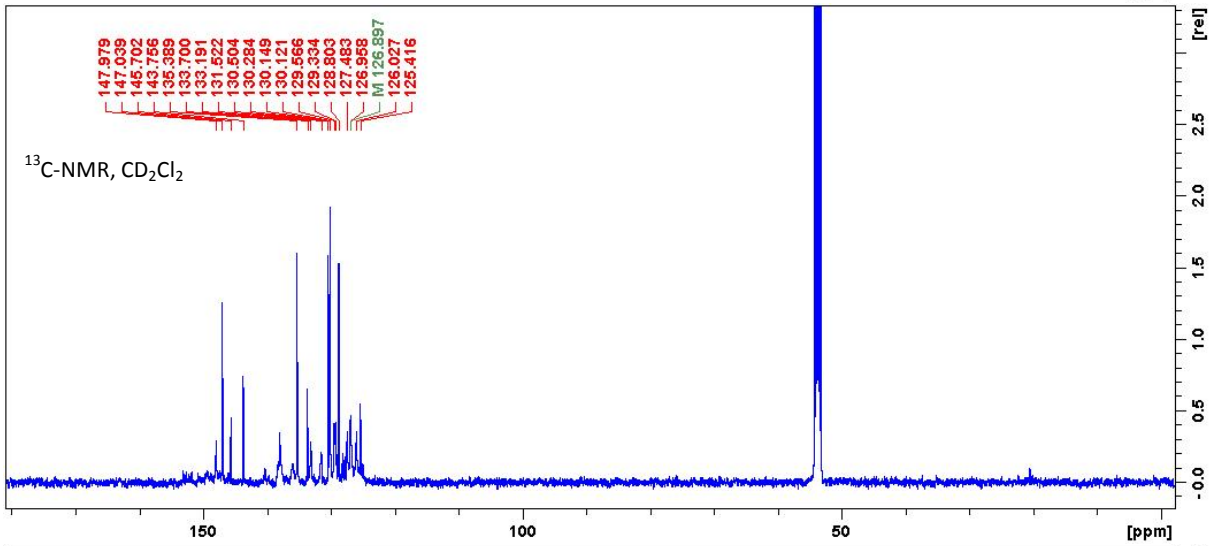

^{13}C-NMR, CD_2Cl_2
148.9365
147.0501
142.2833
139.4309
139.2350
137.8618
137.6630
137.3037
136.1136
135.8215
135.3208
131.7890
131.3989
131.2884
128.6884
127.2278
127.1827
127.1022
126.7434
126.4080
123.0580
119.4273
118.3786
110.1423
60.3741
47.2458
35.8441
28.3235
16.0490
[rel]
[ppm]

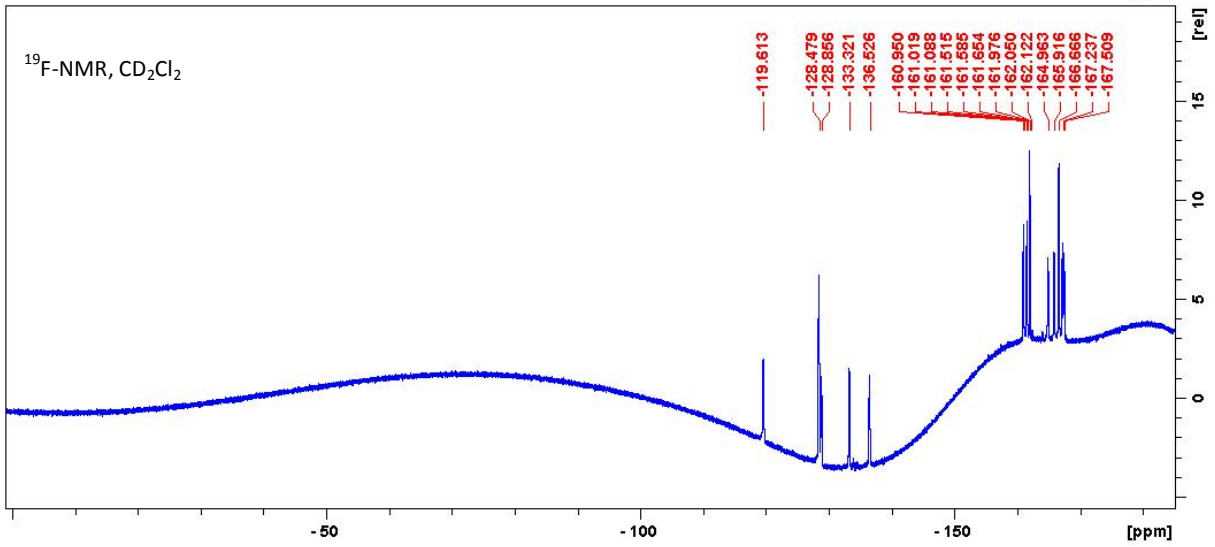

^{19}F-NMR, CD_2Cl_2
-124.8742
-127.2736
-129.5236
-133.4395
-136.0125
-163.3797
-164.0396
-164.7591
-166.2825
-166.6325
-167.6535
-168.2036
[rel]
[ppm]

2.7.8 [6b-B(C_6F_5)$_3$] (7)

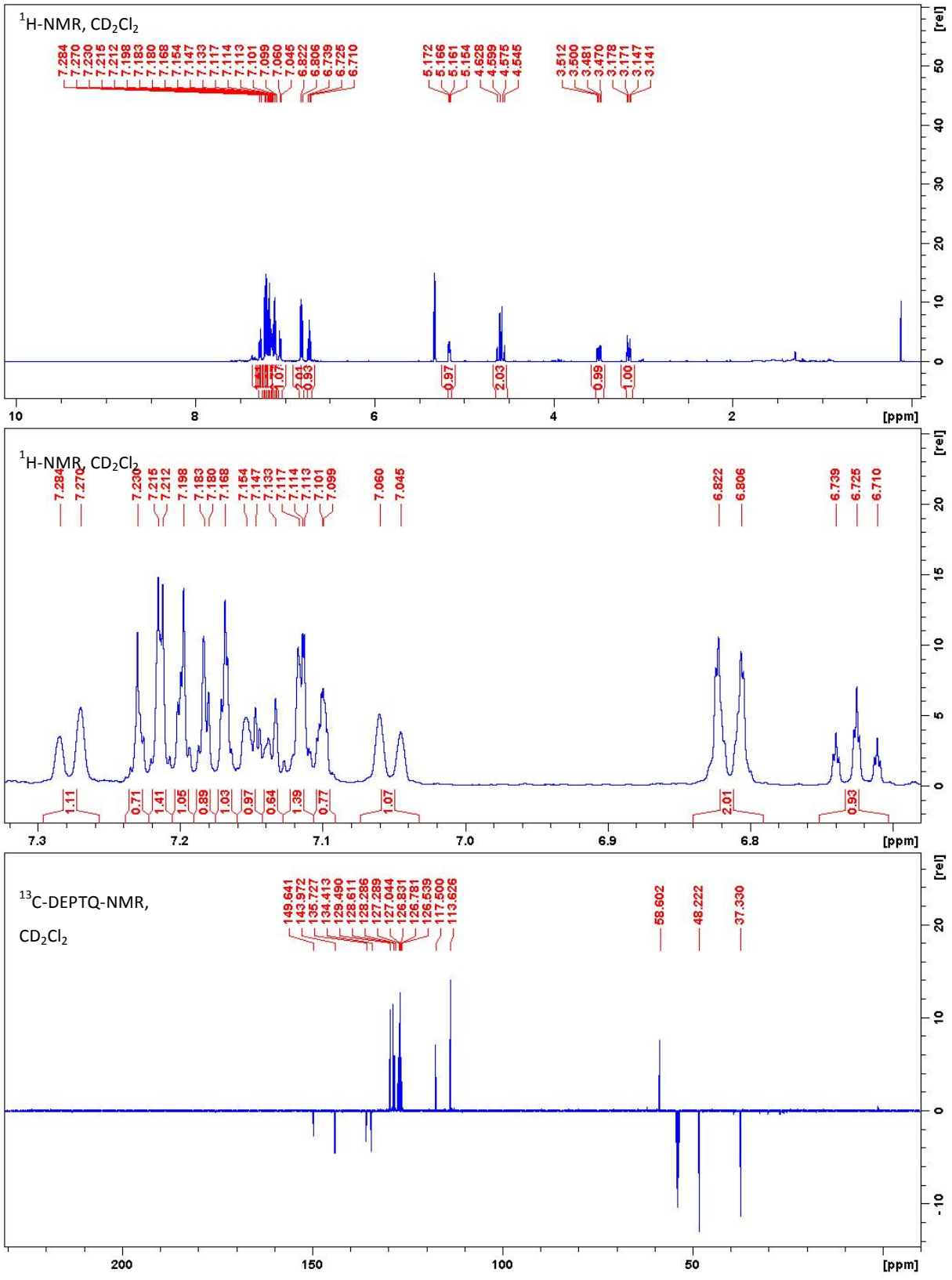



^{11}B-NMR, CD_2Cl_2
-13.556
[rel]
[ppm]


147.979
147.039
145.702
143.756
135.389
133.700
133.191
131.522
130.504
130.284
130.149
130.121
129.566
129.334
128.803
127.483
126.958
M1 126.897
126.027
125.416
^{13}C-NMR, CD_2Cl_2
[rel]
[ppm]


^{19}F-NMR, CD_2Cl_2
-119.613
-128.479
-128.856
-133.321
-136.526
-160.950
-161.019
-161.088
-161.515
-161.585
-161.654
-161.976
-162.050
-162.122
-164.963
-165.916
-166.666
-167.237
-167.509
[rel]
[ppm]

2.7.9 2,3-diphenyl-1,2,3,4-tetrahydro-isoquinoline (8)

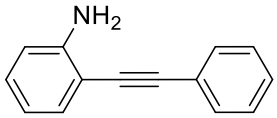


3 Synthesis of starting materials

3.1 General procedure for Sonogashira couplings of anilines

A Schlenk flask was loaded with 2-Iodoaniline (for scale see below, 1.00 eq.), $Pd(PPh_3)_4$ (0.01 eq.) and CuI (0.02 eq.), evacuated and flushed with argon. The alkyne (1.30 eq.) was added first, followed by dry, degassed triethylamine (3.20 eq.) and dry, degassed tetrahydrofurane (0.25 M). The reaction mixture was again carefully degassed by argon stream for a short time and was stirred at room temperature overnight. After completion of the reaction (TLC) a minimal amount of silica was added to the solution and the solvent was evaporated under reduced pressure. The resulting dry powder was subjected to column chromatography.[2]

3.1.1 2-(phenylethynyl) aniline (Ia)

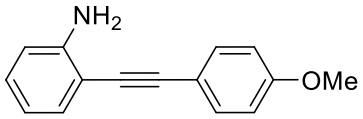


22.80 mmol 2-Iodoaniline, cyclohexane/ ethylacetate 5:1; yellow solid, 72%

^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.46 – 7.39 (m, 3H, H_{Ar}), 7.03 – 6.92 (m, 4H, H_{Ar}), 6.60 – 6.54 (m, 1H, H_{Ar}), 6.34 – 6.29 (m, 1H, H_{Ar}), 3.74 (s, 2H, NH_2).

3.1.2 2-(*para*-ethynylanisol) aniline (Ii)

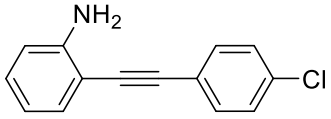
2.90 mmol 2-Iodoaniline, 6 days, cyclohexane/ ethyl acetate 5:1, yellow solid, 99%



^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.51 – 7.46 (m, 1H, H_{Ar}), 7.41 – 7.36 (m, 2H, H_{Ar}), 6.99 – 6.94 (m, 1H, H_{Ar}), 6.64 – 6.56 (m, 3H, H_{Ar}), 6.38 – 6.30 (m, 1H, H_{Ar}), 3.77 (s, 2H, NH_2), 3.19 (s, 3H, CH_3).

3.1.3 2-(*para*-chlorophenylethynyl) aniline (Ij)

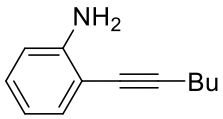
2.80 mmol 2-Iodoaniline, 3 days, cyclohexane/ ethyl acetate 10:1, yellow solid, 98%



^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.44 – 7.39 (m, 1H, H_{Ar}), 7.08 – 7.04 (m, 2H, H_{Ar}), 6.99 – 6.91 (m, 3H, H_{Ar}), 6.60 – 6.55 (m, 1H, H_{Ar}), 6.33 – 6.29 (m, 1H, H_{Ar}), 3.70 (s, 2H, NH_2).

3.1.4 2-(hex-1-yn-1-yl) aniline (Ik)

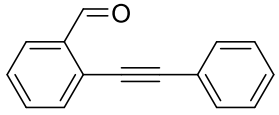
4.86 mmol 2-Iodoaniline in 10 ml NEt_3 as solvent, 15h/ 50 °C, cyclohexane/ ethyl acetate 25:1, pale yellow oil, 72%



^{1}H-NMR (500 MHz, $CDCl_3$, 303 K) δ = 7.25 – 7.23 (m, 1H, H_{Ar}), 7.09 – 7.05 (m, 1H, H_{Ar}), 6.70 – 6.64 (m, 2H, H_{Ar}), 4.15 (s, 2H, N*H*), 2.48 (t, *J* = 7.1 Hz, 2H, CH_2), 1.66 – 1.57 (m, 2H, CH_2), 1.55 – 1.45 (m, 2H, CH_2), 0.96 (t, *J* = 7.3 Hz, 3H, CH_3).

3.2 Synthesis of 2-(phenylethynyl) benzaldehyde (VI)

A Schlenk flask was loaded with $Pd(PPh_3)_4$ (116 mg, 0.10 mmol, 0.01 eq.) and CuI (3.80 mg, 0.20 mmol, 0.02 eq.), evacuated and flushed with argon. Ethynylbenzene (1.32 ml, 1.23 g, 12.0 mmol, 1.20 eq.) and 2-bromobenzaldehyde (1.17 ml, 1.85 g, 10.0 mmol, 1.00 eq.) were added, followed by dry, degassed triethylamine (3.2 eq.) and dry, degassed tetrahydrofurane (0.25 M). The reaction mixture was again carefully degassed by argon stream for a short time and was stirred at room temperature overnight. After completion of the reaction (TLC) a minimal amount of silica was added to the solution and the solvent was evaporated under reduced pressure. The resulting dry powder was subjected to column chromatography (cyclohexane/ ethyl acetate, 50:1 to 25:1 to 10:1) to yield the product as yellow oil (1.92 g, 9.30 mmol, 93%).[3]



^{1}H-NMR (500 MHz, $CDCl_3$, 303 K) δ = 10.66 (d, *J* = 0.8, 1H, C*H*O), 7.99 – 7.92 (m, 1H, H_{Ar}), 7.67 – 7.62 (m, 1H, H_{Ar}), 7.61 – 7.54 (m, 3H, H_{Ar}), 7.48 – 7.43 (m, 1H, H_{Ar}), 7.41 – 7.36 (m, 3H, H_{Ar}).

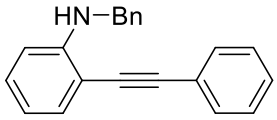
3.3 General procedure for reductive aminations

Under an atmosphere of argon, a suspension of $NaBH_4$ (1.50 eq.) in dichloroethane (0.5 M) was cooled in an ice bath and glacial acetic acid (4.50 eq.) was added dropwise. The resulting mixture was warmed to room temperature and a solution of aniline (1.00 eq.) and aldehyde (1.00 eq.) in dichloroethane (0.5 M) was added via syringe. An additional amount of acetic acid (1.00 eq.) was added and the solution was stirred at room temperature. After full conversion (TLC monitoring, usually 1 – 5 h) the reaction mixture was basified with an equal amount of 1 M NaOH solution and was extracted three times with dichloromethane. The

combined organic layers were dried over Na_2SO_4, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography.[4]

3.3.1 *N*-benzyl-2-(ethynylphenyl) aniline (1a)

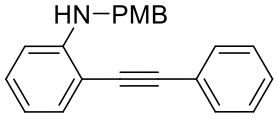
5.17 mmol **Ia**, cyclohexane/ dichloromethane 20:1, yellow oil, 69%



^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.56 – 7.50 (m, 1H, H_{Ar}), 7.44 – 7.38 (m, 2H, H_{Ar}), 7.18 – 7.13 (m, 2H, H_{Ar}), 7.12 – 7.06 (m, 2H, H_{Ar}), 7.06 – 6.93 (m, 5H, H_{Ar}), 6.62 – 6.56 (m, 1H, H_{Ar}), 6.49 – 6.44 (m, 1H, H_{Ar}), 5.18 (t, $^3J_{HH}$ = 5.2 Hz, 1H, NH), 4.00 (d, $^3J_{HH}$ = 5.7 Hz, 2H, NCH_2); **^{13}C-NMR** (126 MHz, C_6D_6, 303 K): δ = 149.40, 139.61, 132.65, 131.78, 130.44, 128.88, 128.67, 128.32, 127.33, 127.22, 123.98, 117.14, 110.56, 108.22, 95.86, 87.11, 47.82.

3.3.2 *N-para*-methoxybenzyl-2-(phenylethynyl) aniline (1b)

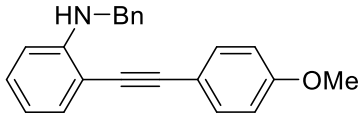
1.40 mmol **Ia**, SiO_2 deactivated with triethylamine, cyclohexane/ dichloromethane 20:1, yellow oil, 60%



^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.57 – 7.52 (m, 1H, H_{Ar}), 7.44 – 7.38 (m, 2H, H_{Ar}), 7.12 – 7.03 (m, 3H, H_{Ar}), 7.00 – 6.92 (m, 3H, H_{Ar}), 6.75 – 6.69 (m, 2H, H_{Ar}), 6.64 – 6.57 (m, 1H, H_{Ar}), 6.56 – 6.51 (m, 1H, H_{Ar}), 5.17 (t, $^3J_{HH}$ = 5.2 Hz, 1H, N*H*), 4.02 (d, $^3J_{HH}$= 5.5 Hz, 2H, NCH_2), 3.28 (s, 3H, CH_3); **^{13}C-NMR** (126 MHz, C_6D_6, 303 K) δ = 159.45, 149.49, 132.64, 131.77, 131.37, 130.44, 128.67, 128.56, 128.30, 123.97, 117.06, 114.46, 110.59, 108.19, 95.87, 87.17, 54.78, 47.41.

3.3.3 *N*-benzyl-2-(*para*-ethynylanisole) aniline (1i)

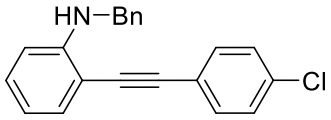
1.40 mmol **Ii**, cyclohexane/ dichloromethane 20:1 to 10:1, yellow oil, 38%



^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.59 – 7.55 (m, 1H, H_{Ar}), 7.41 – 7.36 (m, 2H, H_{Ar}), 7.20 – 7.14 (m, 2H, H_{Ar}), 7.12 – 7.07 (m, 2H, H_{Ar}), 7.06 – 6.99 (m, 2H, H_{Ar}), 6.64 – 6.56 (m, 3H, H_{Ar}), 6.51 – 6.45 (m, 1H, H_{Ar}), 5.23 (t, $^3J_{HH}$ = 5.5 Hz, 1H, NH), 4.02 (d, $^3J_{HH}$ = 5.7 Hz, 2H, NCH_2), 3.18 (s, 3H, CH_3); **^{13}C-NMR** (126 MHz, C_6D_6, 303 K): δ = 160.14, 149.32, 139.72, 133.30, 132.53, 130.13, 128.87, 127.30, 127.26, 117.15, 116.06, 114.48, 110.52, 108.72, 95.92, 85.68, 54.77, 47.87.

3.3.4 *N*-benzyl-2-(*para*-chlorophenylethynyl) aniline (1j)

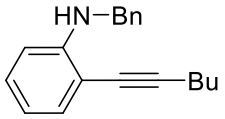
1.40 mmol **Ij**, cyclohexane/ dichloromethane 20:1 to 10:1, yellow solid, 58%



^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.54 – 7.48 (m, 1H, H_{Ar}), 7.17 – 7.13 (m, 2H, H_{Ar}), 7.12 – 7.08 (m, 2H, H_{Ar}), 7.08 – 6.99 (m, 4H, H_{Ar}), 6.91 – 6.87 (m, 2H, H_{Ar}), 6.64 – 6.55 (m, 1H, H_{Ar}), 6.50 – 6.44 (m, 1H, H_{Ar}), 5.08 (t, $^{3}J_{HH}$ = 5.3 Hz, 1H, N*H*), 4.01 (d, $^{3}J_{HH}$ = 5.7 Hz, 2H, NCH_2); **^{13}C-NMR** (126 MHz, C_6D_6, 303 K) δ = 149.42, 139.48, 134.41, 132.91, 132.66, 130.70, 129.00, 128.94, 127.46, 127.28, 122.28, 117.22, 110.64, 107.84, 94.65, 88.03, 47.87.

3.3.5 *N*-benzyl-2-(hex-1-yn-1-yl) aniline (1k)

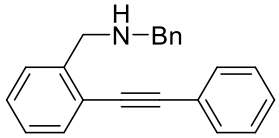
3.51 mmol **Ik**, cyclohexane/ ethyl acetate 100:1, yellow oil, 70%



^{1}H-NMR (500 MHz, $CDCl_3$, 303 K) δ = 7.41 – 7.33 (m, 4H, H_{Ar}), 7.30 – 7.25 (m, 2H, H_{Ar}), 7.14 – 7.08 (m, 1H, H_{Ar}), 6.64 – 6.59 (m, 1H, H_{Ar}), 6.58 – 6.54 (m, 1H, H_{Ar}), 5.02 (s, 1H, N*H*), 4.41 (s, 2H, NCH_2), 2.46 (t, *J* = 7.0 Hz, 2H, CH_2), 1.62 – 1.53 (m, 2H, CH_2), 1.49 – 1.40 (m, 2H, CH_2), 0.91 (t, *J* = 7.3 Hz, 3H, CH_3); **^{13}C-NMR** (126 MHz, $CDCl_3$, 303 K) δ = 148.80 (C), 139.43 (C), 132.05 (CH), 129.19 (CH), 128.77 (CH), 127.38 (CH), 127.31 (CH), 116.63 (CH), 109.82 (CH), 108.82 (C), 96.42 (C), 77.23 (C), 48.00 (CH_2), 31.13 (CH_2), 22.14 (CH_2), 19.50 (CH_2), 13.71 (CH_3).

3.3.6 *N*-benzyl-1-(2-(phenylethynyl)phenyl) methanamine (6a)

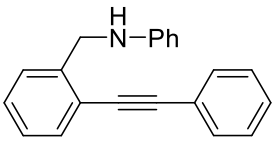
1.21 mmol **VI**, cyclohexane/ ethyl acetate 10:1, yellow oil, 62%.



^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.57 – 7.54 (m, 1H, H_{Ar}), 7.48 – 7.45 (m, 2H, H_{Ar}), 7.40 – 7.37 (m, 1H, H_{Ar}), 7.33 – 7.30 (m, 2H, H_{Ar}), 7.20 – 7.17 (m, 2H, H_{Ar}), 7.12 – 7.06 (m, 2H, H_{Ar}), 7.04 – 6.95 (m, 4H, H_{Ar}), 4.03 (s, 2H, CH_2), 3.67 (s, 2H, CH_2), 1.48 (s, 1H, N*H*). **^{13}C-NMR** (126 MHz, C_6D_6, 303 K) δ = 143.33 (C), 141.28 (C), 132.57 (CH), 131.90 (CH), 128.89 (CH), 128.71 (CH), 128.68 (CH), 128.58 (CH), 128.51 (CH), 128.48 (CH), 127.06 (CH), 126.99 (CH), 124.02 (C), 122.92 (C), 94.45 (C), 88.59 (C), 53.58 (CH), 52.00 (CH).

3.3.7 *N*-(2-(phenylethynyl)benzyl) aniline (6b)

2.42 mmol **VI**, cyclohexane/ ethyl acetate 25:1, yellow oil, 69%.

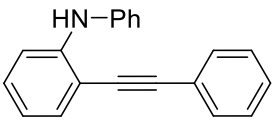


^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.56 – 7.53 (m, 1H, H_{Ar}), 7.46 – 7.43 (m, 2H, H_{Ar}), 7.26 – 7.23 (m, 1H, H_{Ar}), 7.13 – 7.07 (m, 2H, H_{Ar}), 7.03 – 6.92 (m, 5H, H_{Ar}), 6.73 – 6.69 (m, 1H, H_{Ar}), 6.51 – 6.46 (m, 2H, H_{Ar}), 4.43 (s, 2H, CH_2), 3.59 (s, 1H, N*H*). **^{13}C-NMR** (126 MHz, C_6D_6, 303 K) δ = 148.62 (C), 142.03 (C), 132.52 (CH), 131.91 (CH), 129.57 (CH), 128.86 (CH), 128.71 (CH), 128.59 (CH), 128.35 (CH), 127.77 (CH), 127.15 (CH), 123.76 (C), 122.41 (C), 117.85 (CH), 113.23 (CH), 95.41 (C), 87.89 (C), 47.11 (CH_2).

3.4 Synthesis of *N*-phenyl-2-(phenylethynyl) aniline (1c)

In a flask 2-(phenylethynyl) aniline (**Ia**, 250 mg, 1.29 mmol, 1.00 eq.), phenylboronic acid (237 mg, 1.94 mmol, 1.5 eq.) and copper(II) acetate (16 mg, 0.13 mmol, 0.10 eq.) were dissolved in toluene (4 ml), followed by addition of decanoic acid (45 mg, 0.26 mmol, 0.20 eq.) and 2,6-dimethylpyridine (0.23 ml, 208 mg, 1.94 mmol, 1.50 eq.). The mixture was stirred at room temperature overnight. Ethyl acetate (40 ml) was added and the solution was filtered over celite. After evaporation of the solvent under reduced pressure the residue was purified by column chromatography (cyclohexane/ ethyl acetate, 25:1) to yield the product as yellow oil (192 mg, 0.71 mmol, 55%).[5]

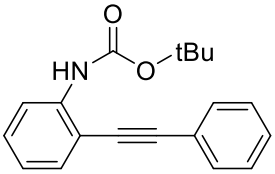
Due to the copper catalyzed synthesis of **1c** a small amount of cyclisation product could not be avoided and the mixture was inseparable by column chromatography. Alternative transition metal catalyzed routes (e.g. Buchwald-Hartwig type starting from **Ia** or a reversed route with final Sonogashira coupling) led to similar or worse product ratios. The yield of the table run experiment with **1c** was corrected by the ratio of **3c** in **1c** (12%).



^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.56 – 7.51 (m, 1H, H_{Ar}), 7.42 – 7.37 (m, 2H, H_{Ar}), 7.22 – 7.19 (m, 1H, H_{Ar}), 7.11 – 7.04 (m, 2H, H_{Ar}), 7.01 – 6.93 (m, 6H, H_{Ar}), 6.88 – 6.83 (m, 1H, H_{Ar}), 6.66 (m, 1H, H_{Ar}), 6.55 (s, 1H, N*H*); **^{13}C-NMR** (126 MHz, C_6D_6, 303 K) δ = 145.59 (C), 142.16 (C), 133.06 (CH), 131.88 (CH), 129.93 (CH), 129.67 (CH), 128.69 (CH), 128.54 (CH), 123.67 (C), 122.78 (CH), 120.65 (CH), 119.73 (CH), 114.17 (CH), 111.00 (C), 96.24 (C), 86.64 (C).

3.5 Synthesis of *tert*-butyl (2-(phenylethynyl)phenyl) carbamate (1d)

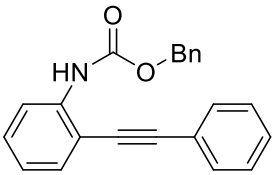
In a round bottom flask 2-(phenylehtynyl) aniline (**Ia**, 800 mg, 4.14 mmol, 1.00 eq.) was dissolved in tetrahydrofuran (20 ml) and di-*tert*-butyldicarbonate (1.72 ml, 1.81 g, 8.28 mmol, 2.00 eq.) was added. The solution was refluxed for 40 h and water (10 ml) was added. The aqueous phase was extracted with ethyl acetate (3x 10 ml). The combined organic layers were washed with saturated sodium bicarbonate solution (30 ml) and dried over sodium sulfate. The solvent was evaporated and the residue was purified by column chromatography on deactivated silica (cyclohexane/ ethyl acetate 10:1, dry silica was suspended in the solvent mixture and triethylamine was added until a persistent smell of amine was present. The column was run without any further triethylamine in the solvent mixture) to yield the product as yellow solid (913 mg, 3.15 mmol, 76%).[6]



^{1}H-NMR (300 MHz, C_6D_6, 298 K) δ = 8.74 – 8.65 (m, 1H, H_{Ar}), 7.63 (s,1H, N*H*), 7.43 – 7.32 (m, 3H, H_{Ar}), 7.12 – 7.03 (m, 1H, H_{Ar}), 6.99 – 6.91 (m, 3H, H_{Ar}), 6.73 – 6.65 (m, 1H, H_{Ar}), 1.37 (s, 9H, C(CH_3)$_3$); **^{13}C-NMR** (126 MHz, C_6D_6, 303 K) δ = 152.39 (C), 140.49 (C), 132.02 (CH), 131.85 (CH), 130.20 (CH), 128.78 (CH), 128.68 (CH), 123.12 (C), 122.39 (CH), 118.08 (CH), 111.42 (C), 96.73 (C), 85.30 (C), 80.44 (C), 28.21 (CH_3).

3.6 Synthesis of benzyl (2-(phenylethynyl)phenyl) carbamate (1e)

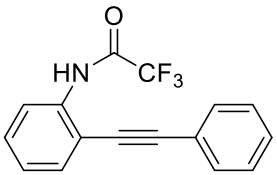
In a round bottom flask 2-(phenylehtynyl) aniline (**Ia**, 100 mg, 0.52 mmol, 1.00 eq.) was dissolved in tetrahydrofuran (1 ml) and benzyl chloroformate (1.72 ml, 1.81 g, 8.28 mmol, 2.00 eq.) and sodiumbicarbonate (47.8 mg, 0.56 mmol, 1.10 eq.) were added. The solution was stirred at ambient temperature. After 16 h the solvent was evaporated and the residue was purified by column chromatography (cyclohexane/ ethyl acetate 10:1) to yield the product as brown solid (126 mg, 0.39 mmol, 74%).[7]



^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 8.67 – 8.59 (m, 1H, H_{Ar}), 7.64 (s, 1H, N*H*), 7.40 – 7.36 (m, 1H, H_{Ar}), 7.35 – 7.31 (m, 2H, H_{Ar}), 7.21 – 7.18 (m, 2H, H_{Ar}), 7.09 – 7.02 (m, 4H, H_{Ar}), 6.96 – 6.90 (m, 3H, H_{Ar}), 6.72 – 6.68 (m, 1H, H_{Ar}), 5.04 (s, 2H, CH_2); **^{13}C-NMR** (126 MHz, C_6D_6, 303 K) δ = 153.07 (C), 139.87 (C), 136.76 (C), 132.00 (CH), 131.83 (CH), 130.18 (CH), 128.81 (CH), 128.71 (CH), 128.68 (CH), 128.60 (CH), 128.33 (CH), 122.93 (C), 122.82 (CH), 118.32 (CH), 111.84 (C), 96.94 (C), 84.99 (C), 67.12 (CH_2).

3.7 Synthesis of 2,2,2-trifluoro-*N*-(2-(phenylethynyl)phenyl) acetamide (1f)

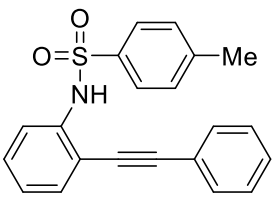
In a round bottom flask 2-(phenylehtynyl) aniline (**Ia**, 100 mg, 0.52 mmol, 1.00 eq.), pyridine (0.084 ml, 82.3 mg, 1.04 mmol, 2.00 eq.) and 4-(dimethylamino)pyridine (3 mg, 0.025 mmol, 0.05 eq.) were dissolved in dichloromethane (1 ml). The solution was cooled in an ice bath and 2,2,2-trifluoroacetanhydride (0.088 ml, 131 mg, 0.62 mmol, 1.20 eq.) was added. After stirring at ambient temperature for 16 h water was added (1 ml) and the mixture was extracted with ethyl acetate (3x 1 ml). The crude product was purified by column chromatography (cyclohexane/ ethyl acetate 25:1) to yield the product as white solid (81.4 mg, 0.282 mmol, 54%).



^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 8.61 (s, 1H, N*H*), 8.45 – 8.40 (m, 1H, H_{Ar}), 7.41 – 7.36 (m, 2H, H_{Ar}), 7.28 – 7.24 (m, 1H, H_{Ar}), 7.01 – 6.97 (m, 3H, H_{Ar}), 6.95 – 6.91 (m, 1H, H_{Ar}), 6.73 – 6.69 (m, 1H, H_{Ar}), **^{19}F-NMR** (282 MHz, C_6D_6, 298 K) δ = −75.86 (s, 3F); **^{13}C-NMR** (126 MHz, C_6D_6 303 K) δ = 154.30 (q, $^{2}J_{CF}$ = 36.9 Hz, CO), 136.88 (C), 131.66 (CH), 131.58 (CH), 130.03 (CH), 129.40 (CH), 128.93 (CH), 125.40 (CH), 122.25 (C), 119.93 (CH), 116.36 (q, $^{1}J_{CF}$ = 289.1 Hz, CF_3), 113.73 (C), 98.37 (C), 83.61 (C).

3.8 Synthesis of *N*-(2-(phenylethynyl)phenyl) toluenesulfonamide (1g)

In a round bottom flask 2-(phenylehtynyl) aniline (**Ia**, 200 mg, 1.03 mmol, 1.00 eq.), 4-toluenesulfonyl chloride (217 mg, 1.14 mmol, 1.10 eq.) and pyridine (0.167 ml, 162.9 mg, 2.06 mmol, 2.00 eq.) were dissolved in dichloromethane (4 ml) and the solution was stirred at room temperature. After 16 h water was added (1 ml), the mixture was extracted with dichloromethane (3x 3 ml), the organic layers were washed with brine (5 ml) and dried over $MgSO_4$. The solvent was evaporated and the crude product was purified by column chromatography (cyclohexane/ ethyl acetate 5:1) to yield the product as light brown solid (334 mg, 0.96 mmol, 93%).

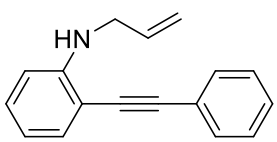


^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.92 – 7.88 (m, 1H, H_{Ar}), 7.74 – 7.70 (m, 2H, H_{Ar}), 7.42 (s, 1H, N*H*), 7.33 – 7.29 (m, 2H, H_{Ar}), 7.14 –7.11 (m, 1H, H_{Ar}), 7.00 – 6.96 (m, 3H, H_{Ar}), 6.92 – 6.87 (m, 1H, H_{Ar}), 6.62 – 6.57 (m, 1H, H_{Ar}), 6.56 – 6.51 (m, 2H, H_{Ar}), 1.66 (s, 3H, C*H*$_3$); **^{13}C-NMR**

(126 MHz, C_6D_6, 303 K) δ = 143.63 (C), 138.67 (C), 137.34 (C), 132.07 (CH), 131.83 (CH), 129.87 (CH), 129.67 (CH), 129.08 (CH), 128.79 (CH), 127.64 (CH), 124.70 (CH), 122.62 (C), 121.18 (CH), 115.19 (C), 96.74 (C), 84.59 (C), 21.00 (CH_3).

3.9 *N*-allyl-2-(phenylethynyl) aniline (1h)

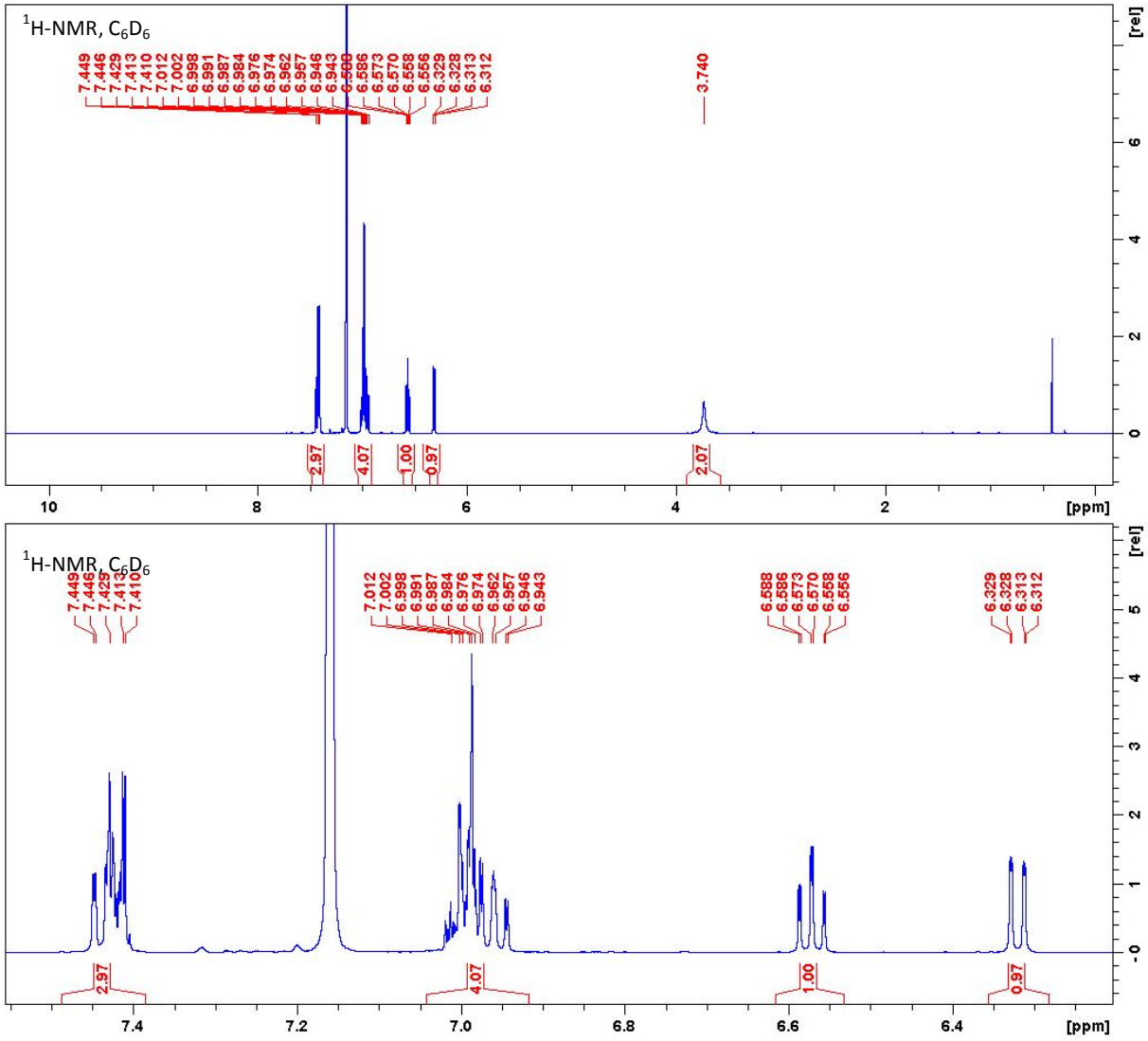
In a round bottom flask *tert*-butyl(2-(phenylethynyl)phenyl) carbamate (**1d**, 211 mg, 0.72 mmol, 1.00 eq.) was evacuated, flushed with argon, dissolved in dry tetrahydrofuran (7 ml) and cooled in an ice bath. Sodium hydride (60% in mineral oil, 65.0 mg, 1.26 mmol, 2.25 eq.) was added and the solution was stirred at 0 °C. After 30 min allyl bromide (0.140 ml, 196 mg, 1.62 mmol, 2.25 eq.) was added and the solution was refluxed overnight. When the reaction was finished (TLC monitoring) diethyl ether (2.5 ml), water (1.5 ml) and brine (1.5 ml) were added and the mixture was extracted with diethyl ether (3x 2ml). The combined organic layers were washed with brine (2 ml) and dried over sodium sulfate. The solvent was evaporated and the residue was dissolved in methanol. The solution was added to an ice cold solution of acetyl chloride (0.514 ml, 0.565 g, 7.2 mmol, 10 eq.) in methanol (3 ml). After 2 h at room temperature the solvent was evaporated, 1 M sodium hydroxide solution was added to the residue and the mixture was extracted with diethyl ether (3x 2ml). After drying of the organic layers over sodium sulfate and evaporation of the solvent, the crude product was purified by column chromatography (cyclohexane/ ethyl acetate 20:1) to yield the product as yellow solid (43 mg, 0.18 mmol, 60%).[8]



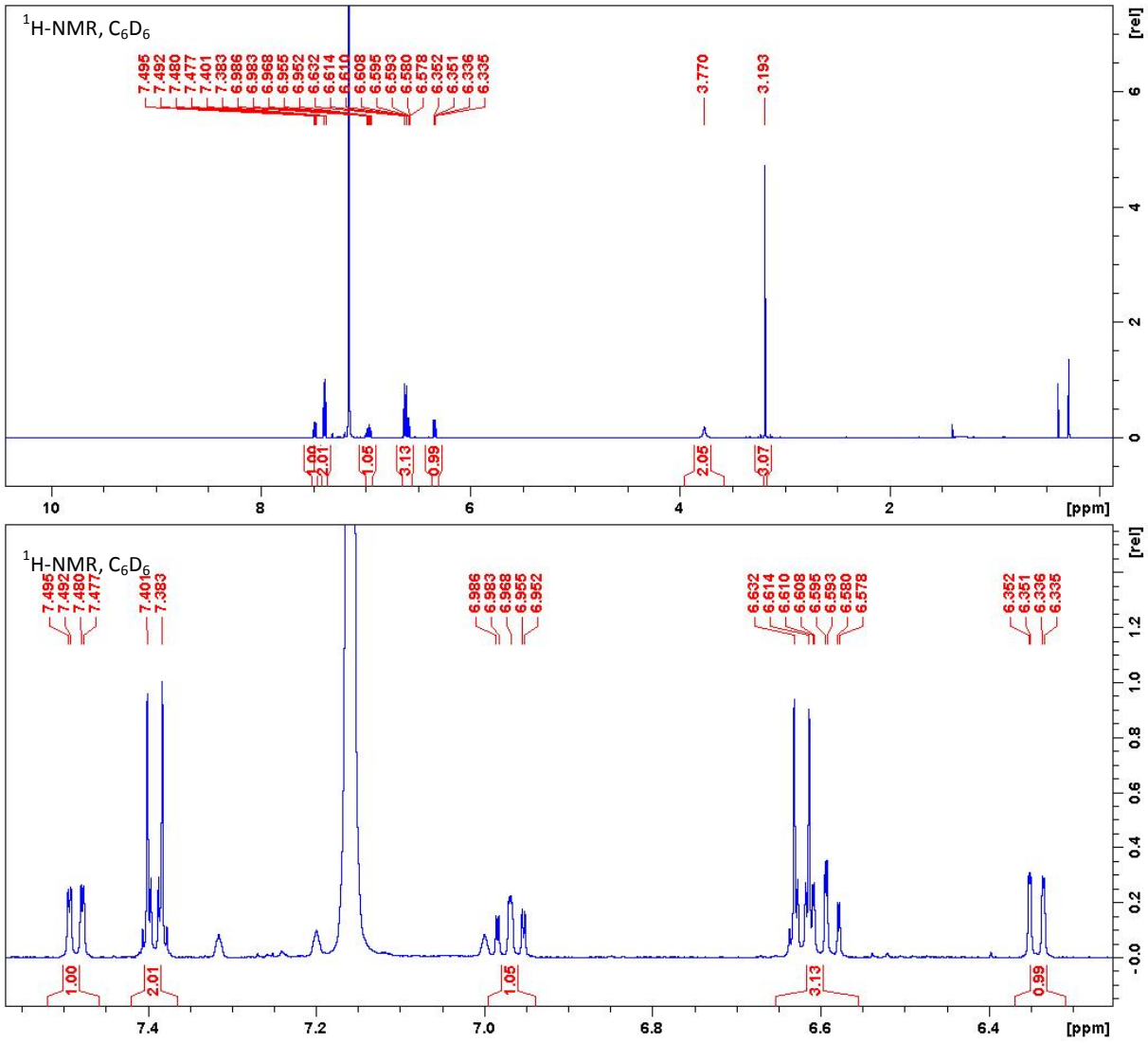
^{1}H-NMR (500 MHz, C_6D_6, 303 K) δ = 7.53 – 7.50 (m, 1H, H_{Ar}), 7.46 – 7.43 (m, 2H, H_{Ar}), 7.11 – 7.07 (m, 1H, H_{Ar}), 7.02 – 6.95 (m, 3H, H_{Ar}), 6.63 – 6.59 (m, 1H, H_{Ar}), 6.50 – 6.46 (m, 1H, H_{Ar}), 5.63 (ddt, *J* = 17.2, 10.2, 5.1 Hz, 1H, CH_{allyl}), 5.13 (dq, *J* = 17.2, 1.8 Hz, 1H, C$H_{2,allyl}$), 4.94 (dq, *J* = 10.3, 1.6 Hz, 1H, C$H_{2,allyl}$), 4.88 (s, 1H, N*H*), 3.40 (dt, *J* = 5.0, 1.7 Hz, 1H, C$H_{2,allyl}$); **^{13}C-NMR** (126 MHz, C_6D_6, 303 K) δ = 149.33 (C), 135.37 (CH), 132.68 (CH), 131.81 (CH), 130.36 (CH), 128.68 (CH), 128.33 (CH), 124.03 (C), 117.00 (CH), 115.82 (CH_2), 110.42 (CH), 108.18 (C), 95.70 (C), 87.10 (C), 46.02 (CH_2).

3.10 NMR spectra of starting materials

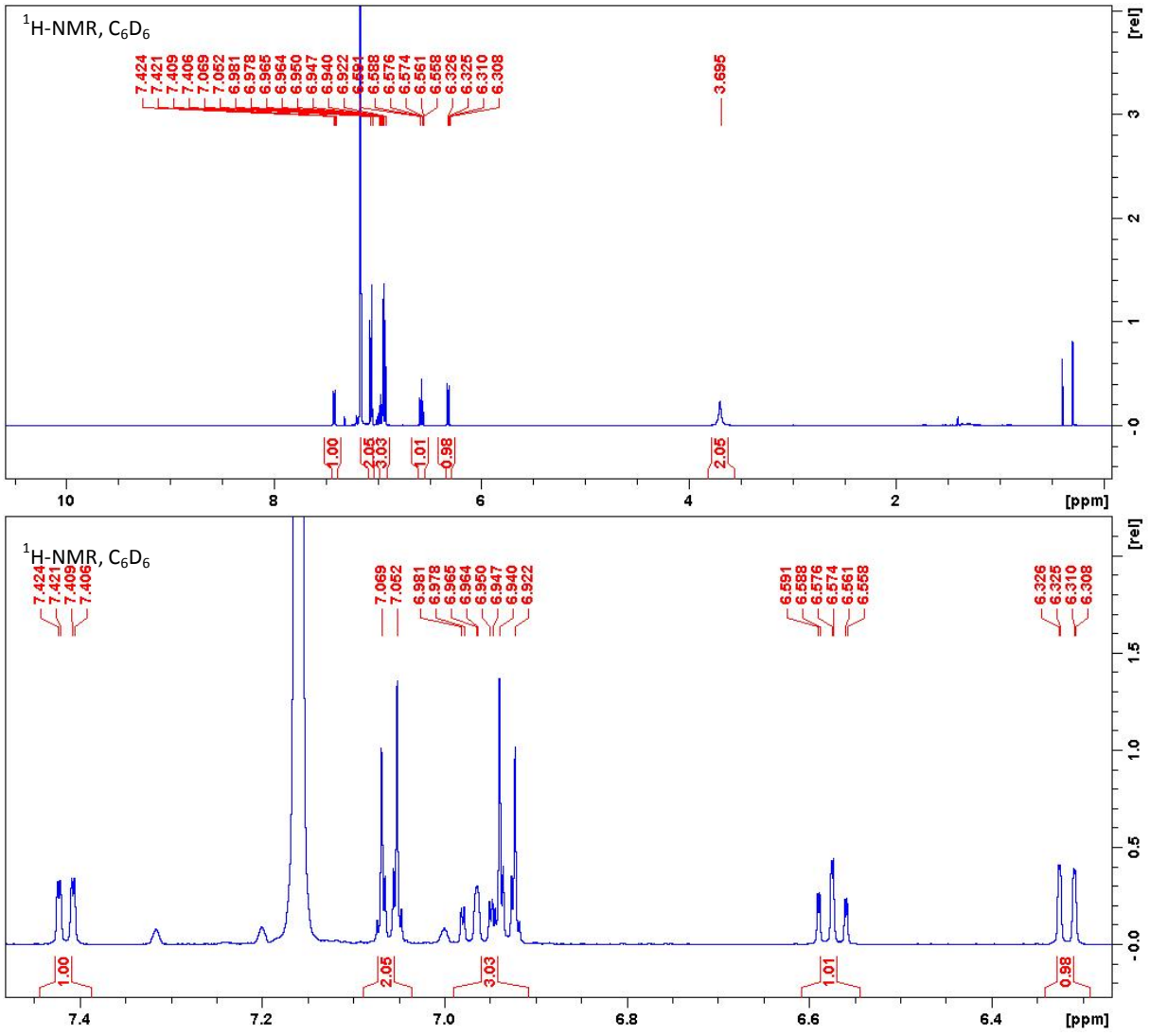
3.10.1 2-(phenylethynyl) aniline (Ia)



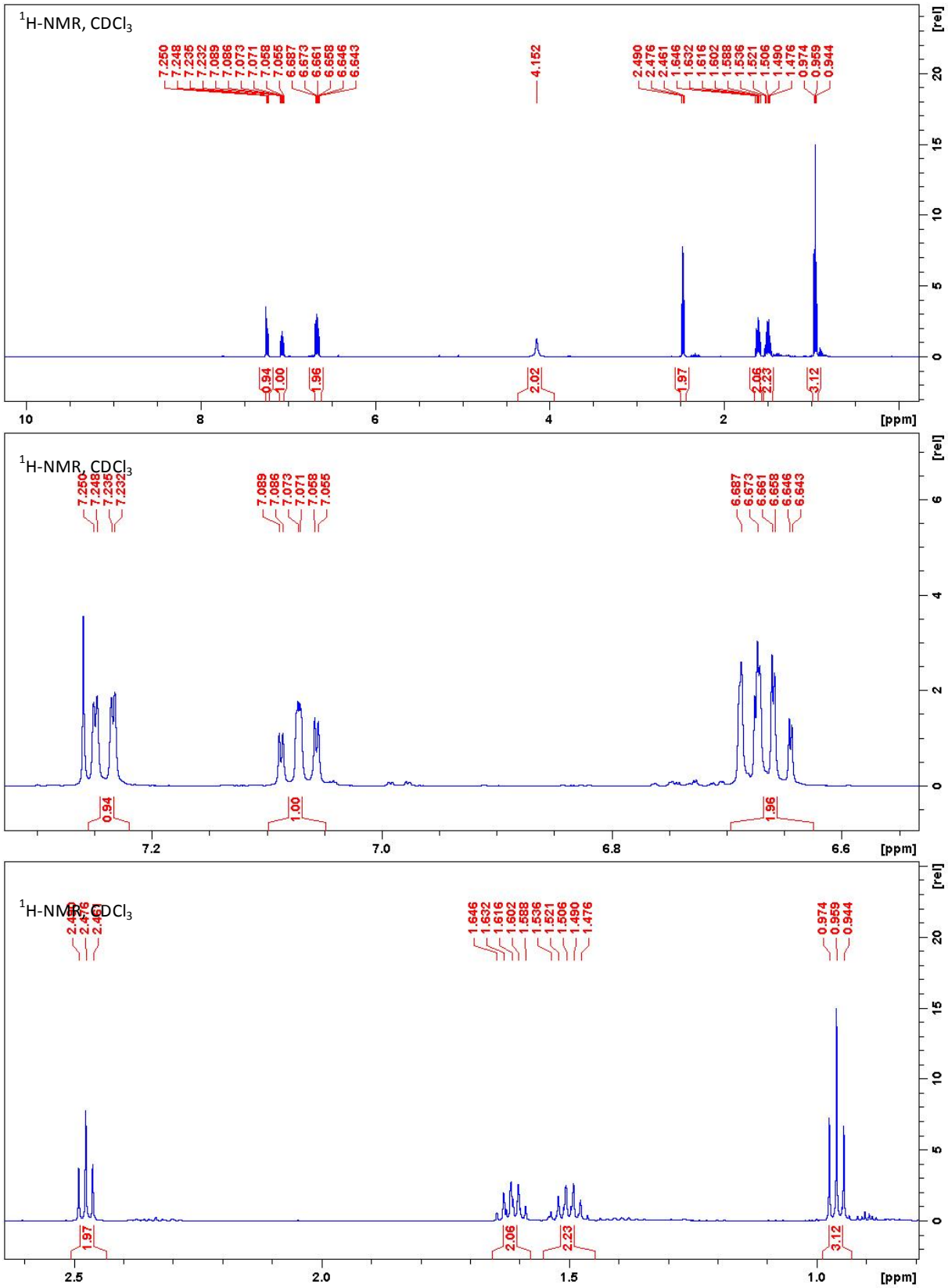
3.10.2 2-(*para*-ethynylanisol) aniline (Ii)



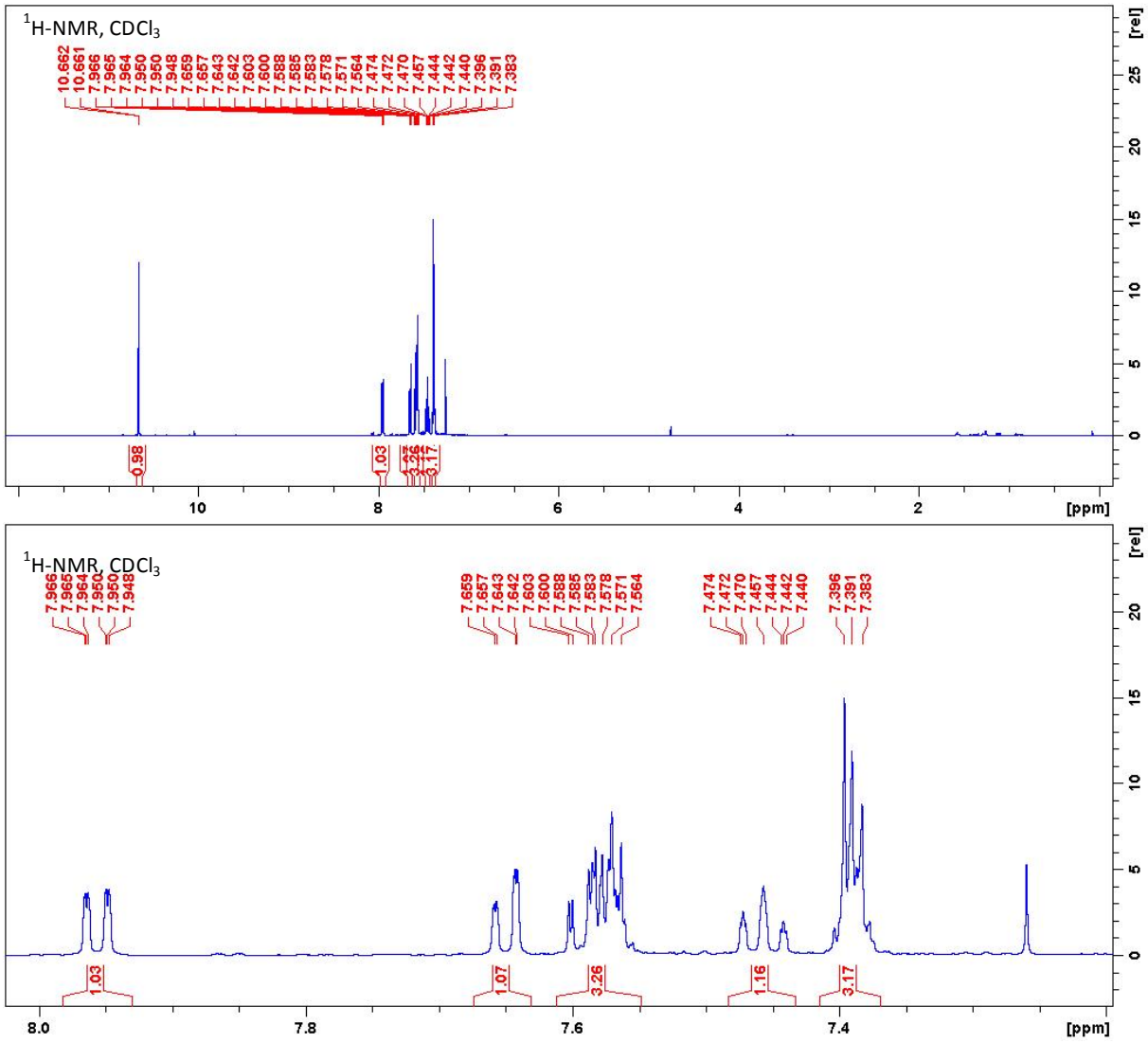
3.10.3 2-(*para*-chlorophenylethynyl) aniline (Ij)



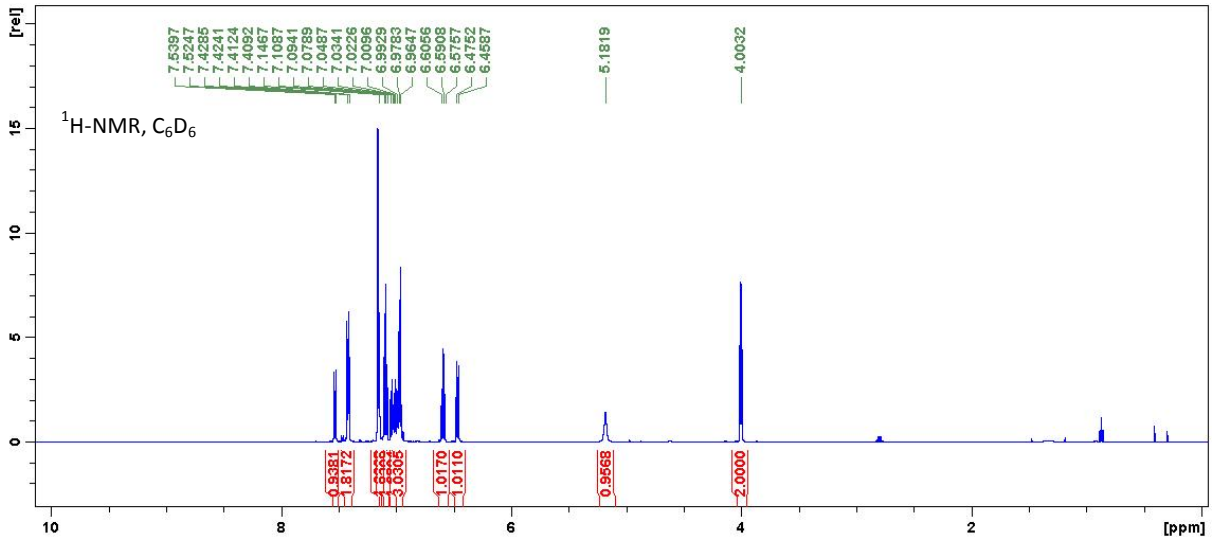
3.10.4 2-(hex-1-yn-1-yl) aniline (Ik)

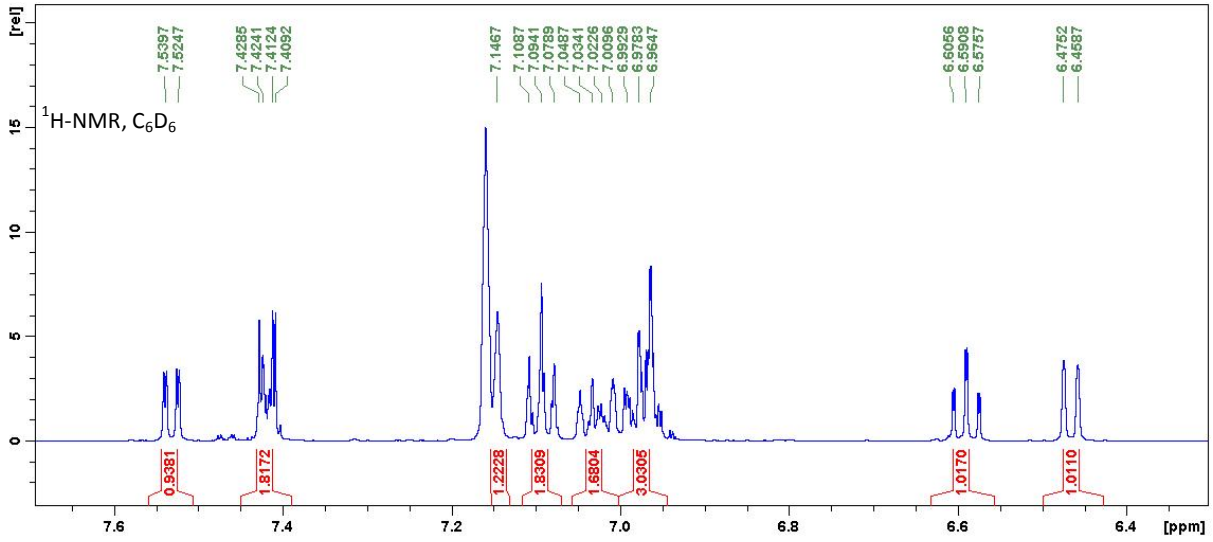


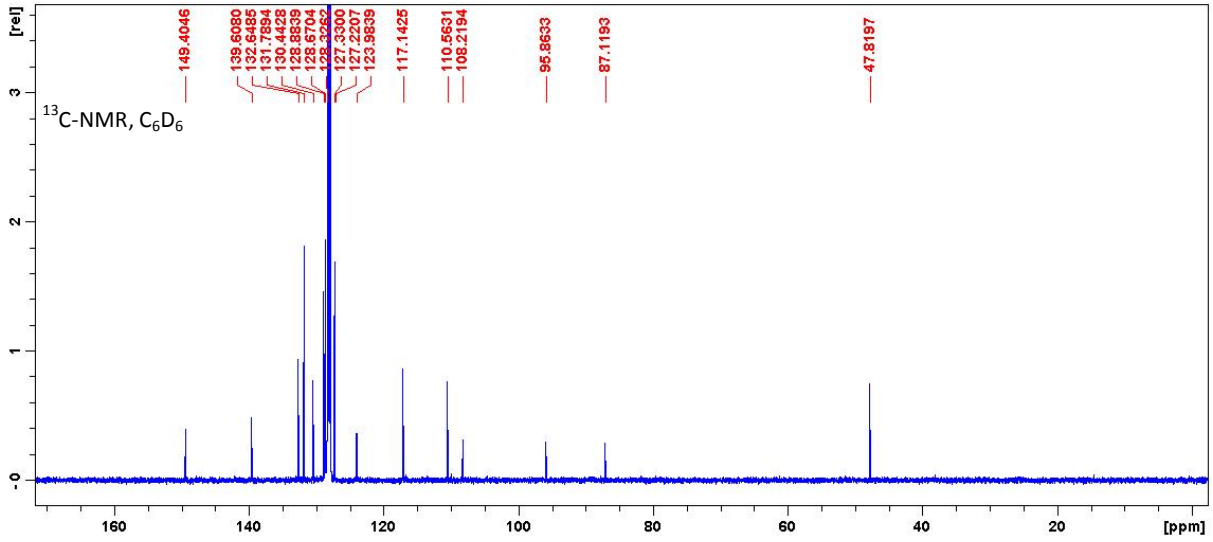
3.10.5 Synthesis of 2-(phenylethynyl) benzaldehyde (VI)



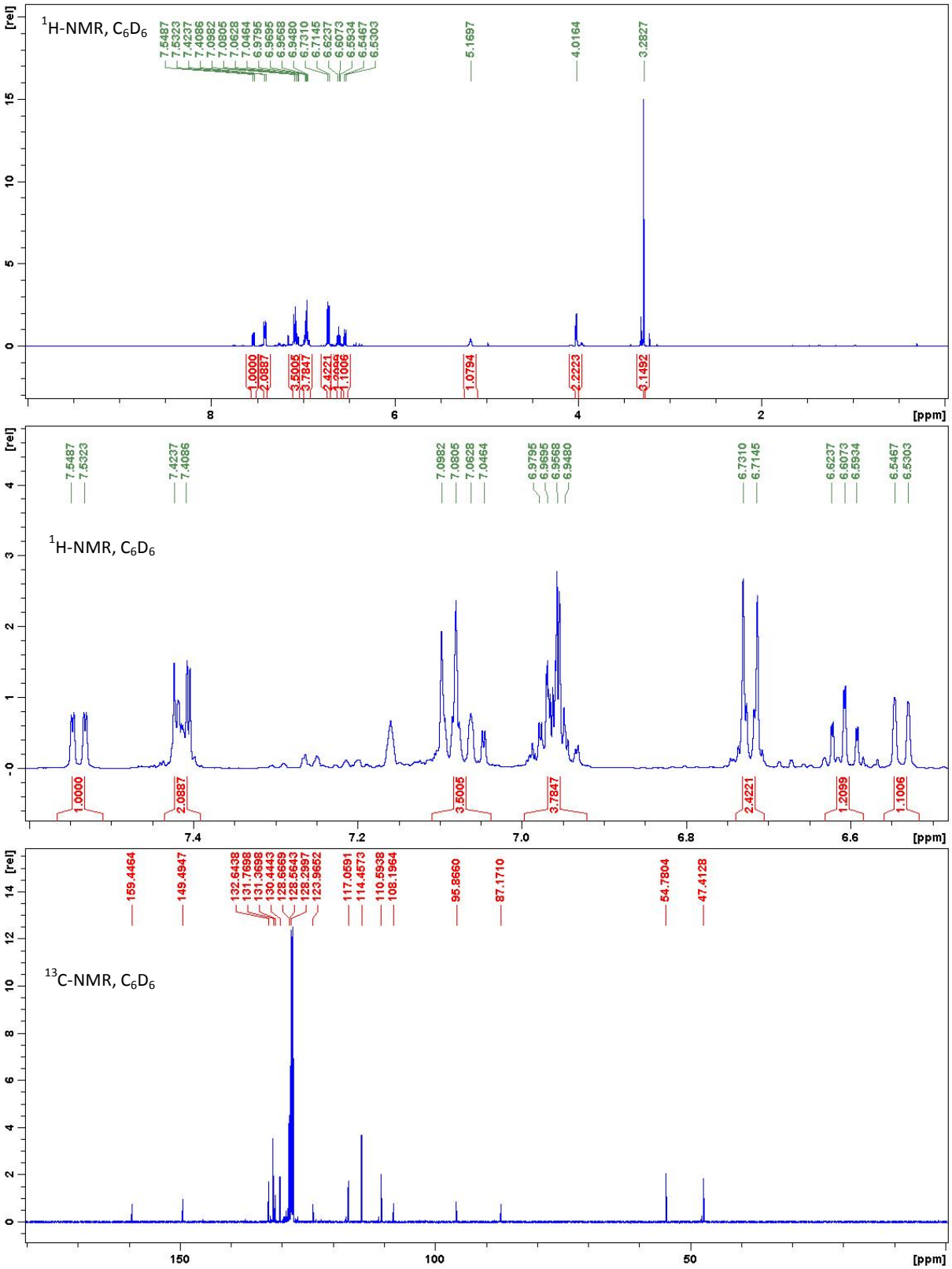
3.10.6 *N*-benzyl-2-(ethynylphenyl) aniline (1a)



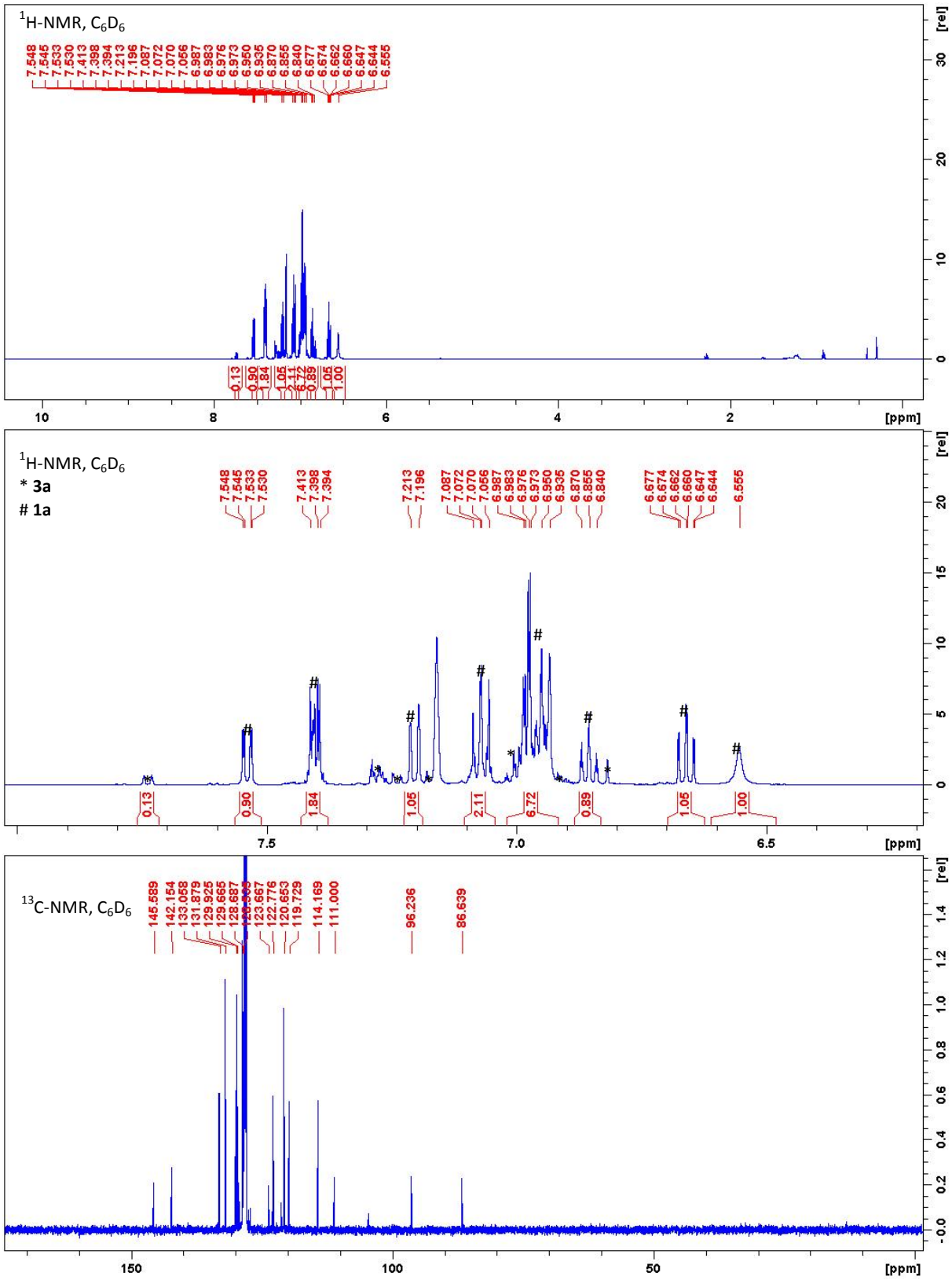




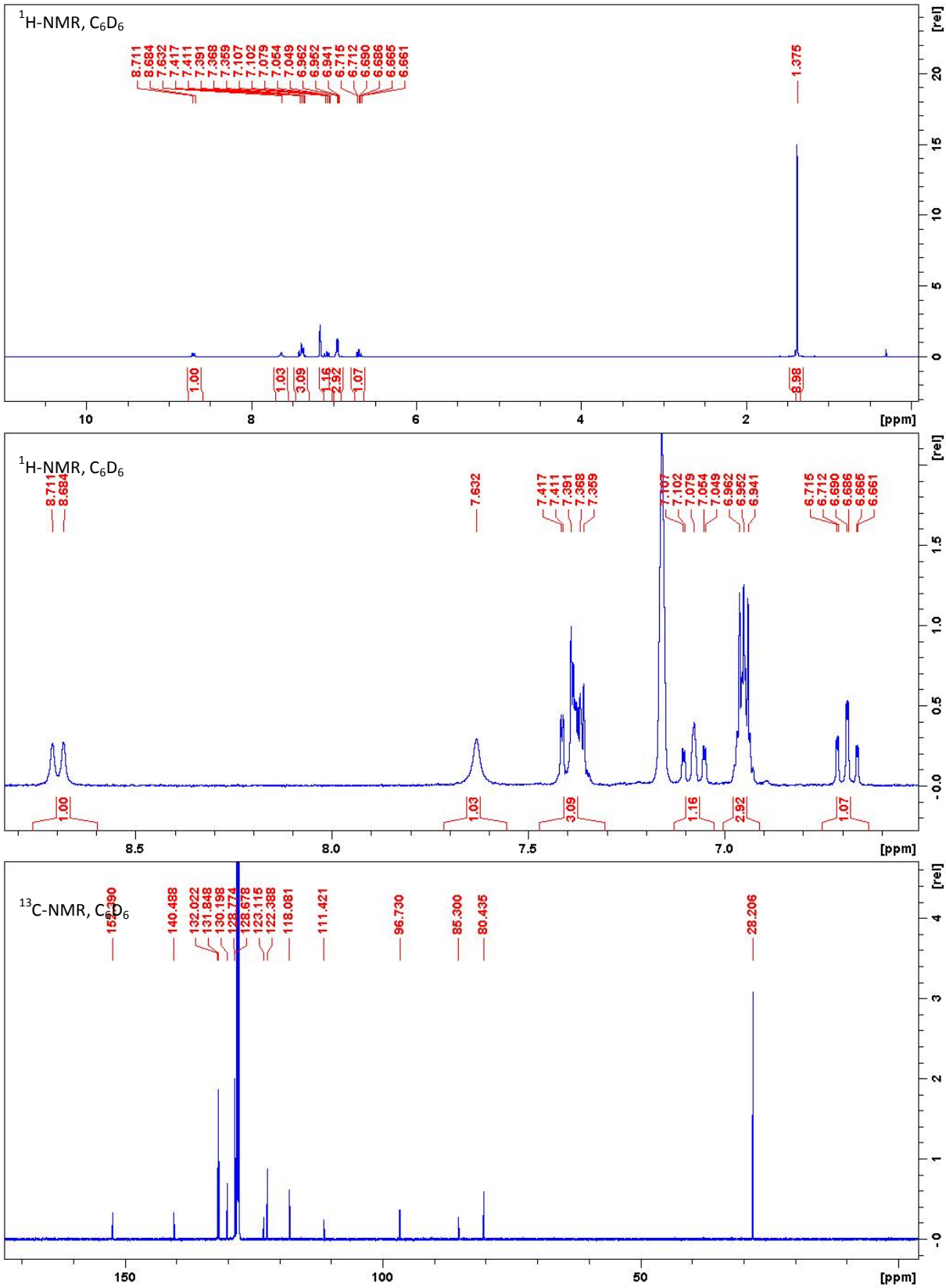
3.10.7 *N-para*-methoxybenzyl-2-(phenylethynyl) aniline (1b)



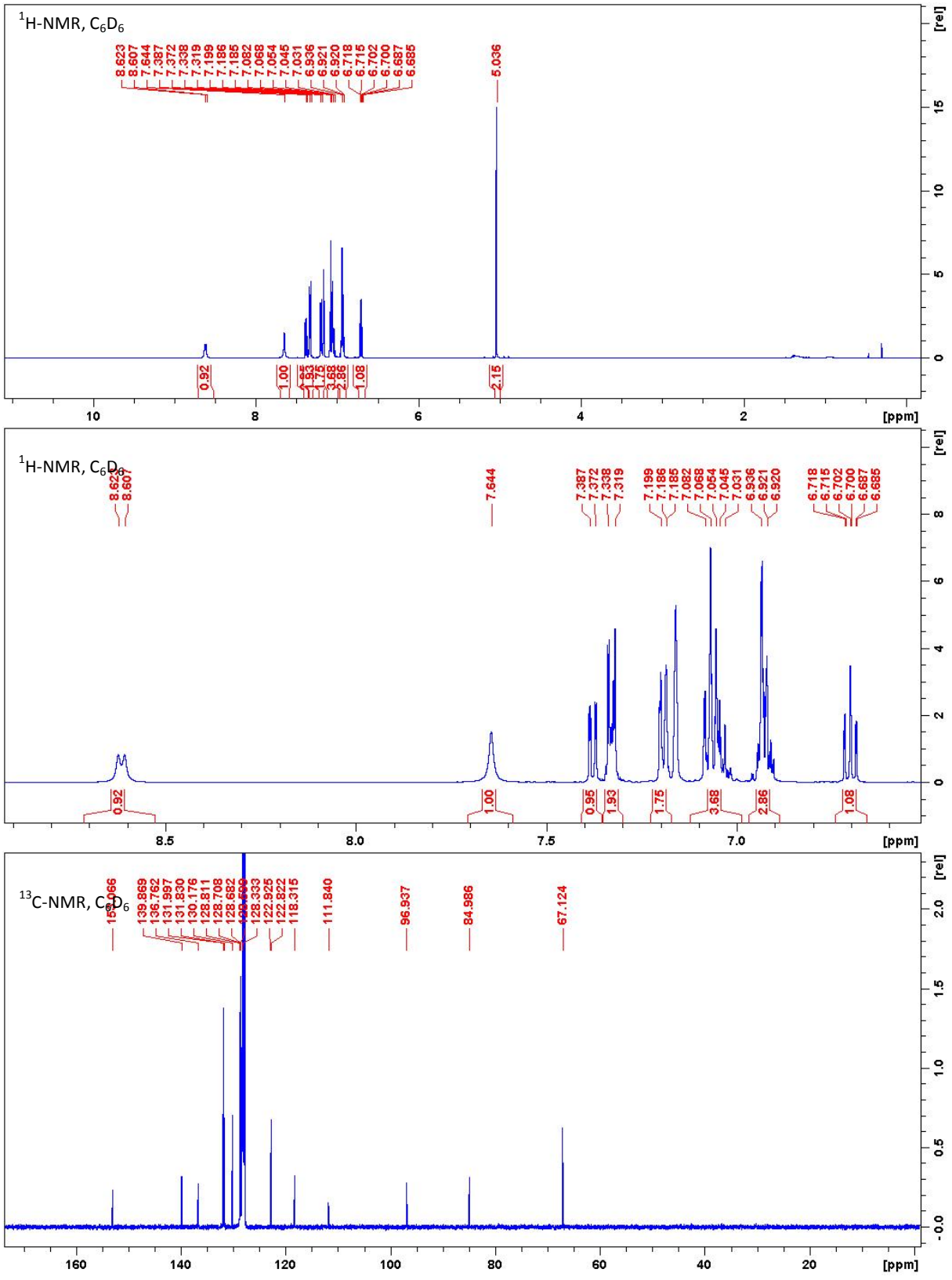
3.10.8 *N*-phenyl-2-(phenylethynyl) aniline (1c)



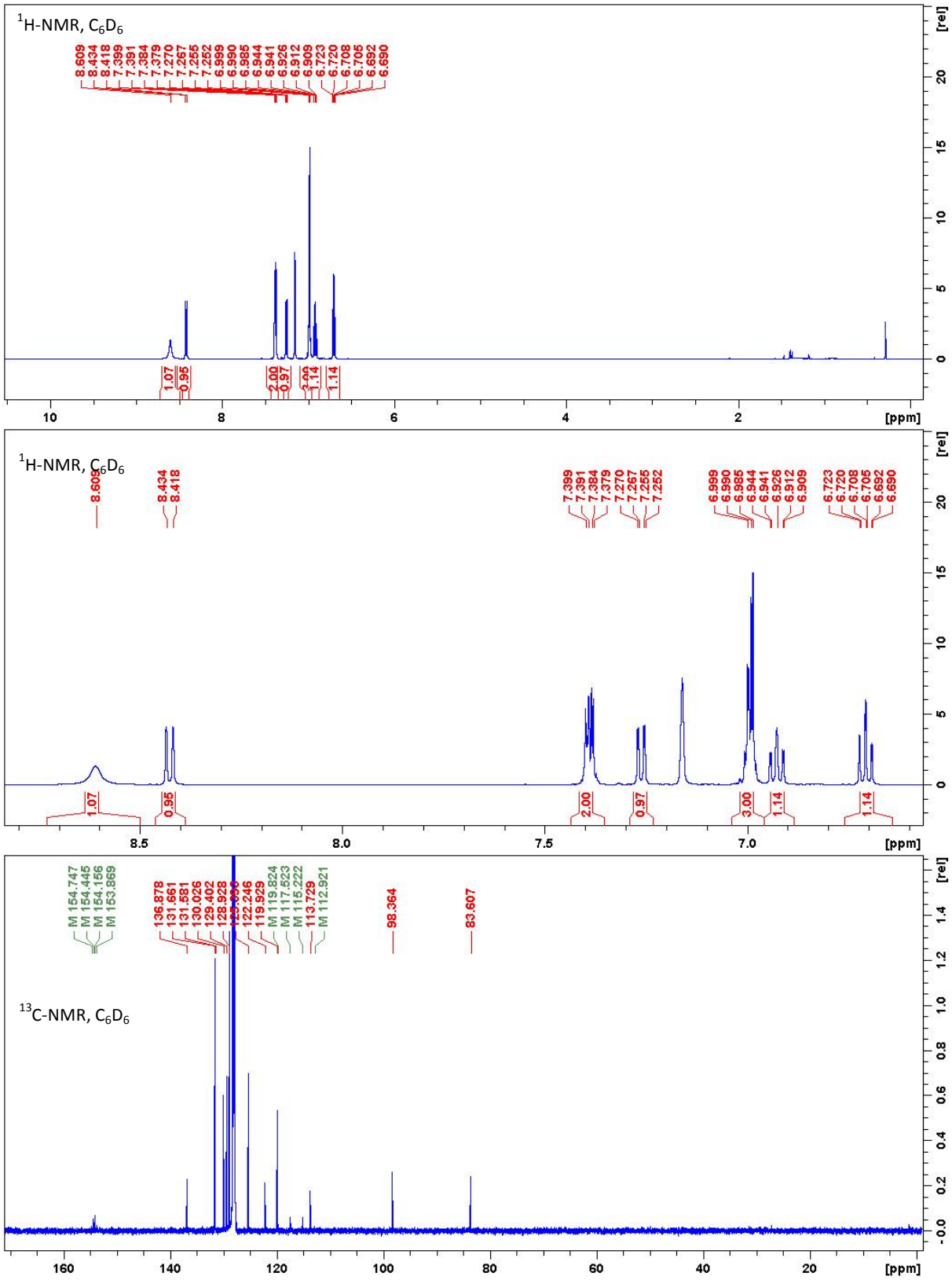
3.10.9 *tert*-butyl (2-(phenylethynyl)phenyl) carbamate (1d)

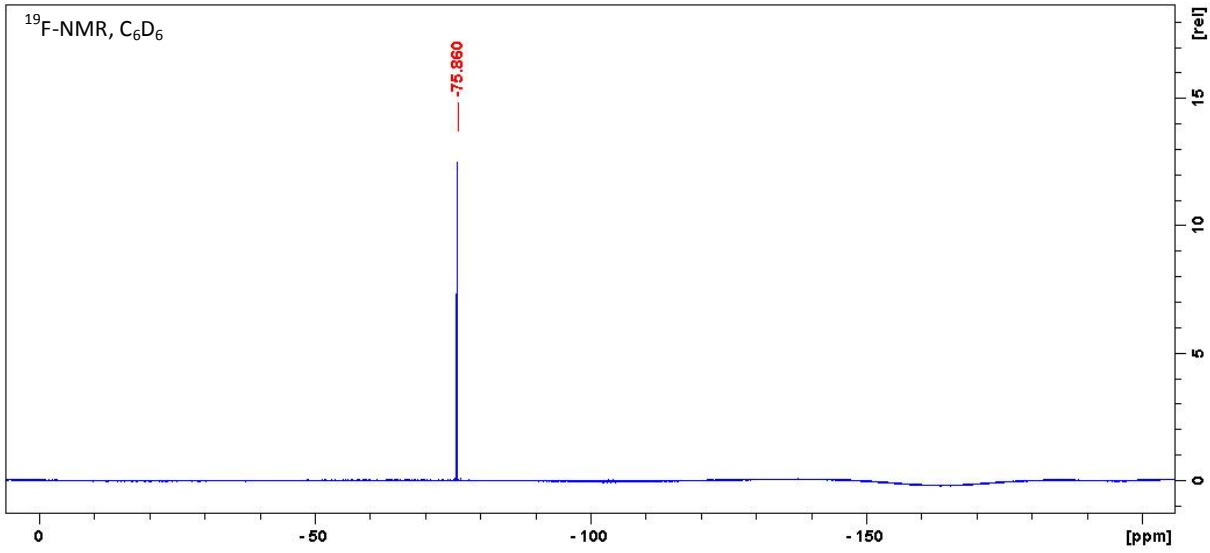


3.10.10 benzyl (2-(phenylethynyl)phenyl) carbamate (1e)

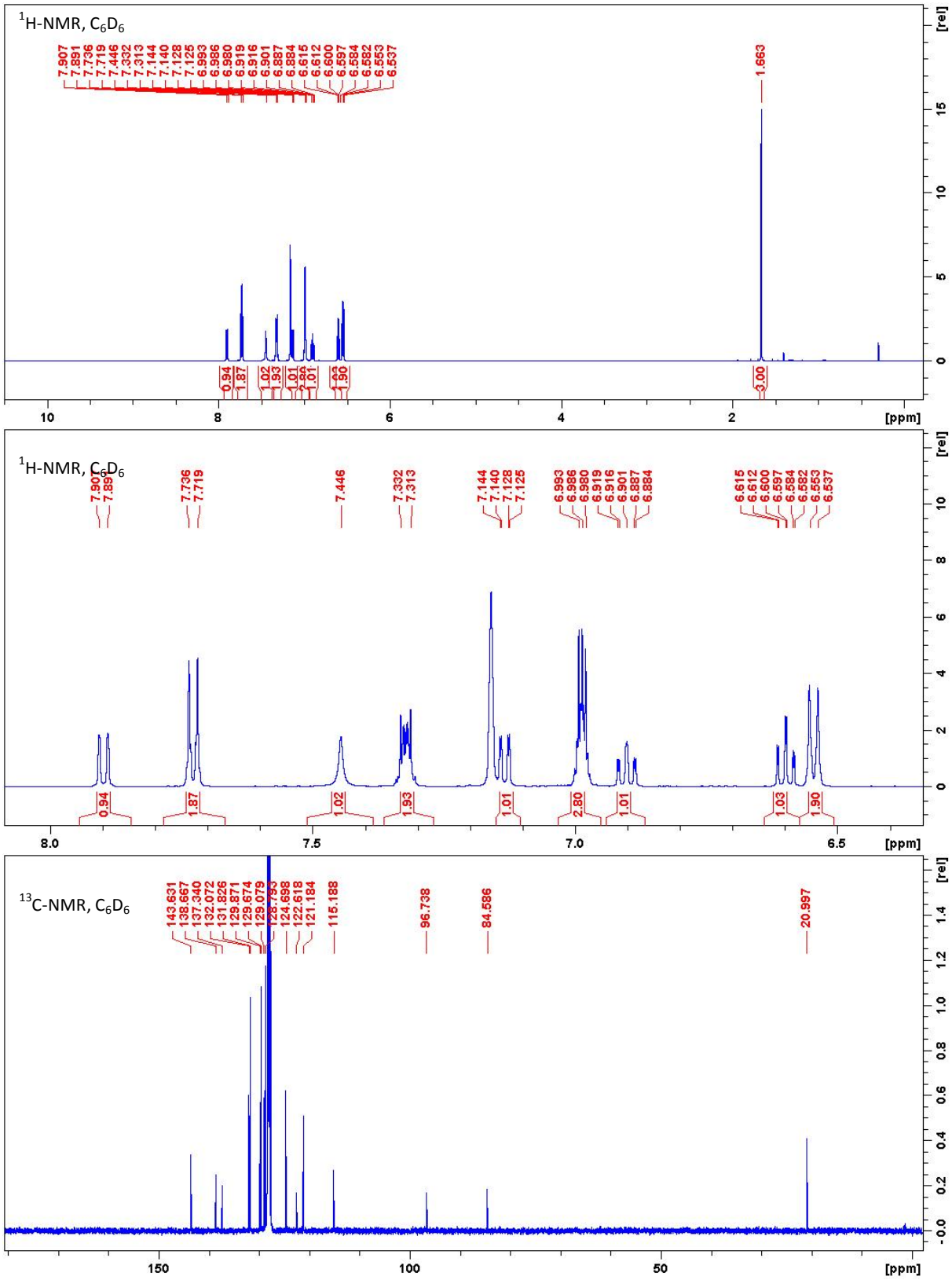


3.10.11 2,2,2-trifluoro-*N*-(2-(phenylethynyl)phenyl) acetamide (1f)

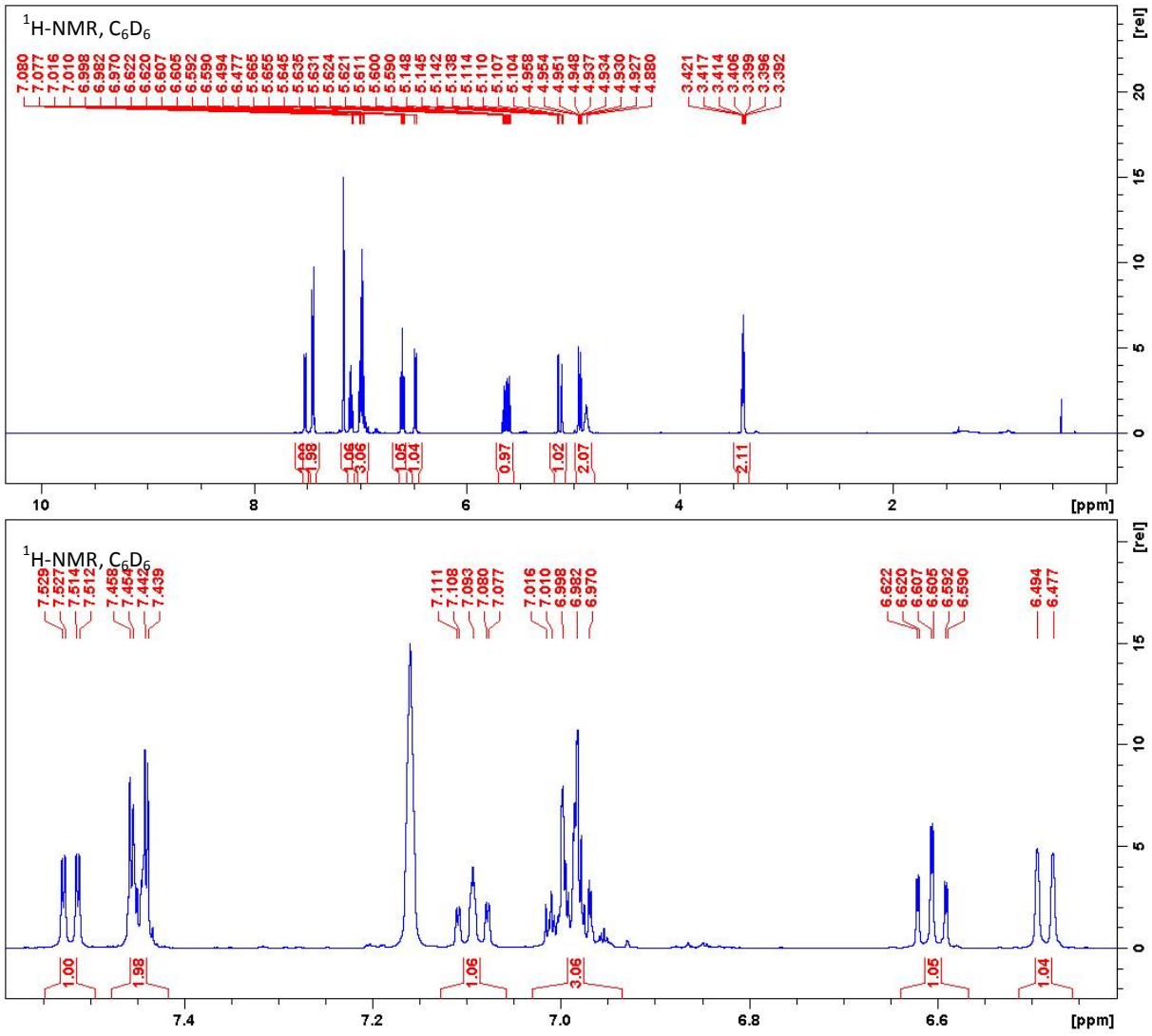


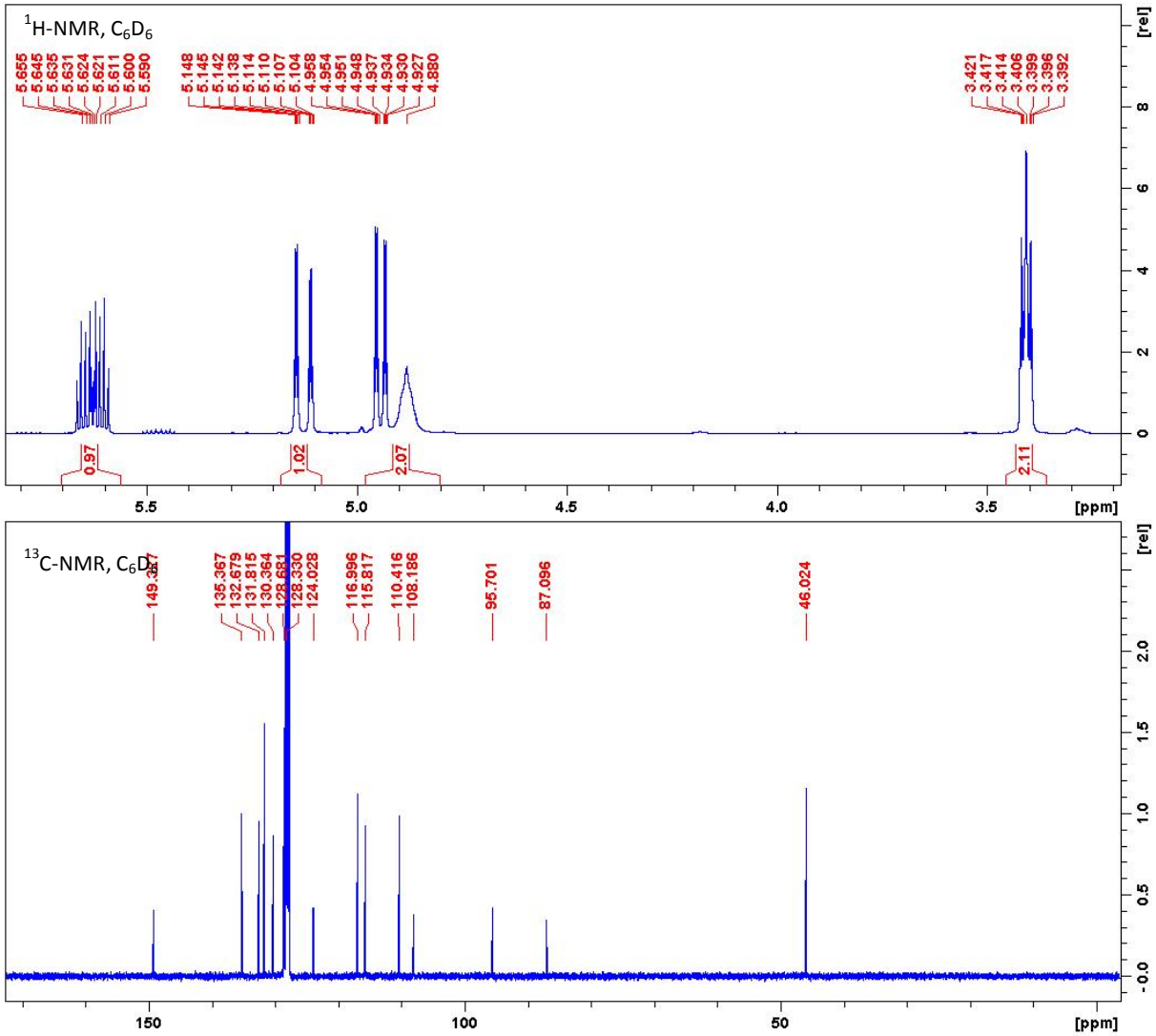

^{19}F-NMR, C_6D_6
-75.860
[rel]
15
10
5
0
0
-50
-100
-150
[ppm]

3.10.12 *N*-(2-(phenylethynyl)phenyl) toluenesulfonamide (1g)

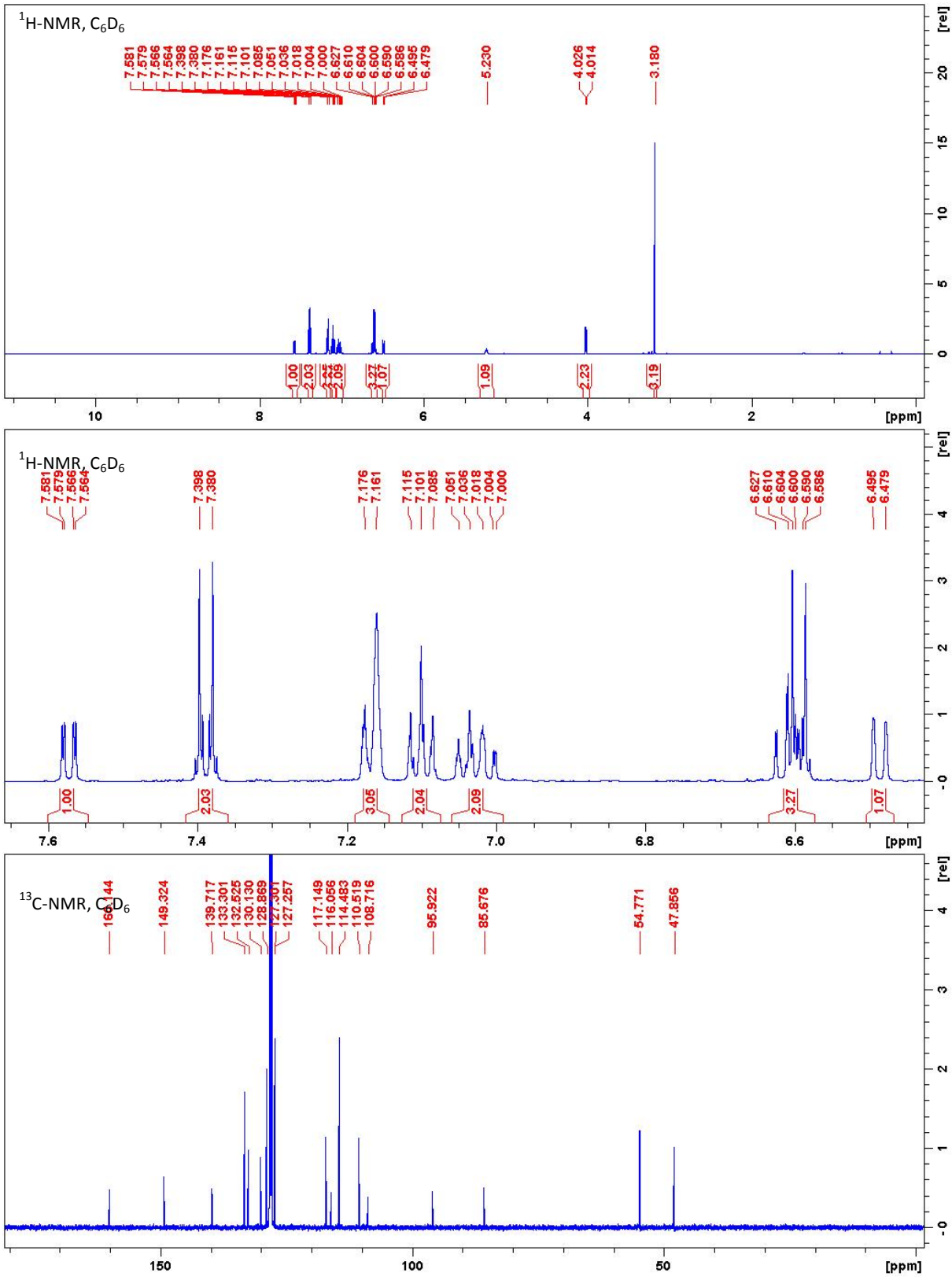


3.10.13 *N*-allyl-2-(phenylethynyl) aniline (1h)

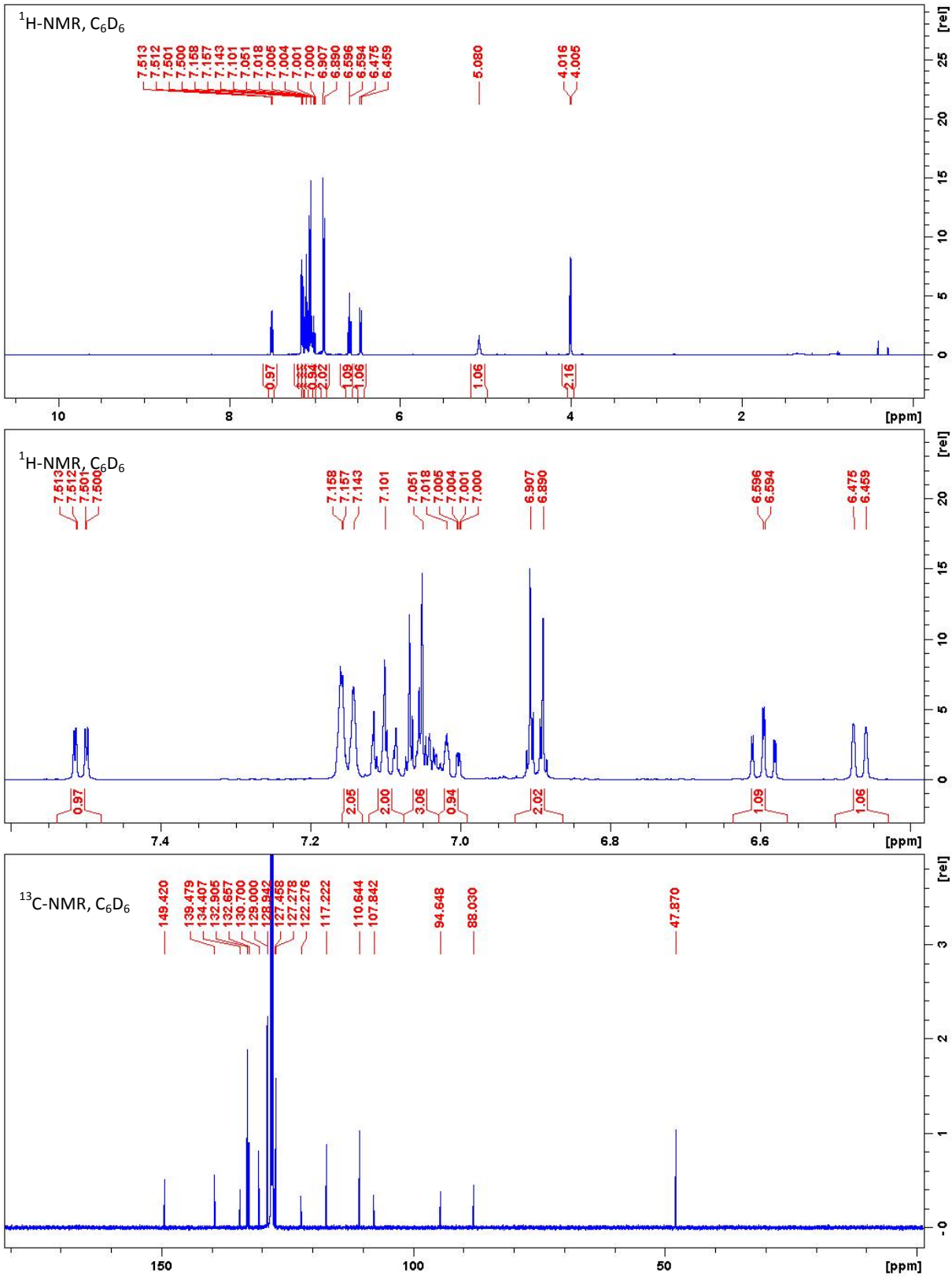



^{1}H-NMR, C_6D_6
5.655
5.645
5.635
5.631
5.624
5.621
5.611
5.600
5.590
5.148
5.145
5.142
5.138
5.114
5.110
5.107
5.104
4.958
4.954
4.951
4.948
4.937
4.934
4.930
4.927
4.880
3.421
3.417
3.414
3.406
3.399
3.396
3.392
0.97
1.02
2.07
2.11
[rel]
[ppm]
^{13}C-NMR, C_6D_6
149.387
135.367
132.679
131.815
130.364
128.681
128.330
124.028
116.996
115.817
110.416
108.186
95.701
87.096
46.024
[rel]
[ppm]

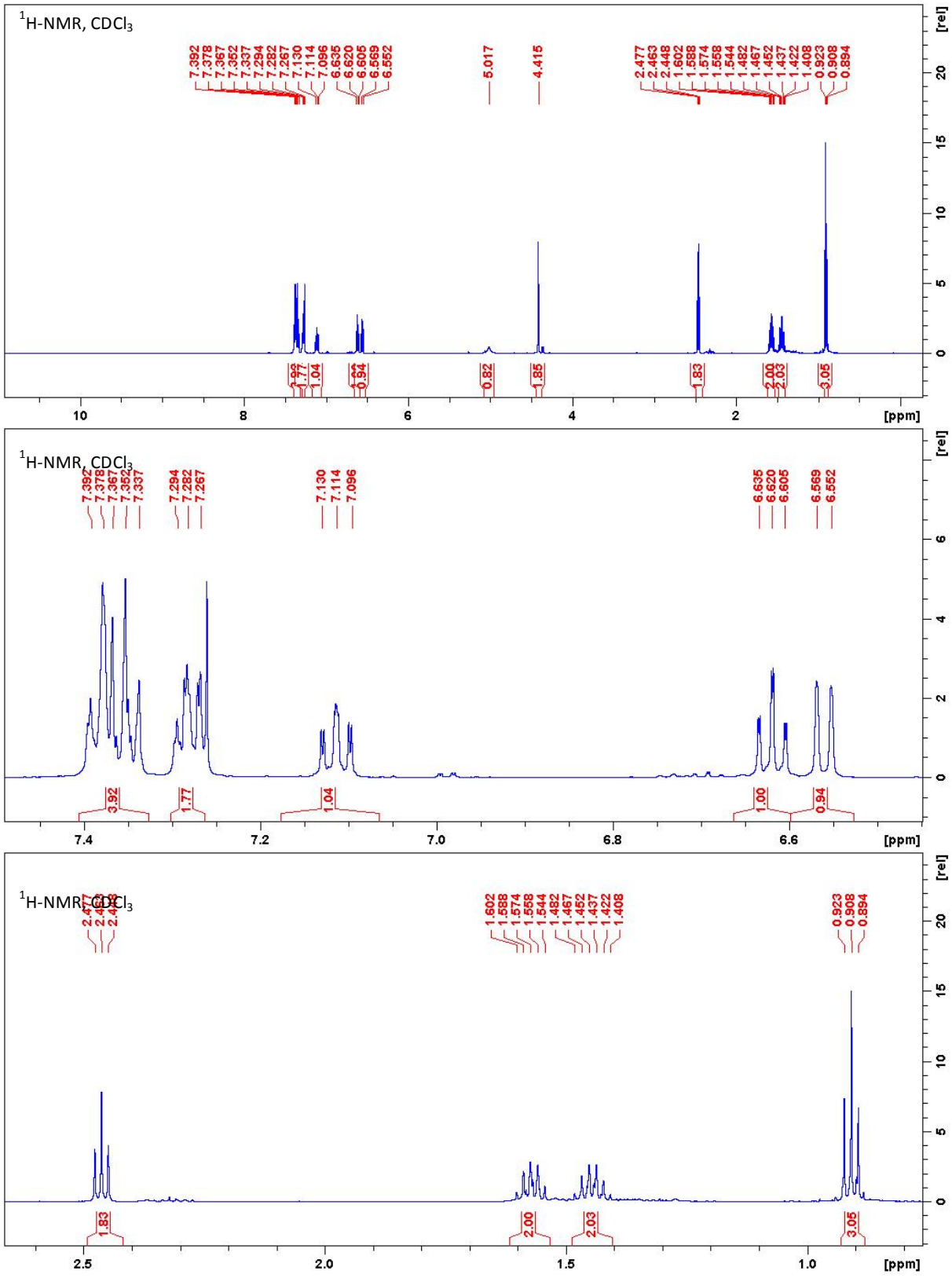
3.10.14 *N*-benzyl-2-(*para*-ethynylanisole) aniline (1i)

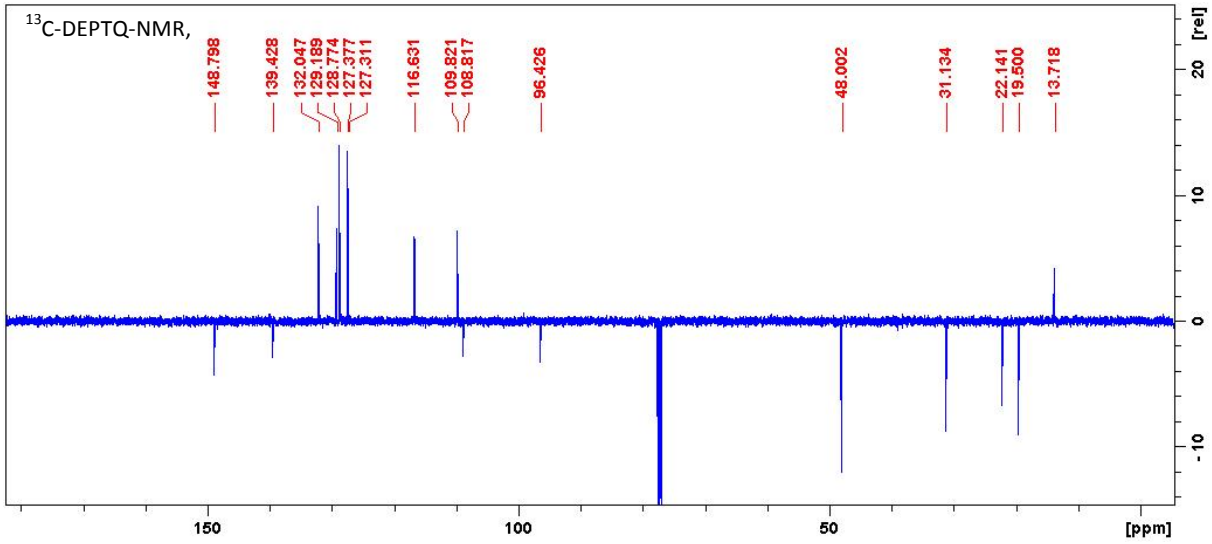


3.10.15 *N*-benzyl-2-(*para*-chlorophenylethynyl) aniline (1j)

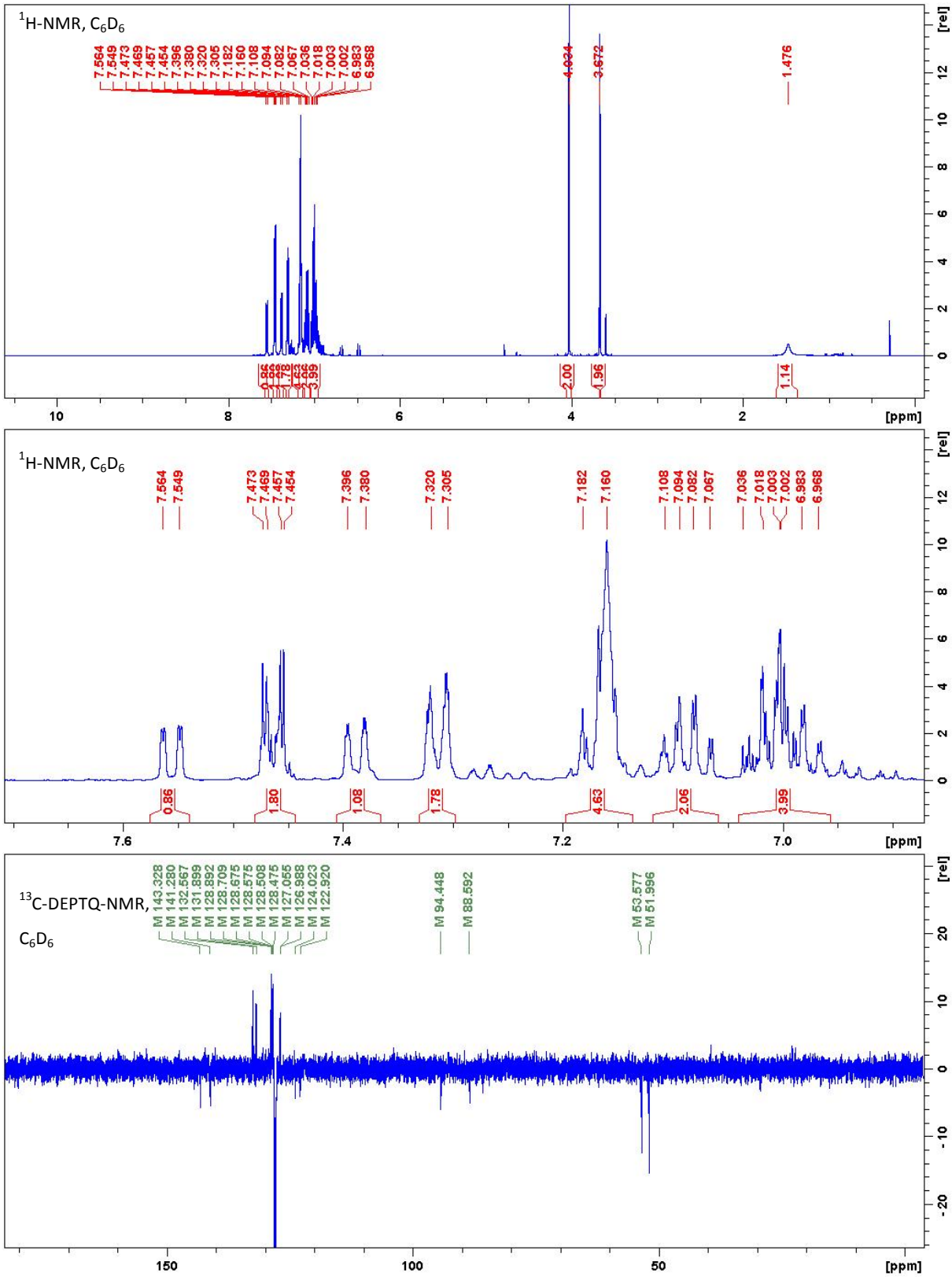


3.10.16 *N*-benzyl-2-(hex-1-yn-1-yl) aniline (1k)

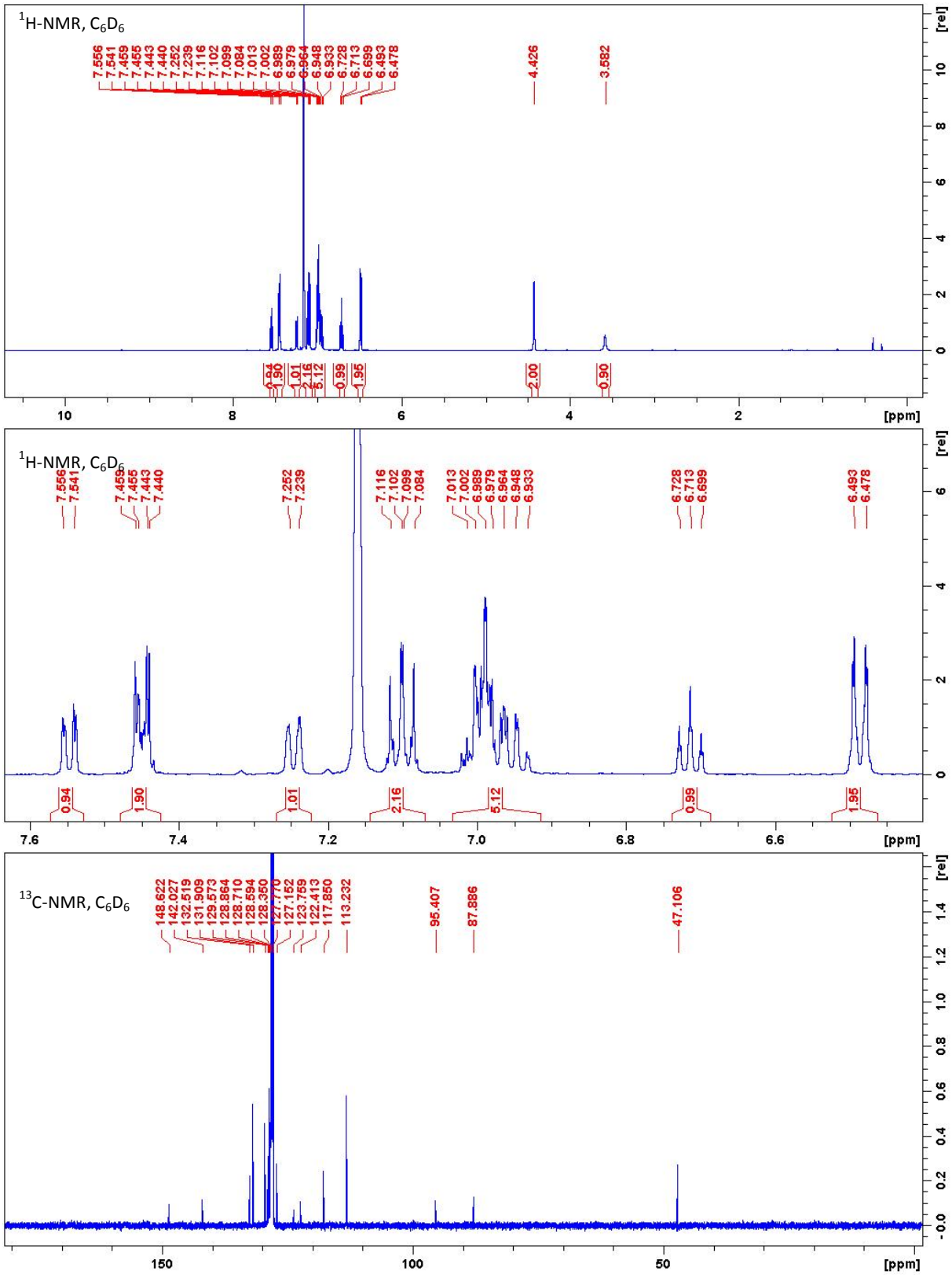



13C-DEPTQ-NMR,
148.798
139.428
132.047
129.189
128.774
127.377
127.311
116.631
109.821
108.817
96.426
48.002
31.134
22.141
19.500
13.718
20
10
0
- 10
[rel]
150
100
50
[ppm]

3.10.17 *N*-benzyl-1-(2-(phenylethynyl)phenyl) methanamine (6a)



3.10.18 *N*-(2-(phenylethynyl)benzyl) aniline (6b)



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