Kinetic resolution of donor-functionalised tertiary alcohols by Cu–H-catalysed stereoselective silylation using a strained silicon-stereogenic silane

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Electronic Supplementary Information

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1 General information

Reagents obtained from commercial suppliers were used without further purification unless otherwise noted. All reactions were performed in flame-dried glassware under a static pressure of argon. Liquids and solutions were transferred with syringes. Solvents were dried prior to use following standard procedures. Technical grade solvents for chromatography (cyclohexane, *t*-butyl methyl ether) were distilled before use. Analytical thin layer chromatography was performed on silica gel SIL G-25 glass plates by *Macherey-Nagel* and flash chromatography on silica gel 60 (40-63 μm, 230-400 mesh, ASTM) by *Merck* using the indicated solvents. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or C_6D_6 on *Bruker* AV 300 and *Bruker* AV 400 instruments. Chemical shifts are reported in ppm with the solvent reference as the internal standard ($CDCl_3$: δ = 7.26, C_6D_6: δ = 7.16). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, m_c = centrosymmetrical multiplet, br = broad), coupling constants (Hz) and integration. AB signals in the ^{1}H NMR spectra were denoted by the symbol "$^{\lozenge}$". Residual solvent peaks for cyclohexane and *t*-butyl methyl ether in the ^{1}H and ^{13}C NMR spectra were shown with a star (∗). Infrared spectra were recorded on a *Digilab* Excalibur Series FTS 4000 spectrometer. Intensities of the bands are abbreviated as broad (br), strong (s), medium (m), and weak (w). Gas liquid chromatography (GLC) was performed on a *Shimadzu* GC-17A with a SE-54 (30 m × 0.32 mm × 0.25 μm film thickness) column by *CS-Chromatographie Service* using the following program: column flow 1.7 mL/min N_2, start at 40°C, heat rate 10°C/min to 280°C, 5 min at 280°C. Enantiomeric ratios were determined by analytical HPLC analysis on an *Agilent* 1200 Series instrument with a chiral stationary phase using *Daicel Chiralpak* IA and *Daicel Chiralpak* IB columns (*n*-heptane:*i*-propanol mixtures as solvent). Optical rotations were measured on a *Perkin Elmer* 341 polarimeter. Melting points (m.p.) were determined with a *Stuart Scientific MP3* apparatus and are not corrected. High resolution mass spectrometry (HRMS) was performed by electron spray ionization mass spectrometry (ESI-MS) using a *Bruker* MicroTOF instrument, elemental analysis were obtained using a *Elementaranalysensysteme* VarioEL III instrument.

2 Characterisation data of 14–24, 26 and 28

(^{Si}*S**,*R**)-2-[2-(1-*tert*-Butyl-1-silaindan-1-yloxy)-2-phenyl-4-(trimethylsilanyl)-but-3-ynyl]pyridine [(^{Si}*S**,*R**)-14]

Analytical data for (^{Si}*S**,*R**)-**14**: Yield: 51%. GLC (SE-54): t_R = 26.6, 26.8 min. R_f = 0.59 (cyclohexane–*t*-butyl methyl ether = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.07 (s, 9H, Si(CH_3)$_3$), 0.83$^{\lozenge}$ (ddd, 15.5, 9.1, 4.3 Hz, 1H, 2''-H_A), 0.96$^{\lozenge}$ (m_c, 1H, 2''-H_B), 0.96 (s, 9H, C(CH_3)$_3$), 2.66$^{\lozenge}$ (ddd, *J* = 16.9, 9.9, 4.0 Hz, 1H, 3''-H_A), 2.75$^{\lozenge}$ (ddd, *J* = 16.9, 9.1, 6.4 Hz, 1H, 3''-H_B), 3.26$^{\lozenge}$ (d, *J* = 12.8 Hz, 1H, 1-H_A), 3.47$^{\lozenge}$ (d, *J* = 12.8 Hz, 1H, 1-H_B), 6.95 (dd, *J* = *J* = 7.2 Hz, 1H, Ar-H), 7.02–7.20 (m, 7H, Ar-H), 7.31 (d, *J* = 7.7 Hz, 1H, 3'-H), 7.45 (dd, *J* = 7.8, 1.8 Hz, 2H, Ar-H), 7.53 (ddd, *J* = *J* = 7.7 Hz, *J* = 1.7 Hz, 1H, 4'-H), 8.46 (ddd, *J* = 4.8, 1.7, 0.8 Hz, 1H, 6'-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.2, 6.9, 19.2, 26.2, 30.2, 55.8, 75.6, 94.1,

106.2, 121.7, 125.1, 125.4, 125.9, 126.2, 127.5, 127.8, 129.5, 133.0, 135.1, 135.6, 144.5, 148.7, 153.5, 157.0. IR (film) 2173 (w, C≡C) cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{37}NOSi_2$ (M + Na^+): 506.2306; found: 506.2298. Anal. calcd for $C_{30}H_{37}NOSi_2$ (483.80): C, 74.48; H, 7.71; N, 2.90; found: C, 74.26; H, 7.86; N, 2.78. The diastereomeric ratio was determined by integration of baseline separated ^{1}H NMR signals of Si(CH_3)$_3$ at –0.04 (s, 9H, minor diastereomer) and 0.07 (s, 9H, major diastereomer) ppm.

Analytical data for (^{Si}*S*,*R*)-**14** (d.r. = 76:24, Entry 1, Table 2): Yield: 58%. $[\alpha]_D^{20}$ = –29.9, $[\alpha]_{578}^{20}$ = –31.3, $[\alpha]_{546}^{20}$ = –35.3, $[\alpha]_{436}^{20}$ = –62.5, $[\alpha]_{365}^{20}$ = –102 (*c* = 0.515, $CHCl_3$).

(^{Si}*R*,S)-2-[2-(1-*tert*-Butyl-1-silaindan-1-yloxy)-2-*p*-tolyl-4-(trimethylsilanyl)-but-3-ynyl]pyridine [(^{Si}*R*,S**)-15]**

Analytical data for (^{Si}*R**,S*)-**15**: Yield: 61%. R_f = 0.58 (cyclohexane–*t*-butyl methyl ether = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.05 (s, 9H, Si(CH_3)$_3$), 0.81$^\diamond$ (ddd, 15.4, 9.0, 4.4 Hz, 1H, 2''-H_A), 0.94 (s, 9H, C(CH_3)$_3$), 0.95$^\diamond$ (m_c, 1H, 2''-H_B), 2.69 (m_c, 2H, 3''-H), 3.25$^\diamond$ (d, *J* = 12.9 Hz, 1H, 1-H_A), 3.46$^\diamond$ (d, *J* = 12.9 Hz, 1H, 1-H_B), 6.93–6.97 (m, 3H, Ar-H), 7.02 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.09–7.13 (m, 2H, 5'-H, Ar-H), 7.17 (ddd, *J* = *J* = 7.5 Hz, *J* = 1.3 Hz, 1H, Ar-H), 7.32–7.34 (m, 3H, 3'-H, Ar-H), 7.54 (ddd, *J* = *J* = 7.7 Hz, *J* = 1.8 Hz, 1H, 4'-H), 8.46 (ddd, *J* = 4.9, 1.8, 0.8 Hz, 1H, 6'-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.2, 7.0, 19.2, 21.3, 26.2, 30.3, 55.8, 75.5, 93.9, 106.5, 121.7, 125.1, 125.4, 125.9, 126.1, 128.5, 129.4, 133.1, 135.1, 135.7, 137.1, 141.7, 148.7, 153.5, 157.2. IR (film) 2172 (w, C≡C) cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{39}NOSi_2$ (M + Na^+): 520.2462; found: 520.2452. Anal. calcd for $C_{31}H_{39}NOSi_2$ (597.83): C, 74.79; H, 7.90; N, 2.81; found: C, 74.59; H, 8.01; N, 2.70. The diastereomeric ratio was determined by integration of baseline separated ^{1}H NMR signals of Si(CH_3)$_3$ at –0.06 (s, 9H, minor diastereomer) and 0.05 (s, 9H, major diastereomer) ppm.

Analytical data for (^{Si}*R*,S)-**15** (d.r. = 78:22, Entry 2, Table 2): Yield: 58%. $[\alpha]_D^{20}$ = +21.6, $[\alpha]_{578}^{20}$ = +21.9, $[\alpha]_{546}^{20}$ = +25.5, $[\alpha]_{436}^{20}$ = +45.2, $[\alpha]_{365}^{20}$ = +73.3 (*c* = 0.660, $CHCl_3$).

(^{Si}*S*,R)-2-[2-(1-*tert*-Butyl-1-silaindan-1-yloxy)-2-(2-methoxyphenyl)-4-(trimethylsilanyl)-but-3-ynyl]pyridine [(^{Si}*S*,R**)-16]**

Analytical data for (^{Si}*S**,*R**)-**16**: Yield: 59%. R_f = 0.42 (cyclohexane–*t*-butyl methyl ether = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.02 (s, 9H, Si(CH_3)$_3$), 0.77$^\diamond$ (ddd, 15.4, 9.4, 4.4 Hz, 1H, 2''-H_A), 0.95$^\diamond$ (m_c, 1H, 2''-H_B), 0.94 (s, 9H, C(CH_3)$_3$), 2.60$^\diamond$ (ddd, *J* = 16.1, 10.0, 4.5 Hz, 1H, 3''-H_A), 2.73$^\diamond$ (ddd, *J* = 16.1, 9.3, 5.9 Hz, 1H, 3''-H_B), 3.60$^\diamond$ (d, *J* = 13.1 Hz, 1H, 1-H_A), 3.80$^\diamond$ (d, *J* = 13.1 Hz, 1H, 1-H_B), 3.68 (s, 3H, OCH_3), 6.72 (dd, *J* = 8.2, 1.0 Hz, 1H, Ar-H), 6.77 (ddd, *J* = *J* = 7.6 Hz, *J* = 1.1 Hz, 1H, Ar-H), 6.99–7.04 (m, 2H, Ar-H), 7.10 (ddd, *J* = 7.6, 5.0, 1.1 Hz, 1H, 5'-H), 7.16–7.20 (m, 2H, Ar-H), 7.29 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.34 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.52 (ddd, *J* = *J* = 7.6 Hz, *J* = 1.9 Hz, 1H, 4'-H), 7.57 (dd, *J* = 7.7, 1.7 Hz, 1H, Ar-H), 8.48 (ddd, *J* = 5.0, 1.9, 0.9 Hz, 1H, 6'-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.2, 7.1, 19.3, 26.3, 30.2, 50.7, 55.1, 74.7, 92.1, 106.9, 111.5, 119.9, 121.4, 125.0, 125.5, 125.9, 128.1, 129.1, 129.3, 131.5, 133.1, 134.9, 136.2, 148.7, 153.4, 157.0, 158.0. IR (ATR) 2170 (w, C≡C) cm^{-1}.

HRMS (ESI) calcd for $C_{31}H_{39}NO_2Si_2$ (M + H^+): 514.2592; found: 514.2580. Anal. calcd for $C_{31}H_{39}NO_2Si_2$ (513.83): C, 72.46; H, 7.65; N, 2.73; found: C, 72.44; H, 7.95; N, 2.65. The diastereomeric ratio was determined by integration of baseline separated ^{1}H NMR signals of Si(CH_3)$_3$ at –0.08 (s, 9H, minor diastereomer) and 0.02 (s, 9H, major diastereomer) ppm.

Analytical data for (^{Si}*S*,*R*)-**16** (d.r. = 81:19, Entry 3, Table 2): Yield: 64%. $[\alpha]_D^{20}$ = –19.2, $[\alpha]_{578}^{20}$ = –20.1, $[\alpha]_{546}^{20}$ = –22.7, $[\alpha]_{436}^{20}$ = –37.9, $[\alpha]_{365}^{20}$ = –55.6 (*c* = 0.885, $CHCl_3$).

(^Si^*R,S*)-2-[2-(1-*tert*-Butyl-1-silaindan-1-yloxy)-2-(4-methoxyphenyl)-4-(trimethylsilanyl)-but-3-ynyl]pyridine [(^Si^*R**,*S**)-17]**

Analytical data for (^{Si}*R**,*S**)-**17**: Yield: 54%. R_f = 0.43 (cyclohexane–*t*-butyl methyl ether = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.07 (s, 9H, Si(CH_3)$_3$), 0.81$^\diamond$ (ddd, 15.3, 9.1, 4.5 Hz, 1H, 2''-H_A), 0.93 (s, 9H, C(CH_3)$_3$), 0.97$^\diamond$ (m_c, 1H, 2''-H_B), 2.65$^\diamond$ (m_c, 1H, 3''-H_A), 2.74$^\diamond$ (ddd, *J* = 16.8, 9.2, 6.4 Hz, 1H, 3''-H_B), 3.27$^\diamond$ (d, *J* = 12.9 Hz, 1H, 1-H_A), 3.51$^\diamond$ (d, *J* = 12.9 Hz, 1H, 1-H_B), 3.77 (s, 3H, OCH_3), 6.67 (m_c, 2H, Ar-H), 6.97 (dd, *J* = *J* = 7.6 Hz, 1H, Ar-H), 7.10 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.10–7.20 (m, 3H, 5'-H, Ar-H), 7.32–7.37 (m, 3H, Ar-H), 7.59 (ddd, *J* = *J* = 7.7 Hz, *J* = 1.7 Hz, 1H, 4'-H), 8.47 (ddd, *J* = 5.0, 1.7, 0.8 Hz, 1H, 6'-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.2, 6.9, 19.1, 26.2, 30.2, 55.3, 55.4, 75.2, 94.0, 106.3, 113.1, 122.0, 125.1, 125.7, 125.9, 127.5, 129.5, 133.0, 135.6, 135.9, 136.4, 147.9, 153.6, 156.8, 159.0. IR (film) 2172 (w, C≡C) cm^{-1}.HRMS (ESI) calcd for $C_{31}H_{39}NO_2Si_2$ (M + Na^+): 536.2412; found: 536.2416. Anal. calcd for $C_{31}H_{39}NO_2Si_2$ (513.83): C, 72.46; H, 7.65; N, 2.73; found: C, 72.27; H, 7.90; N, 2.56. The diastereomeric ratio was determined by integration of baseline separated ^{1}H NMR signals of Si(CH_3)$_3$ at –0.04 (s, 9H, minor diastereomer) and 0.07 (s, 9H, major diastereomer) ppm.

Analytical data for (^{Si}*R*,*S*)-**17** (d.r. = 78:22, Entry 4, Table 2): Yield: 56%. $[\alpha]_D^{20}$ = +23.2, $[\alpha]_{578}^{20}$ = +24.4, $[\alpha]_{546}^{20}$ = +27.8, $[\alpha]_{436}^{20}$ = +47.7, $[\alpha]_{365}^{20}$ = +74.1 (*c* = 0.640, $CHCl_3$).

(^Si^*R,*S**)-2-[2-(1-*tert*-Butyl-1-silaindan-1-yloxy)-2-(4-fluorophenyl)-4-(trimethylsilanyl)-but-3-ynyl]pyridine [(^Si^*R**,*S**)-18]**

Analytical data for (^{Si}*R**,*S**)-**18**: Yield: 59%. R_f = 0.57 (cyclohexane–*t*-butyl methyl ether = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.07 (s, 9H, Si(CH_3)$_3$), 0.84$^\diamond$ (ddd, 15.5, 9.1, 4.5 Hz, 1H, 2''-H_A), 0.95 (s, 9H, C(CH_3)$_3$), 0.99$^\diamond$ (m_c, 1H, 2''-H_B), 2.73 (m_c, 2H, 3''-H), 3.26$^\diamond$ (d, *J* = 13.0 Hz, 1H, 1-H_A), 3.47$^\diamond$ (d, *J* = 13.0 Hz, 1H, 1-H_B), 6.79–6.85 (m, 2H, Ar-H), 6.97 (dd, *J* = *J* = 7.3 Hz, 1H, Ar-H), 7.04 (d, *J* = 7.3 Hz, 1H, Ar-H), 7.08 (d, *J* = 7.3 Hz, 1H, Ar-H), 7.12 (ddd, *J* = 7.6, 4.9, 1.0 Hz, 1H, 5'-H), 7.19 (ddd, *J* = *J* = 7.5 Hz, *J* = 1.3 Hz, 1H, Ar-H), 7.32 (d, *J* = 7.6 Hz, 1H, 3'-H), 7.35–7.40 (m, 2H, Ar-H), 7.55 (ddd, *J* = *J* = 7.6 Hz, *J* = 1.7 Hz, 1H, 4'-H), 8.44 (ddd, *J* = 4.9, 1.7, 0.8 Hz, 1H, 6'-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.3, 6.9, 19.1, 26.1, 30.2, 55.6, 75.2, 94.4, 106.0, 114.5 (d, J_{C-F} = 21.3 Hz), 121.9, 125.2, 125.5, 126.0, 128.1 (d, J_{C-F} = 8.1 Hz), 129.7, 132.9, 135.4, 135.5, 140.1 (d, J_{C-F} = 2.9 Hz), 148.5, 153.6, 156.7, 162.3 (d, J_{C-F} = 244.2 Hz). IR (film) 2172 (w, C≡C) cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{36}FNOSi_2$ (M + H^+): 524.2212; found: 524.2204. Anal. calcd for $C_{30}H_{36}FNOSi_2$ (501.79): C, 71.81; H, 7.23; N,

2.79; found: C, 72.03; H, 7.56; N, 3.18. The diastereomeric ratio was determined by integration of baseline separated ^{1}H NMR signals of Si(CH_3)$_3$ at –0.03 (s, 9H, minor diastereomer) and 0.07 (s, 9H, major diastereomer) ppm.

Analytical data for (^{Si}*R*,*S*)-**18** (d.r. = 81:19, Entry 5, Table 2): Yield: 55%. $[\alpha]_D^{20}$ = +27.8, $[\alpha]_{578}^{20}$ = +29.0, $[\alpha]_{546}^{20}$ = +33.3, $[\alpha]_{436}^{20}$ = +58.9, $[\alpha]_{365}^{20}$ = +96.9 (*c* = 0.710, $CHCl_3$).

(^{Si}*S,*R**)-2-[2-(1-*tert*-Butyl-1-silaindan-1-yloxy)-2-(4-chlorophenyl)-4-(trimethylsilanyl)-but-3-ynyl]pyridine [(^{Si}*S**,*R**)-19]**

Analytical data for (^{Si}*S**,*R**)-**19**: Yield: 58%. R_f = 0.58 (cyclohexane–*t*-butyl methyl ether = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.07 (s, 9H, Si(CH_3)$_3$), 0.85$^{\diamond}$ (ddd, 15.5, 8.5, 4.8 Hz, 1H, 2''-H_A), 0.95 (s, 9H, C(CH_3)$_3$), 0.97$^{\diamond}$ (m_c, 1H, 2''-H_B), 2.75 (m_c, 2H, 3''-H), 3.25$^{\diamond}$ (d, *J* = 12.8 Hz, 1H, 1-H_A), 3.45$^{\diamond}$ (d, *J* = 12.8 Hz, 1H, 1-H_B), 6.97 (dd, *J* = *J* = 7.2 Hz, 1H, Ar-H), 7.04–7.13 (m, 5H, Ar-H), 7.20 (ddd, *J* = *J* = 7.5 Hz, *J* = 1.3 Hz, 1H, Ar-H), 7.31–7.36 (m, 3H, 3'-H, Ar-H), 7.55 (ddd, *J* = *J* = 7.7 Hz, *J* = 1.7 Hz, 1H, 4'-H), 8.44 (ddd, *J* = 5.0, 1.7, 0.8 Hz, 1H, 6'-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ –0.3, 6.9, 19.1, 26.2, 30.3, 55.7, 75.2, 94.5, 105.8, 121.9, 125.2, 125.4, 126.0, 127.7, 127.9, 129.7, 132.9, 133.3, 135.2, 135.4, 143.1, 148.8, 153.6, 156.6. IR (film) 2172 (w, C≡C) cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{36}ClNOSi_2$ (M + Na^+) : 518.2097; found: 518.2083. Anal. calcd for $C_{30}H_{36}ClNOSi_2$ (517.25): C, 69.53; H, 7.00; N, 2.70; found: C, 69.62; H, 7.24; N, 2.60. The diastereomeric ratio was determined by integration of baseline separated ^{1}H NMR signals of Si(CH_3)$_3$ at –0.04 (s, 9H, minor diastereomer) and 0.07 (s, 9H, major diastereomer) ppm.

Analytical data for (^{Si}*S*,*R*)-**19** (d.r. = 79:21, Entry 6, Table 2): Yield: 59%. $[\alpha]_D^{20}$ = –18.2, $[\alpha]_{578}^{20}$ = –19.1, $[\alpha]_{546}^{20}$ = –21.7, $[\alpha]_{436}^{20}$ = –35.9, $[\alpha]_{365}^{20}$ = –53.3 (*c* = 0.695, $CHCl_3$).

(^{Si}*S,*R**)-2-[2-(1-*tert*-Butyl-1-silaindan-1-yloxy)-2,4-diphenyl-but-3-ynyl]pyridine [(^{Si}*S**,*R**)-20]**

Analytical data for (^{Si}*S**,*R**)-**20**: Yield: 61%. R_f = 0.46 (cyclohexane–*t*-butyl methyl ether = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82 (m_c, 2H, 2''-H), 0.99 (s, 9H, C(CH_3)$_3$), 2.56$^{\diamond}$ (ddd, *J* = 17.0, 8.3, 5.8 Hz, 1H, 3''-H_A), 2.68$^{\diamond}$ (m_c, 1H, 3''-H_B), 3.39$^{\diamond}$ (d, *J* = 12.9 Hz, 1H, 1-H_A), 3.59$^{\diamond}$ (d, *J* = 12.9 Hz, 1H, 1-H_B), 6.94 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.02 (d, *J* = 6.8 Hz, 1H, Ar-H), 7.06–7.09 (m, 2H, Ar-H), 7.14–7.27 (m, 8H, 5'-H, Ar-H), 7.38 (d, *J* = 7.8 Hz, 1H, 3'-H), 7.58–7.64 (m, 3H, 4'-H, Ar-H), 8.56 (d, *J* = 4.2 Hz, 1H, 6'-H).^{13}C NMR (100 MHz, $CDCl_3$): 6.8, 19.2, 26.2, 30.2, 55.4, 75.5, 89.7, 90.3, 122.1, 122.5, 125.1, 125.8, 125.9, 126.2, 127.7, 128.0, 128.2, 128.6, 129.5, 131.7, 133.0, 135.5, 135.9, 145.0, 148.2, 153.7, 156.9. IR (film) 2233 (w, C≡C) cm^{-1}. HRMS (ESI) calcd for $C_{33}H_{33}NOSi$ (M + Na^+): 510.2224; found: 510.2223. Anal. calcd for $C_{33}H_{33}NOSi$ (487.72): C, 81.27; H, 6.82; N, 2.87; found: C, 81.22; H, 7.35; N, 2.65. The diastereomeric ratio was determined by integration of baseline separated ^{1}H NMR signals of 6'-H at 8.49 (d, 1H, minor diastereomer) and 8.56 (d, 1H, major diastereomer) ppm.

Analytical data for ($^{Si}S,R$)-**20** (d.r. = 72:28, Entry 7, Table 2): Yield: 62%. $[\alpha]_D^{20}$ = –78.1, $[\alpha]_{578}^{20}$ = –81.6, $[\alpha]_{546}^{20}$ = –94.6, $[\alpha]_{436}^{20}$ = –182, $[\alpha]_{365}^{20}$ = –346 (*c* = 0.645, $CHCl_3$).

($^{Si}R^*,S^*$)-2-[2-(1-*tert*-Butyl-1-silaindan-1-yloxy)-2-(4-methoxyphenyl)-4-phenyl-but-3-ynyl]pyridine [($^{Si}R^*,S^*$)-21]

Analytical data for ($^{Si}R^*,S^*$)-**21**: Yield: 64%. R_f = 0.35 (cyclohexane–*t*-butyl methyl ether = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83 (m_c, 2H, 2''-H), 0.97 (s, 9H, C(CH_3)$_3$), 2.56$^\diamond$ (ddd, *J* = 16.9, 9.5, 4.9 Hz, 1H, 3''-H_A), 2.67$^\diamond$ (m_c, 1H, 3''-H_B), 3.33$^\diamond$ (d, *J* = 12.8 Hz, 1H, 1-H_A), 3.54$^\diamond$ (d, *J* = 12.8 Hz, 1H, 1-H_B), 3.80 (s, 3H, OCH_3), 6.74–6.78 (m, 2H, Ar-H), 6.95 (dd, *J* = *J* = 7.0 Hz, 2H, Ar-H), 7.04–7.07 (m, 3H, Ar-H), 7.13–7.30 (m, 5H, Ar-H), 7.34 (d, *J* = 7.7 Hz, 1H, 3'-H), 7.44–7.48 (m, 2H, Ar-H), 7.57 (ddd, *J* = *J* = 7.7, 1.7 Hz, 1H, 4'-H), 8.54 (ddd, *J* = 4.9, 1.7, 0.8 Hz, 1H, 6'-H). ^{13}C NMR (100 MHz, $CDCl_3$): 6.8, 19.2, 26.2, 30.2, 55.4, 55.9, 75.2, 89.4, 90.6, 113.2, 121.8, 122.7, 125.1, 125.6, 125.9, 127.4, 128.2, 128.5, 129.4, 131.7, 133.0, 135.3, 135.7, 137.4, 148.8, 153.7, 157.3, 159.1. IR (ATR) 2232 (w, C≡C) cm^{-1}. HRMS (ESI) calcd for $C_{34}H_{35}NO_2Si$ (M + Na^+): 540.2329; found: 540.2322. Anal. calcd for $C_{34}H_{35}NO_2Si$ (517.74): C, 78.88; H, 6.81; N, 2.71; found: C, 78.74; H, 7.21; N, 2.46. The diastereomeric ratio was determined by integration of baseline separated ^{1}H NMR signals of 6'-H at 8.48 (ddd, 1H, minor diastereomer) and 8.54 (ddd, 1H, major diastereomer) ppm.

($^{Si}R^*,S^*$)-2-[2-(1-*tert*-Butyl-1-silaindan-1-yloxy)-2-methyl-4-(trimethylsilanyl)-but-3-ynyl]pyridine [($^{Si}R^*,S^*$)-22]

Analytical data for ($^{Si}R^*,S^*$)-**22**: Yield: 61%. R_f = 0.54 (cyclohexane–*t*-butyl methyl ether = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ –0.03 (s, 9H, Si(CH_3)$_{3minor}$), 0.01 (s, 9H, Si(CH_3)$_{3major}$), 0.91 (s, 9H, C(CH_3)$_3$), 0.97$^\diamond$ (m_c, 1H, 2''-H_A), 1.13$^\diamond$ (m_c, 1H, 2''-H_B), 1.38 (s, 3H, CH_{3major}), 1.43 (s, 3H, CH_{3minor}), 2.90$^\diamond$ (m_c, 1H, 3''-H_A), 3.12$^\diamond$ (m_c, 1H, 3''-H_B), 3.14 (s, 2H, 1-H_{minor}), 3.16 (s, 2H, 1-H_{major}), 7.11–7.59 (m, 7H, Ar-H), 8.49–8.52 (m, 1H, 6'-H). ^{13}C NMR (75 MHz, $CDCl_3$) (Major diastereomer): δ –0.2, 6.9, 18.9, 25.9, 30.3, 30.9, 53.2, 70.4, 89.5, 108.8, 121.7, 125.4, 125.5, 126.3, 129.8, 133.1, 135.4, 136.3, 148.8, 153.8, 157.6. ^{13}C NMR (Minor diastereomer): δ –0.2, 7.5, 18.9, 25.9, 30.3, 30.6, 53.3, 70.4, 89.6, 108.9, 121.7, 125.3, 125.5, 126.2, 129.8, 133.4, 135.4, 136.0, 148.8, 153.6, 157.6. IR (film) 2168 (w, C≡C) cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{35}NOSi_2$ (M + H^+): 422.2330; found: 422.2332. Anal. calcd for $C_{25}H_{35}NOSi_2$ (421.73): C, 71.20; H, 8.37; N, 3.32; found: C, 70.93; H, 8.44; N, 3.81. The diastereomeric ratio was determined by integration of baseline separated ^{1}H NMR signals of Si(CH_3)$_3$ at –0.03 (s, 9H, minor diastereomer) and 0.01 (s, 9H, major diastereomer) ppm.

($^{Si}R^*,S^*$)-2-[2-(1-*tert*-Butyl-1-silaindan-1-yloxy)-2-isopropyl-4-(trimethylsilanyl)-but-3-ynyl]pyridine [($^{Si}R^*,S^*$)-23]

Analytical data for ($^{Si}R^*,S^*$)-**23**: Yield: 47%. R_f = 0.68 (cyclohexane–*t*-butyl methyl ether = 3 : 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ –0.10 (s, 9H, Si(CH_3)$_{3minor}$), –0.04 (s, 9H, Si(CH_3)$_{3major}$), 0.69 (m_c, 2H, 2''-H_{minor}), 0.91 (s, 9H, C(CH_3)$_{3minor}$), 0.94 (s, 9H, C(CH_3)$_{3major}$), 1.00 (m_c, 1H, 2''-H_{Amajor}), 1.05 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_{2minor}$), 1.08 (d, *J* = 6.8 Hz, 3H, CH(CH_3)$_{2major}$), 1.09 (d, *J* = 6.8 Hz, 3H, CH(CH_3)$_{2major}$), 1.28 (m_c, 1H, 2''-H_{Bmajor}), 1.76 (qq, J = J = 6.8 Hz, 1H, CH(CH$_3$)$_{2major}$), 1.83 (sep, 1H, CH(CH$_3$)$_{2minor}$),

2.93 (m_c, 2H, 3''-H), 3.08$^{\diamond}$ (d, J = 12.8 Hz, 1H, 1-H_{Aminor}), 3.15$^{\diamond}$ (d, J = 12.8 Hz, 1H, 1-H_{Bminor}), 3.12 (s, 2H, 1-H_{major}), 7.07–7.18 (m, 3H, Ar-H), 7.24–7.34 (m, 2H, Ar-H), 7.42 (m_c, 1H, Ar-H), 7.47 (ddd, J = J = 7.7 Hz, J = 1.8 Hz, 1H, 4'-H_{major}), 7.55 (ddd, J = J = 7.7 Hz, J = 1.8 Hz, 1H, 4'-H_{minor}), 7.61 (m_c, 1H, Ar-H), 8.48 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H, 6'-H_{major}), 8.52 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H, 6'-H_{minor}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.3 [0.3], 6.8 [7.4], 17.4 [17.8], 17.8 [17.9], 19.3 [19.4], 26.1 [26.1], 30.2 [30.4], 37.5 [38.5], 47.3 [47.9], 76.6 [76.7], 92.1 [92.3], 106.9, [107.4], 121.6 [121.8], 125.2 [125.3], 125.7 [125.8], 126.3 [126.3], 129.5 [129.7], 133.0 [133.3], 135.5 [135.5], 136.3 [136.3], 148.6 [148.6], 153.3 [153.3], 157.6 [157.8]. IR (film) 2165 (w, C≡C) cm^{-1}. HRMS (ESI) calcd for $C_{27}H_{39}NOSi_2$ (M + H^+): 450.2643; found: 450.2651. Anal. calcd for $C_{27}H_{39}NOSi_2$ (449.78): C, 72.10; H, 8.74; N, 3.11; found: C, 71.80; H, 8.79; N, 3.48. The diastereomeric ratio was determined by integration of baseline separated ^{1}H NMR signals of Si(CH_3)$_3$ at –0.10 (s, 9H, minor diastereomer) and –0.04 (s, 9H, major diastereomer) ppm.

(^{Si}***R*,S**)-2-[2-(1-*tert*-Butyl-1-silaindan-1-yloxy)-2-cyclohexyl-4-phenyl-but-3-ynyl]pyridine [(**^{Si}***R*,S**)-24]**

Analytical data for (^{Si}*R*,S**)-**24**: Yield: 51%. Major diastereomer: R_f = 0.57 (cyclohexane–*t*-butyl methyl ether = 9 : 2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (s, 9H, C(CH_3)$_3$), 1.01$^{\diamond}$ (m_c, 1H, 2''-H_A), 1.15–1.81 (m, 10H, 2''-H_B and Cy-H), 2.12 (d, J = 11.6 Hz, 1H, Cy-H), 2.20 (d, J = 11.6 Hz, 1H, Cy-H), 2.80$^{\diamond}$ (ddd, J = 17.0, 9.3, 6.1 Hz, 1H, 3''-H_A), 2.91$^{\diamond}$ (ddd, J = 17.0, 10.5, 3.9 Hz, 1H, 3''-H_B), 3.22 (d, J = 13.1 Hz, 1H, 1-H_A), 3.26 (d, J = 13.1 Hz, 1H, 1-H_B), 6.92–6.95 (m, 2H, Ar-H), 7.02 (d, J = 7.6 Hz, 1H, 3'-H), 7.09 (dd, J = J = 7.2 Hz, J = 0.7 Hz, 1H, Ar-H), 7.13 (ddd, J = 7.6, 4.9, 1.1 Hz, 1H, 5'-H), 7.17–7.24 (m, 4H, Ar-H), 7.33 (d, J = 7.8 Hz, 2H, Ar-H), 7.50 (ddd, J = J = 7.6 Hz, J = 1.8 Hz, 1H, 4'-H), 8.54 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H, 6'-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 7.4, 19.3, 26.2, 26.7, 27.5, 28.0, 30.3, 47.5, 48.3, 76.5, 88.1, 91.7, 121.6, 122.9, 125.3, 125.7, 126.3, 128.1, 128.2, 129.6, 131.6, 133.0, 135.5, 136.5, 148.9, 153.8, 157.9. IR (film) 2229 (w, C≡C) cm^{-1}. HRMS (ESI) calcd for $C_{33}H_{39}NOSi$ (M + H^+): 494.2874; found: 494.2866. Analytical data for (^{Si}*S*,S**)-**24** (Minor diastereomer): R_f = 0.46 (cyclohexane–*t*-butyl methyl ether = 9 : 2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.54$^{\diamond}$ (ddd, J = 15.5, 9.8, 6.4 Hz, 1H, 2''-H_A), 0.69$^{\diamond}$ (ddd, J = 15.5, 8.8, 4.4 Hz, 1H, 2''-H_B), 0.95 (s, 9H, C(CH_3)$_3$), 1.15–1.33 (m, 5H, Cy-H), 1.61–1.82 (m, 4H, Cy-H), 1.63 (m_c, 2H, Cy-H), 2.74 (m_c, 2H, 3''-H), 3.31 (s, 2H, 1-H), 6.86 (m_c, 2H, Ar-H), 7.00 (d, J = 7.5 Hz, 1H, Ar-H), 7.13–7.29 (m, 6H, Ar-H), 7.56–7.66 (m, 2H, Ar-H), 7.73 (dd, J = J = 7.1 Hz, 1H, Ar-H), 8.60 (ddd, J = 4.9, 1.8, 0.8 Hz, 1H, 6'-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 6.7, 19.3, 26.2, 26.7, 27.1, 27.9, 30.1, 47.8, 48.8, 76.4, 88.3, 91.2, 121.7, 122.8, 125.3, 125.8, 126.3, 128.0, 128.2, 129.4, 131.5, 133.2, 135.4, 136.6, 150.0, 153.6, 158.1. HRMS (ESI) calcd for $C_{33}H_{39}NOSi$ (M + H^+): 494.2874; found: 494.2870. The diastereomeric ratio was determined by integration of baseline separated ^{1}H NMR signals of 6'-H at 8.54 (ddd, 1H, major diastereomer) and 8.60 (ddd, 1H, minor diastereomer) ppm.

(^{Si}*S,*R**)-2-[2-(1-*tert*-Butyl-1-silaindan-1-yloxy)-2,4-diphenyl-but-3-ynyl]-6-methylpyridine [(^{Si}*S**,*R**)-26]**

Analytical data for (^{Si}*S**,*R**)-**26**: Yield : 60%. R_f = 0.57 (cyclohexane–*t*-butyl methyl ether = 3 : 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.79 (m_c, 2H, 2''-H), 0.99 (s, 9H, C(C*H*$_3$)$_3$), 2.53 (s, 3H, C*H*$_3$), 2.62 (m_c, 2H, 3''-H), 3.30$^{◊}$ (d, *J* = 12.9 Hz, 1H, 1-H_A), 3.52$^{◊}$ (d, *J* = 12.9 Hz, 1H, 1-H_B), 6.94 (m_c, 2H, Ar-H), 7.01–7.07 (m, 4H, Ar-H), 7.13–7.28 (m, 8H, Ar-H), 7.47 (dd, *J* = *J* = 7.7 Hz, 1H, Ar-H), 7.59–7.62 (m, 2H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 6.8, 19.2, 24.7, 26.2, 30.2, 55.8, 75.5, 89.5, 90.5, 121.3, 122.6, 122.7, 125.1, 125.9, 126.2, 127.5, 127.9, 128.1, 128.5, 129.4, 131.7, 133.0, 135.6, 135.7, 145.4, 153.7, 156.5, 157.2. IR (film) 2232 (w, C≡C) cm^{-1}. HRMS (ESI) calcd for $C_{34}H_{35}NOSi$ (M + H^+): 502.2561; found: 502.2553. The diastereomeric ratio was determined by integration of baseline separated ^{1}H NMR signals of C*H*$_3$ at 2.46 (s, 3H, minor diastereomer) and 2.53 (s, 3H, major diastereomer) ppm.

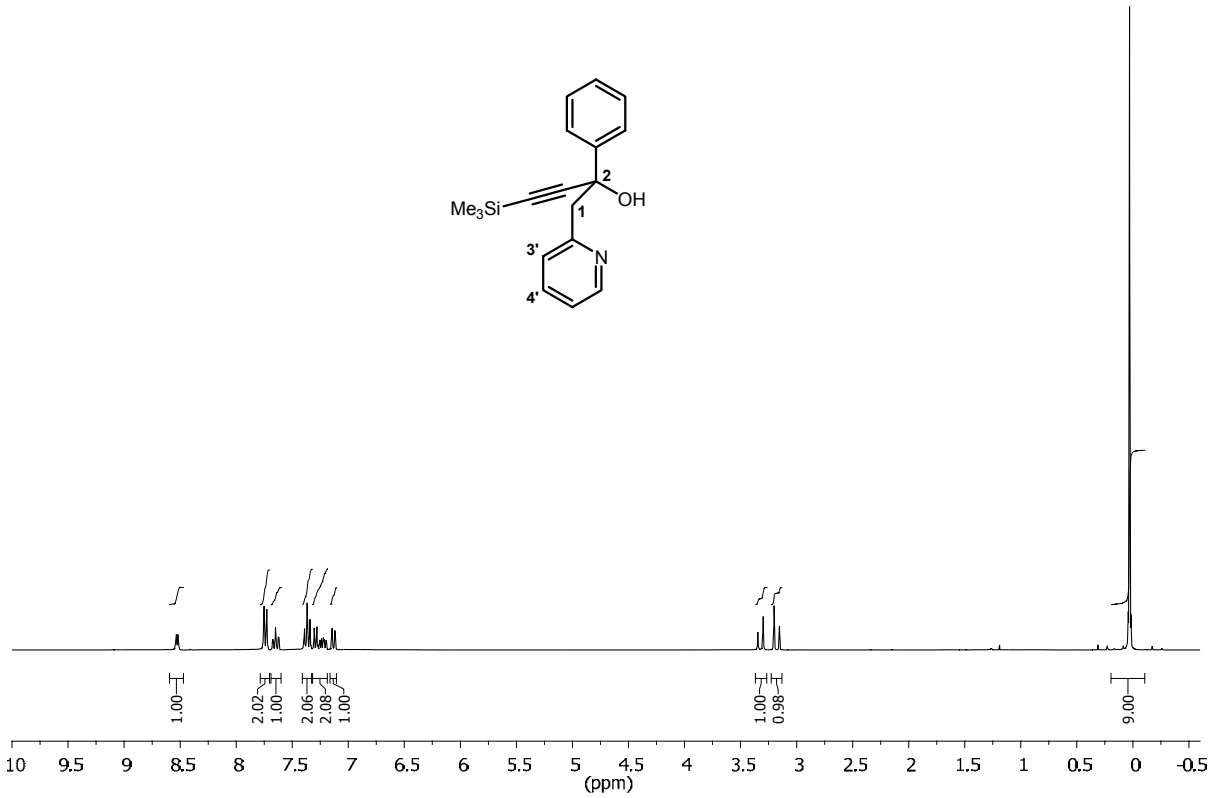
Analytical data for (^{Si}*S*,*R*)-**26** (d.r. = 75:25, Scheme 3): $[\alpha]_D^{20}$ = –60.5, $[\alpha]_{578}^{20}$ = –63.7, $[\alpha]_{546}^{20}$ = –73.8, $[\alpha]_{436}^{20}$ = –142, $[\alpha]_{365}^{20}$ = –273 (*c* = 0.745, $CHCl_3$).

(^{Si}*S,*R**)-2-[2-(1-*tert*-Butyl-1-silaindan-1-yloxy)-2,4-diphenyl-but-3-ynyl]quinoline [(^{Si}*S**,*R**)-28]**

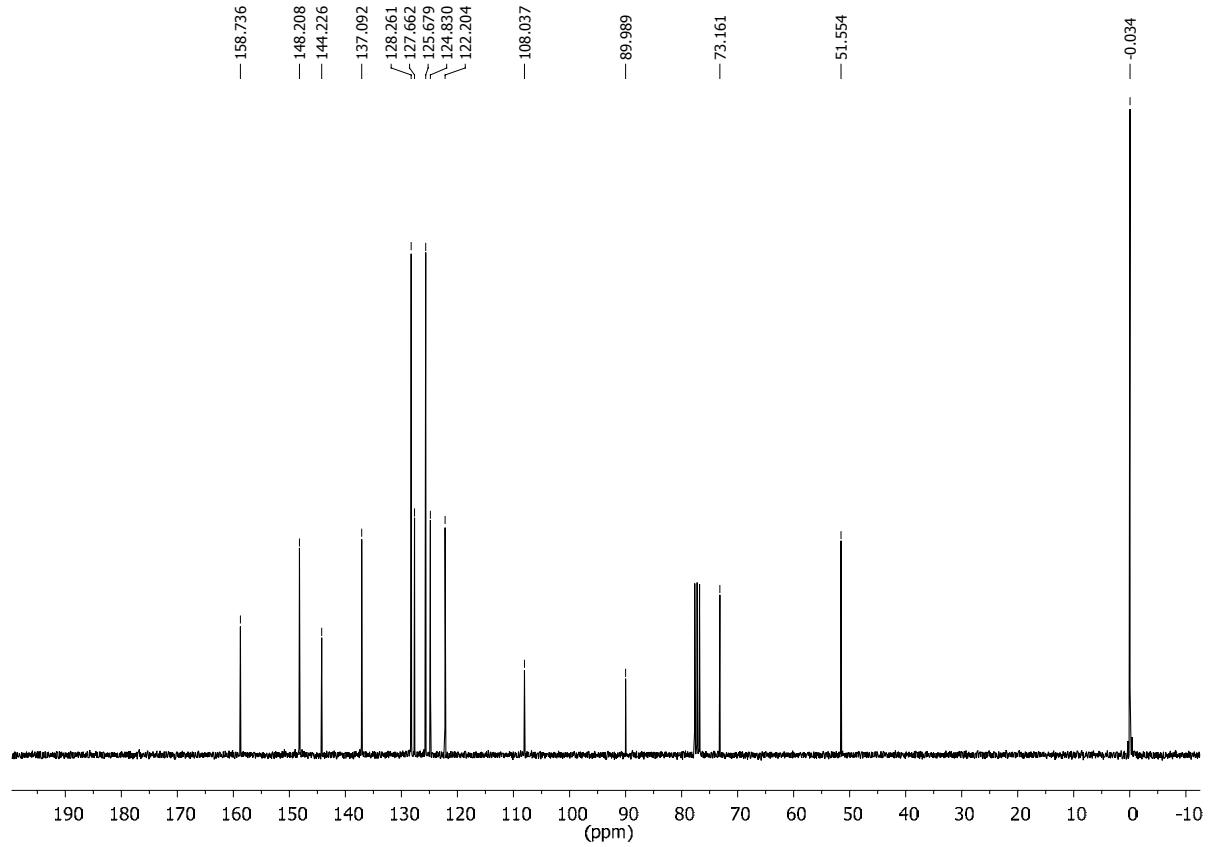
Analytical data for (^{Si}*S**,*R**)-**28**: R_f = 0.70 (cyclohexane–*t*-butyl methyl ether = 3 : 1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.71 (m_c, 2H, 2''-H), 1.00 (s, 9H, C(C*H*$_3$)$_3$), 2.57 (m_c, 2H, 3''-H), 3.53$^{◊}$ (d, *J* = 12.7 Hz, 1H, 1-H_A), 3.75$^{◊}$ (d, *J* = 12.7 Hz, 1H, 1-H_B), 6.90–7.01 (m, 4H, Ar-H), 7.12–7.40 (m, 8H, Ar-H), 7.46–7.51 (m, 2H, Ar-H), 7.64–7.81 (m, 4H, Ar-H), 8.02 (d, *J* = 11.2, 1H, Ar-H), 8.10 (d, *J* = 11.2 Hz, 1H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 6.8, 19.1, 26.2, 30.1, 56.5, 75.6, 89.9, 90.2, 122.5, 123.9, 125.1, 125.9, 126.0, 126.2, 127.2, 127.6, 127.7, 128.0, 128.1, 128.5, 129.2, 129.4, 129.4, 131.7, 133.0, 134.9, 135.5, 145.2, 147.9, 153.7, 157.8. IR (film) 2232 (w, C≡C) cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{35}NOSi$ (M + H^+): 538.2561; found: 538.2567. The diastereomeric ratio was determined by integration of baseline separated ^{1}H NMR signals of 1-H_B at 3.71 (d, 1H, minor diastereomer) and 3.75 (d, 1H, major diastereomer) ppm.

Analytical data for (^{Si}*S*,*R*)-**28** (d.r. = 77:23, Scheme 3): Yield : 55%. $[\alpha]_D^{20}$ = –66.0, $[\alpha]_{578}^{20}$ = –69.2, $[\alpha]_{546}^{20}$ = –80.5, $[\alpha]_{436}^{20}$ = –156 (*c* = 0.655, $CHCl_3$).

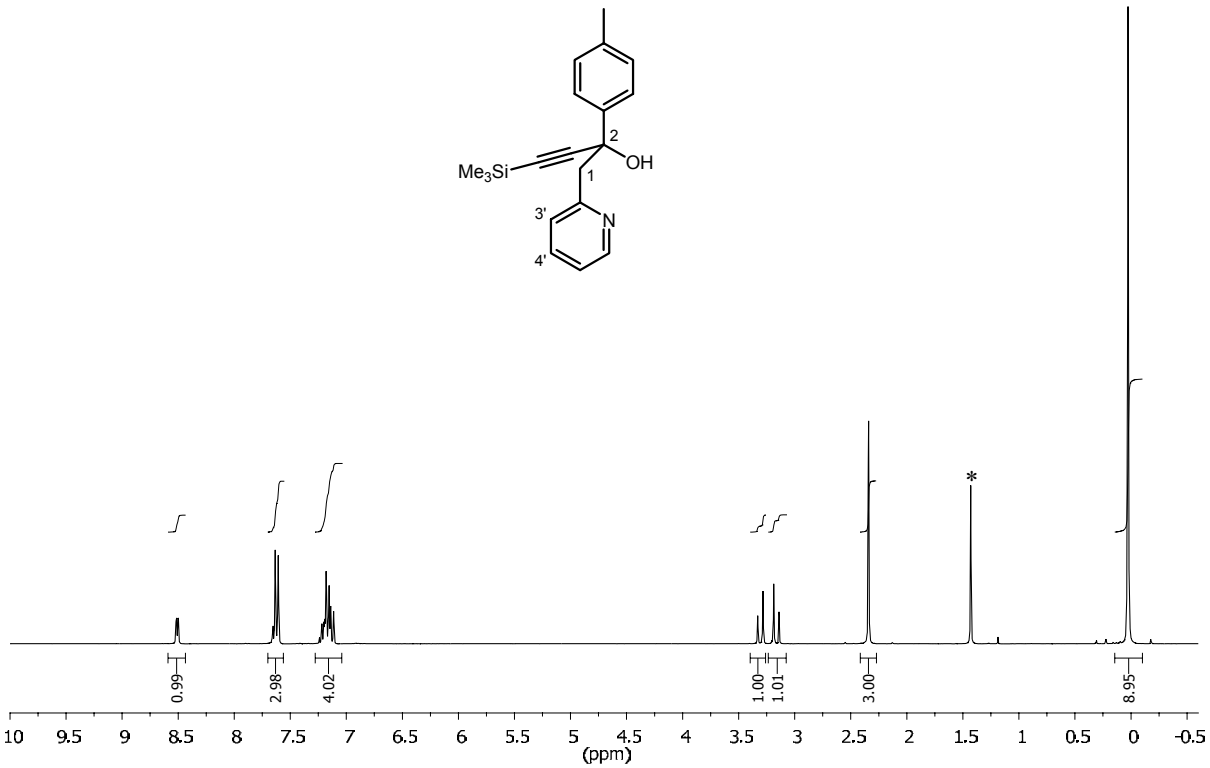
rac-**3** (^{1}H):



rac-**3** (^{13}C):



rac-**4** (^{1}H):



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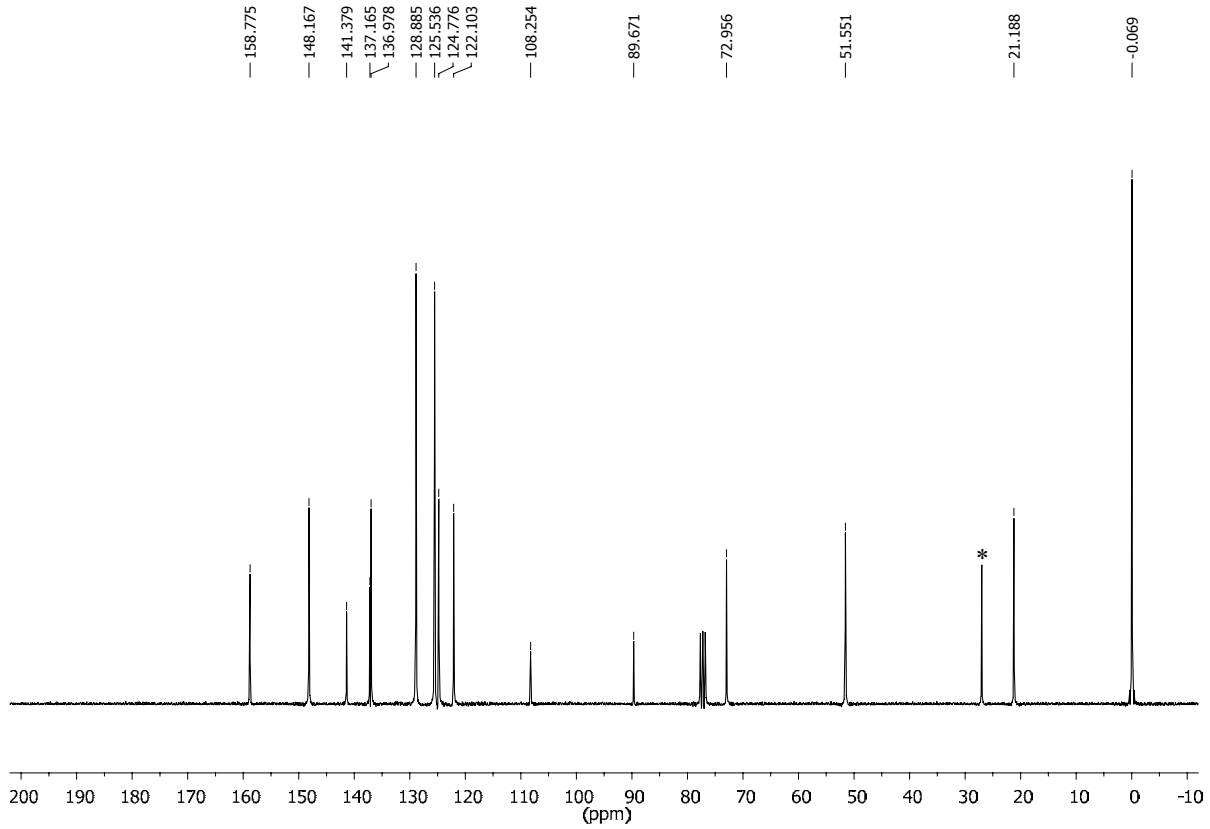

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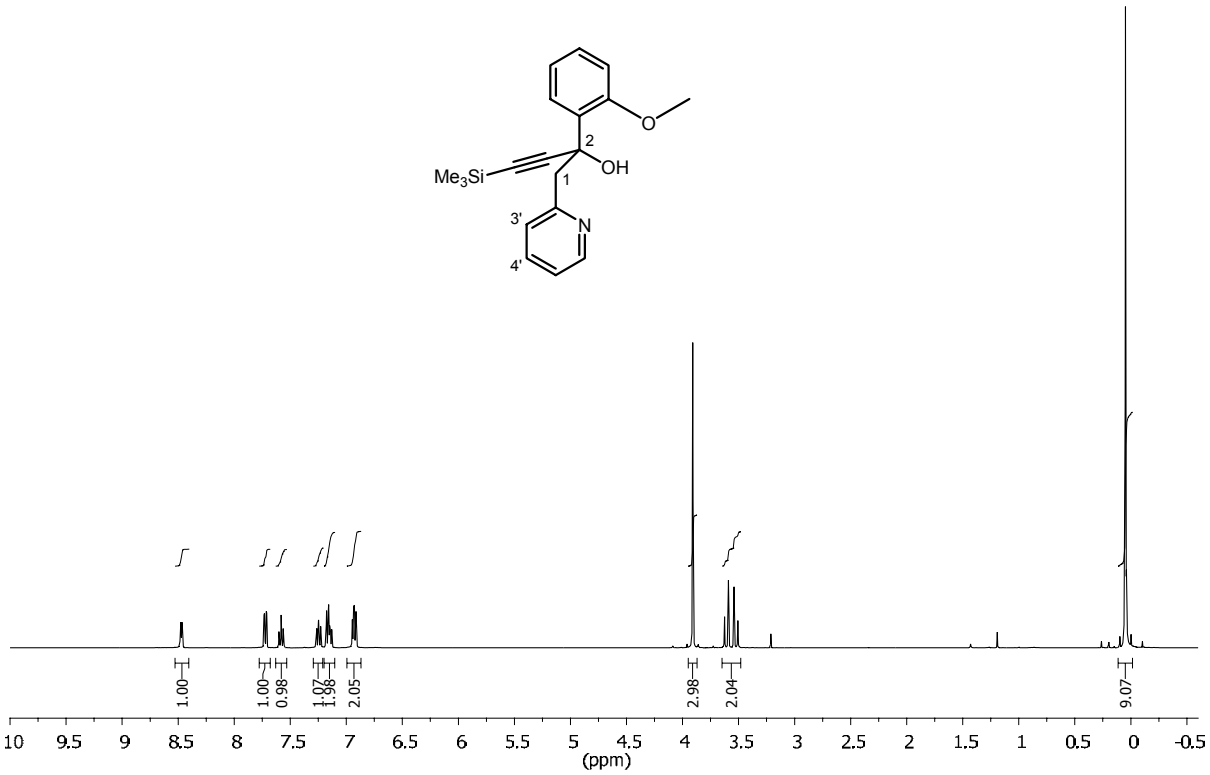

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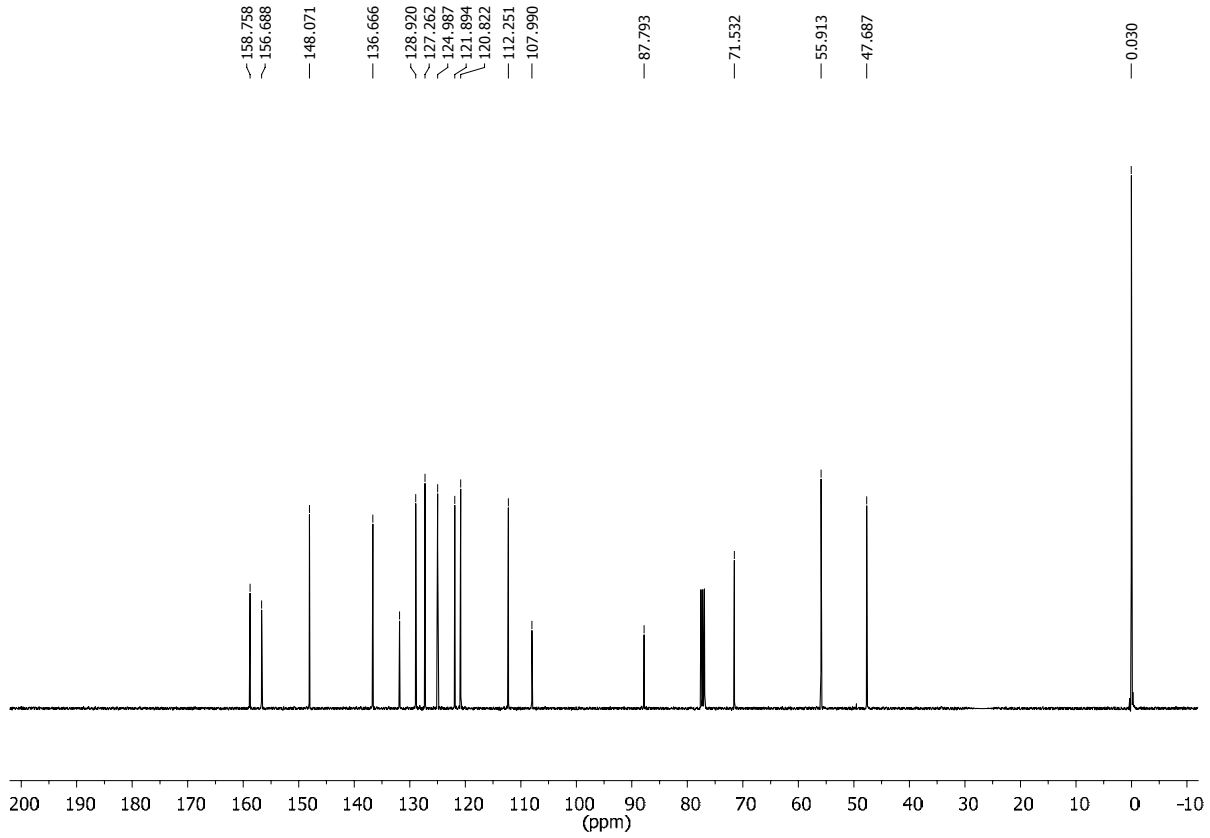
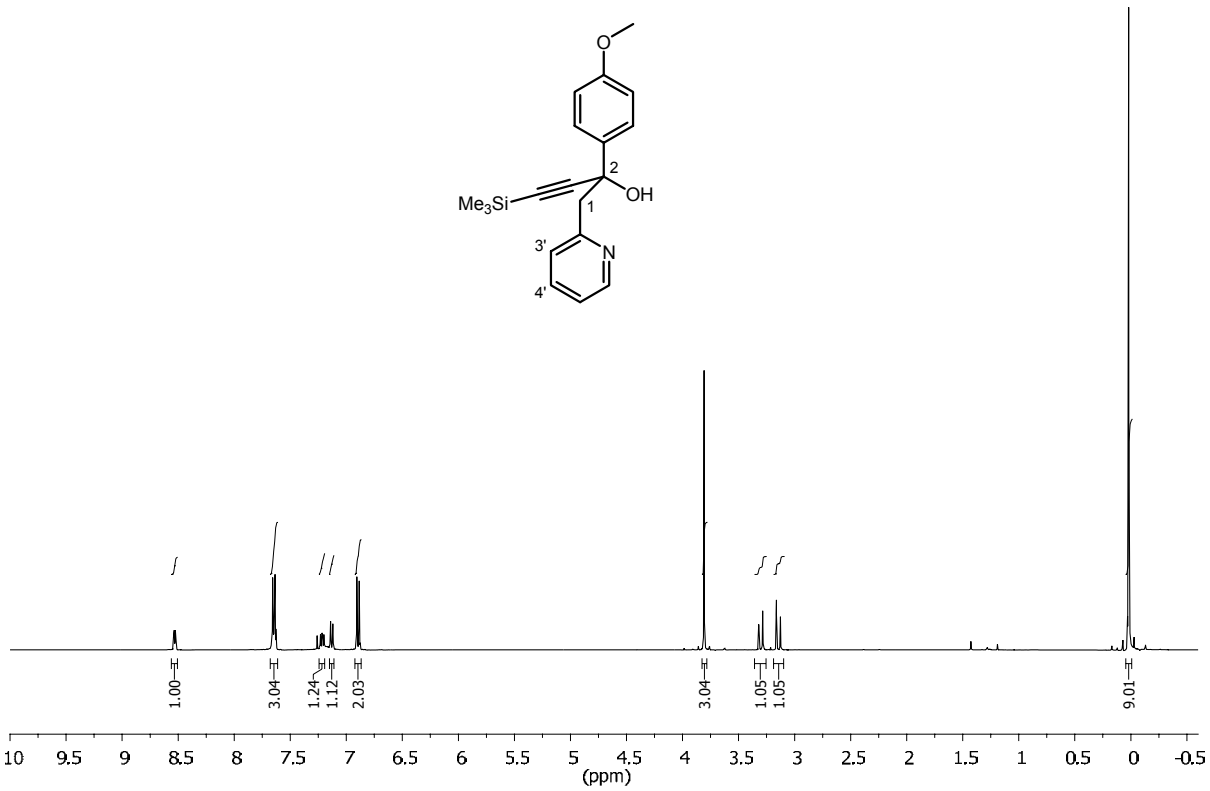


rac-**6** (^{1}H):



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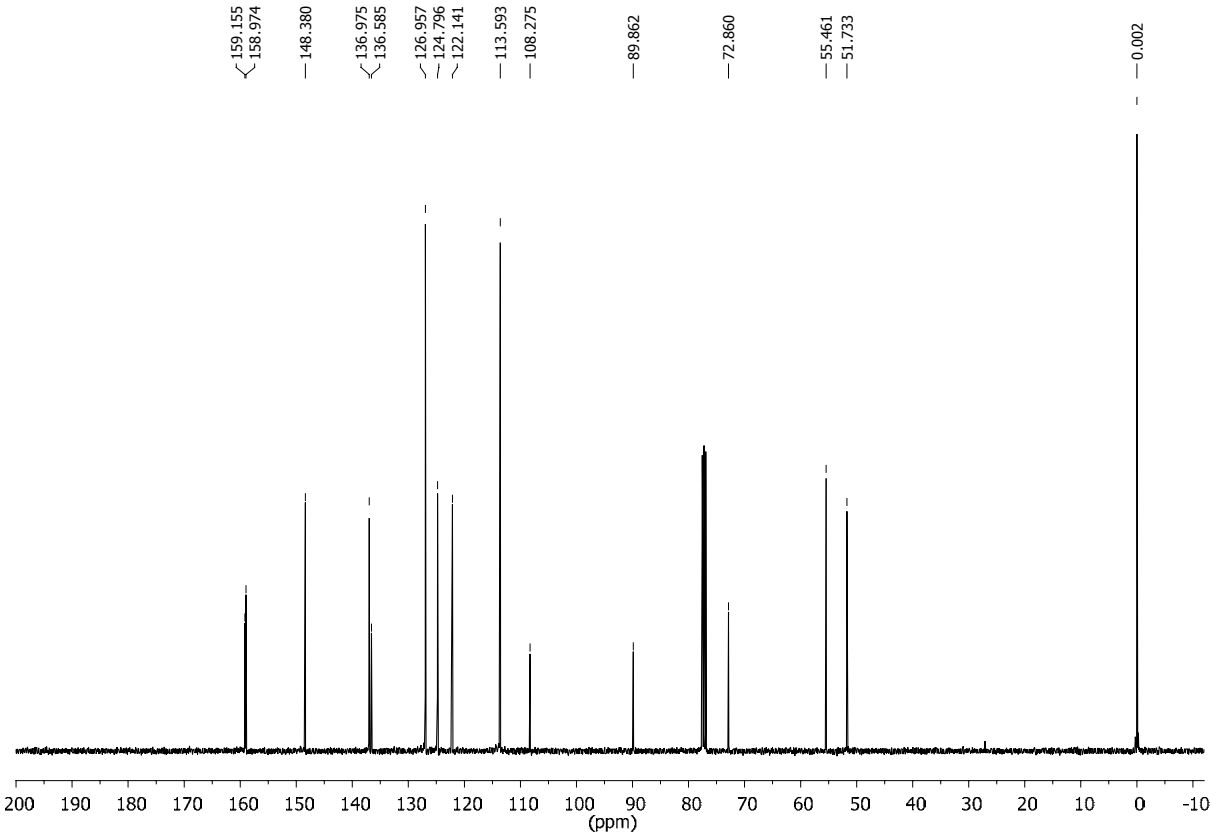
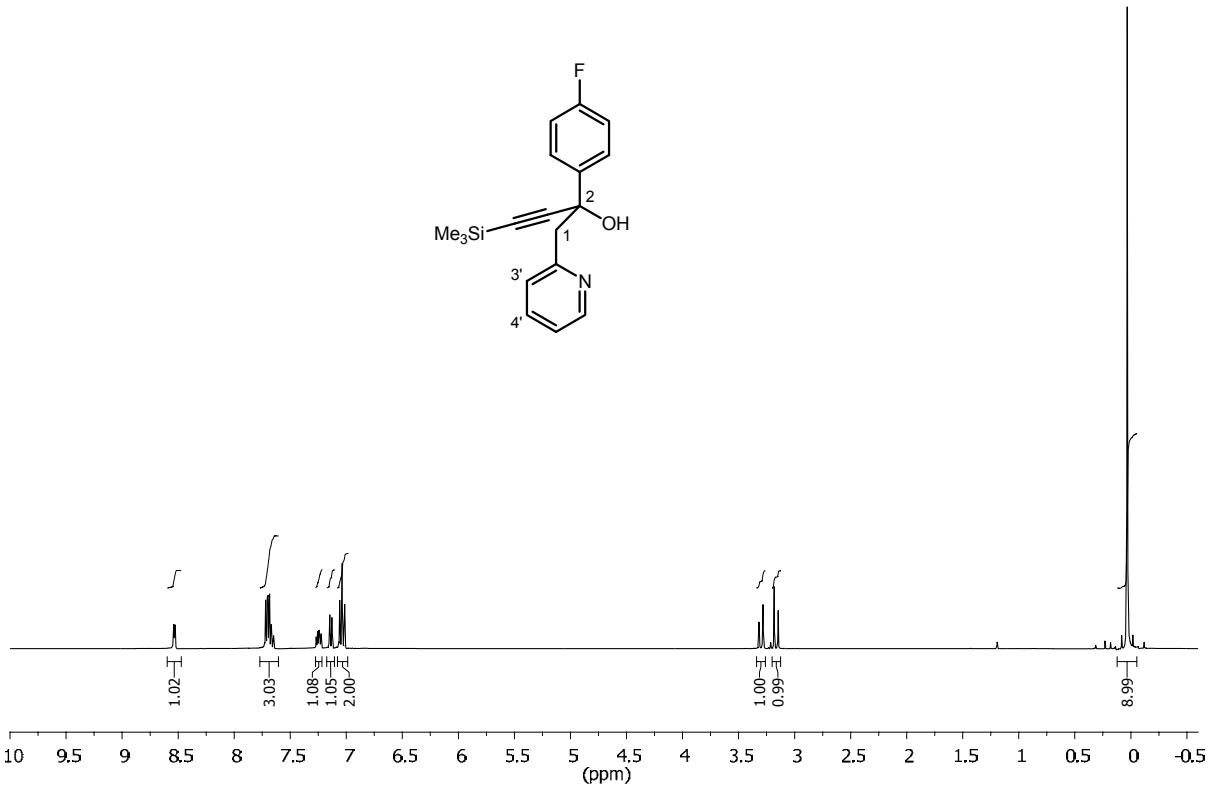
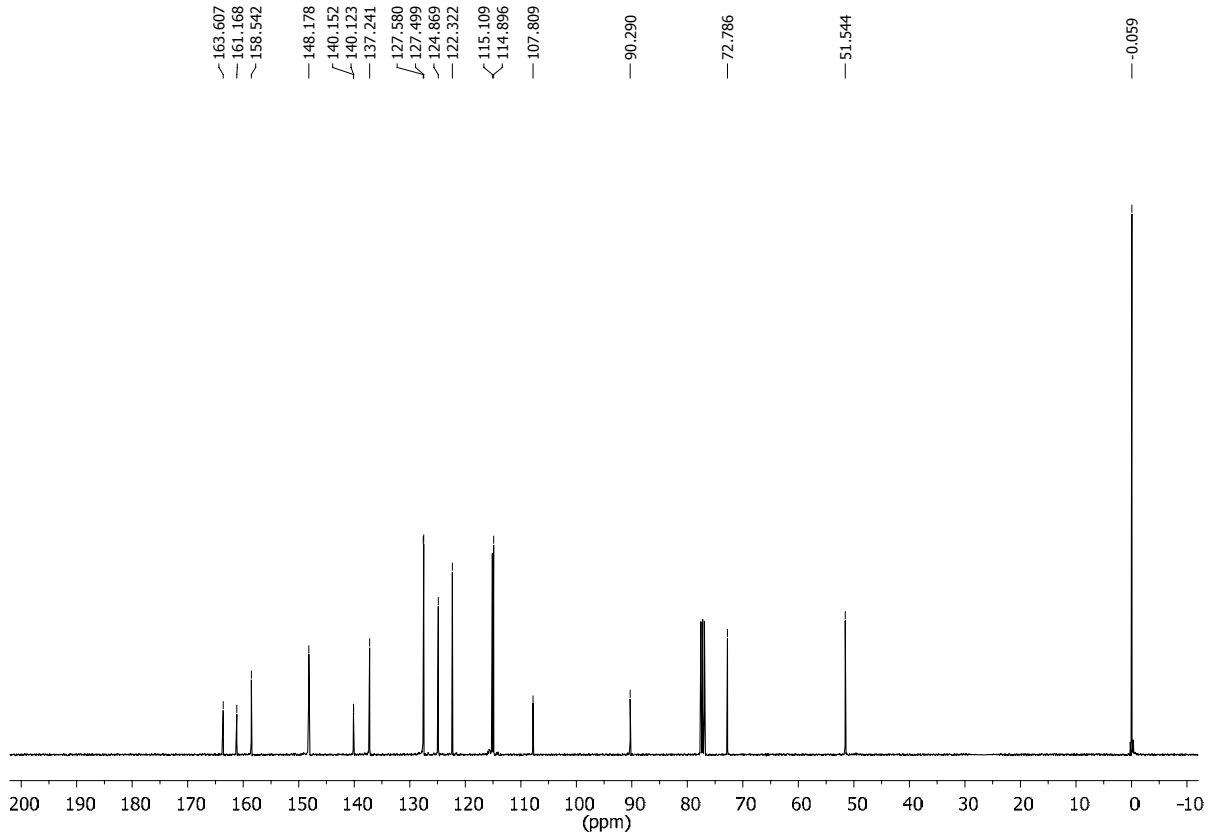


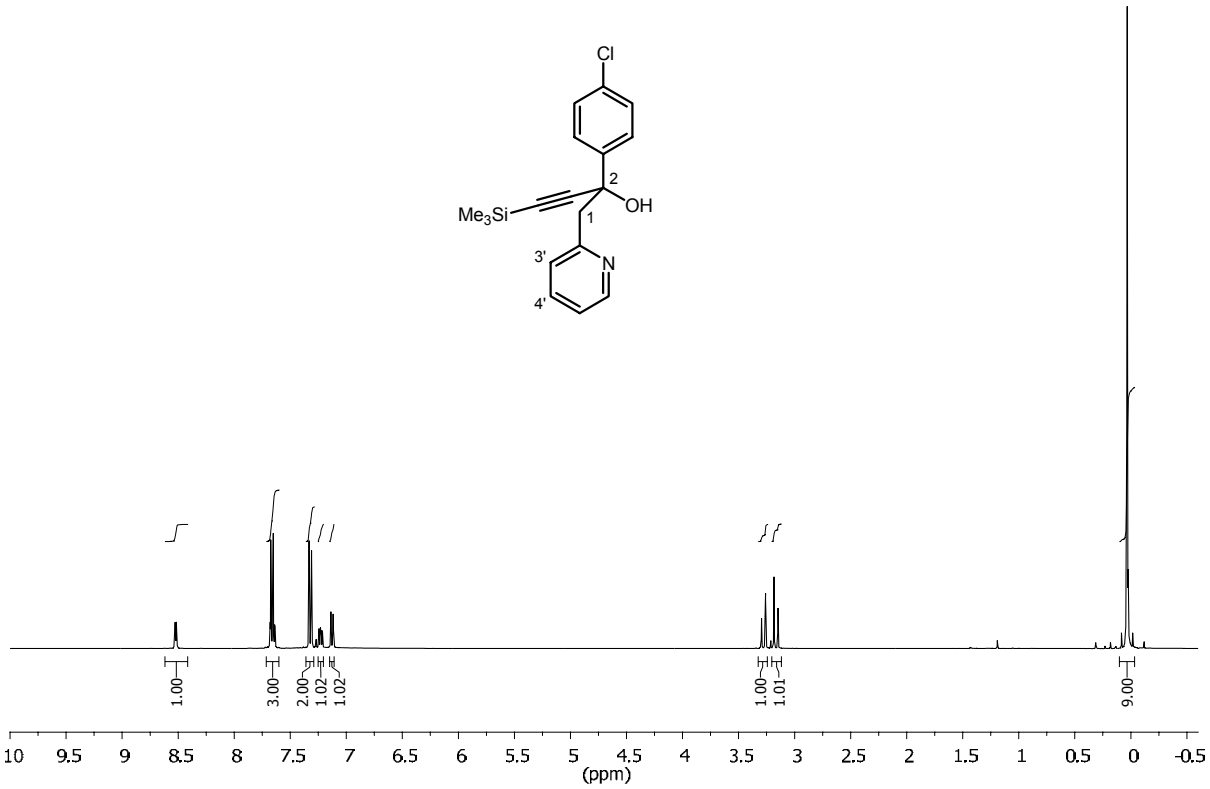
rac-**7** (^{1}H):



rac-**7** (^{13}C):



rac-**8** (^{1}H):



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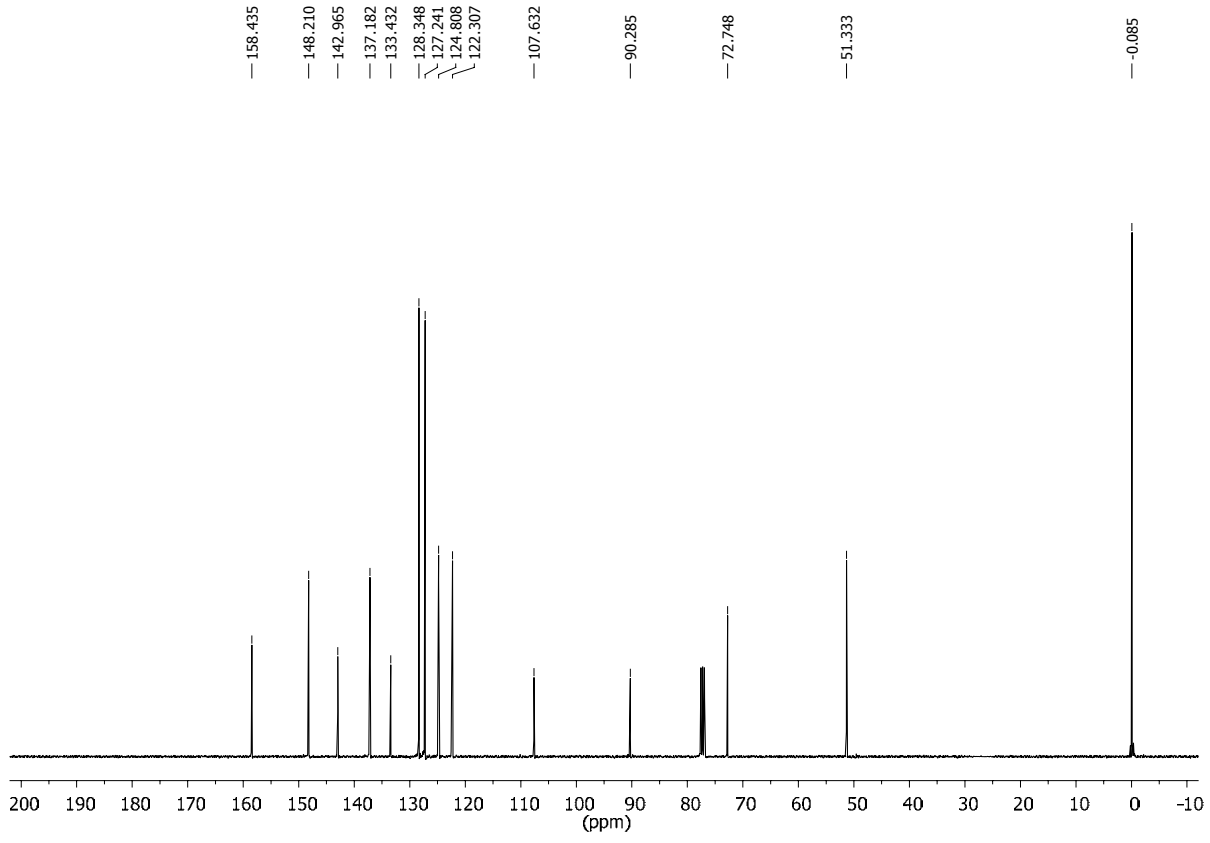

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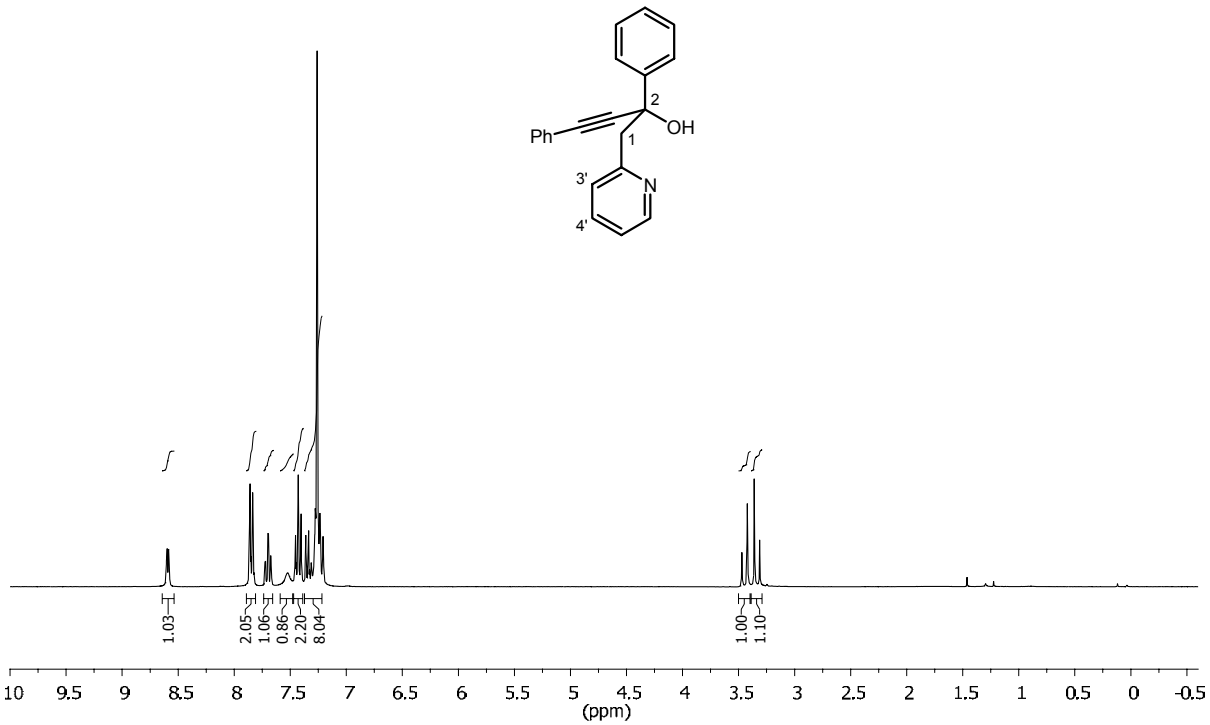
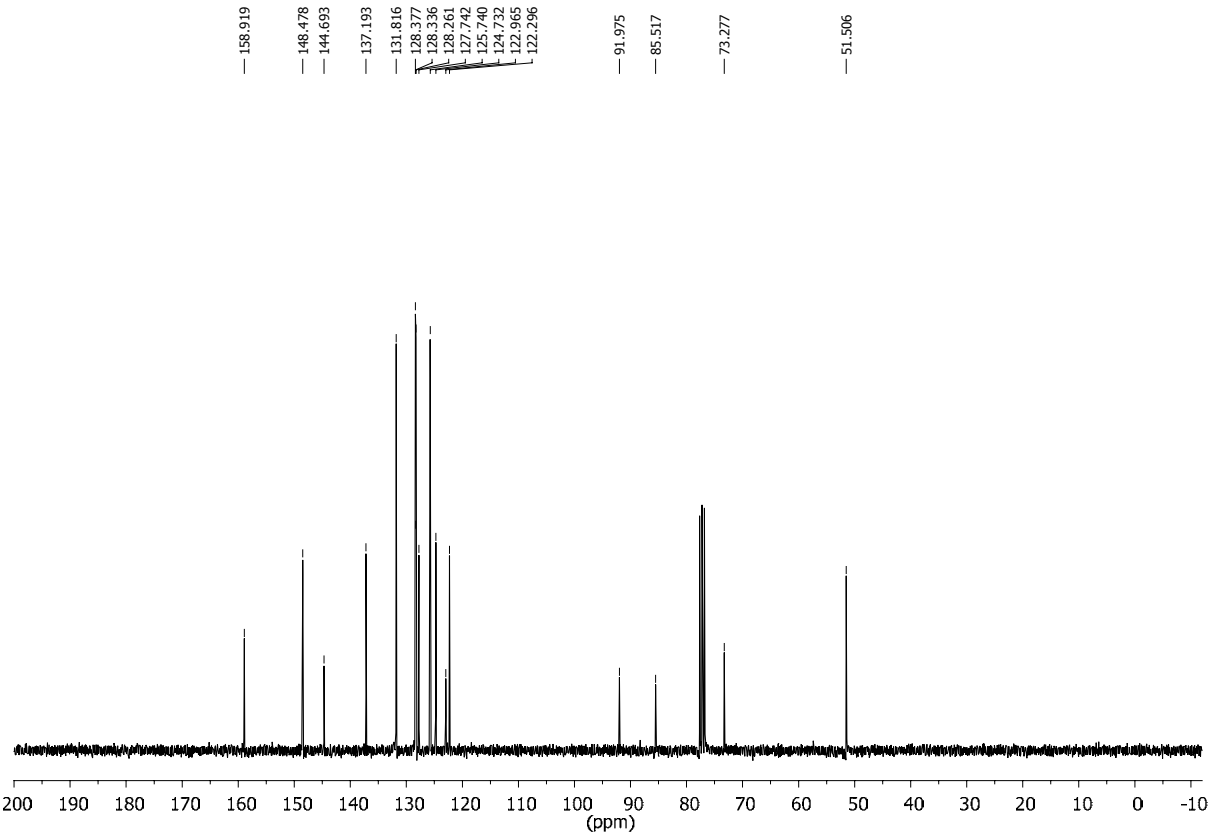
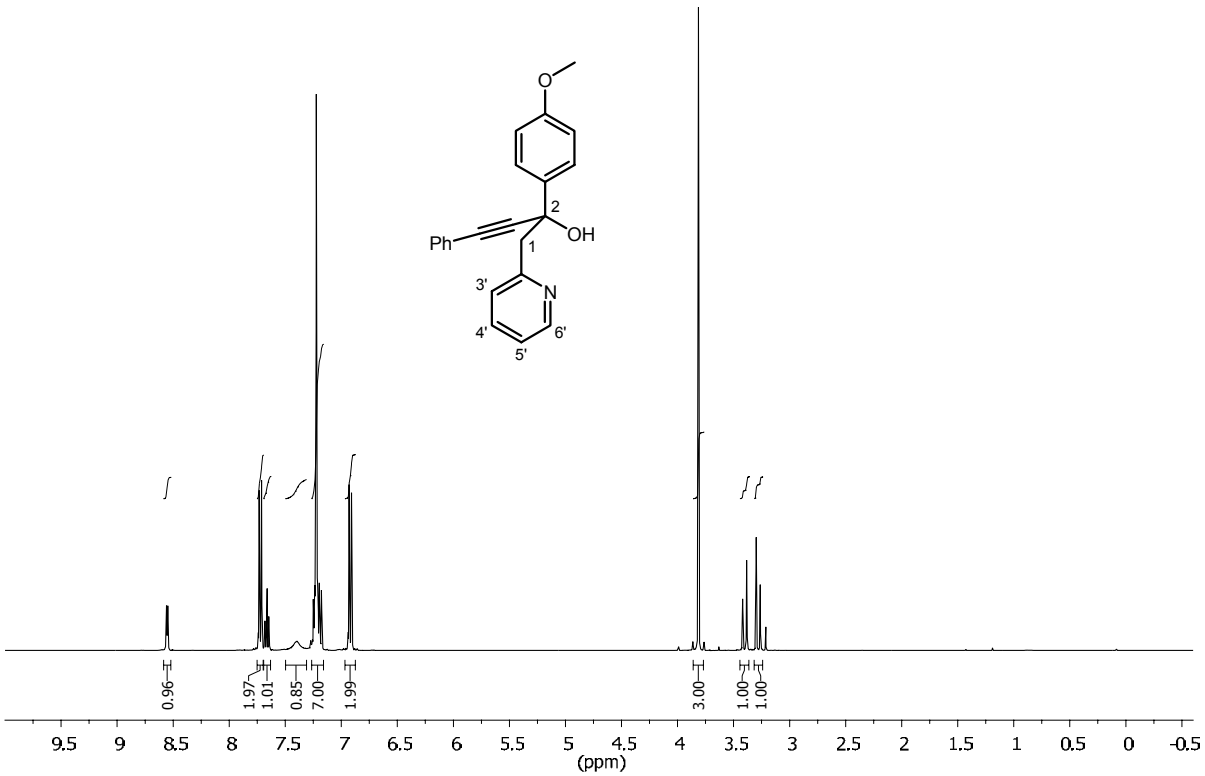


rac-**9** (^{13}C):



rac-**10** (^{1}H):



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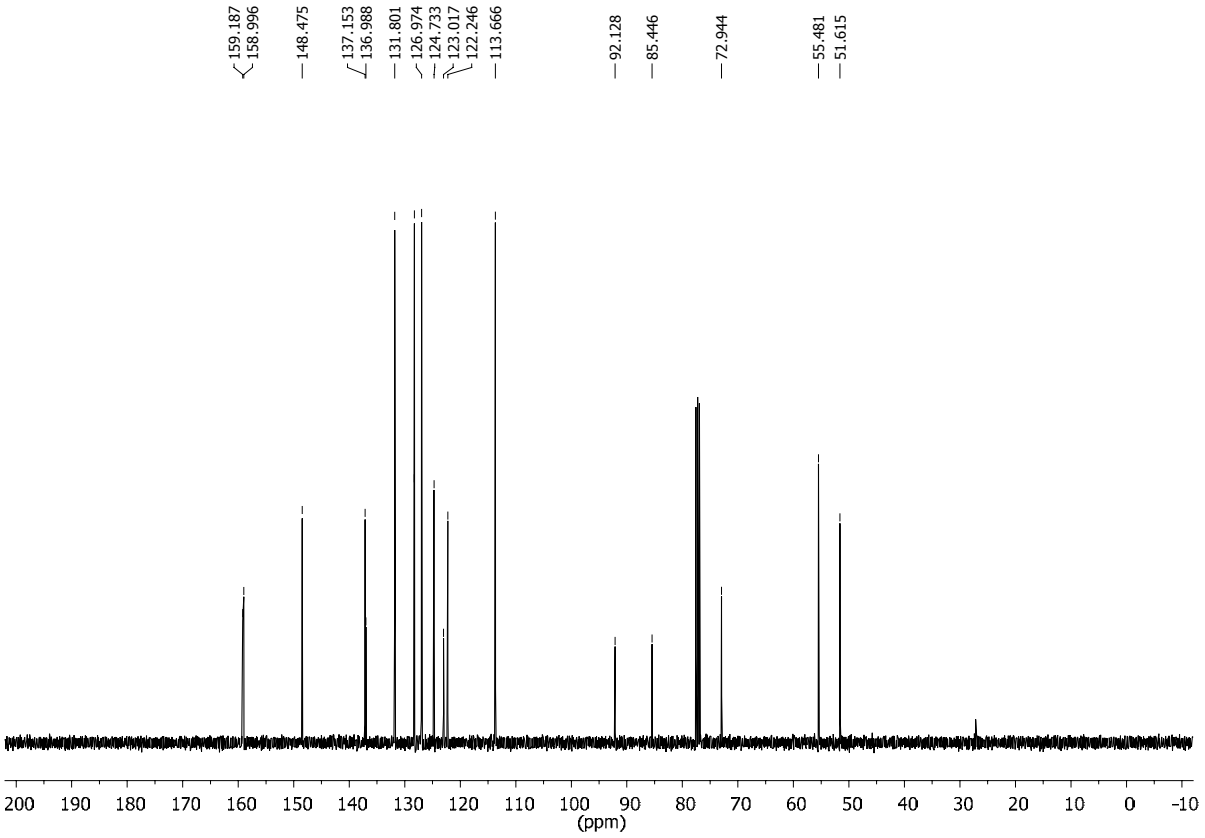

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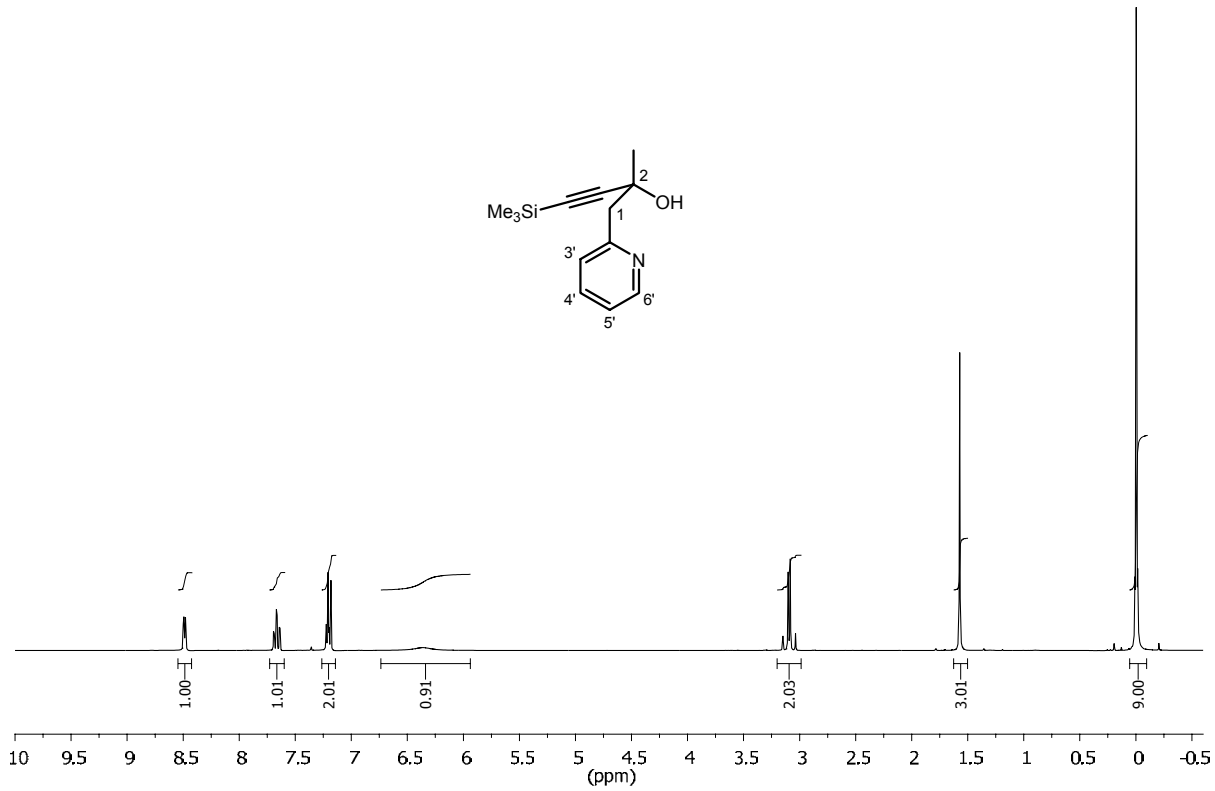
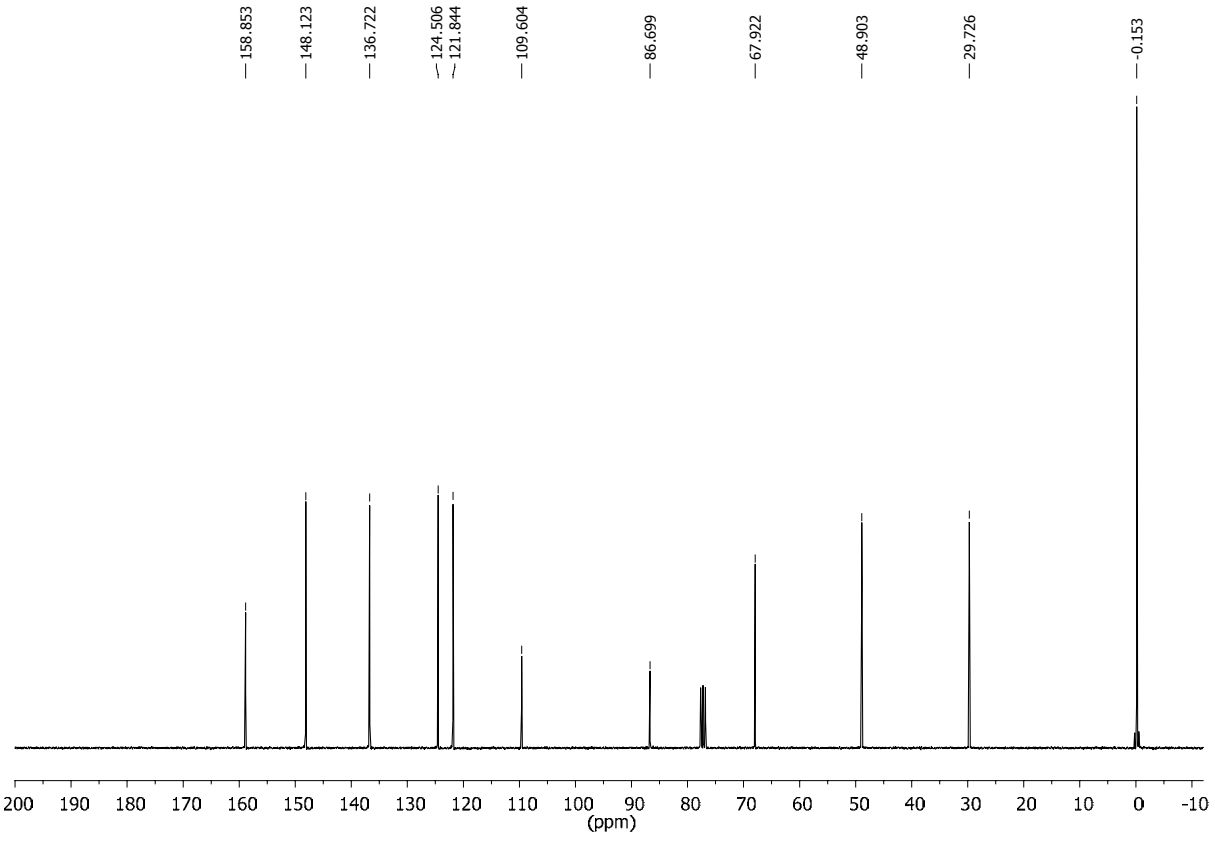
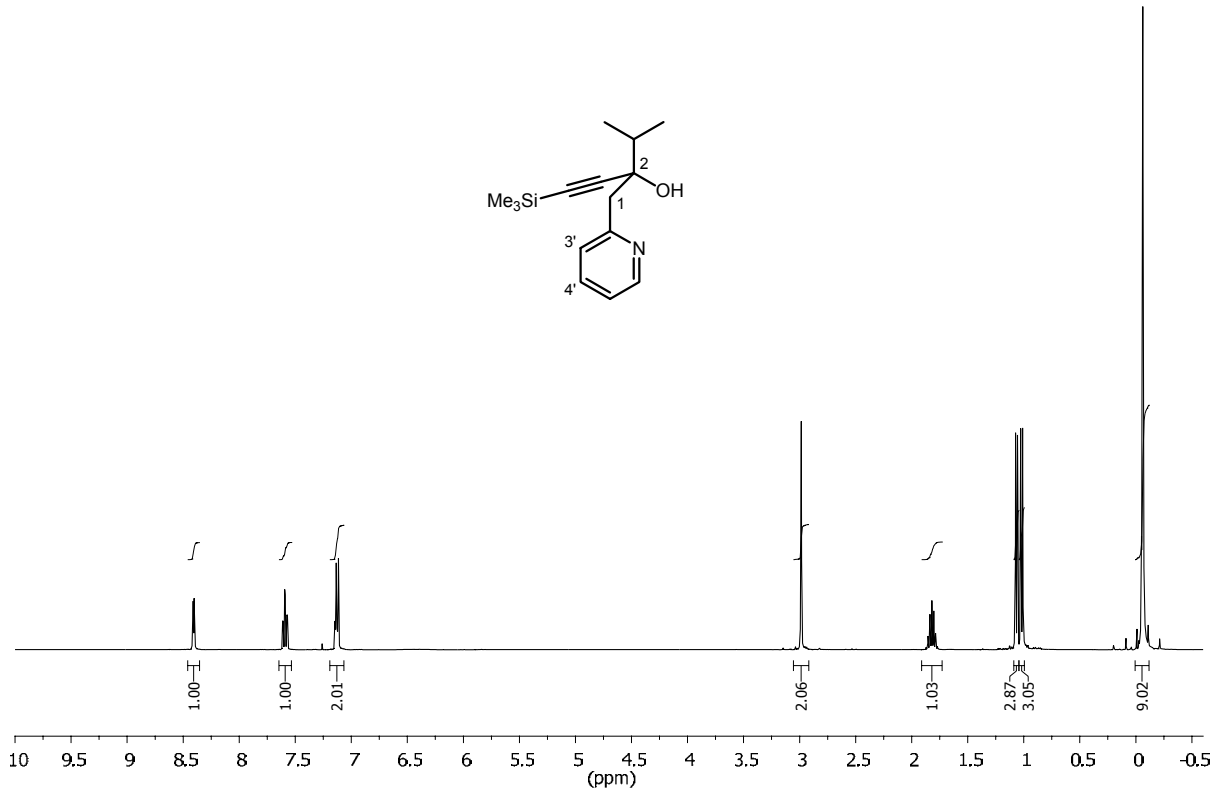


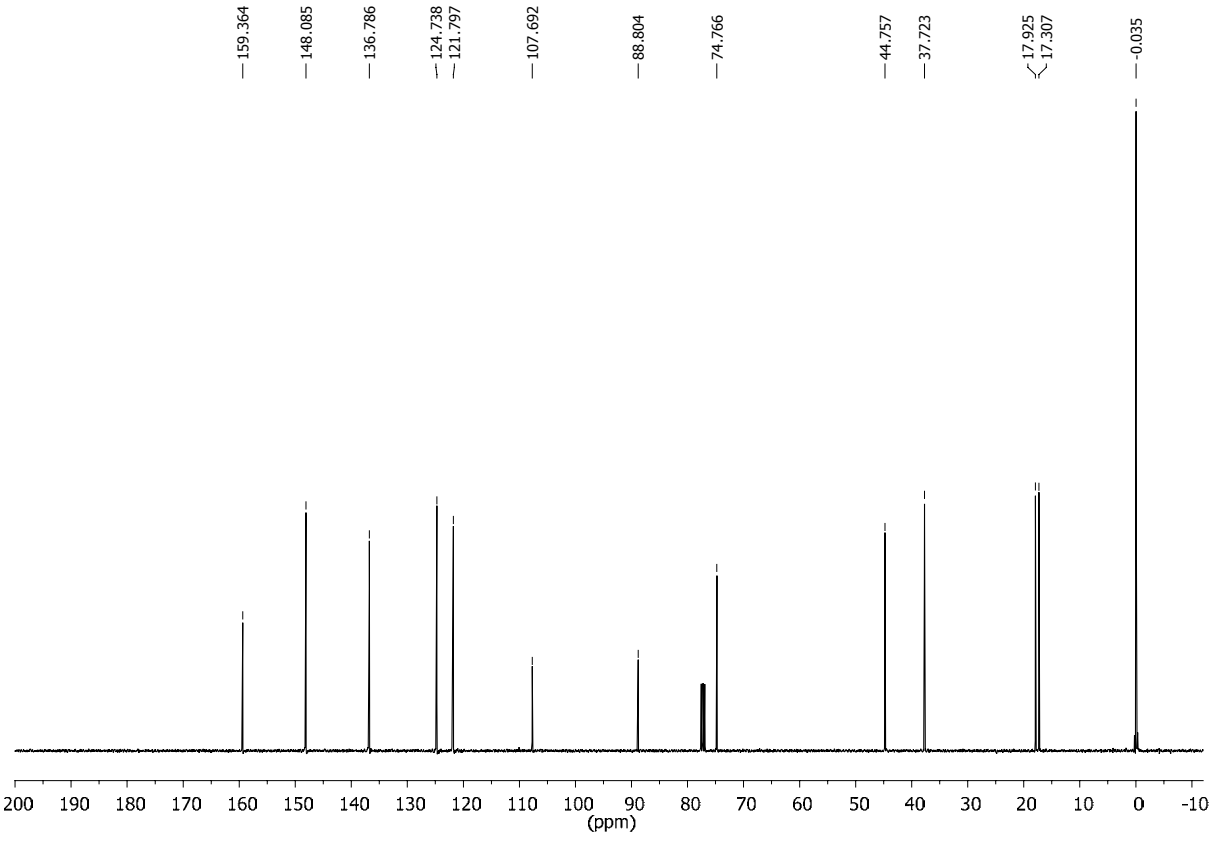
rac-**11** (^{13}C):



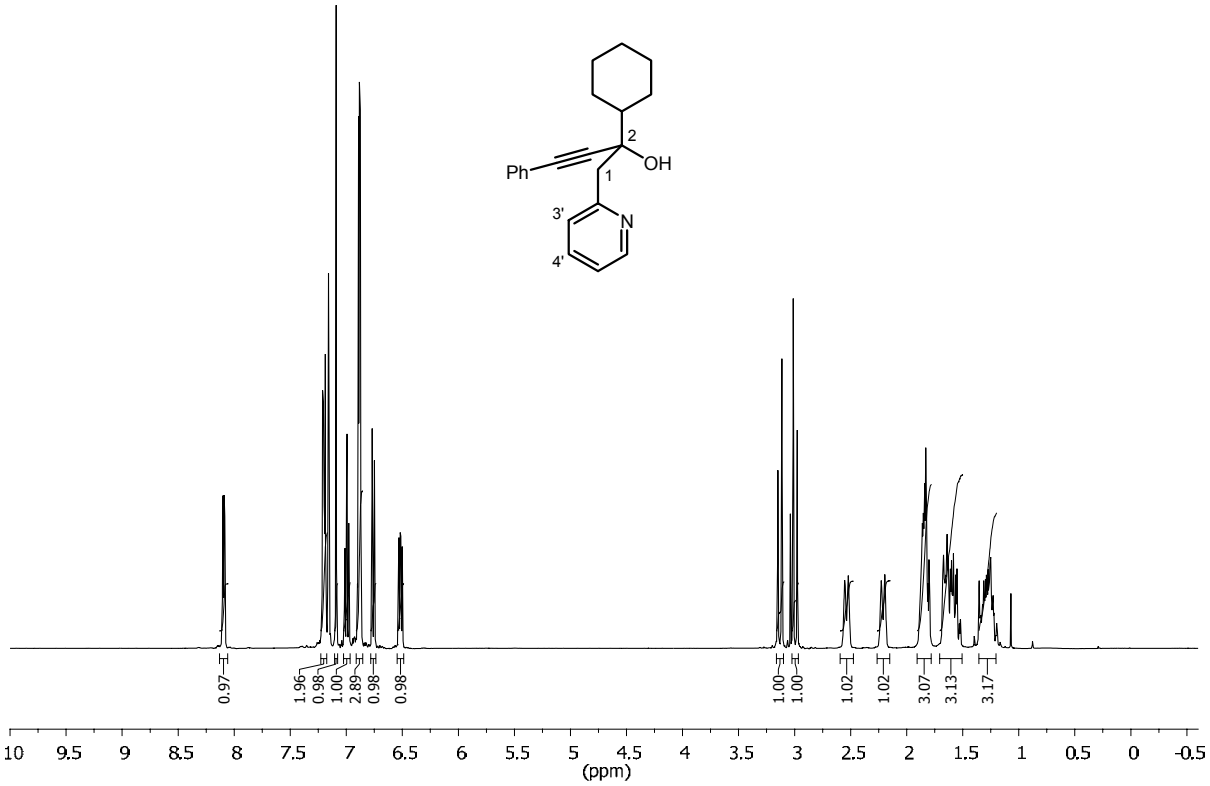
rac-**12** (^{1}H):



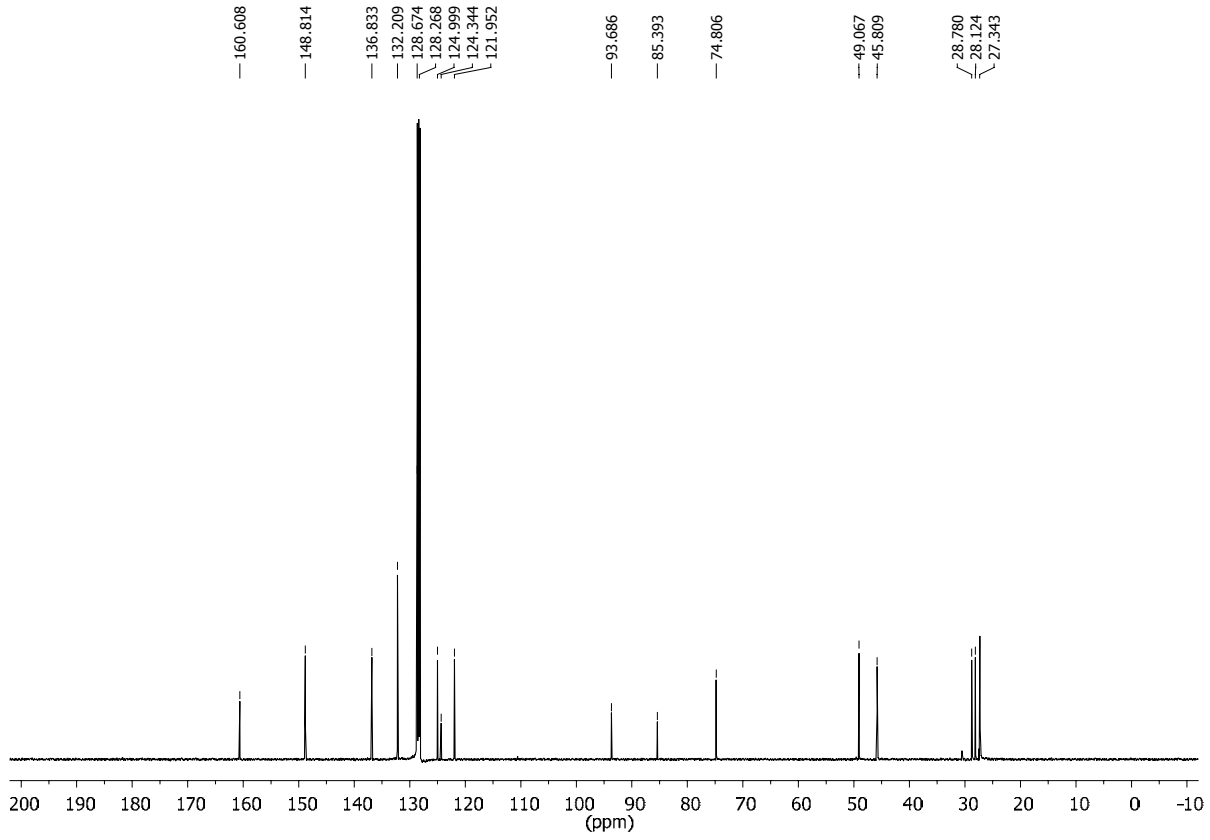
rac-**12** (^{13}C):



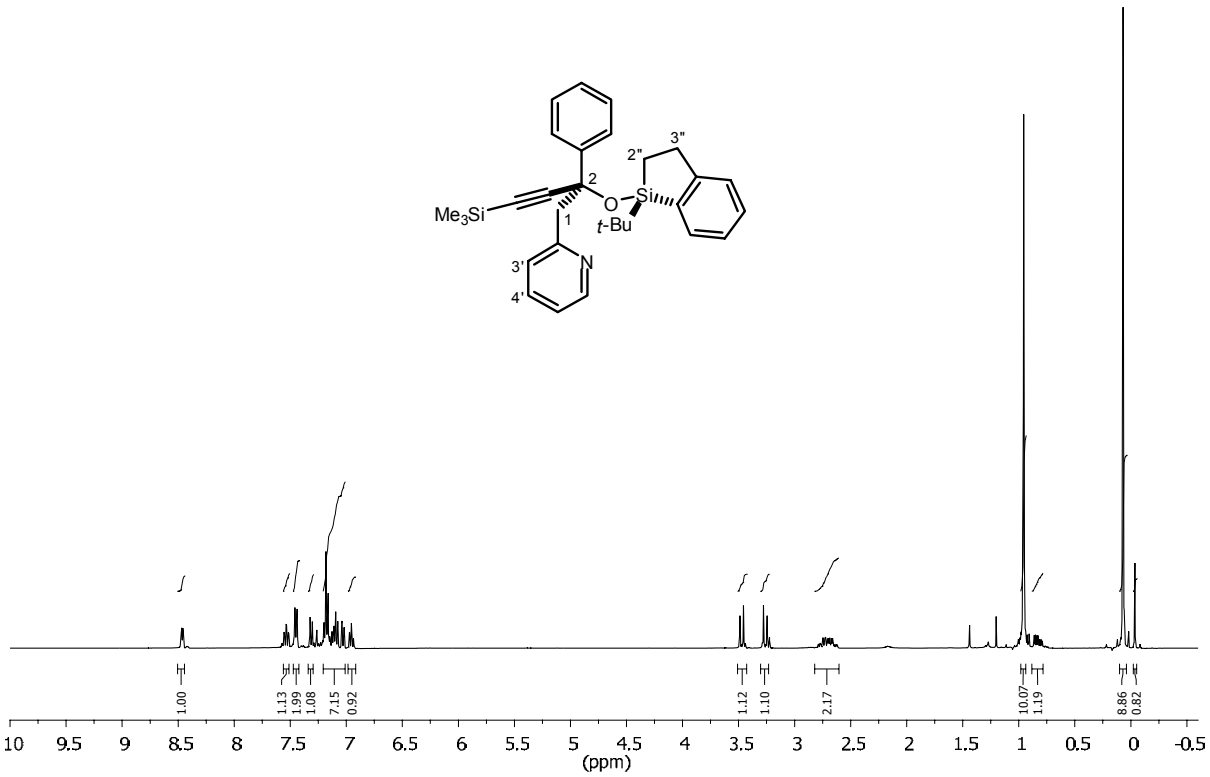
rac-**13** (^{1}H):



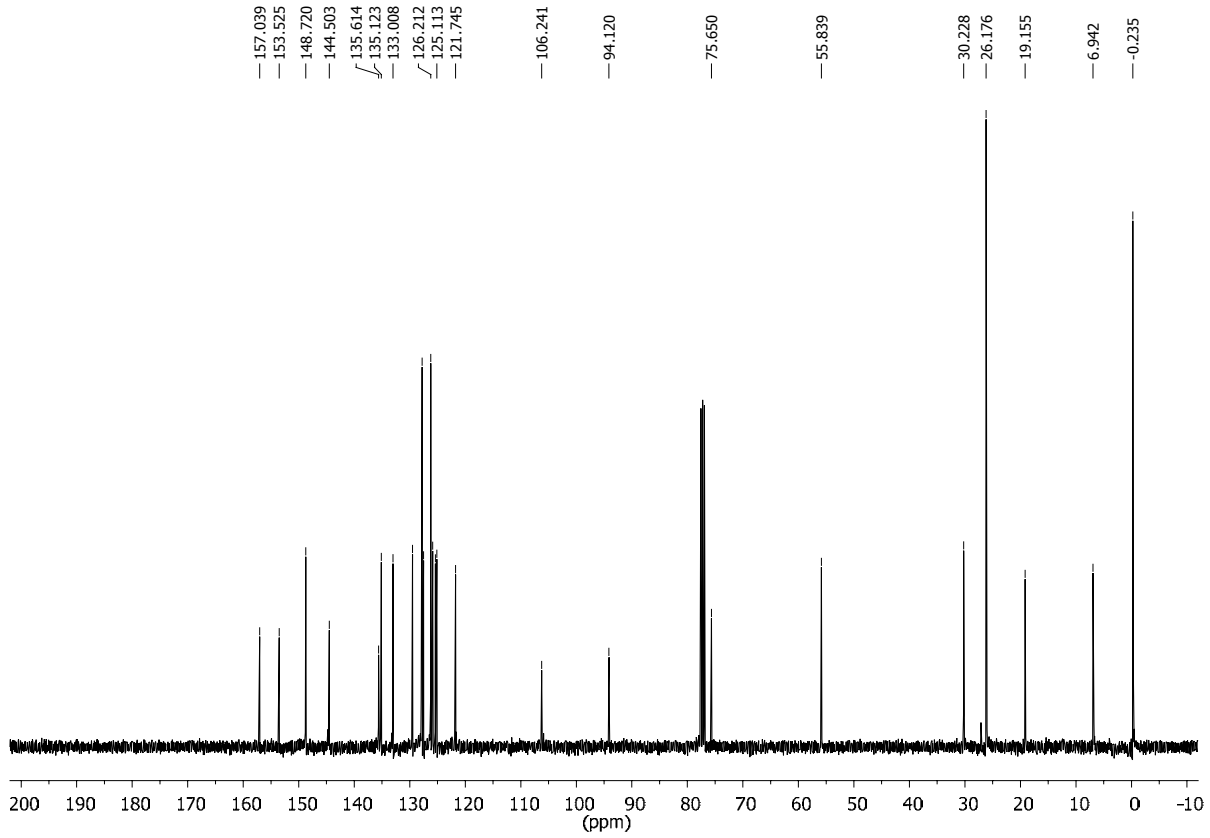
rac-**13** (^{13}C):



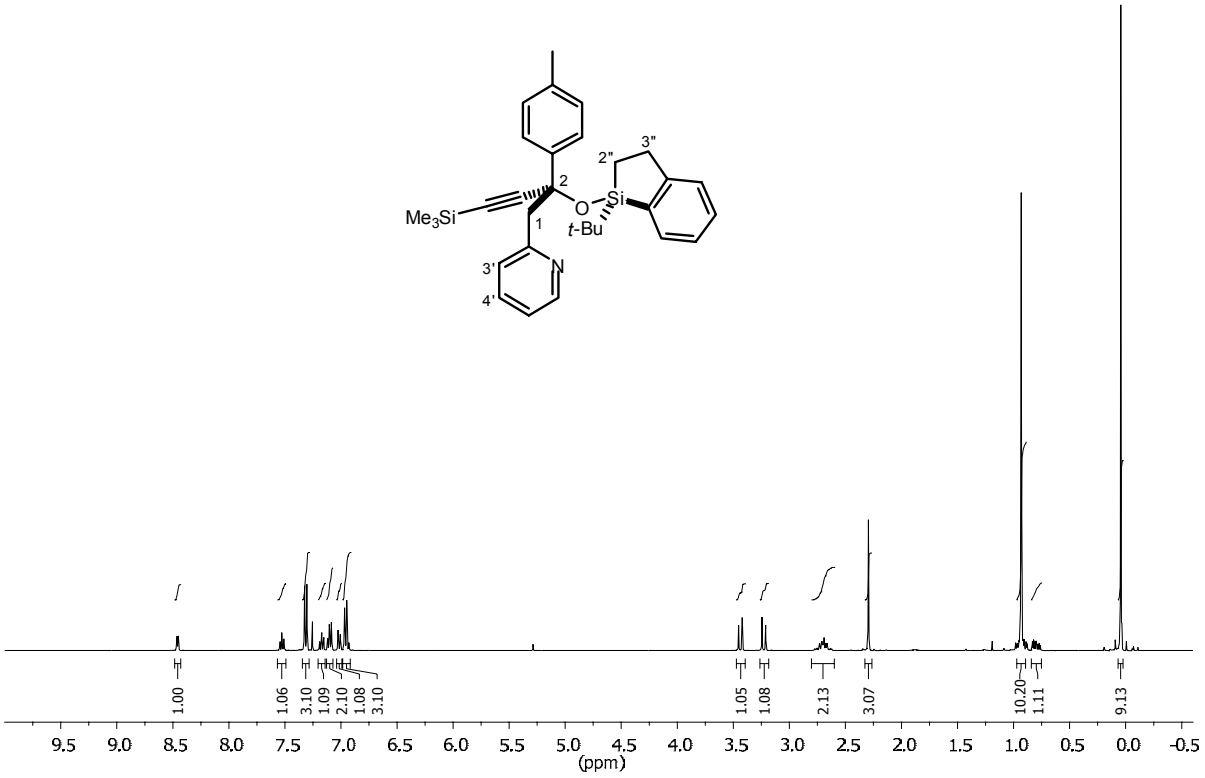
(^{Si}S*,*R**)-**14** (^{1}H):



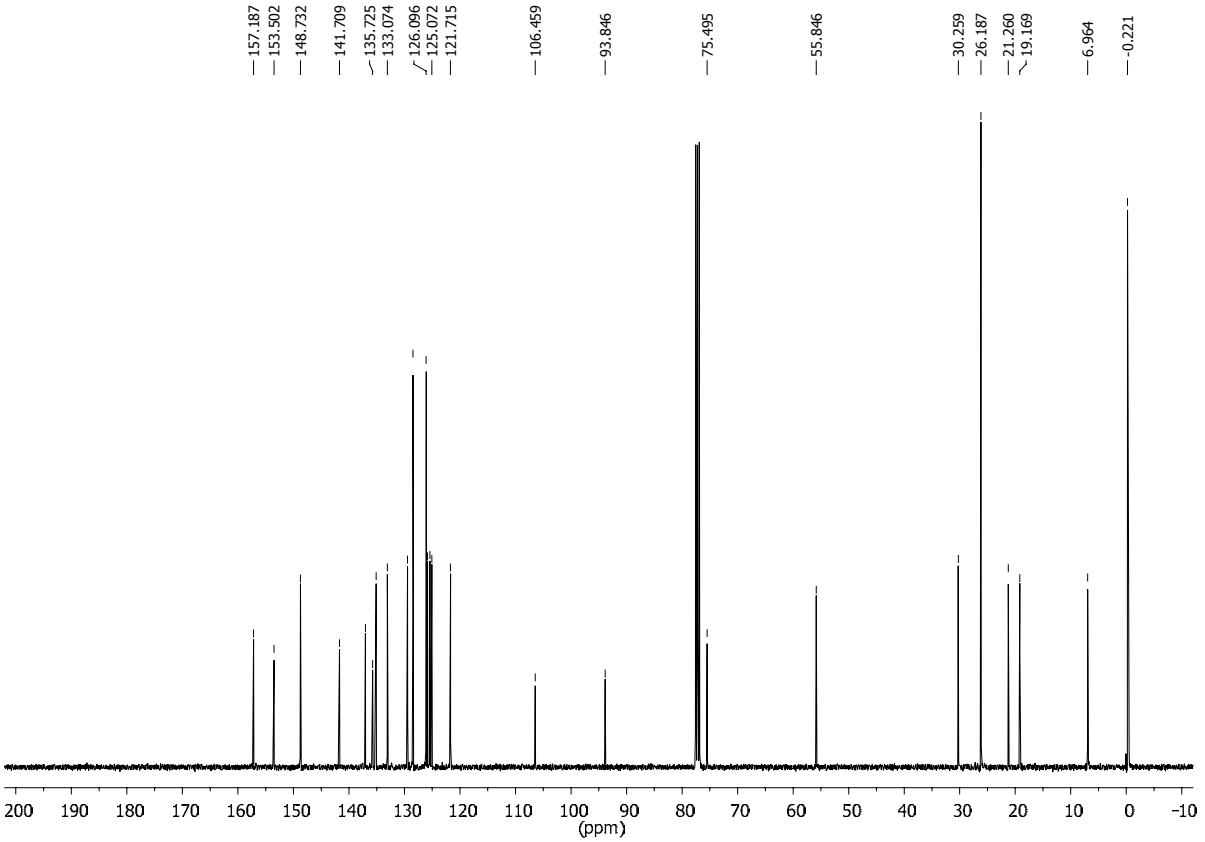
(^{Si}S*,*R**)-**14** (^{13}C):



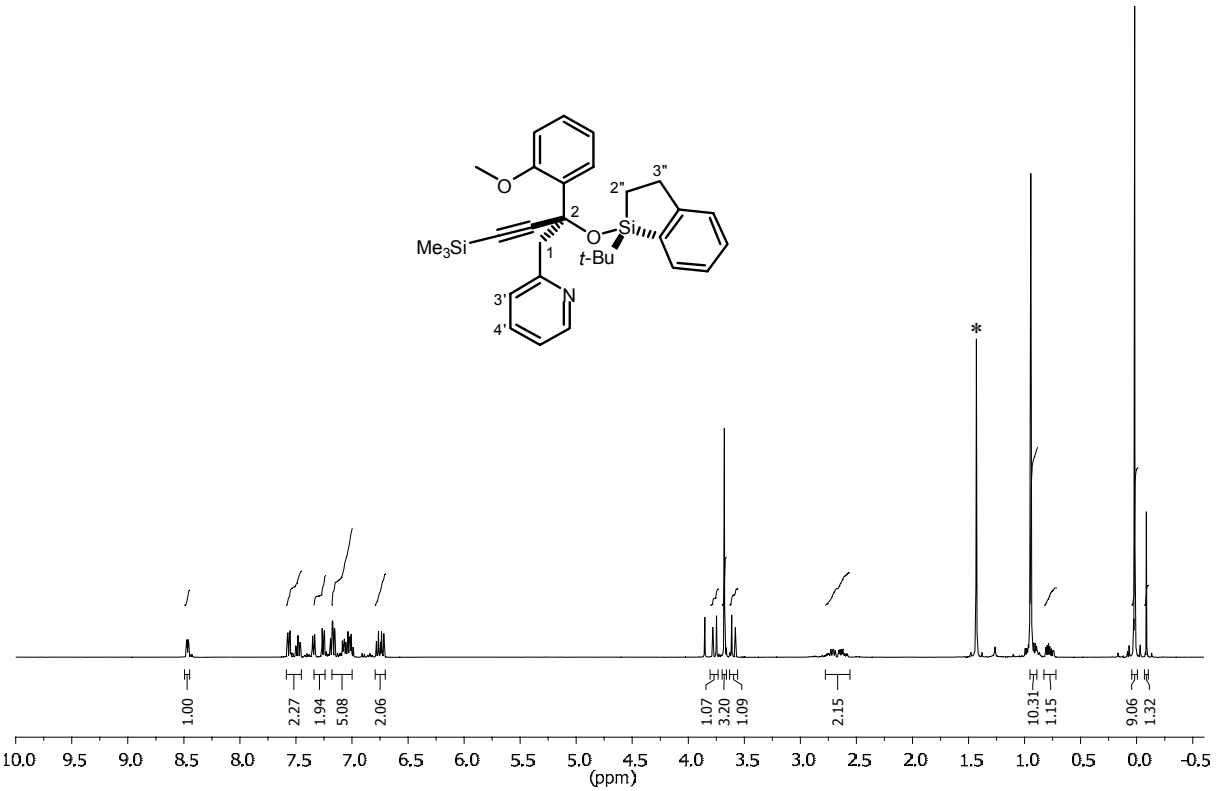
(^{Si}*R**,*S**)-**15** (^{1}H):



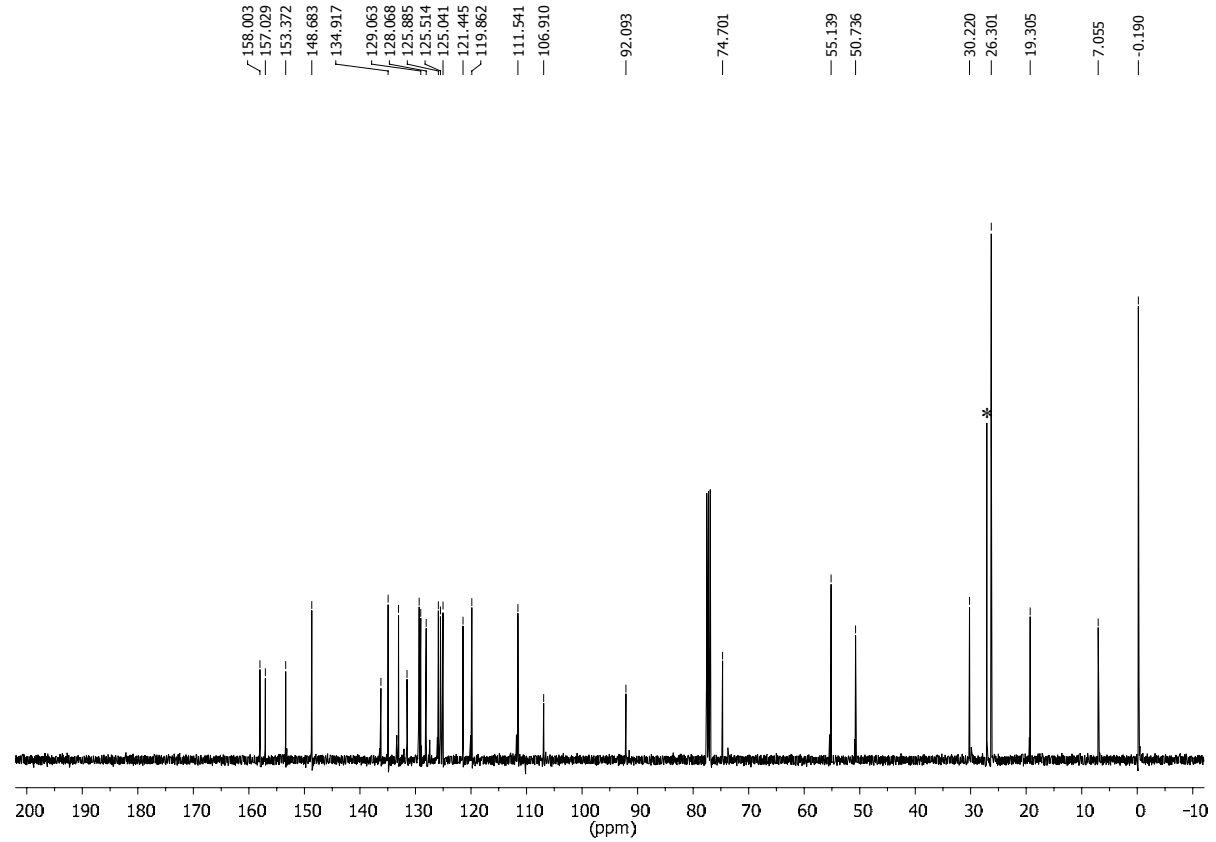
(^{Si}*R**,*S**)-**15** (^{13}C):



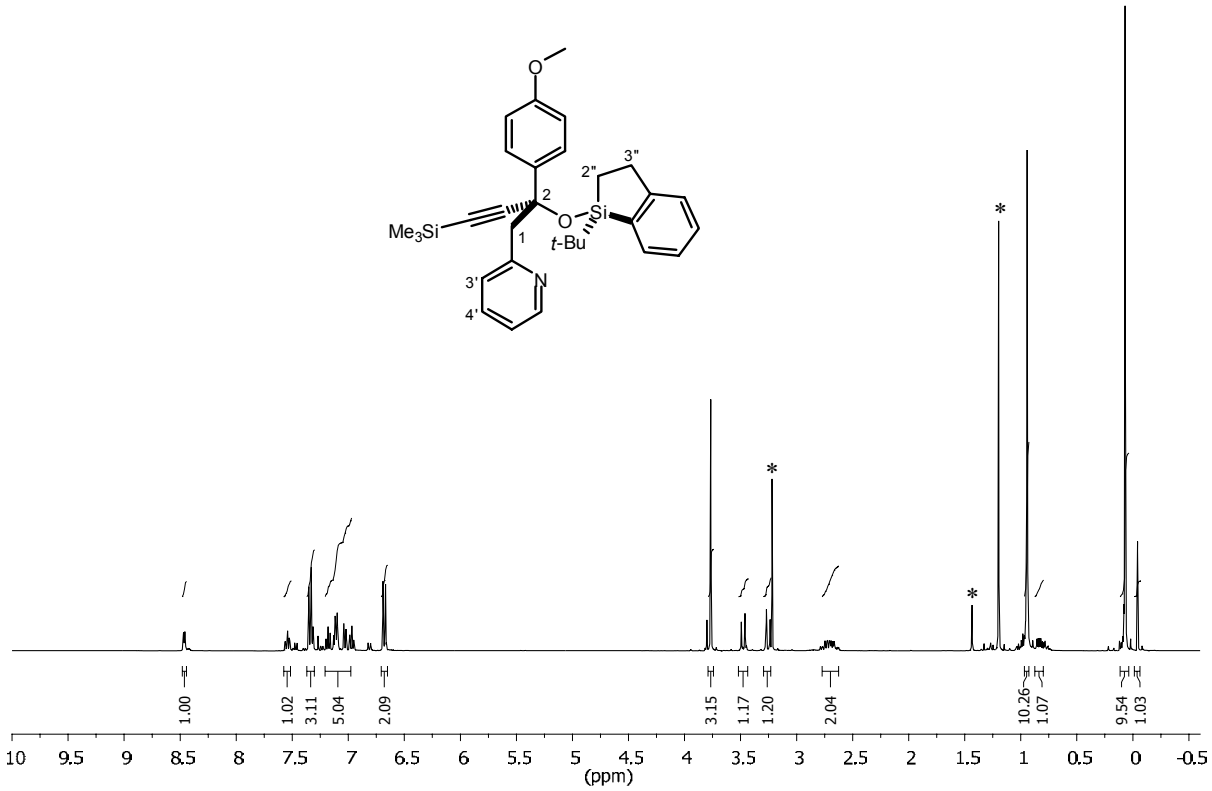
($^{Si}S^*,R^*$)-**16** (^{1}H):



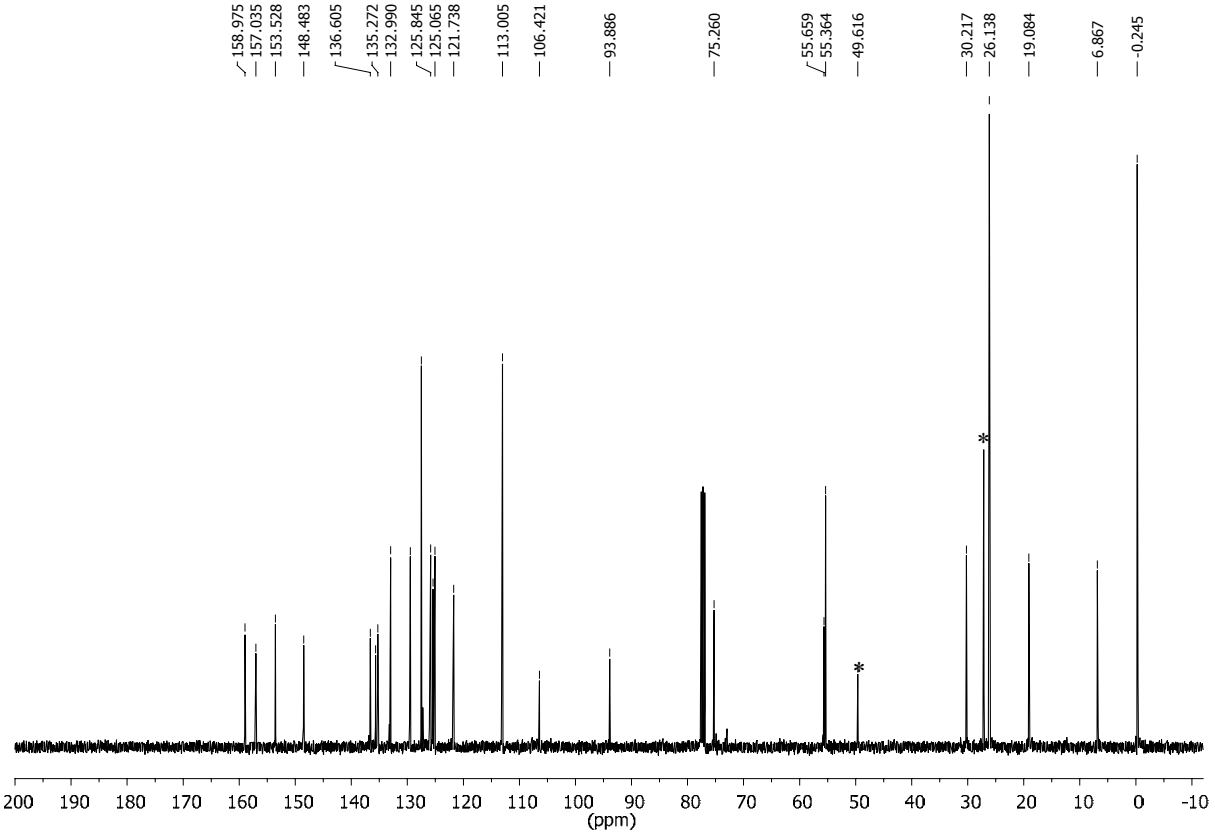
($^{Si}S^*,R^*$)-**16** (^{13}C):



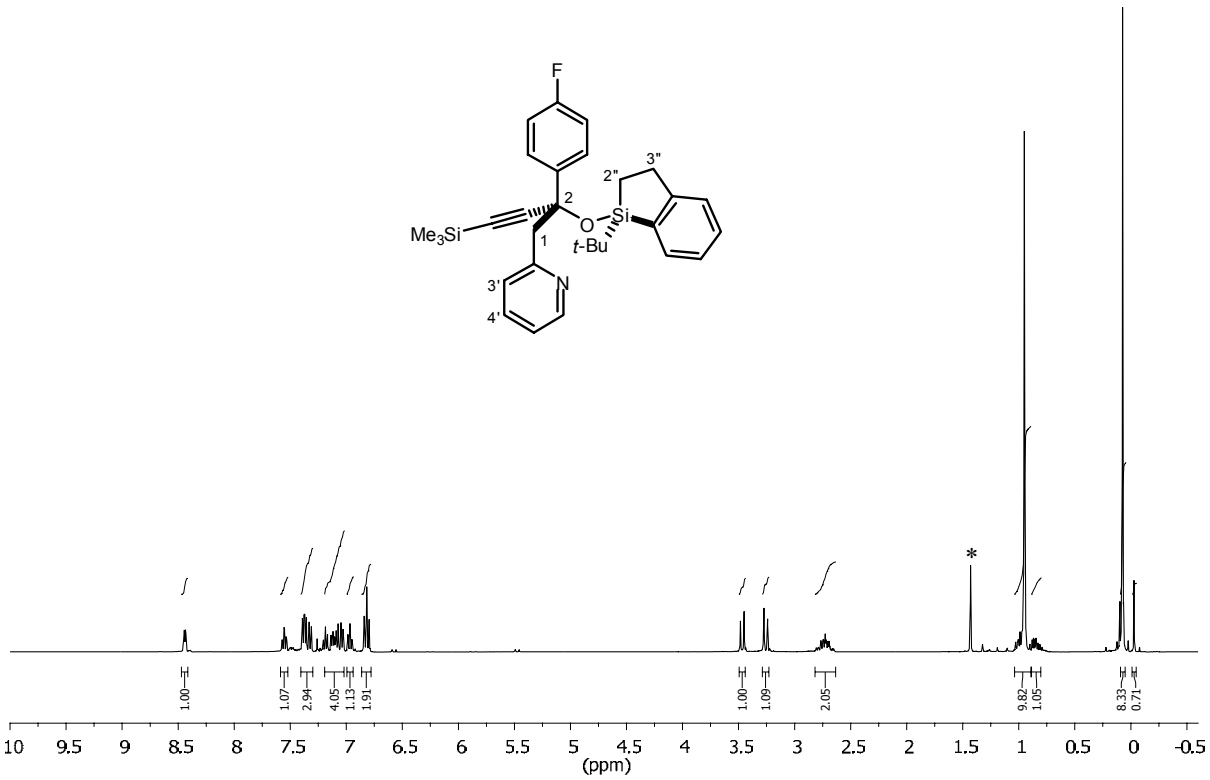
($^{Si}R^*,S^*$)-**17** (^{1}H):



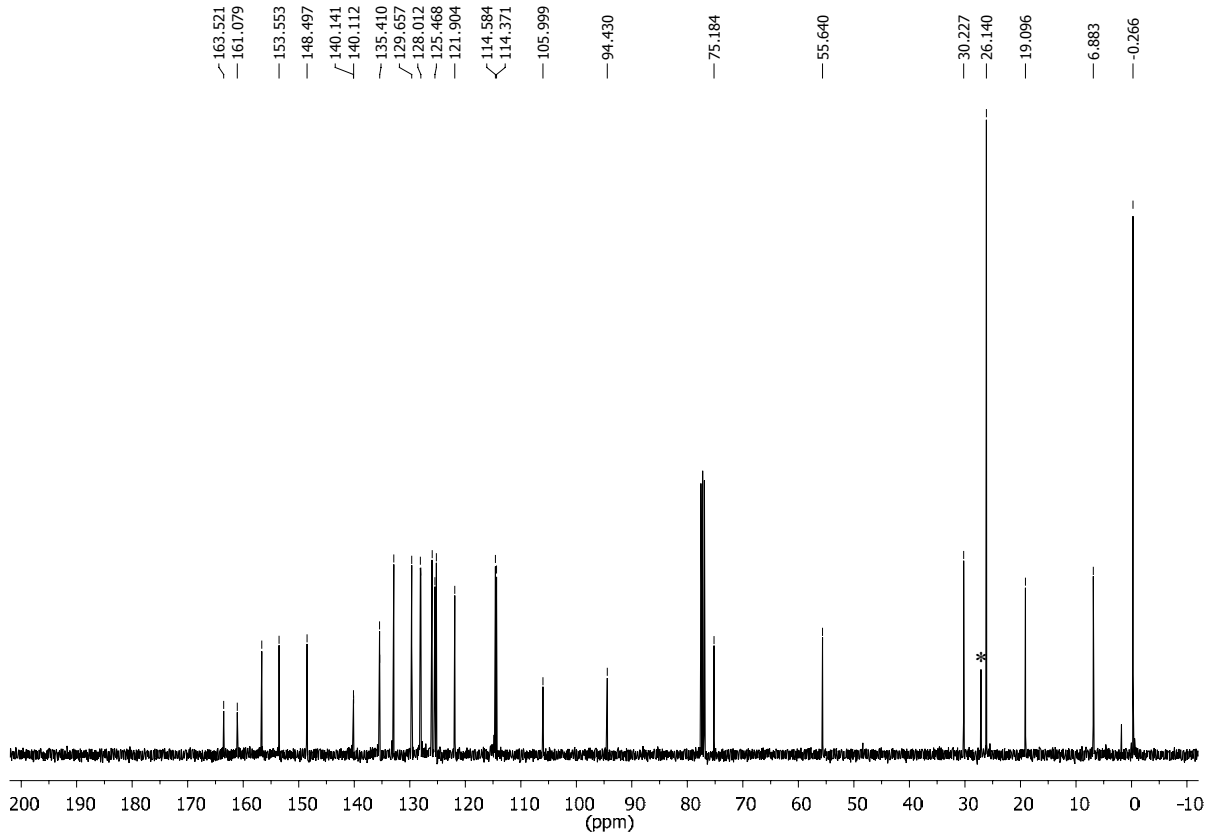
($^{Si}R^*,S^*$)-**17** (^{13}C):



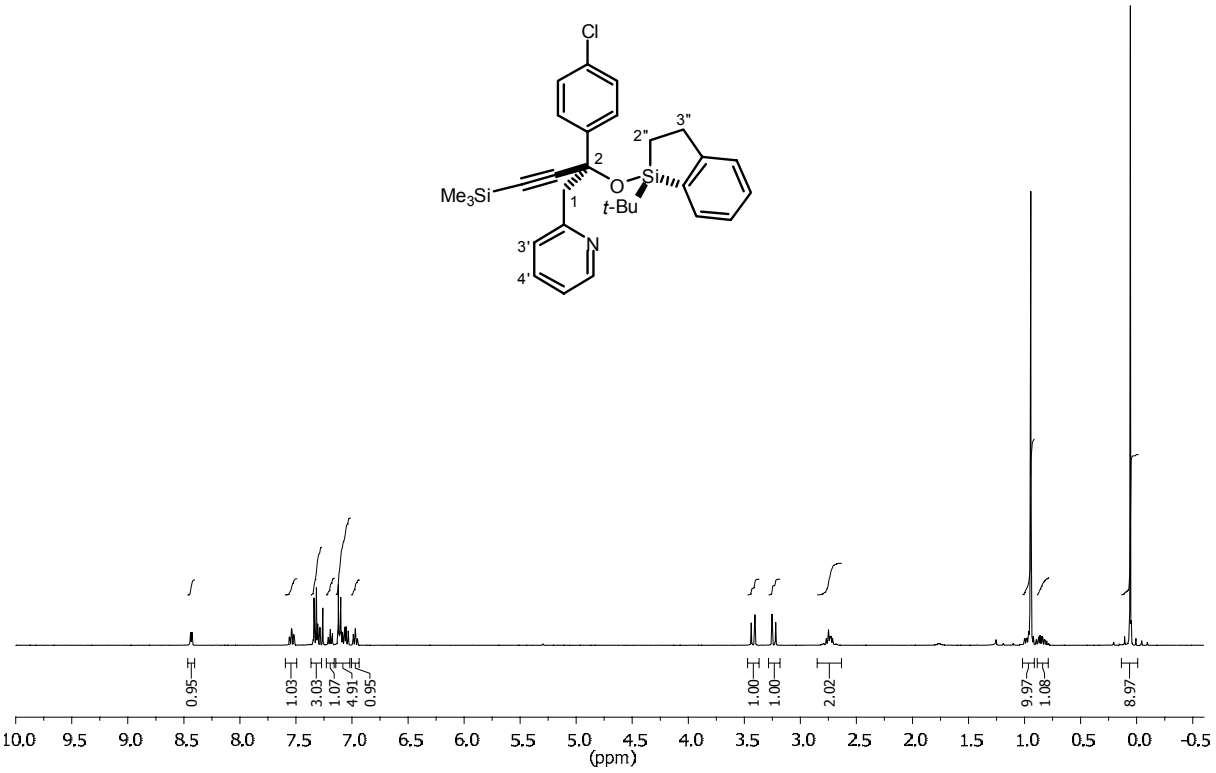
(^{Si}*R**,*S**)-**18** (^{1}H):



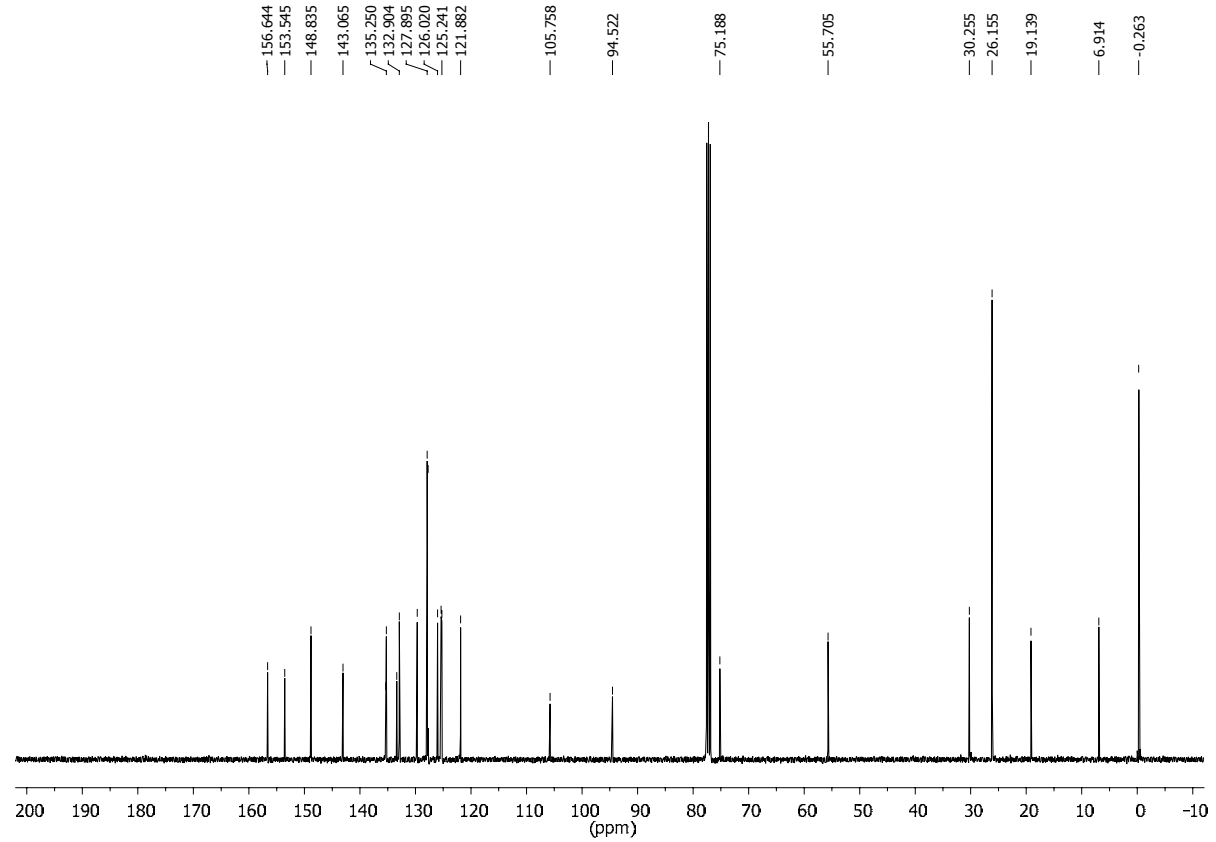
(^{Si}*R**,*S**)-**18** (^{13}C):



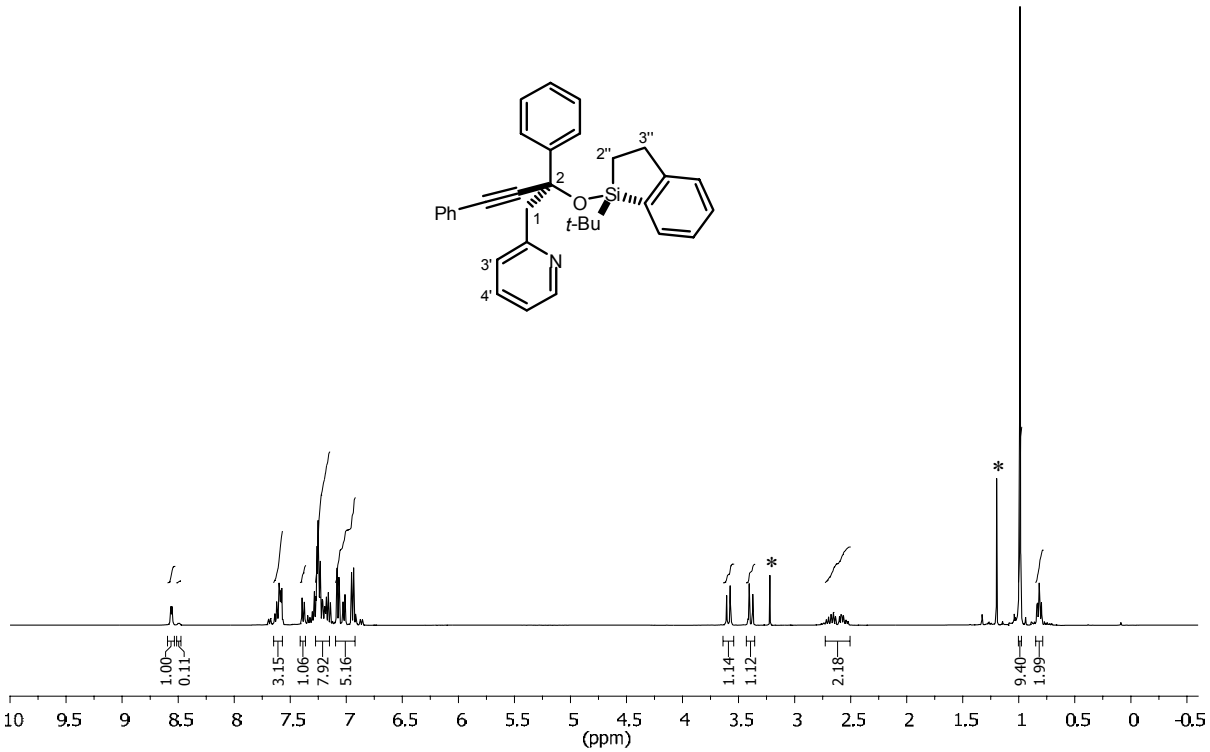
(^{Si}S*,*R**)-**19** (^{1}H):



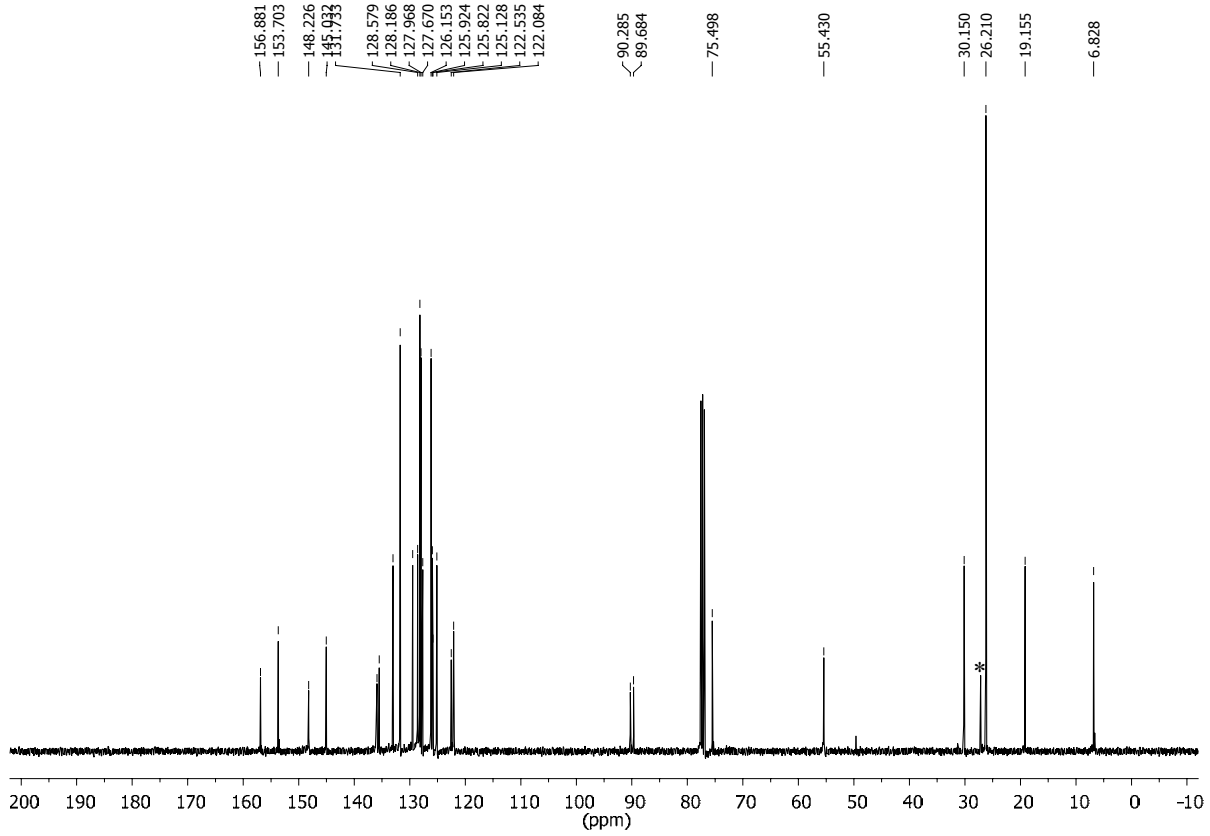
(^{Si}S,*R*)-**19** (^{13}C):



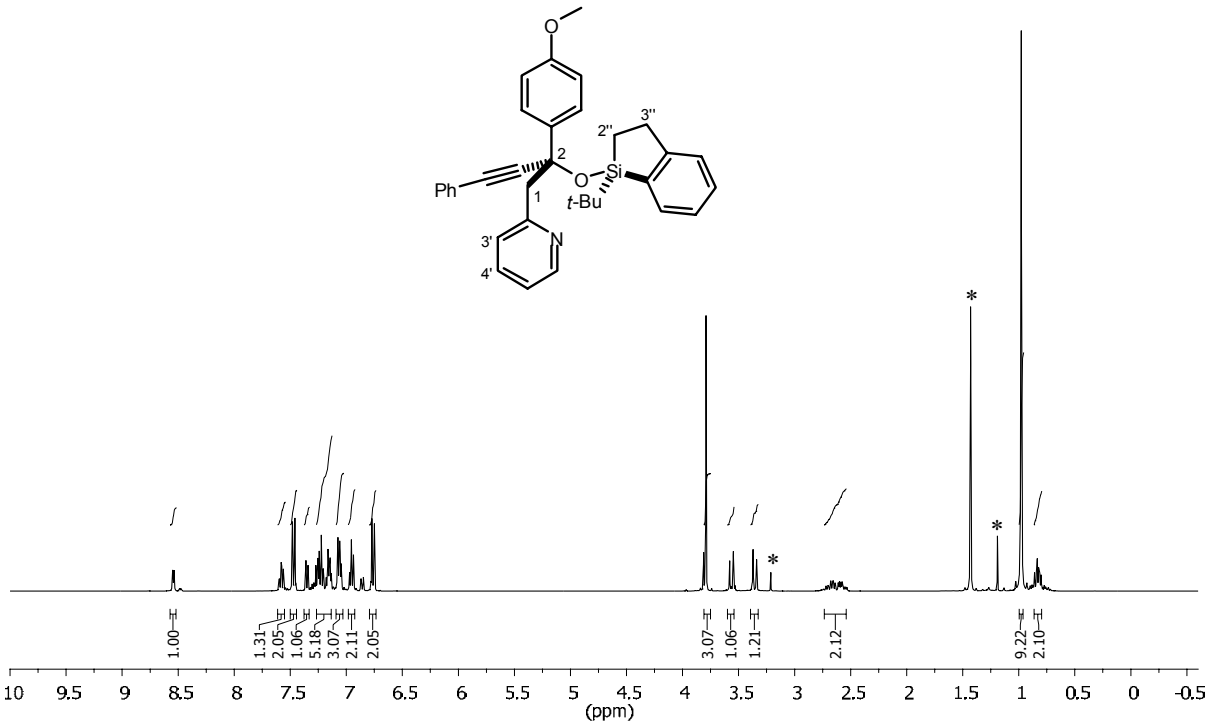
(^{Si}S*,R*)-**20** (^{1}H):



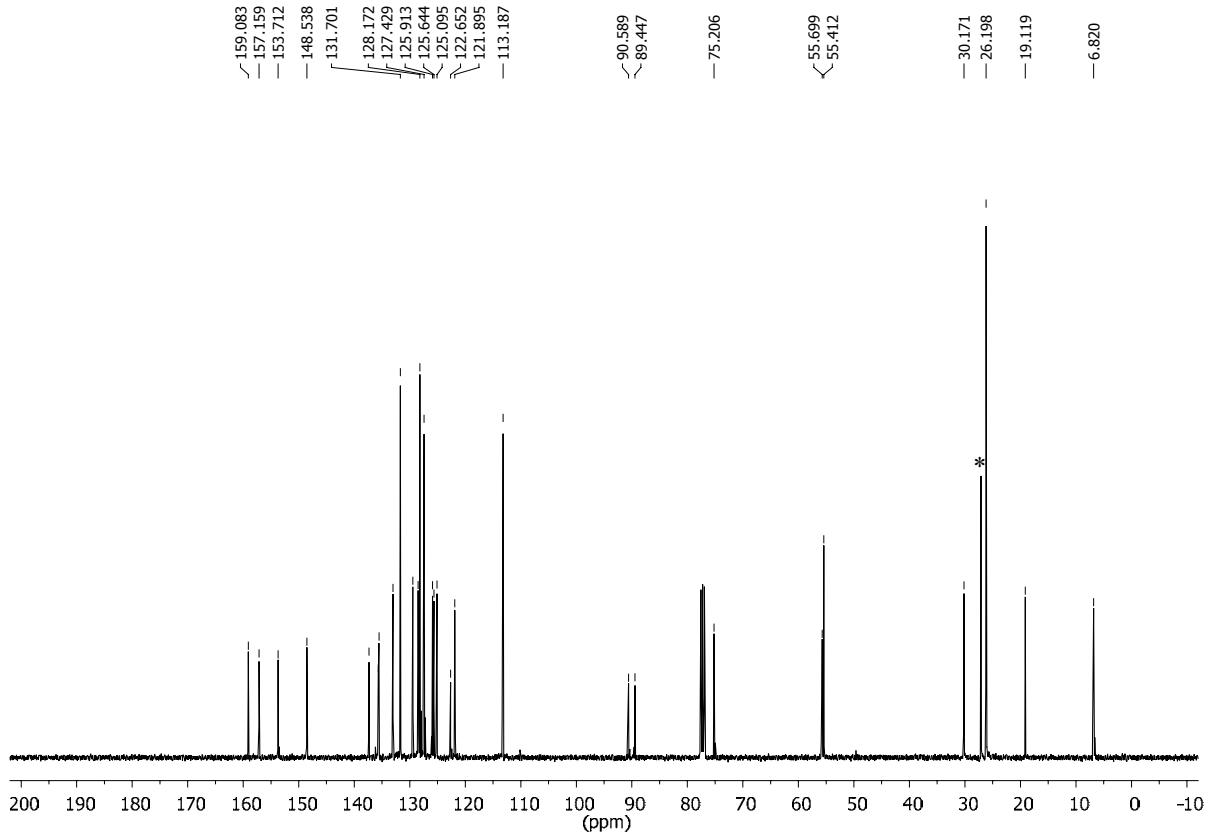
(^{Si}S*,R*)-**20** (^{13}C):



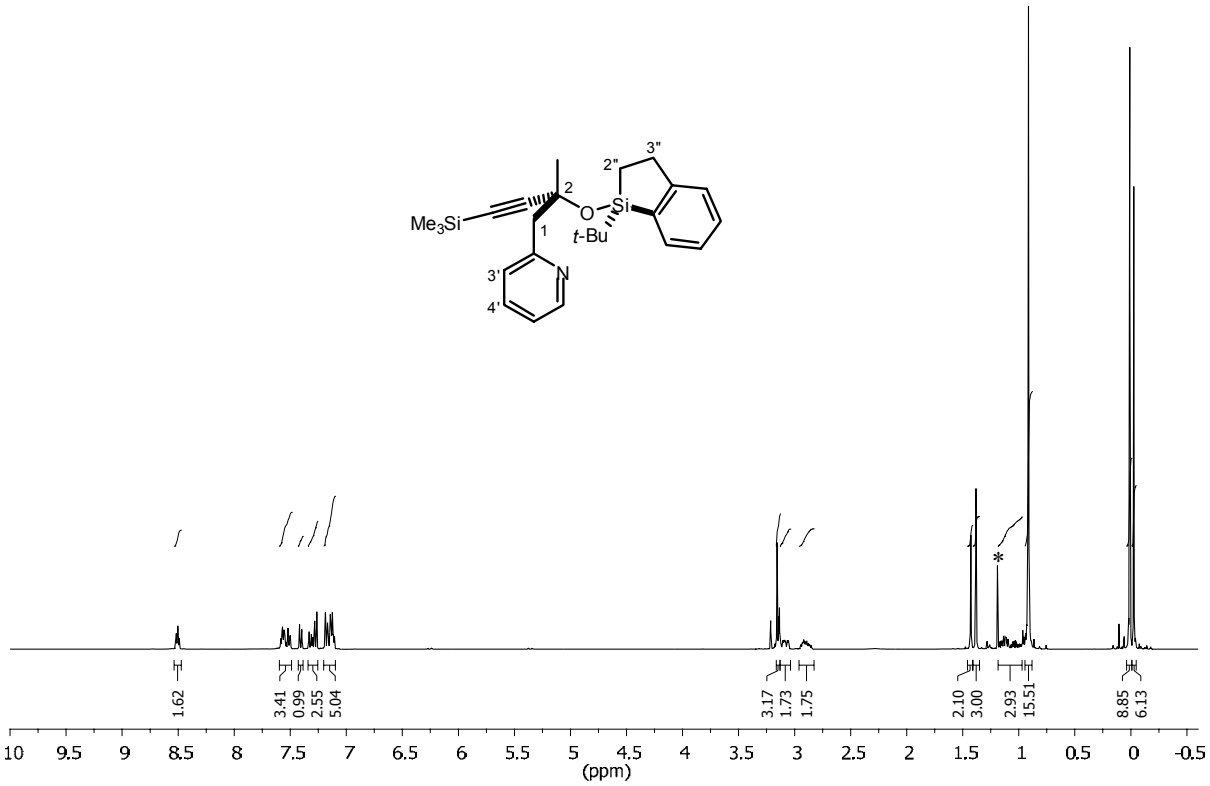
(^{Si}*R**,*S**)-**21** (^{1}H):



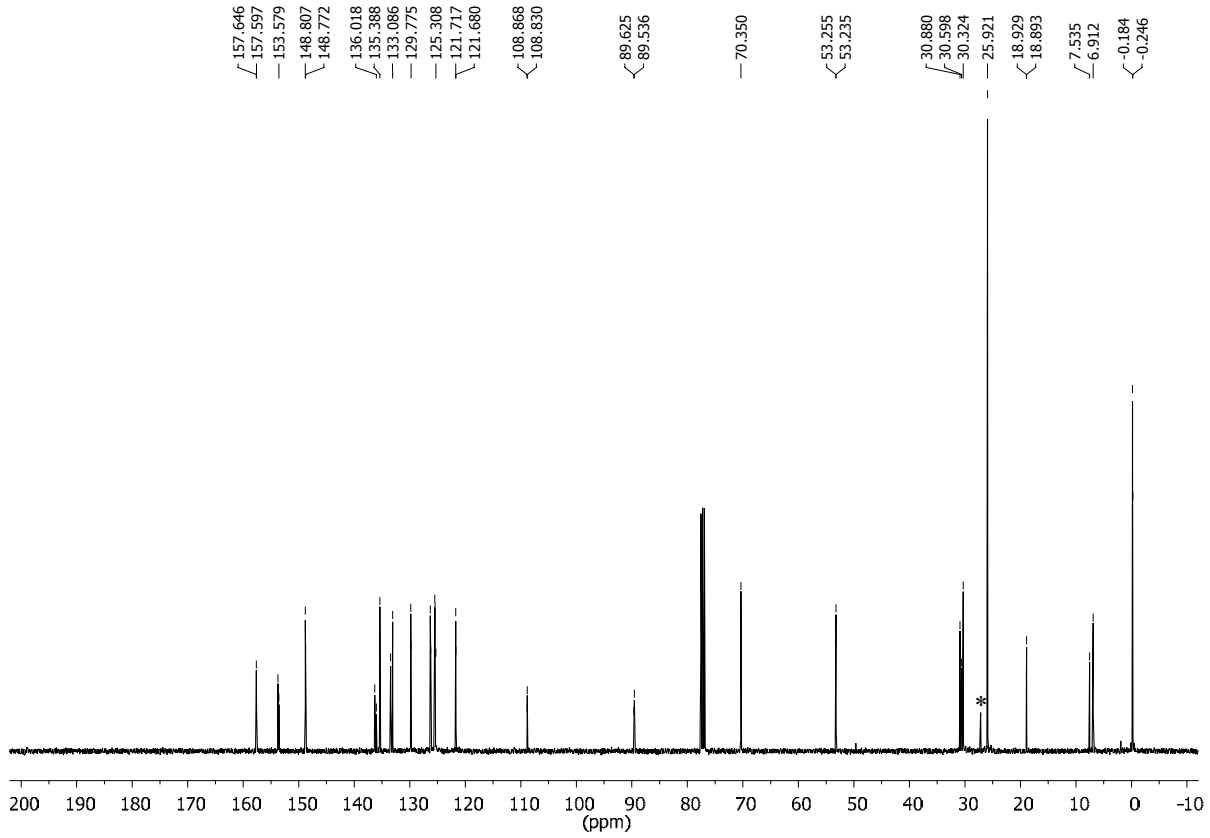
(^{Si}*R**,*S**)-**21** (^{13}C):



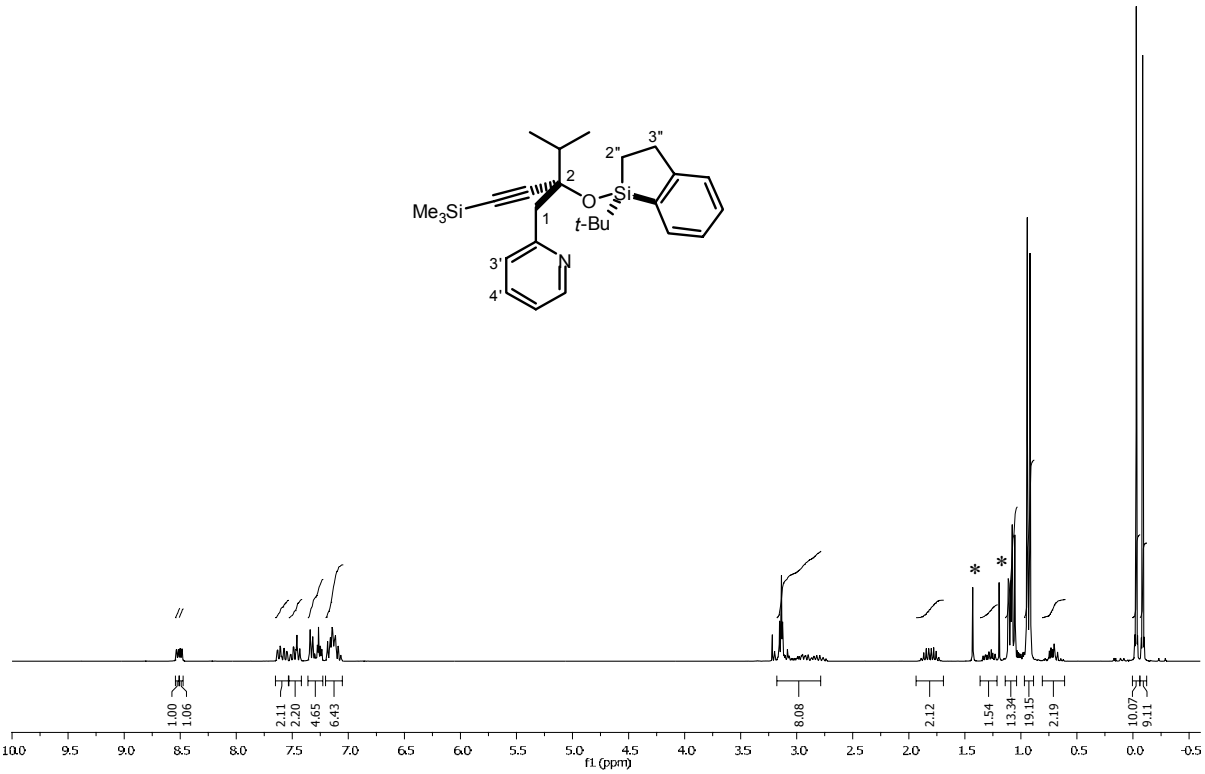
(^{Si}*R**,*S**)-**22** (^{1}H):



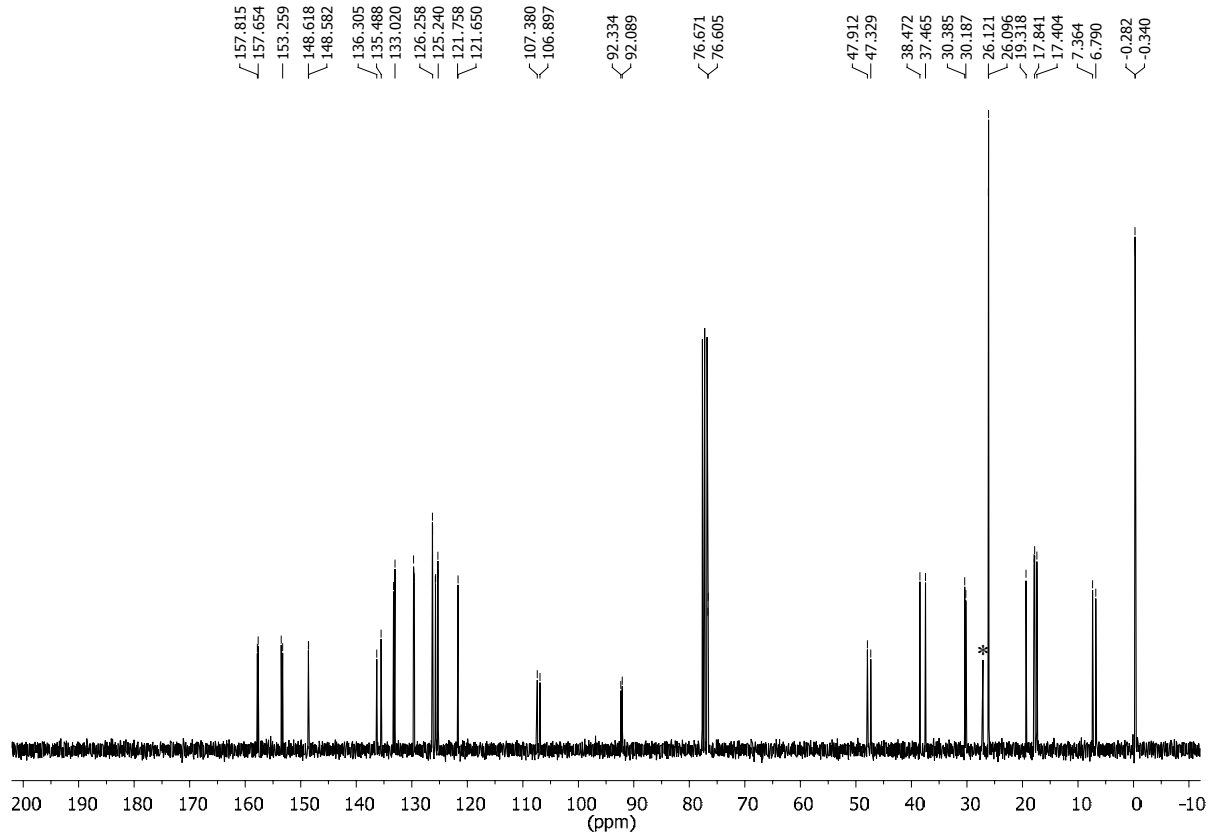
(^{Si}*R**,*S**)-**22** (^{13}C):



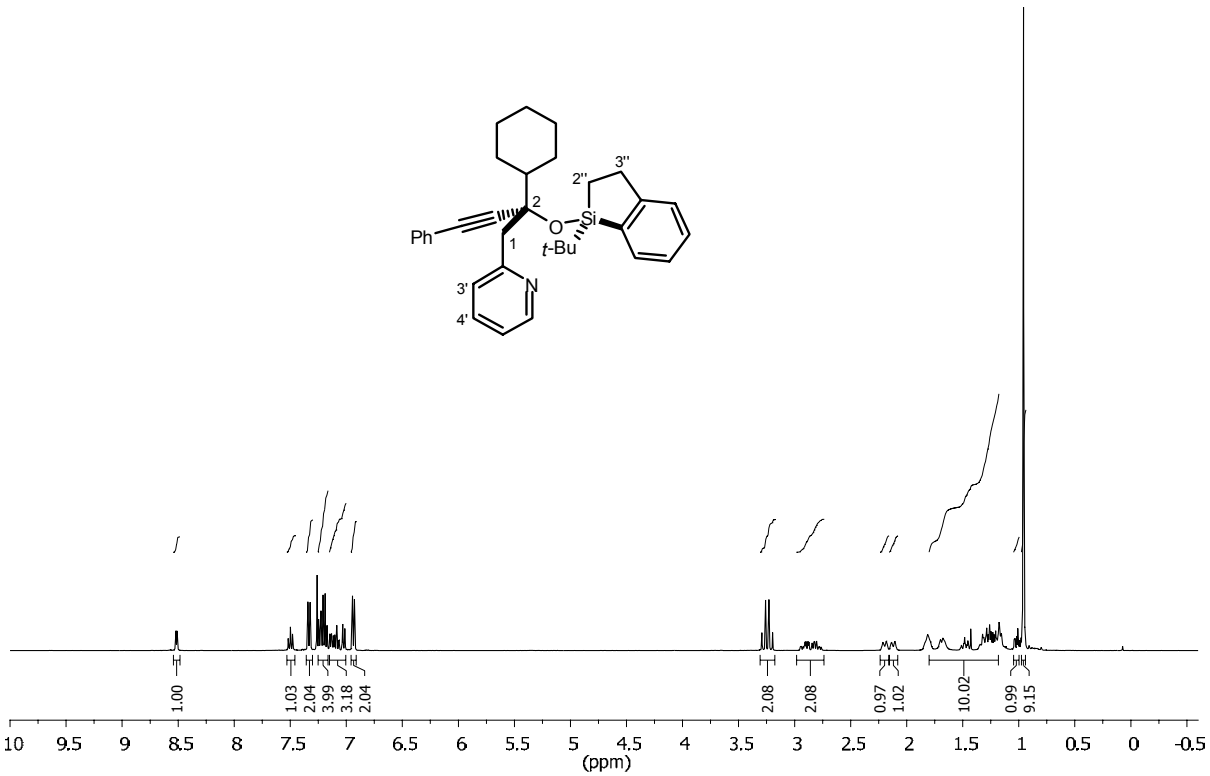
(^{Si}*R**,*S**)-**23** (^{1}H):



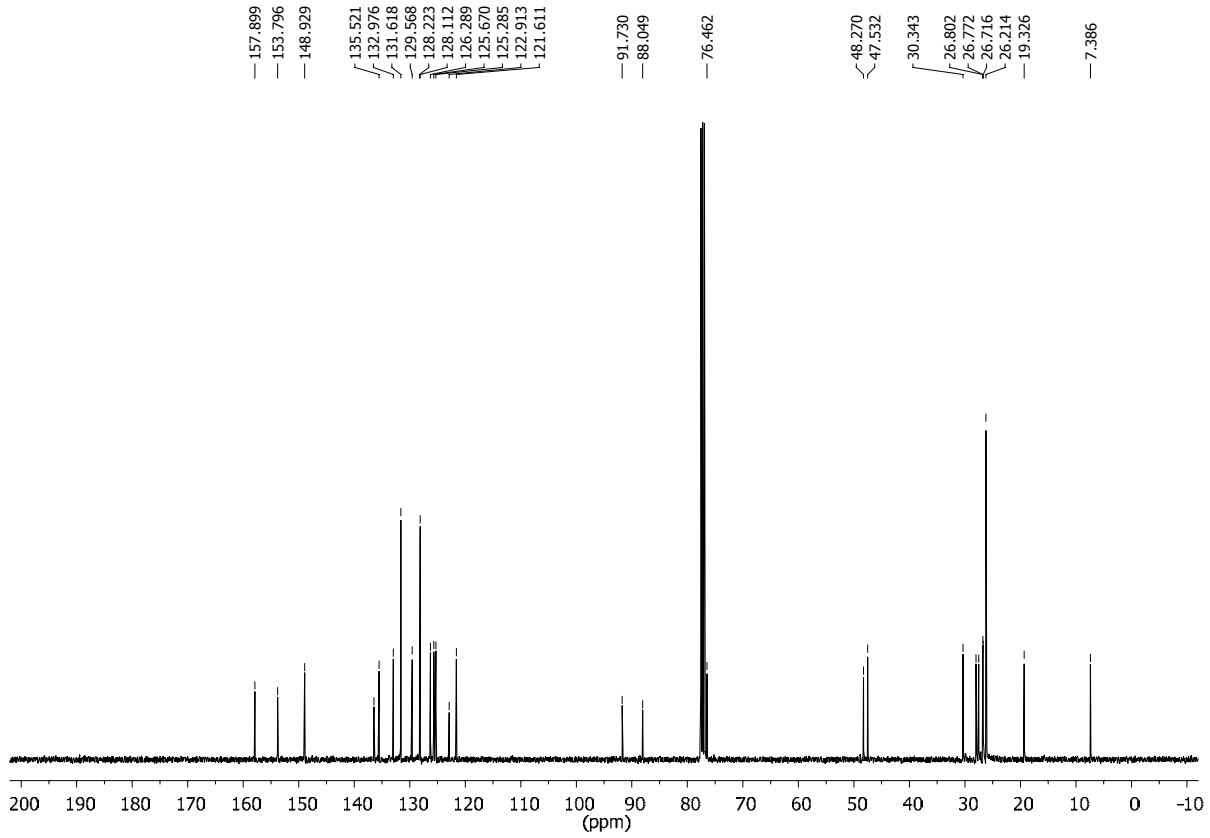
(^{Si}*R**,*S**)-**23** (^{13}C):



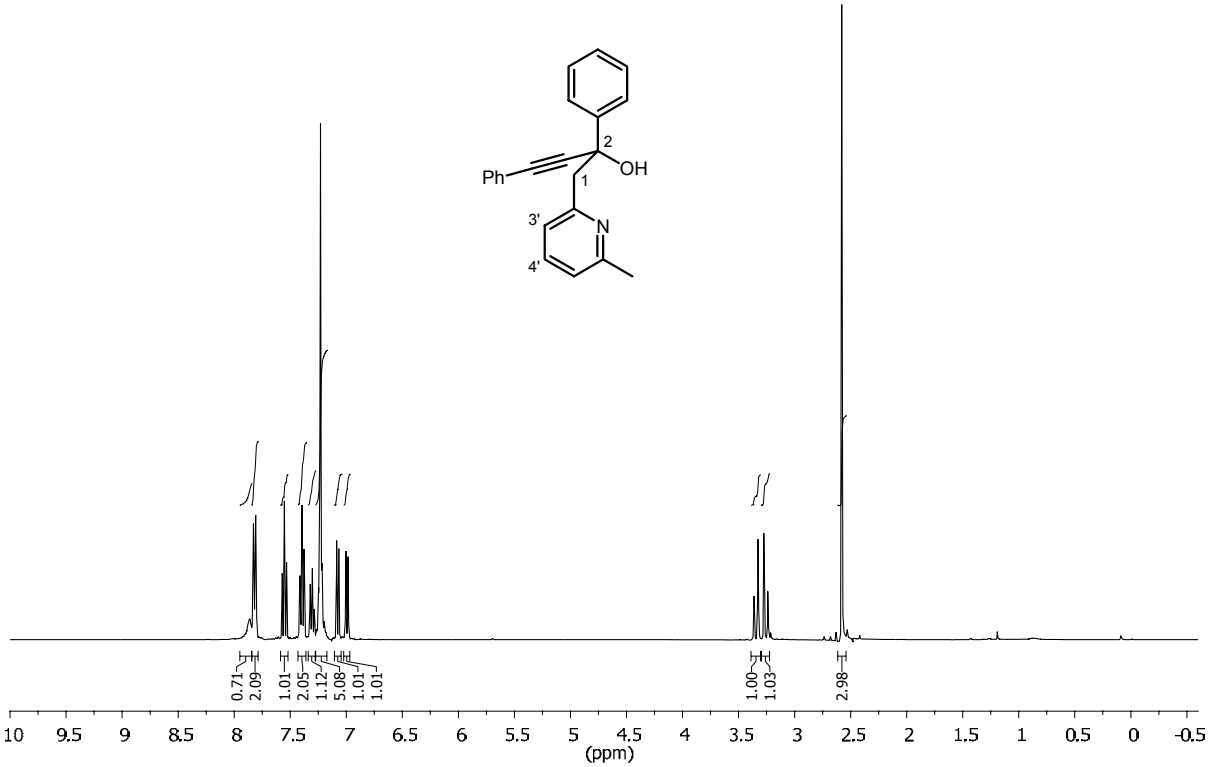
($^{Si}R^*,S^*$)-**24** (^{1}H): (Major diastereomer)



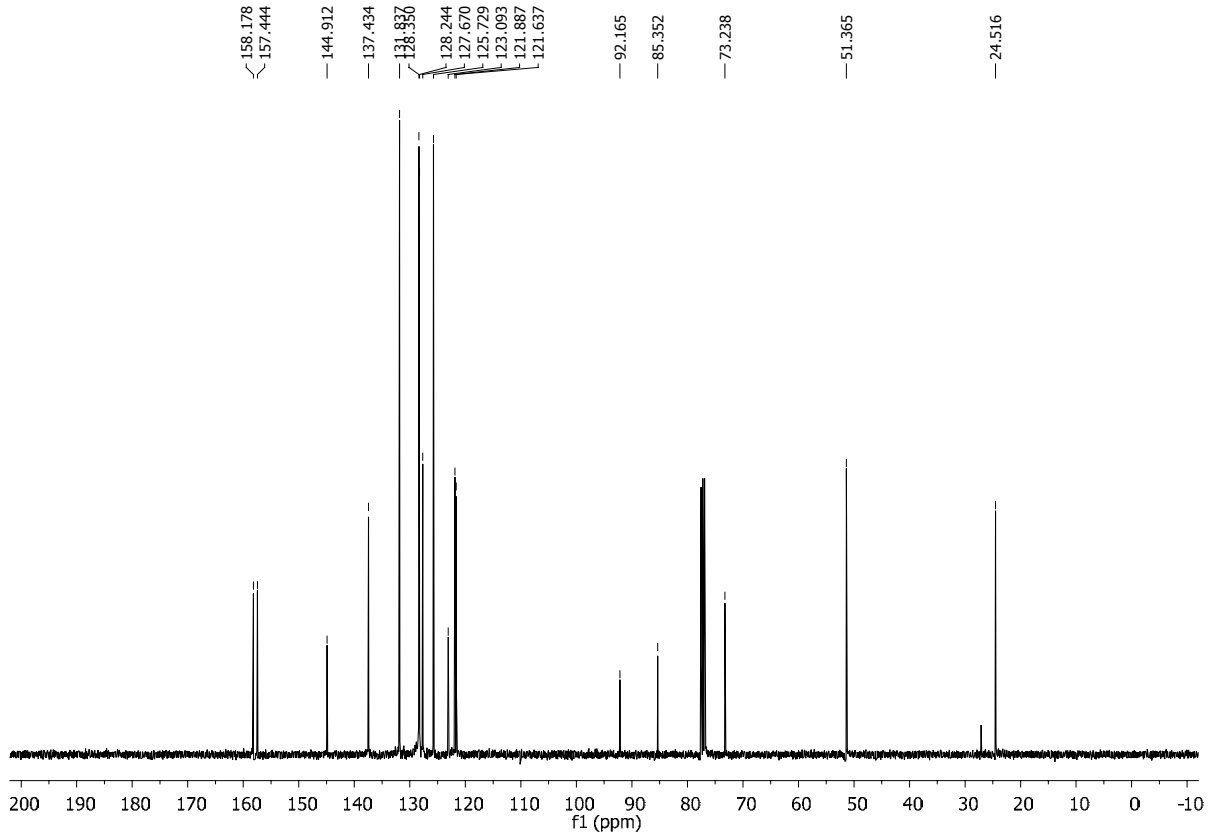
($^{Si}R^*,S^*$)-**24** (^{13}C):



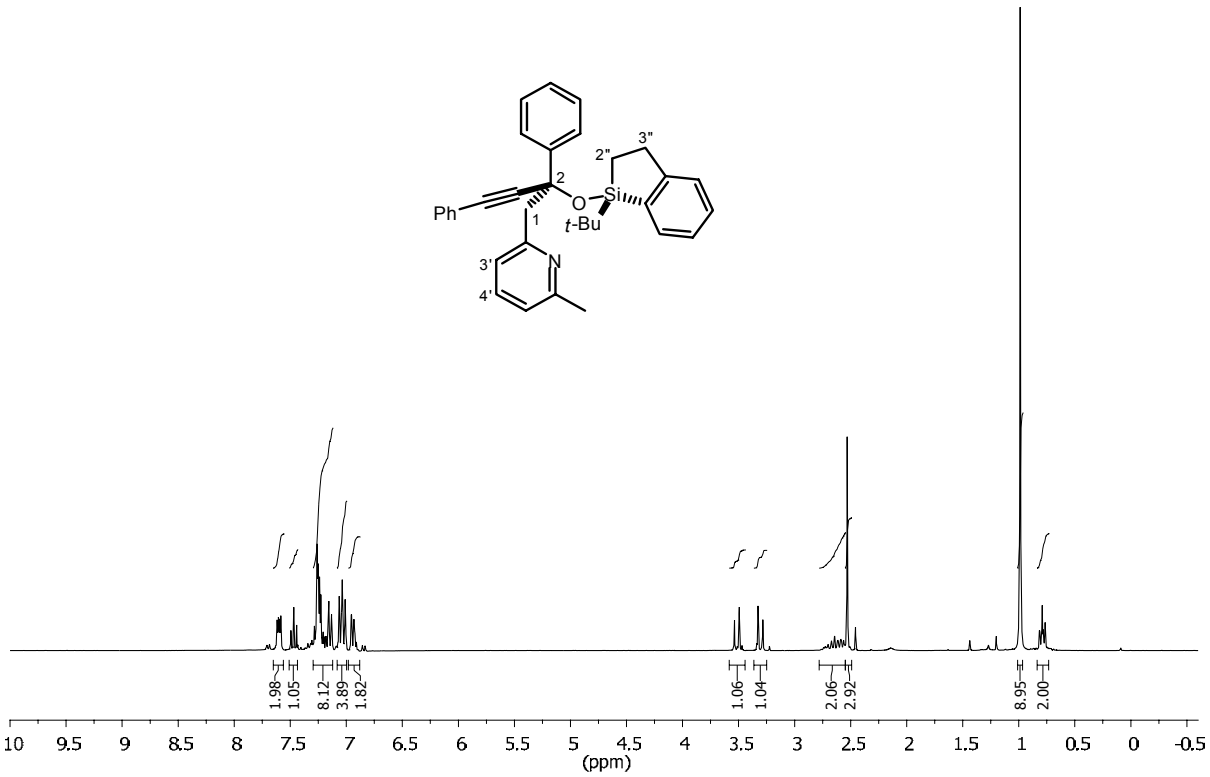
rac-**25** (^{1}H):



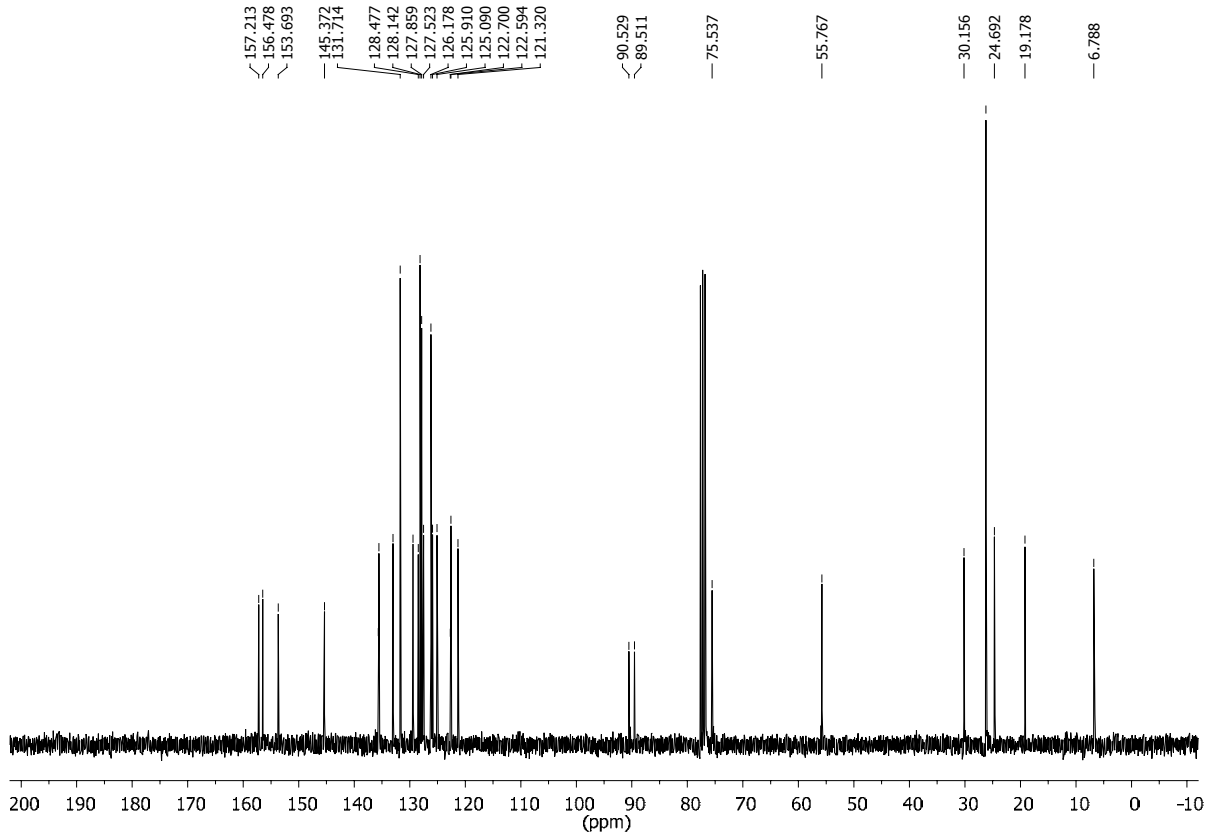
rac-**25** (^{13}C):



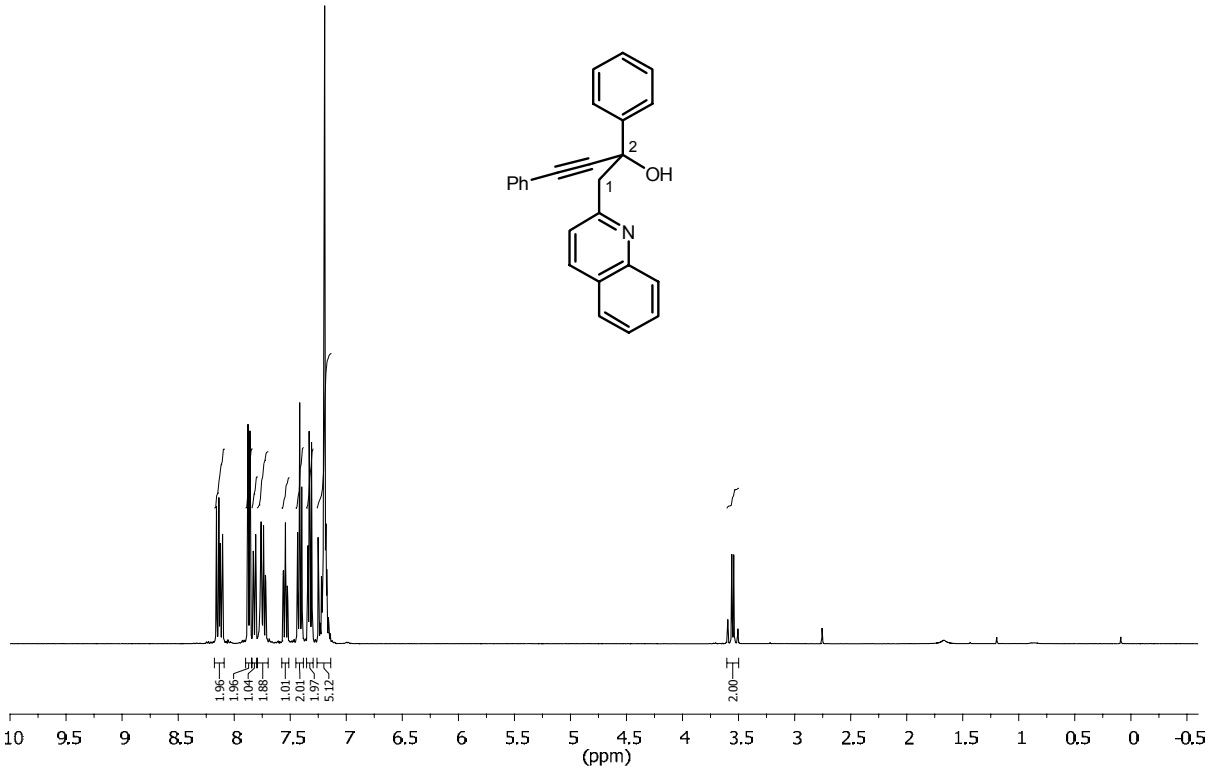
(^{Si}S*,*R**)-**26** (^{1}H):



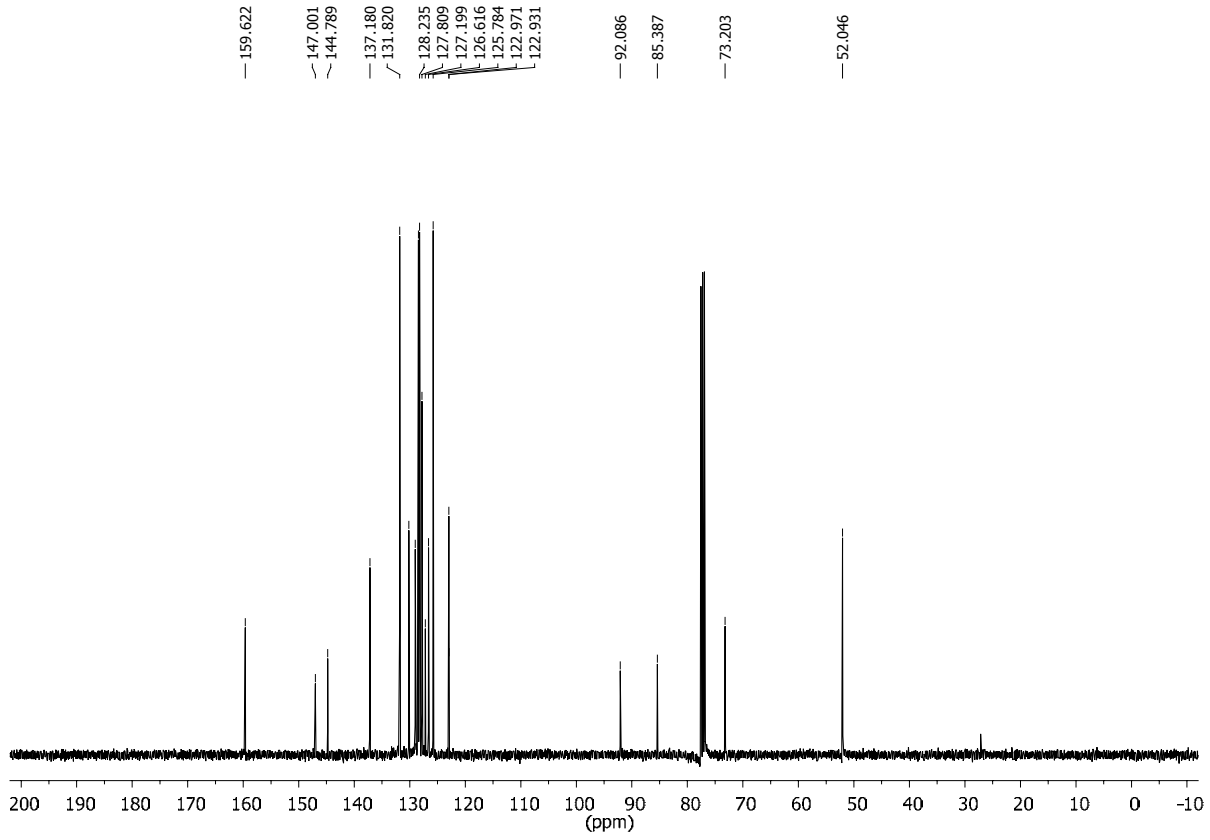
(^{Si}S*,*R**)-**26** (^{13}C):



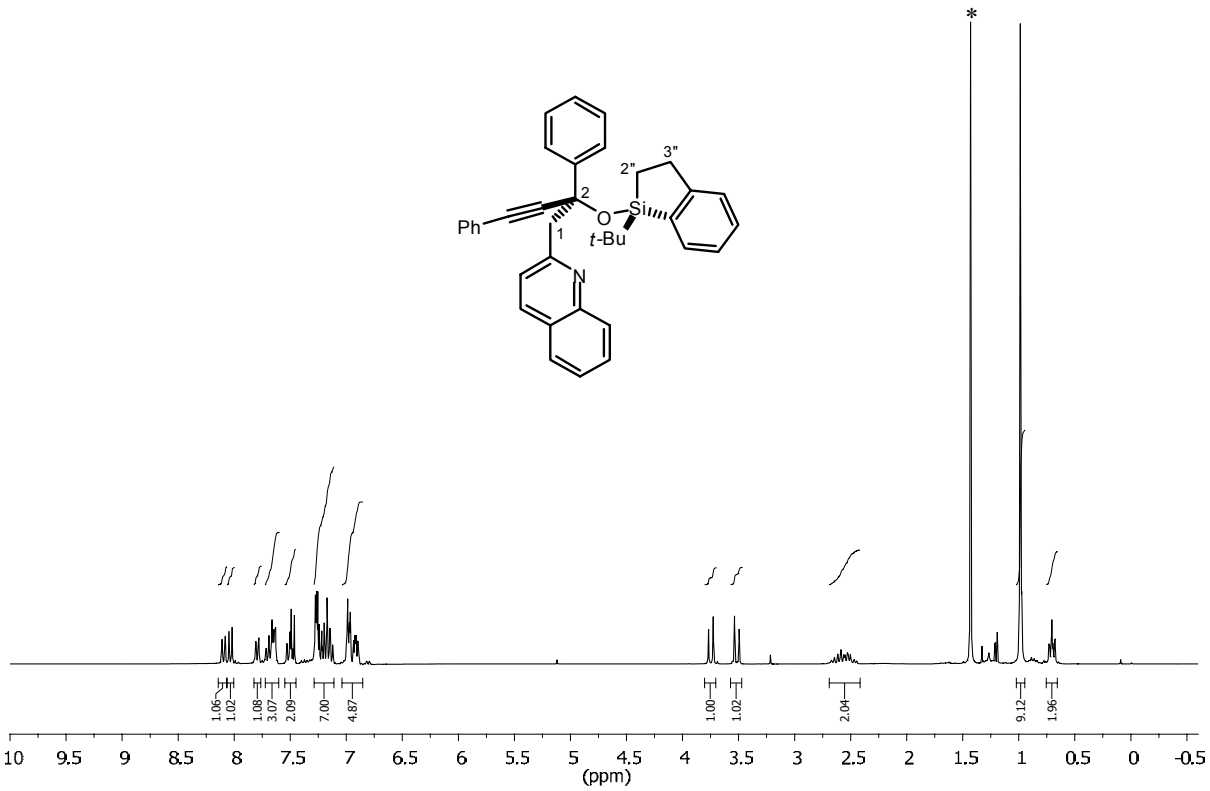
rac-**27** (^{1}H):



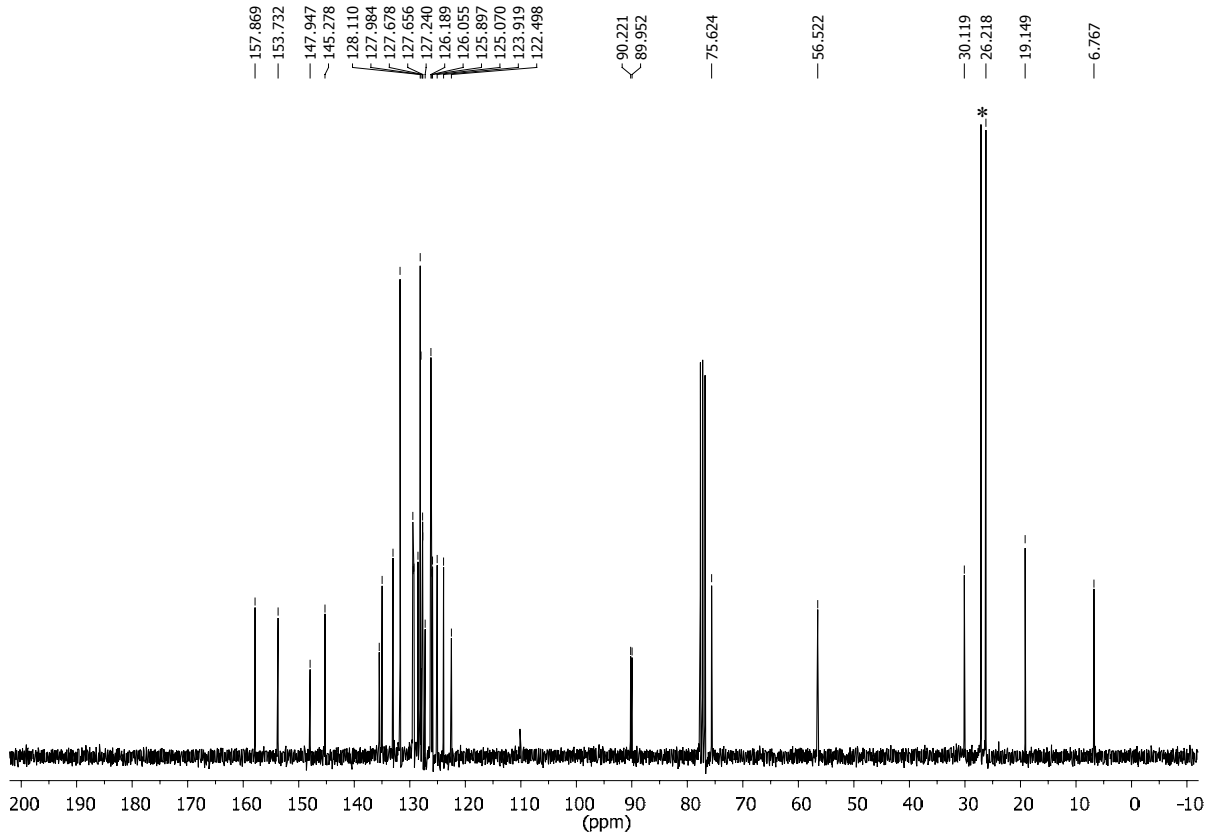
rac-**27** (^{13}C):



(^{Si}S*,*R**)-**28** (^{1}H):

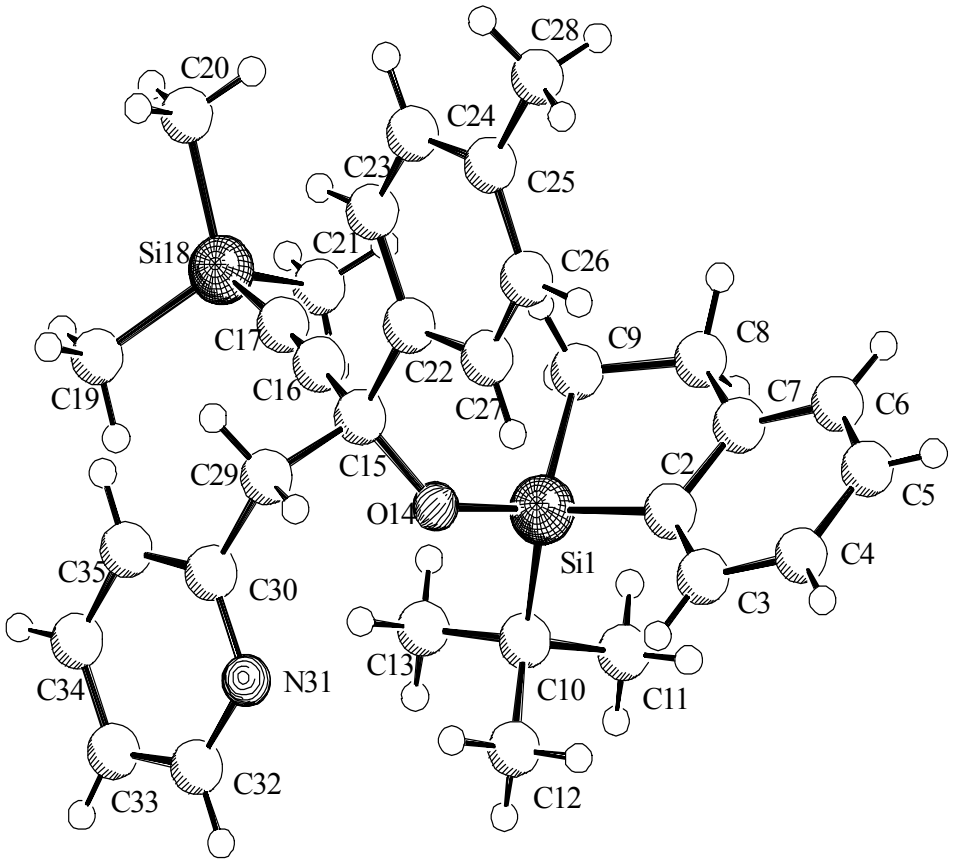


(^{Si}S*,*R**)-**28** (^{13}C):

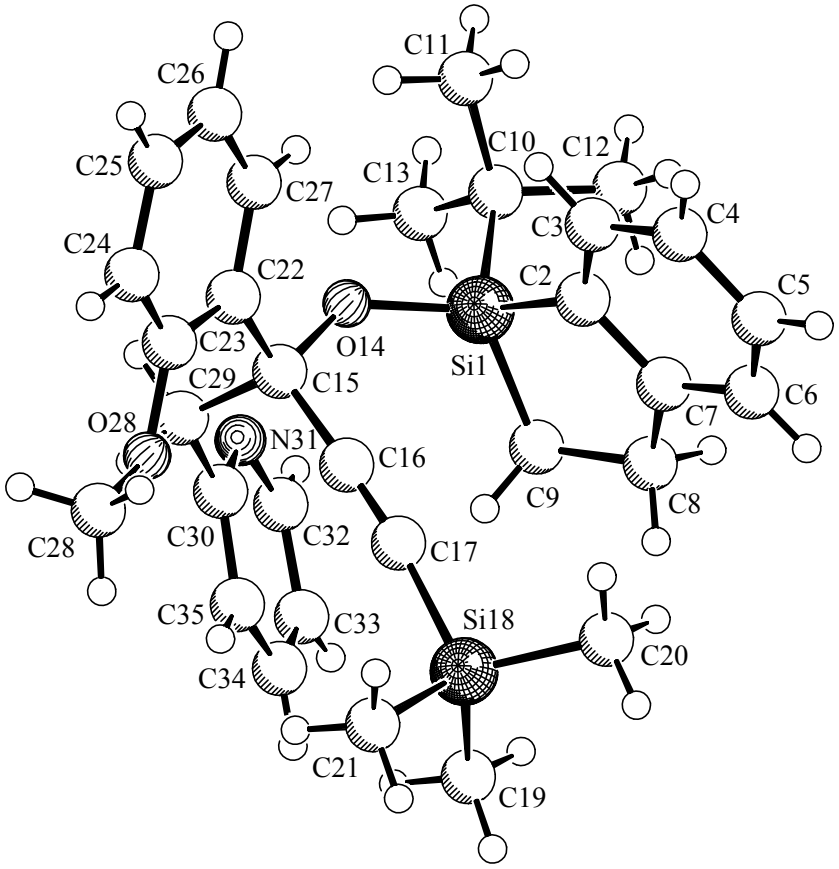


4 Molecular structures of *rac*-15, *rac*-16 and *rac*-19 (relative configuration) as well as (*S*)-8 (absolute configuration)

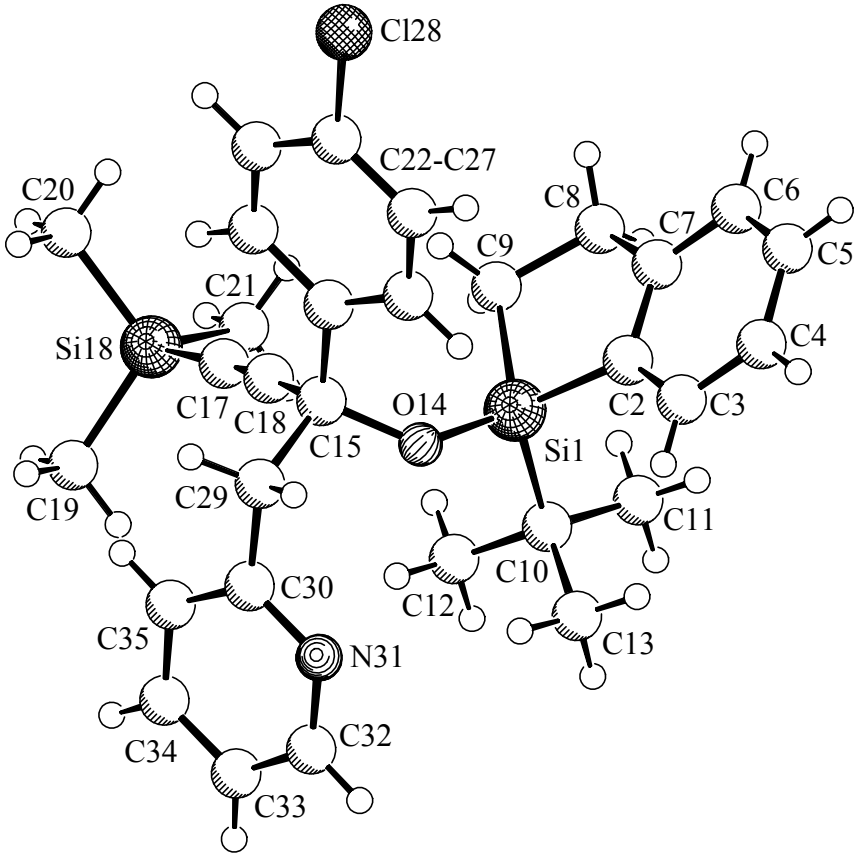
rac-**15** [(^{Si}*R**;*S**)-**15**]: Crystal data for $C_{31}H_{39}NOSi_2$, *M* = 497.81, triclinic, space group *P*1bar (No. 2), *a* = 10.2158(3), *b* = 10.5173(3), *c* = 16.3911(5) Å, *α* = 72.213(2), *β* = 81.203(2), *γ* = 61.845(4)°, *V* = 1478.42(8) Å^3, D_c = 1.118 g cm^{-3}, *μ* = 1.249 mm^{-1}, *Z* = 2, *λ* = 1.54178 Å, *T* = 223(2) K, 18283 reflections collected (±*h*, ±*k*, ±*l*), [(*sinθ*)/*λ*] = 0.60 Å^{-1}, 5176 independent (R_{int} = 0.038) and 4699 observed reflections [$I \geq 2\sigma(I)$], 323 refined parameters, R = 0.043, wR^2 = 0.117, CCDC 668299



rac-**16** [($^{Si}S^*$,R^*)-**16**]: Crystal data for $C_{31}H_{39}NO_2Si_2$, M = 513.81, monoclinic, space group $P2_1/n$ (No. 14), a = 14.6545(4), b = 21.6938(6), c = 19.1708(5) Å, β = 101.885(2)°, V = 5964.0(3) Å^3, D_c = 1.144 g cm^{-3}, μ = 1.279 mm^{-1}, Z = 8, λ = 1.54178 Å, T = 223(2) K, 55533 reflections collected (±h, ±k, ±l), [($\sin\theta$)/λ] = 0.60 Å^{-1}, 10655 independent (R_{int} = 0.068) and 8195 observed reflections [$I \geq 2\sigma(I)$], 694 refined parameters, R = 0.055, wR^2 = 0.138, CCDC 668298



rac-**19** [(^{Si}*R**,*S**)-**19**]: Crystal data for $C_{30}H_{36}ClNOSi_2$, *M* = 518.23, triclinic, space group *P*1bar (No. 2), *a* = 10.2053(4), *b* = 10.5866(5), *c* = 16.1920(8) Å, *α* = 72.052(2), *β* = 80.971(2), *γ* = 62.274(4)°, *V* = 1472.97(12) Å^3, D_c = 1.168 g cm^{-3}, *μ* = 2.088 mm^{-1}, *Z* = 2, *λ* = 1.54178 Å, *T* = 223(2) K, 17954 reflections collected (±*h*, ±*k*, ±*l*), [(*sinθ*)/*λ*] = 0.60 Å^{-1}, 5153 independent (R_{int} = 0.035) and 4833 observed reflections [$I \geq 2\sigma(I)$], 322 refined parameters, R = 0.038, wR^2 = 0.114, CCDC 668297



(*S*)-**8**: Crystal data for $C_{18}H_{20}ClNOSi$, M = 329.89, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 5.9900(3), b = 15.6120(8), c = 19.9389(10) Å, V = 1864.60(13) Å^3, D_c = 1.175 g cm^{-3}, μ = 2.428 mm^{-1}, Z = 4, λ = 1.54178 Å, T = 223(2) K, 10021 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 3219 independent (R_{int} = 0.050) and 2928 observed reflections [$I \geq 2\sigma(I)$], 203 refined parameters, R = 0.041, wR^2 = 0.100, Flack parameter 0.00(2), CCDC 668300