Supplementary Information

Construction of dibenzo-fused seven- to nine-membered carbocycles via Brønsted acid promoted intramolecular Friedel–Crafts type alkenylation

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Contents

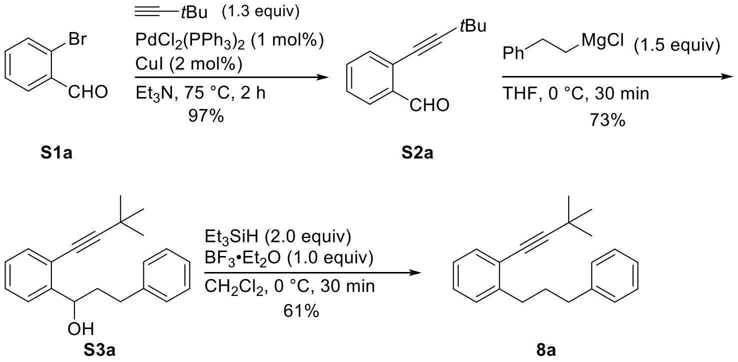
1. Synthesis

1.1. General information

All melting points were determined on a Yanaco melting point apparatus and are uncorrected. Infrared spectra were recorded on a Horiba FT-710 model spectrophotometer. ^{1}H and ^{13}C NMR spectral data were recorded at 25 °C unless otherwise noted, on one of the following instruments: Bruker Avance-600, Bruker Avance DPX-400, JEOL JNM-LA 500, or JEOL JNM-AL 300. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet, br = broad, app = apparent), coupling constant (J) in Hertz (Hz), and integration. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS, δ = 0 for ^{1}H NMR) or $CDCl_3$ (δ = 77.0, center line, for ^{13}C NMR). HRMS analysis were performed on Bruker Daltonics microTOF or JEOL JMS-700.

1.2. Synthesis of *o*-alkynyl(arylalkyl)benzenes 8

1.2.1. Synthesis of 8a (typical synthetic procedure for 8a and 8i-l).



Scheme S1. Preparation of 1-(3,3-dimethylbut-1-yn-1-yl)-2-(3-phenylpropyl)benzene (**8a**).

To a mixture of $PdCl_2(PPh_3)_2$ (71.0 mg, 101 μmol, 1 mol%), CuI (40.1 mg, 211 μmol, 2 mol%), 2-bromobenzaldehyde (**S1a**) (1.20 mL, 10.0 mmol), and triethylamine (50 mL) at room temperature was added 3,3-dimethyl-1-butyne (1.60 mL, 13.0 mmol). The mixture was then heated at 75°C for 2 h, cooled to room temperature, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using ethyl acetate/hexane = 1/50 to give 2-(3,3-dimethylbut-1-yn-1-yl)benzaldehyde (**S2a**)[1] as a yellow liquid (1.80 g, 9.66 mmol, 97%).

To a solution of **S2a** (192 mg, 1.0 mmol) in THF (1.0 mL) at 0 °C was added 1.0 M THF solution of benzylmagnesium chloride (1.50 mL, 1.50 mmol). The mixture was stirred for 30 min at 0 °C, quenched with saturated aqueous NH_4Cl, and then extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by silica gel column chromatography using ethyl acetate/hexane = 1/16 as an eluent to give 1-(2-(3,3-dimethylbut-1-yn-1-yl)phenyl)-3-phenylpropan-1-ol (**S3a**) as a colorless liquid (213 mg, 730 μmol, 73%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (s, 9H, Me (*t*-Bu)), 2.00–2.18 (m, 2H, CH_2), 2.26 (d, J = 4.5 Hz,

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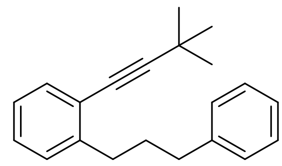
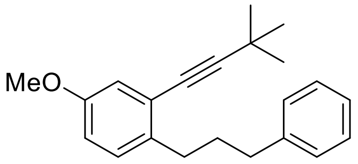
[1] A. S. K. Hashmi, M. Bührle, R. Salathé and J. W. Bats, *Adv. Synth. Catal.*, 2008, **350**, 2059.

1H, OH), 2.64–2.79 (m, 1H, CH_2), 2.79–2.94 (m, 1H, CH_2), 5.12 (td, *J* = 5.0, 7.6 Hz, 1H, C*H*OH), 7.15–7.31 (m, 7H, Ar), 7.36 (dd, *J* = 1.1, 7.7 Hz, 1H, Ar), 7.44 (d, *J* = 7.7 Hz, 1H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1 (C), 30.9 ($3CH_3$), 32.4 (CH_2), 39.4 (CH_2), 72.0 (CH), 76.9 (C), 103.6 (C), 121.1 (C), 125.2 (CH), 125.7 (CH), 126.8 (CH), 127.9 (CH), 128.3 (2CH), 128.3 (2CH), 132.1 (CH), 142.0 (C), 146.1 (C); HRMS-ESI *m/z* $[M+Na]^+$ calcd for $C_{21}H_{24}NaO$: 315.1719, found: 315.1717.

1-(3,3-Dimethylbut-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8a). To a CH_2Cl_2 solution (3 mL) of 1-(2-(3,3-dimethylbut-1-yn-1-yl)phenyl)-3-phenylpropan-1-ol (**S3a**) (112 mg, 0.38 mmol) at 0 °C were added triethylsilane (110 µL, 0.76 mmol) and boron trifluoride etherate (50 µL, 0.35 mmol). The mixture was then stirred at 0 °C for 30 min, quenched with saturated aqueous $NaHCO_3$, and then extracted with ethyl acetate (2 × 3 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexane as an eluent to give 1-(3,3-dimethylbut-1-yn-1-yl)-2-(3-phenylpropyl)benzene (**8a**) as a colorless liquid (64.4 mg, 0.23 mmol, 61%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (s, 9H, Me (*t*-Bu)), 1.90–2.05 (m, 2H, CH_2), 2.68 (t, *J* = 7.8 Hz, 2H, CH_2), 2.80 (t, *J* = 7.8 Hz, 2H, CH_2), 7.10–7.32 (m, 8H, Ar), 7.35 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 28.1 (C), 31.1 ($3CH_3$), 32.1 (CH_2), 34.5 (CH_2), 35.9 (CH_2), 77.7 (C), 102.1 (C), 123.3 (C), 125.6 (CH), 125.7 (CH), 127.5 (CH), 128.3 (2CH), 128.4 (2CH), 128.6 (CH), 132.0 (CH), 142.4 (C), 144.1 (C); HRMS-ESI *m/z* $[M+Na]^+$ calcd for $C_{21}H_{24}Na$: 299.1770, found: 299.1771.

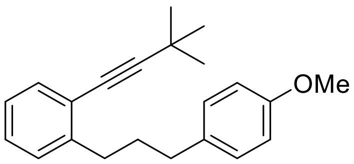


1.2.2. 2-(3,3-Dimethylbut-1-yn-1-yl)-4-methoxy-1-(3-phenylpropyl)benzene (8i).



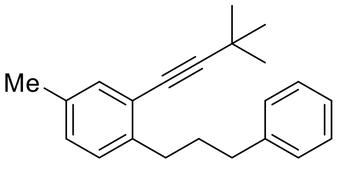
The title compound was synthesized using the same procedure described above. Colorless liquid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.32 (s, 9H, Me (*t*-Bu)), 1.93 (quint, *J* = 8.3 Hz, 2H, CH_2), 2.66 (t, *J* = 7.7 Hz, 2H, CH_2), 2.74 (t, *J* = 7.7 Hz, 2H, CH_2), 3.77 (s, 3H, OMe), 6.75 (dd, *J* = 2.8, 8.5 Hz, 1H, Ar), 6.89 (d, *J* = 2.7 Hz, 1H, Ar), 7.05 (d, *J* = 8.4 Hz, 1H, Ar), 7.16 (d, *J* = 7.4 Hz, 1H, Ar), 7.19 (d, *J* = 7.3 Hz, 2H, Ar), 7.26 (s, 1H, Ar), 7.28 (d, *J* = 7.0 Hz, 1H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.1 (C), 31.1 ($3CH_3$), 32.4 (CH_2), 33.6 (CH_2), 35.9 (CH_2), 55.3 (CH_3), 77.8 (C), 101.9 (C), 114.3 (CH), 116.3 (CH), 124.0 (C), 125.6 (CH), 128.3 (2CH), 128.4 (2CH), 129.6 (CH), 136.5 (C), 142.5 (C), 157.3 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{22}H_{26}O$: 306.1984, found: 306.1985.

1.2.3. 1-(3,3-Dimethylbut-1-yn-1-yl)-2-(3-(4-methoxyphenyl)propyl)benzene (8j).



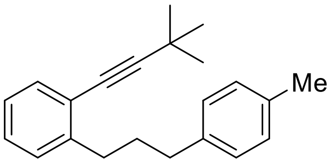
The title compound was synthesized using the same procedure described above. Colorless liquid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.32 (s, 9H, Me (*t*-Bu)), 1.93 (quint, *J* = 7.7 Hz, 2H, CH_2), 2.62 (t, *J* = 7.7 Hz, 2H, CH_2), 2.78 (t, *J* = 7.7 Hz, 2H, CH_2), 3.78 (s, 3H, OMe), 6.82 (d, *J* = 8.1 Hz, 2H, Ar), 7.06–7.20 (m, 5H, Ar), 7.35 (d, *J* = 7.7 Hz, 1H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.2 (C), 31.1 ($3CH_3$), 32.4 (CH_2), 34.5 (CH_2), 35.0 (CH_2), 55.3 (CH_3), 77.7 (C), 102.1 (C), 113.7 (2CH), 123.3 (C), 125.6 (CH), 127.5 (CH), 128.6 (CH), 129.3 (2CH), 132.0 (CH), 134.6 (C), 144.2 (C), 157.7 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{22}H_{26}O$: 306.1984, found: 306.1984.

1.2.4. 2-(3,3-Dimethylbut-1-yn-1-yl)-4-methyl-1-(3-phenylpropyl)benzene (8k).



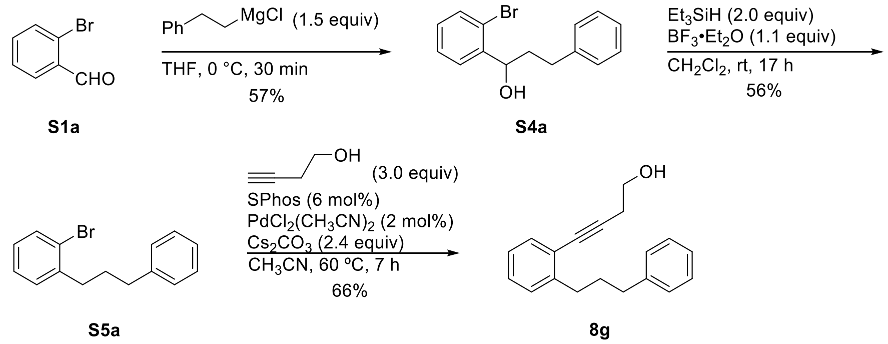
The title compound was synthesized using the same procedure described above. Colorless liquid: ^{1}H NMR (600 MHz, CDCl$_3$) δ 1.31 (s, 9H, Me (*t*-Bu)), 1.91–2.01 (m, 2H, CH$_2$), 2.26 (s, 3H, CH$_3$ (*p*-tol)), 2.67 (t, J = 8.0 Hz, 2H, CH$_2$), 2.76 (t, J = 8.0 Hz, 2H, CH$_2$), 6.95–7.07 (m, 2H, Ar), 7.13–7.22 (m, 4H, Ar), 7.24–7.29 (m, 2H, Ar); ^{13}C NMR (150 MHz, CDCl$_3$) δ 20.7 (CH$_3$), 28.1 (C), 31.1 (3CH$_3$), 32.3 (CH$_2$), 34.1 (CH$_2$), 35.9 (CH$_2$), 77.8 (C), 101.7 (C), 123.1 (C), 126.6 (CH), 128.2 (2CH), 128.4 (CH), 128.4 (2CH), 128.5 (CH), 132.5 (CH), 135.0 (C), 141.0 (C), 142.5 (C); HRMS-EI *m/z* [M]$^+$ calcd for C$_{22}$H$_{26}$: 290.2035, found: 290.2038.

1.2.5. 1-(3,3-Dimethylbut-1-yn-1-yl)-2-(3-(*p*-tolyl)propyl)benzene (8l).



The title compound was synthesized using the same procedure described above. Colorless liquid: ^{1}H NMR (600 MHz, CDCl$_3$) δ 1.31 (s, 9H, Me (*t*-Bu)), 1.94 (quint, J = 7.8 Hz, 2H, CH$_2$), 2.30 (s, 3H, CH$_3$ (*p*-tol)), 2.64 (t, J = 7.8 Hz, 2H, CH$_2$), 2.79 (t, J = 7.8 Hz, 2H, CH$_2$), 7.05–7.11 (m, 5H, Ar), 7.11–7.18 (m, 2H, Ar), 7.35 (d, J = 7.7 Hz, 1H, Ar); ^{13}C NMR (150 MHz, CDCl$_3$) δ 21.0 (CH$_3$), 28.1 (C), 31.1 (3CH$_3$), 32.3 (CH$_2$), 34.5 (CH$_2$), 35.5 (CH$_2$), 77.7 (C), 102.1 (C), 123.3 (C), 125.6 (CH), 127.5 (CH), 128.3 (2CH), 128.6 (CH), 129.0 (2CH), 131.9 (CH), 135.0 (C), 139.3 (C), 144.2 (C); HRMS-EI *m/z* [M]$^+$ calcd for C$_{22}$H$_{26}$: 290.2035, found: 290.2036.

1.2.6. Synthesis of 4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-ol (8g) (typical synthetic procedure for 8g and 8b-e).

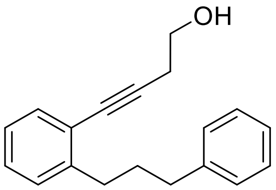


Scheme S2. Preparation of 4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-ol (**8g**).

To a mixture of 2-bromobenzaldehyde (**S1a**) (2.30 mL, 20.0 mmol) in THF (150 mL) at 0 °C was added 1.0 M THF solution of benzylmagnesium chloride (30.0 mL, 30.0 mmol). The mixture was stirred at 0 °C for 30 min, quenched with saturated aqueous NH$_4$Cl, and then extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using ethyl acetate/hexane = 1/8 as an eluent to give 1-(2-bromophenyl)-3-phenylpropan-1-ol (**S4a**) as a white solid (3.31 g, 11.4 mmol, 57%): ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.93–2.15 (m, 3H, CH$_2$, OH), 2.69–2.93 (m, 2H,

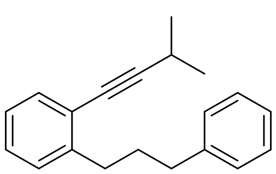
CH_2), 5.08 (dt, *J* = 3.9, 8.9 Hz, 1H, CH), 7.12 (td, *J* = 1.7, 7.7 Hz, 1H, Ar), 7.15–7.30 (m, 5H, Ar), 7.33 (td, *J* = 1.1, 7.7 Hz, 1H, Ar), 7.50 (dd, *J* = 1.0, 8.0 Hz, 1H, Ar), 7.57 (dd, *J* = 1.8, 7.8 Hz, 1H, Ar).

To a CH_2Cl_2 solution (110 mL) of 1-(2-bromophenyl)-3-phenylpropan-1-ol (**S4a**) (3.20 g, 11.0 mmol) at 0 °C were added triethylsilane (3.50 mL, 22.0 mmol) and boron trifluoride etherate (1.72 mL, 12.1 mmol). The mixture was then stirred at room temperature for 17 h, quenched with saturated aqueous $NaHCO_3$, and then extracted with ethyl acetate (2 × 10 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexane as an eluent to give 1-bromo-2-(3-phenylpropyl)benzene (**S5a**) as a colorless liquid (1.69 g, 6.13 mmol, 56%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.95 (quint, *J* = 7.1 Hz, 2H, CH_2), 2.69 (t, *J* = 7.5 Hz, 2H, CH_2), 2.77 (t, *J* = 7.5 Hz, 2H, CH_2), 7.03 (td, *J* = 2.4, 6.7 Hz, 1H, Ar), 7.13–7.32 (m, 7H, Ar), 7.51 (d, *J* = 7.5 Hz, 1H, Ar).



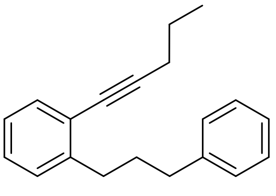
4-(2-(3-Phenylpropyl)phenyl)but-3-yn-1-ol (8g). A mixture of 1-bromo-2-(3-phenylpropyl)benzene (**S5a**) (155 mg, 560 μmol), SPhos (13.1 mg, 31.9 μmol, 6 mol%), $PdCl_2(CH_3CN)_2$ (2.6 mg, 10 μmol, 2 mol%), Cs_2CO_3 (391 mg, 1.20 mmol), dry CH_3CN (5.0 mL), and 3-butyn-1-ol (114 μL, 1.50 mmol) was heated at 60 °C for 7 h. After being cooled to room temperature, the reaction mixture was diluted with ethyl acatate and filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel with ethyl acetate/hexane = 1/4 as an eluent to give 4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-ol (**8g**) (98.5 mg, 372 μmol, 66%) as a yellow liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.91–2.01 (m, 3H, CH_2, OH), 2.63 (t, *J* = 7.0 Hz, 2H, CH_2), 2.67 (t, *J* = 7.7 Hz, 2H, CH_2), 2.79 (t, *J* = 8.1 Hz, 2H, CH_2), 3.74 (t, *J* = 6.3 Hz, 2H, CH_2), 7.10 (td, *J* = 1.7, 7.5 Hz, 1H, CH_2), 7.14–7.22 (m, 5H, Ar), 7.27 (t, *J* = 7.5 Hz, 2H, Ar), 7.37 (d, *J* = 7.7 Hz, 1H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.8 (CH_2), 32.0 (CH_2), 34.2 (CH_2), 35.6 (CH_2), 61.2 (CH_2), 81.0 (C), 89.7 (C), 122.6 (C), 125.7 (2CH), 128.0 (CH), 128.2 (2CH), 128.4 (2CH), 128.6 (CH), 132.2 (CH), 142.2 (C), 144.2 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{19}H_{20}O$: 264.1514, found: 264.1517.

1.2.7. 1-(3-Methylbut-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8b).



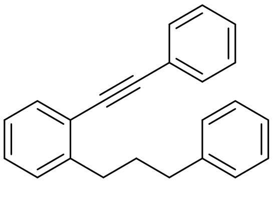
The title compound was synthesized using the same procedure described above. Yellow liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (d, *J* = 6.9 Hz, 6H, Me (*i*-Pr)), 1.97 (quint, *J* = 7.6 Hz, 2H, CH_2), 2.68 (t, *J* = 7.7 Hz, 2H, CH_2), 2.75–2.85 (m, 3H, CH, CH_2), 7.10 (td, *J* = 2.1, 7.3 Hz, 1H, Ar), 7.14–7.21 (m, 5H, Ar), 7.27 (t, *J* = 7.6 Hz, 2H, Ar), 7.35 (d, *J* = 7.6 Hz, 1H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3 (CH), 23.1 ($2CH_3$), 32.1 (CH_2), 34.4 (CH_2), 35.9 (CH_2), 78.4 (C), 99.3 (C), 123.3 (C), 125.6 (CH), 125.7 (CH), 127.5 (CH), 128.2 (2CH), 128.4 (2CH), 128.6 (CH), 132.0 (CH), 142.4 (C), 144.1 (C); HRMS-ESI *m/z* $[M]^+$ calcd for $C_{20}H_{22}$: 262.1722, found: 262.1726.

1.2.8. 1-(Pent-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8c).



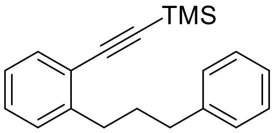
The title compound was synthesized using the same procedure described above. Colorless liquid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.10 (t, J = 7.2 Hz, 3H, Me (n-Pr)), 1.66 (sext, J = 7.2 Hz, 2H, CH_2 (n-Pr)), 2.01 (quint, J = 7.7 Hz, 2H, CH_2), 2.42 (t, J = 6.9 Hz, 2H, CH_2 (n-Pr)), 2.72 (t, J = 7.7 Hz, 2H, CH_2), 2.85 (t, J = 7.7 Hz, 2H, CH_2), 7.14 (dt, J = 1.6, 7.5 Hz, 1H, Ar), 7.18–7.26 (m, 5H, Ar), 7.31 (dd, J = 7.1, 7.3 Hz, 2H, Ar), 7.41 (d, J = 7.5 Hz, 1H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.6 (CH_3), 21.5 (CH_2), 22.3 (CH_2), 32.2 (CH_2), 34.4 (CH_2), 35.8 (CH_2), 79.3 (C), 93.7 (C), 123.4 (C), 125.6 (CH), 125.7 (CH), 127.5 (CH), 128.2 (2CH), 128.4 (2CH), 128.6 (CH), 132.2 (CH), 142.4 (C), 144.1 (C); HRMS-EI m/z $[M]^+$ calcd for $C_{20}H_{22}$: 262.1722, found: 262.1721.

1.2.9. 1-(Phenyleth-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8d).



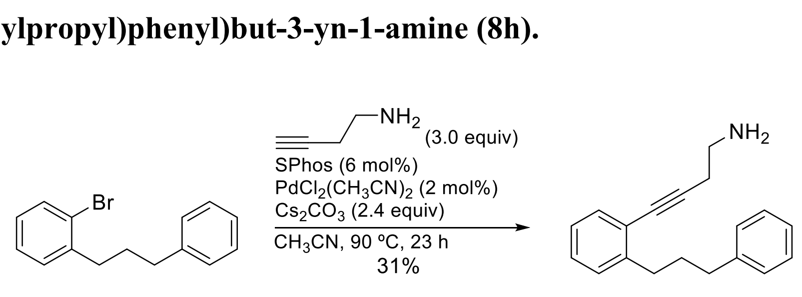
The title compound was synthesized using the same procedure described above. Yellow liquid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.05 (quint, J = 7.7 Hz, 2H, CH_2), 2.72 (d, J = 7.7 Hz, 2H, CH_2), 2.91 (t, J = 7.7 Hz, 2H, CH_2), 7.13–7.29 (m, 8H, Ar), 7.30–7.40 (m, 3H, Ar), 7.46 (dd, J = 2.0, 6.6 Hz, 2H, Ar), 7.51 (d, J = 7.6 Hz, 1H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$) δ 32.2 (CH_2), 34.4 (CH_2), 35.8 (CH_2), 88.2 (C), 92.9 (C), 122.6 (C), 123.5 (C), 125.7 (CH), 125.8 (CH), 128.1 (CH), 128.3 (2CH), 128.3 (2CH), 128.4 (CH), 128.5 (2CH), 128.8 (CH), 131.5 (2CH), 132.2 (CH), 142.3 (C), 144.4 (C); HRMS-EI m/z $[M]^+$ calcd for $C_{23}H_{20}$: 296.1565, found: 296.1562.

1.2.10. Trimethyl((2-(3-phenylpropyl)phenyl)ethynyl)silane (8e).



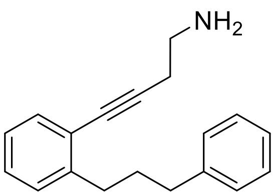
The title compound was synthesized using the same procedure described above. Yellow liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.26 (s, 9H, Me (TMS)), 1.98 (quint, J = 7.7 Hz, 2H, CH_2), 2.68 (t, J = 7.7 Hz, 2H, CH_2), 2.83 (t, J = 7.7 Hz, 2H, CH_2), 7.12 (td, J = 1.2, 7.4 Hz, 1H, Ar), 7.17 (d, J = 7.7 Hz, 2H, Ar), 7.20 (d, J = 7.0 Hz, 2H, Ar), 7.23 (td, J = 1.2, 7.5 Hz, 1H, Ar), 7.28 (t, J = 7.6 Hz, 2H, Ar), 7.43 (dd, J = 1.2, 7.7 Hz, 1H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.0 ($3CH_3$), 32.2 (CH_2), 34.5 (CH_2), 35.9 (CH_2), 97.8 (C), 103.9 (C), 122.5 (C), 125.7 (CH), 125.7 (CH), 128.3 (2CH), 128.4 (2CH), 128.6 (CH), 128.7 (CH), 132.5 (CH), 142.4 (C), 144.9 (C); HRMS-EI m/z $[M]^+$ calcd for $C_{20}H_{24}Si$: 292.1647, found: 292.1651.

1.2.11. 4-(2-(3-Phenylpropyl)phenyl)but-3-yn-1-amine (8h).



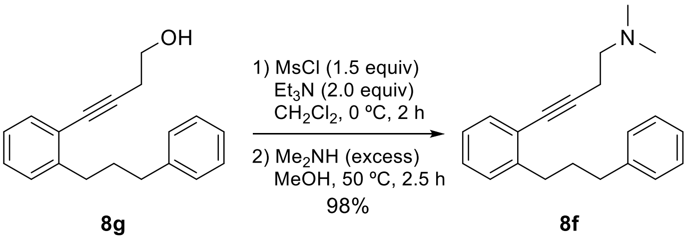
S5a **8h**

Scheme S3. Preparation of 4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-amine (**8h**).

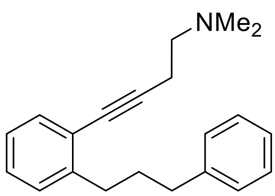


1-Bromo-2-(3-phenylpropyl)benzene (**S5a**) (50.3 mg, 180 μmol), SPhos (4.1 mg,10 μmol, 6 mol%), $PdCl_2(CH_3CN)_2$ (1.0 mg, 3.8 μmol, 2 mol%), Cs_2CO_3 (144 mg, 440 μmol) and dry CH_3CN (1.8 mL) and 3-butynylamine (50 μL, 550 μmol) were added to a dried shield tube and the mixture was heated with stirring at 90 °C for 23 h. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel with methanol/chloroform = 1/5 as an eluent to give 4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-amine (**8h**) (14.5 mg, 55 μmol, 31%) as a yellow liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63 (app. br s, 2H, CH_2), 1.93–2.04 (m, 2H, CH_2), 2.54 (t, J = 6.4 Hz, 2H, CH_2), 2.68 (t, J = 7.7 Hz, 2H, CH_2), 2.80 (t, J = 7.2 Hz, 2H, CH_2), 2.89 (app. br s, 2H, NH_2), 7.11–7.25 (m, 6H, Ar), 7.28 (t, J = 7.6 Hz, 2H, Ar), 7.38 (d, J = 7.6 Hz, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 24.6 (CH_2), 32.1 (CH_2), 34.2 (CH_2), 35.7 (CH_2), 41.3 (CH_2), 80.6 (C), 91.2 (C), 122.9 (C), 125.7 (2CH), 127.8 (CH), 128.2 (2CH), 128.4 (2CH), 128.6 (CH), 132.3 (CH), 142.3 (C), 144.1 (C); HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{19}H_{22}N$: 264.1752, found: 264.1741.

1.2.12. *N*,*N*-Dimethyl-4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-amine (8f).



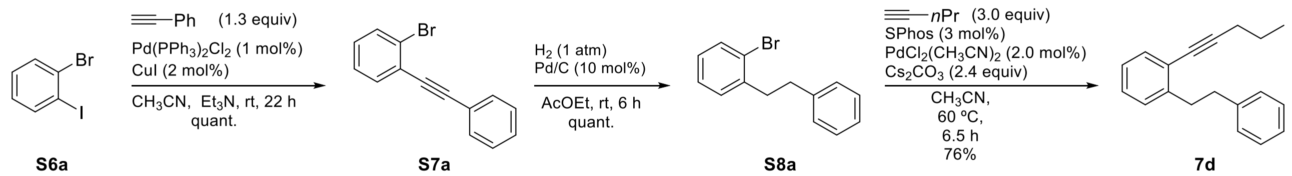
Scheme S4. Preparation of *N*,*N*-dimethyl-4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-amine (**8f**).



To a mixture of 4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-ol (**8g**) (36.1 mg, 140 μmol), triethylamine (40 μL, 270 μmol) and CH_2Cl_2 (1.5 mL) at 0 °C was added methanesulfonyl chloride (30 μL, 400 μmol). The mixture was stirred at 0 °C for 2 h, quenched with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were washed with brine and dried over Na_2SO_4, and evaporated. To the residue was added 50% aqueous solution of dimethylamine (1.00 mL, 11 mmol) and ethanol (1 mL). The mixture was stirred at 50 °C for 2.5 h, cooled to room temperature and then extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by silica gel column chromatography using ethyl acetate as an eluent to give *N*,*N*-dimethyl-4-(2-(3-phenylpropyl)phenyl)- but-3-yn-1-amine (**8f**) as a yellow liquid (38.9 mg, 130 μmol, 93%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.97 (quint, J = 8.0 Hz, 2H, CH_2), 2.30 (s, 6H, NMe_2), 2.55–2.60 (m, 4H, CH_2), 2.68 (t, J = 7.7 Hz, 2H, CH_2), 2.80 (t, J = 8.0 Hz, 2H, CH_2), 7.10 (td, J = 1.4, 7.3 Hz, 1H, Ar), 7.13–7.23 (m, 5H, Ar), 7.28 (t, J = 7.5 Hz, 2H, Ar), 7.36 (d, J = 7.8 Hz, 1H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.5 (CH_2), 32.1 (CH_2), 34.2 (CH_2), 35.7 (CH_2), 45.2 ($2CH_3$), 58.5 (CH_2), 79.9 (C), 91.7 (C), 123.1 (C), 125.6 (CH), 125.7 (CH), 127.7 (CH), 128.2 (2CH), 128.4 (2CH), 128.6 (CH), 132.2 (CH), 142.4 (C), 144.2 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{21}H_{25}N$: 291.1987, found: 291.1983.

1.3. Synthesis of *o*-alkynyl(arylalkyl)benzenes 7

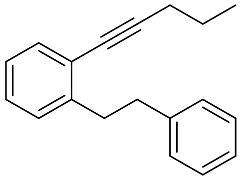
1.3.1. Synthesis of 7d (typical synthetic procedure for 7c–e and 7g–i).



Scheme S5. Preparation of 1-(pent-1-yn-1-yl)-2-phenethylbenzene (**7d**).

To a mixture of 1-bromo-2-iodobenzene (**S6a**) (1.25 mL, 10.0 mmol), triethylamine (40 mL) and CH_3CN (40 mL) were added $PdCl_2(PPh_3)_2$ (70.2 mg, 100 μmol, 1 mol%) and CuI (38.5 mg, 202 μmol, 2 mol%). The mixture was cooled to 0 °C, to which ethynylbenzene (1.43 mL, 13.0 mmol) was added. The mixture was stirred at room temperature for 22 h, quenched with saturated aqueous $NaHCO_3$, and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by silica gel column chromatography using ethyl acetate/hexane = 1/50 as an eluent to give 1-bromo-2-(phenylethynyl)benzene (**S7a**)[2] as a colorless liquid (2.57 g, 9.98 mmol, 100%).

A suspension of **S7a** (974 mg, 3.78 mmol) and 10% Pd/C (200 mg, 188 μmol) in ethyl acetate (15 mL) was stirred under a balloon of hydrogen for 6 h at room temperature. The reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was evaporated, and the residue was chromatographed on silica gel with hexane as an eluent to give 1-bromo-2-phenethylbenzene (**S8a**)[3] (988 mg, 3.78 mmol, 100%) as a colorless liquid.



1-(Pent-1-yn-1-yl)-2-phenethylbenzene (7d). To a mixture of 1-bromo-2-phenethylbenzene (**S8a**) (131 mg, 500 μmol), SPhos (12.3 mg, 30.0 μmol, 6 mol%), $PdCl_2(CH_3CN)_2$ (2.6 mg, 10 μmol, 2 mol%), Cs_2CO_3 (391 mg, 1.20 mmol) and dry CH_3CN (5 mL) were added 1-pentyne (146 μL, 1.5 mmol), and the mixture was stirred at 60 °C for 6.5 h. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel with hexane as an eluent to give 1-(pent-1-yn-1-yl)-2-phenethylbenzene (**7d**) (93.9 mg, 378 μmol, 76%) as an orange liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 1.05 (td, $J = 2.3, 7.4$ Hz, 3H, Me (*n*-Pr)), 1.64 (sext, $J = 7.1$ Hz, 2H, CH_2 (*n*-Pr)), 2.44 (td, $J = 2.3, 7.0$ Hz, 2H, CH_2 (*n*-Pr)), 2.86–2.96 (m, 2H, CH_2), 2.99–3.11 (m, 2H, CH_2), 7.07–7.29 (m, 8H, Ar), 7.36–7.45 (m, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.6 (CH_3), 21.6 (CH_2), 22.3 (CH_2), 37.0 ($2CH_2$), 79.3 (C), 93.9 (C), 123.4 (C), 125.8 (2CH), 127.5 (CH), 128.2 (2CH), 128.4 (2CH), 128.7 (CH), 132.2 (CH), 142.1 (C), 143.4 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{19}H_{20}$: 248.1565, found: 248.1569.

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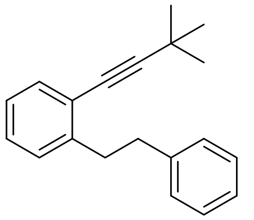
[2] Z. U. Levi and T. D. Tilley, *J. Am. Chem. Soc.*, 2009, **131**, 2796.

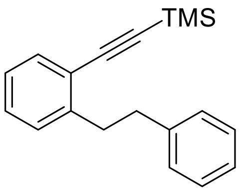
[3] D. S. Roman, Y. Takahashi and A. B. Charette, *Org. Lett.*, 2011, **13**, 3242.

1.3.2. 1-(3,3-Dimethylbut-1-yn-1-yl)-2-phenethylbenzene (7c).



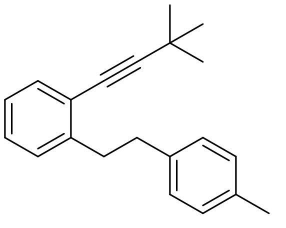
The title compound was synthesized using the same procedure described above. Colorless liquid: ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.35 (s, 9H, Me (*t*-Bu)), 2.91 (d, J = 7.4 Hz, 1H, CH$_2$), 2.93 (d, J = 5.2 Hz, 1H, CH$_2$), 3.04 (d, J = 5.2 Hz, 1H, CH$_2$), 3.06 (d, J = 7.4 Hz, 1H, CH$_2$), 7.10–7.26 (m, 6H, Ar), 7.29 (t, J = 7.5 Hz, 2H, Ar), 7.39 (dd, J = 1.9, 7.5 Hz, 1H, Ar); ^{13}C NMR (125 MHz, CDCl$_3$) δ 28.2 (C), 31.2 (3CH$_3$), 37.0 (2CH$_2$), 77.6 (C), 102.2 (C), 123.2 (C), 125.8 (2CH), 127.6 (CH), 128.3 (2CH), 128.4 (2CH), 128.9 (CH), 132.2 (CH), 142.1 (C), 143.4 (C); HRMS-ESI *m/z* [M+Na]$^+$ calcd for C$_{20}$H$_{22}$Na: 285.1614, found: 285.1614.

1.3.3. Trimethyl((2-phenethylphenyl)ethynyl)silane (7e).



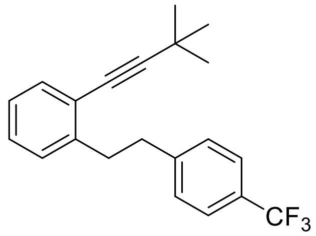
The title compound was synthesized using the same procedure described above. Light brown liquid: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.08 (s, 9H, TMS), 2.67–2.77 (m, 2H, CH$_2$), 2.78–2.94 (m, 2H, CH$_2$), 6.89–7.10 (m, 8H, Ar), 7.27 (d, J = 7.7 Hz, 1H, Ar); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 15.5 (3CH$_3$), 45.1 (CH$_2$), 45.1 (CH$_2$), 93.7 (C), 98.4 (C), 113.4 (C), 116.1 (2CH), 118.0 (2CH), 118.1 (2CH), 118.3 (CH), 118.5 (CH), 121.5 (CH), 129.0 (C), 130.7 (C); HRMS-EI *m/z* [M]$^+$ calcd for C$_{19}$H$_{22}$Si: 278.1491, found: 278.1489.

1.3.4. 1-(3,3-Dimethylbut-1-yn-1-yl)-2-(4-methylphenethyl)benzene (7g).



The title compound was synthesized using the same procedure described above. Yellow solid: mp 34.0–34.5 °C: ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.34 (s, 9H, CH$_3$ (*t*-Bu)), 2.30 (s, 3H, CH$_3$ (*p*-tol)), 2.80–2.92 (m, 2H, CH$_2$), 2.96–3.09 (m, 2H, CH$_2$), 7.01–7.16 (m, 7H, Ar), 7.33–7.41 (m, 1H, Ar); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 21.0 (CH$_3$), 28.1 (C), 31.1 (3CH$_3$), 36.6 (CH$_2$), 37.1 (CH$_2$), 77.7 (C), 102.0 (C), 123.2 (C), 125.8 (CH), 127.6 (CH), 128.2 (2CH), 128.8 (CH), 129.0 (2CH), 132.1 (CH), 135.1 (C), 139.0 (C), 143.5 (C); HRMS-EI *m/z* [M]$^+$ calcd for C$_{21}$H$_{24}$: 276.1878, found: 276.1877.

1.3.5. 1-(3,3-Dimethylbut-1-yn-1-yl)-2-(4-(trifluoromethyl)phenethyl)benzene (7h).

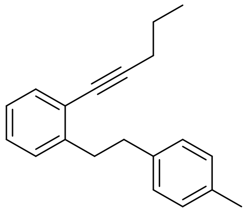


The title compound was synthesized using the same procedure described above. Colorless liquid: ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.34 (s, 9H, CH$_3$ (*t*-Bu)), 2.95–3.02 (m, 2H, CH$_2$), 3.02–3.09 (m, 2H, CH$_2$), 7.08 (dd, J = 1.5, 7.2 Hz, 1H, Ar), 7.11–7.20 (m, 2H, Ar), 7.29 (d, J = 8.0 Hz, 2H, Ar), 7.39 (dd, J = 1.9, 7.2 Hz, 1H, Ar), 7.53 (d, J = 8.2 Hz, 2H, Ar); ^{13}C NMR (125 MHz, CDCl$_3$) δ 28.2 (C), 31.1 (3CH$_3$), 36.5 (CH$_2$), 36.7 (CH$_2$), 77.5 (C), 102.3 (C), 123.3 (C), 124.5 (q, ^1J = 268.4 Hz, CF$_3$), 125.2 (q, ^3J = 3.6 Hz, 2CH), 126.0 (CH), 127.6 (CH), 128.2 (q, ^2J = 32.4 Hz, C), 128.7 (2CH), 128.8 (CH), 132.3 (CH), 142.6 (C), 146.1 (C); HRMS-EI *m/z* [M]$^+$ calcd for C$_{21}$H$_{21}$F$_3$: 330.1595, found: 330.1599.

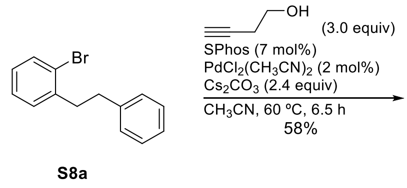
1.3.6. 1-(4-Methylphenethyl)-2-(pent-1-yn-1-yl)benzene (7i).

The title compound was synthesized using the same procedure described above. Colorless liquid: ^{1}H NMR

(300 MHz, CDCl$_3$) δ 1.06 (td, J = 1.6, 7.3 Hz, 3H, Me (n-Pr)), 1.65 (sext, J = 7.2 Hz, 2H, CH$_2$ (n-Pr)), 2.31 (s, 3H, CH$_3$ (p-tol)), 2.44 (td, J = 1.3, 7.0 Hz, 2H, CH$_2$ (n-Pr)), 2.82–2.94 (m, 2H, CH$_2$), 2.97–3.10 (m, 2H, CH$_2$), 7.02–7.17 (m, 7H, Ar), 7.36–7.45 (m, 1H, Ar); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 13.6 (CH$_3$), 21.0 (CH$_3$), 21.6 (CH$_2$), 22.3 (CH$_2$), 36.6 (CH$_2$), 37.1 (CH$_2$), 79.3 (C), 93.8 (C), 123.4 (C), 125.8 (CH), 127.6 (CH), 128.3 (2CH), 128.7 (CH), 129.0 (2CH), 132.2 (CH), 135.2 (C), 139.0 (C), 143.6 (C); HRMS-EI m/z [M]$^+$ calcd for $C_{20}H_{22}$: 262.1722, found: 262.1714.

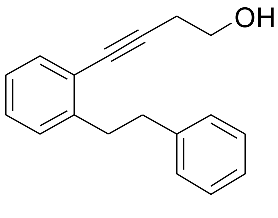


1.3.7. 4-(2-Phenethylphenyl)but-3-yn-1-ol (7f).

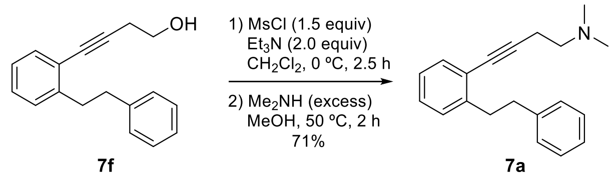


Scheme S6. Preparation of 4-(2-phenethylphenyl)but-3-yn-1-ol (**7f**).

To a mixture of 1-bromo-2-phenethylbenzene (**S8a**) (261 mg, 1.00 mmol), SPhos (27.6 mg, 67.2 µmol, 7 mol%), PdCl$_2$(CH$_3$CN)$_2$ (5.2 mg, 20 µmol, 2 mol%), Cs$_2$CO$_3$ (793 mg, 2.43 mmol) and dry CH$_3$CN (10 mL) were added 3-butyn-1-ol (230 µL, 3.00 mmol), and the mixture was stirred at 60 °C for 6.5 h. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel with ethyl acetate/hexane = 1/4 as an eluent to give 4-(2-phenethylphenyl)but-3-yn-1-ol (**7f**) (144 mg, 575 µmol, 58%) as a colorless liquid: ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.93 (app. br s, 1H, OH), 2.72 (t, J = 6.4 Hz, 2H, CH$_2$), 2.86–2.98 (m, 2H, CH$_2$), 2.99–3.11 (m, 2H, CH$_2$), 3.73–3.86 (m, 2H, CH$_2$), 7.08–7.34 (m, 8H, Ar), 7.37–7.45 (m, 1H, Ar); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 23.9 (CH$_2$), 36.8 (CH$_2$), 37.0 (CH$_2$), 61.2 (CH$_2$), 81.0 (C), 89.9 (C), 122.7 (C), 125.9 (2CH), 128.0 (CH), 128.3 (2CH), 128.4 (2CH), 128.8 (CH), 132.4 (CH), 141.9 (C), 143.6 (C); HRMS-EI m/z [M]$^+$ calcd for $C_{18}H_{18}O$: 250.1358, found: 250.1358.

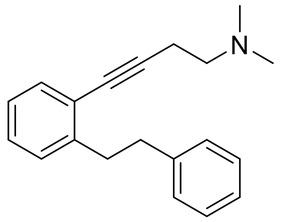


1.3.8. *N*,*N*-Dimethyl-4-(2-phenethylphenyl)but-3-yn-1-amine (7a).



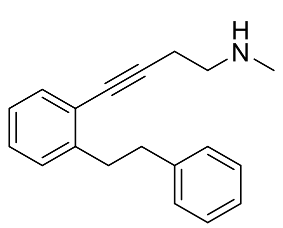
Scheme S7. Preparation of *N*,*N*-dimethyl-4-(2-phenethylphenyl)but-3-yn-1-amine (**7a**).

To a mixture of 4-(2-phenethyl- phenyl)but-3-yn-1-ol (**7f**) (53.6 mg, 214 µmol), triethylamine (60 µL, 400 µmol) and CH$_2$Cl$_2$ (2.0 mL) was added methanesulfonyl chloride (40.0 µL, 300 µmol) at 0 °C. The mixture was stirred at 0 °C for 2.5 h, quenched with saturated aqueous NaHCO$_3$, and extracted with CH$_2$Cl$_2$ (2 × 5.0



mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Then the solvent was removed under reduced pressure. To the residue were added 50% aqueous solution of dimethylamine (400 μL, 5.0 mmol) and ethanol (1.6 mL), and the mixture was stirred at 50 °C for 2 h. The mixture was extracted with CH_2Cl_2, and the organic layer was washed with brine and dried over Na_2SO_4. Then the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using ethyl acetate as an eluent to give *N*,*N*-dimethyl-4-(2-phenethylphenyl)but-3-yn-1-amine (**7a**) as a yellow liquid (41.8 mg, 151 μmol, 71%): ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 2.30 (s, 6H, CH_3 (NMe_2)), 2.63 (app. br s, 4H, CH_2 (Bn)), 2.88–2.96 (m, 2H, CH_2), 3.01–3.10 (m, 2H, CH_2), 7.09–7.23 (m, 6H, Ar), 7.26–7.32 (m, 2H, Ar), 7.37–7.41 (m, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) *δ* 30.2 (CH_2), 44.9 (CH_2), 45.0 (CH_2), 51.5 ($2CH_3$), 62.2 (CH_2), 79.3 (C), 88.8 (C), 113.8 (C), 116.1 (2CH), 117.6 (CH), 118.0 (2CH), 118.1 (2CH), 118.4 (CH), 121.2 (CH), 129.1 (C), 130.3 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{20}H_{23}N$: 277.1830, found: 277.1825.

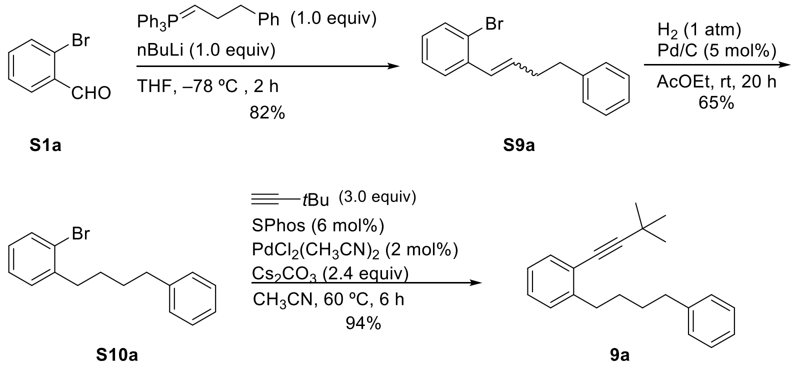
1.3.9. *N*-Methyl-4-(2-phenethylphenyl)but-3-yn-1-amine (7b).



The title compound was synthesized using the same procedure described above. Light brown liquid: ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 2.46 (s, 3H, CH_3), 2.69 (dd, *J* = 6.5, 13.2 Hz, 2H, CH_2 (Bn)), 2.85 (t, *J* = 6.5 Hz, 2H, CH_2 (Bn)), 2.91 (d, *J* = 7.1 Hz, 1H, CH_2), 2.93 (d, *J* = 5.3 Hz, 1H, CH_2), 3.04 (d, *J* = 5.3 Hz, 1H, CH_2), 3.06 (d, *J* = 7.1 Hz, 1H, CH_2), 3.10–3.22 (m, 1H, N*H*CH_3), 7.11–7.16 (m, 2H, Ar), 7.17–7.22 (m, 4H, Ar), 7.26–7.31 (m, 2H, Ar), 7.38–7.43 (m, 1H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) *δ* 31.6 (CH_2), 43.9 (CH_3), 44.9 (CH_2), 44.9 (CH_2), 55.5 (CH_3), 79.7 (C), 88.4 (C), 113.7 (C), 116.1 (2CH), 117.7 (CH), 118.1 (2CH), 118.1 (2CH), 118.4 (CH), 121.3 (CH), 129.0 (C), 130.2 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{19}H_{21}N$: 263.1674, found: 263.1672.

1.4. Synthesis of *o*-alkynyl(arylalkyl)benzenes 9

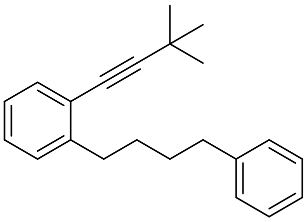
1.4.1. 1-(3,3-Dimethylbut-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9a) (typical synthetic procedure for 9a–c).



Scheme S8. Preparation of 1-(3,3-dimethylbut-1-yn-1-yl)-2-(4-phenylbutyl)benzene (**9a**).

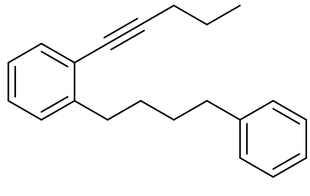
A mixture of (3-iodopropyl)benzene (670 μL, 4.16 mmol), triphenylphosphine (1.13 g, 4.32 mmol) and toluene (1.0 mL) was stirred at 100 °C for 7.5 h and cooled to room temperature. The resulting precipitate was collected by filtration and washed with dry Et_2O to give the phosphonium salt (1.81 g, 3.56 mmol, 86%) as white needles. To a cold solution of the salt (762 mg, 1.50 mmol) in dry THF (15 mL) at 0 °C was added 1.63 M hexane solution of *n*BuLi (920 µL, 1.50 mmol). The mixture was stirred at 0 °C for 2 h, cooled to –78 °C, and 2-bromobenzaldehyde (**S1a**) (173 µL, 1.50 mmol) was added. The resulting mixture was stirred at –78 °C for 2 h and then allowed to warm to room temperature over 30 min. Water was added and the mixture was then extracted with $CHCl_3$. The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using hexane as an eluent to give a mixture of *E*- and *Z*-alkenes **S9a** as a yellow liquid (352 mg, 1.23 mmol, 82%).

A suspension of the mixure of *E*- and *Z*-alkenes **S9a** (352 mg, 1.23 mmol) and 10% Pd/C (63.8 mg, 60.0 µmol) in ethyl acetate (12 mL) was stirred under a balloon of hydrogen for 20 h at room temperature. The reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel with hexane as an eluent to give 1-bromo-2-(4-phenylbutyl)benzene (**S10a**) (230 mg, 795 µmol, 65%) as a colorless liquid.



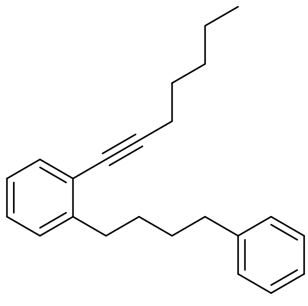
1-(3,3-Dimethylbut-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9a). To a mixture of 1-bromo-2-(4-phenylbutyl)benzene (**S10a**) (86.7 mg, 300 µmol), SPhos (7.4 mg, 18 µmol, 6 mol%), $PdCl_2(CH_3CN)_2$ (1.6 mg, 6.2 µmol, 2 mol%), Cs_2CO_3 (235 mg, 720 mmol) and dry CH_3CN (3.0 mL) were added 3,3-dimethyl-1-butyne (110 µL, 900 µmol), and the mixture was stirred at 60 °C for 6 h. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel with hexane as an eluent to give 1-(3,3-dimethylbut-1-yn-1-yl)-2-(4-phenylbutyl)benzene (**9a**) (82 mg, 282 µmol, 94%) as a colorless liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 9H, Me (*t*-Bu)), 1.62–1.74 (m, 4H, CH_2), 2.58–2.69 (m, 2H, CH_2), 2.72–2.83 (m, 2H, CH_2), 7.05–7.20 (m, 6H, Ar), 7.21–7.30 (m, 2H, Ar), 7.34 (d, *J* = 7.4 Hz, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 28.1 (C), 30.2 (CH_2), 31.1 ($3CH_3$), 31.5 (CH_2), 34.7 (CH_2), 35.9 (CH_2), 77.8 (C), 102.0 (C), 123.2 (C), 125.5 (CH), 125.6 (CH), 127.5 (CH), 128.2 (2CH), 128.4 (2CH), 128.6 (CH), 131.9 (CH), 142.6 (C), 144.3 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{22}H_{26}$: 290.2035, found: 290.2028.

1.4.2. 1-(Pent-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9b).



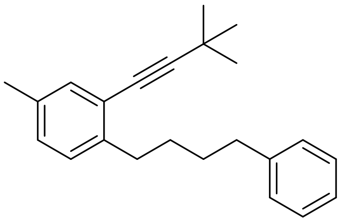
The title compound was synthesized using the same procedure described above. Yellow liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 1.05 (td, *J* = 3.7, 7.2 Hz, 3H, Me (*n*-Pr)), 1.61 (sext, *J* = 3.7 Hz, 2H, CH_2 (*n*-Pr)), 1.66–1.75 (m, 4H, CH_2), 2.40 (td, *J* = 3.5, 6.9 Hz, 2H, CH_2 (*n*-Pr)), 2.55–2.71 (m, 2H, CH_2), 2.73–2.90 (m, 2H, CH_2), 7.12–7.28 (m, 8H, Ar), 7.34–7.41 (m, 1H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.6 (CH_3), 21.5 (CH_2), 22.3 (CH_2), 30.2 (CH_2), 31.3 (CH_2), 34.5 (CH_2), 35.8 (CH_2), 79.4 (C), 93.6 (C), 123.4 (C), 125.5 (CH), 125.6 (CH), 127.5 (CH), 128.2 (2CH), 128.4 (2CH), 128.6 (CH), 132.1 (CH), 142.7 (C), 144.3 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{21}H_{24}$: 276.1878, found: 276.1880.

1.4.3. 1-(Hept-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9c).



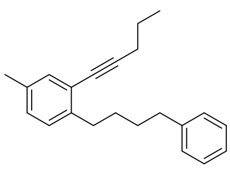
The title compound was synthesized using the same procedure described above. Colorless liquid: ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.94 (dt, *J* = 1.0, 7.4 Hz, 3H, Me), 1.36–1.42 (m, 2H, CH$_2$), 1.45–1.51 (m, 2H, CH$_2$), 1.60–1.66 (m, 2H, CH$_2$), 1.71–1.74 (m, 4H, 2CH$_2$), 2.44 (t, *J* = 7.0 Hz, 2H, Me), 2.67 (t, *J* = 6.6 Hz, 2H, CH$_2$), 2.82 (t, *J* = 6.9 Hz, 2H, CH$_2$), 7.11–7.13 (m, 1H, Ar), 7.15–7.22 (m, 5H, Ar), 7.27 (t, *J* = 8.3 Hz, 2H, Ar), 7.39 (d, *J* = 8.0 Hz, 1H, Ar); ^{13}C NMR (125 MHz, CDCl$_3$) δ 14.0 (CH$_3$), 19.5 (CH$_2$), 22.2 (CH$_2$), 28.5 (CH$_2$), 30.2 (CH$_2$), 31.1 (CH$_2$), 31.3 (CH$_2$), 34.5 (CH$_2$), 35.8 (CH$_2$), 79.3 (C), 93.9 (C), 123.4 (C), 125.5 (CH), 125.6 (CH), 127.5 (CH), 128.2 (2CH), 128.4 (2CH), 128.6 (CH), 132.1 (CH), 142.7 (C), 144.3 (C); HRMS-ESI *m/z* [M+Na]$^+$ calcd for C$_{23}$H$_{28}$Na: 327.2083, found: 327.2092.

1.4.4. 2-(3,3-Dimethylbut-1-yn-1-yl)-4-methyl-1-(4-phenylbutyl)benzene (9d).



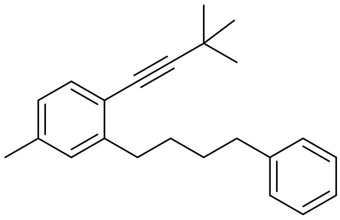
The title compound was synthesized using the same procedure described above. Yellow liquid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.30 (s, 9H, Me (*t*-Bu)), 1.62–1.72 (m, 4H, CH$_2$), 2.25 (s, 3H, Me (*p*-tol)), 2.63 (t, *J* = 6.9 Hz, 2H, CH$_2$), 2.73 (t, *J* = 6.9 Hz, 2H, CH$_2$), 6.96 (dd, *J* = 1.4, 7.7 Hz, 1H, Ar), 7.02 (d, *J* = 7.7 Hz, 1H, Ar), 7.12–7.20 (m, 4H, Ar), 7.25 (t, *J* = 8.3 Hz, 2H, Ar); ^{13}C NMR (75.5 MHz, CDCl$_3$) δ 20.7 (CH$_3$), 28.1 (C), 30.4 (CH$_2$), 31.1 (3CH$_3$), 31.5 (CH$_2$), 34.2 (CH$_2$), 35.9 (CH$_2$), 77.9 (C), 101.6 (C), 123.0 (C), 125.6 (CH), 128.2 (2CH), 128.3 (CH), 128.4 (2CH), 128.5 (CH), 132.4 (CH), 135.0 (C), 141.3 (C), 142.7 (C); HRMS-EI *m/z* [M]$^+$ calcd for C$_{23}$H$_{28}$: 304.2191, found: 304.2188.

1.4.5. 4-Methyl-2-(pent-1-yn-1-yl)-1-(4-phenylbutyl)benzene (9e).



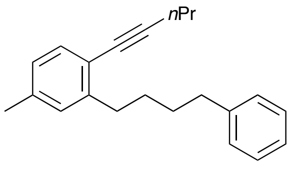
The title compound was synthesized using the same procedure described above. Yellow liquid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.03 (t, *J* = 7.4 Hz, 3H, CH$_3$), 1.55–1.70 (m, 6H, CH$_2$), 2.25 (s, 3H, Me (*p*-tol)), 2.38 (t, *J* = 6.9 Hz, 2H, CH$_2$), 2.62 (br t, *J* = 5.8 Hz, 2H, CH$_2$), 2.73 (br t, *J* = 5.8 Hz, 2H, CH$_2$), 6.96 (br d, *J* = 7.7 Hz, 1H, Ar), 7.01 (br d, *J* = 7.7 Hz, 1H, Ar), 7.12–7.18 (m, 4H, Ar), 7.23 (d, *J* = 7.4 Hz, 2H, Ar); ^{13}C NMR (76 MHz, CDCl$_3$) δ 13.6 (CH$_3$), 20.7 (CH$_3$), 21.5 (CH$_2$), 22.3 (CH$_2$), 30.4 (CH$_2$), 31.3 (CH$_2$), 34.0 (CH$_2$), 35.8 (CH$_2$), 79.5 (C), 93.2 (C), 123.1 (C), 125.6 (CH), 128.2 (2CH), 128.4 (3CH), 128.5 (CH), 132.6 (CH), 135.0 (C), 141.3 (C), 142.8 (C); HRMS-ESI *m/z* [M+Na]$^+$ calcd for C$_{22}$H$_{26}$Na: 313.1927, found: 313.1927.

1.4.6. 1-(3,3-Dimethylbut-1-yn-1-yl)-4-methyl-2-(4-phenylbutyl)benzene (9f).



The title compound was synthesized using the same procedure described above. Yellow liquid: ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.22 (s, 9H, Me (*t*-Bu)), 1.58–1.63 (m, 4H, CH$_2$), 2.21 (s, 3H, Me), 2.53–2.61 (m, 2H, CH$_2$), 2.61–2.70 (m, 2H, CH$_2$), 6.80–6.84 (m, 1H, Ar), 6.85–6.88 (m, 1H, Ar), 7.07–7.11 (m, 3H, Ar), 7.14–7.21 (m, 3H, Ar); ^{13}C NMR (125 MHz, CDCl$_3$) δ 21.4 (CH$_3$), 28.1 (C), 30.3 (CH$_2$), 31.1 (3CH$_3$), 31.6 (CH$_2$), 34.7 (CH$_2$), 36.0 (CH$_2$), 77.8 (C), 101.2 (C), 120.2 (C), 125.6 (CH), 126.3 (CH), 128.2 (2CH), 128.4 (2CH), 129.5 (CH), 131.8 (CH), 137.3 (C), 142.7 (C), 144.2 (C); HRMS-ESI *m/z* [M+Na]$^+$ calcd for C$_{23}$H$_{28}$: 327.2083, found: 327.2089.

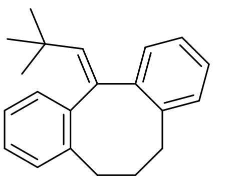
1.4.7. 4-Methyl-1-(pent-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9g).



The title compound was synthesized using the same procedure described above. Yellow liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (t, J = 7.6 Hz, 3H, CH_3), 1.63 (sext, J = 7.6 Hz, 2H, CH_2), 1.68–1.72 (m, 4H, CH_2), 2.31 (s, 3H, Me), 2.43 (t, J = 7.8 Hz, 2H, CH_2), 2.66 (t, J = 7.4 Hz, 2H, CH_2), 2.77 (t, J = 7.4 Hz, 2H, CH_2), 6.93 (dd, J = 1.4, 7.7 Hz, 1H, Ar), 6.97 (br s, J = 7.7 Hz, 1H, Ar), 7.17–7.20 (m, 3H, Ar), 7.26–7.30 (m, 3H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.6 (CH_3), 21.4 (CH_3), 21.5 (CH_2), 22.4 (CH_2), 30.3 (CH_2), 31.4 (CH_2), 34.4 (CH_2), 35.9 (CH_2), 79.4 (C), 92.8 (C), 120.3 (C), 125.6 (CH), 126.4 (CH), 128.2 (2CH), 128.4 (2CH), 129.4 (CH), 132.0 (CH), 137.4 (C), 142.8 (C), 144.2 (C); HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{22}H_{27}$: 291.2107, found: 291.2108.

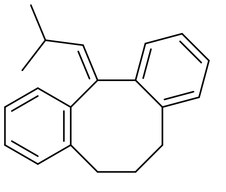
1.5. Synthesis of alkylidenedibenzo[*a,d*]cycloheptenes, -octenes, and -nonenes

1.5.1. 12-(2,2-Dimethylpropylidene)-5,6,7,12-tetrahydro-dibenzo[*a,d*]cyclooctene (2a) (Table 1, entry 4).



TfOH (8.8 μL, 100 μmol) was added to a mixture of 1-(3,3-dimethylbut-1-yn-1-yl)-2-(3-phenylpropyl)benzene (**8a**) (30.0 mg, 109 μmol) in CH_2Cl_2 (1 mL) at 0 °C. After being stirred at 0 °C for 10 min, the mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (3 × 1 mL). The combined organic layers were washed with brine and dried over Na_2SO_4 and evaporated. The residue was purified by silica gel column chromatography using ethyl acetate/hexane = 1/8 as an eluent to give **2a** as a colorless solid (29.8 mg, 108 μmol, 99%): mp 53.3–53.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.96 (s, 9H, CH_3 (*t*-Bu)), 1.36–2.44 (m, 2H, CH_2), 2.49–3.49 (m, 4H, CH_2), 5.62 (s, 1H, CH (vinyl)), 6.93–7.17 (m, 7H, Ar), 7.23 (d, J = 7.1 Hz, 1H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.9 (C), 30.6 ($3CH_3$), 34.1 (CH_2), 36.0–38.5 ($2CH_2$), 125.7 (CH), 126.2 (CH), 126.6 (CH), 126.7 (CH), 128.4 (CH), 128.7 (CH), 129.6 (CH), 129.9 (CH), 139.3 (CH), 140.0 (C), 140.1 (C), 141.9 (C), 146.4 (2C); HRMS-ESI *m/z* $[M+Na]^+$ calcd for $C_{21}H_{24}Na$: 299.1770, found: 299.1771.

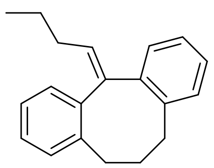
1.5.2. 5,6,7,12-Tetrahydro-12-(2-methylpropylidene)-dibenzo[*a,d*]cyclooctene (2b) (Table 2, entry 1).



The title compound was synthesized using the same procedure described above. Yellow liquid: ^{1}H NMR (600 MHz, $CDCl_3$, 320K) δ 0.96 (d, J = 6.8 Hz, 6H, CH_3 (*i*-Pr)), 1.97 (app. br s, 2H, CH_2), 2.05–2.15 (m, 1H, CH (*i*-Pr)), 2.66 (app. br s, 2H, CH_2), 2.91 (t, J = 6.5 Hz, 2H, CH_2), 5.60 (d, J = 9.7 Hz, 1H, CH (vinyl)), 7.00 (d, J = 7.2 Hz, 1H, Ar), 7.05–7.16 (m, 6H, Ar), 7.33 (d, J = 7.6 Hz, 1H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$, 320K) δ 22.8 ($2CH_3$), 28.5 (CH), 29.5 (CH_2), 34.7–35.5 ($2CH_2$), 126.1 (CH), 126.2 (CH), 126.8 (CH), 127.1 (CH), 128.3 (CH), 128.4 (CH), 129.1 (CH), 130.5 (CH), 138.5 (CH), 140.2 (C), 140.4 (C), 140.7 (C), 141.0 (C), 143.5 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{20}H_{22}$: 262.1722, found: 262.1719.

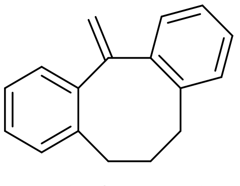
1.5.3. 12-Butylidene-5,6,7,12-tetrahydrodibenzo[*a,d*]cyclooctene (2c) (Table 2, entry 2).

The title compound was synthesized using the same procedure described above. Colorless liquid: ^{1}H NMR



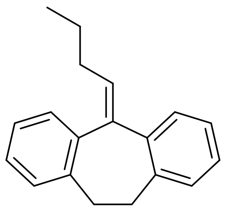
(400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.3 Hz, 3H, CH_3 (n-Pr)), 1.41 (sext, J = 7.3 Hz, 2H, CH_2 (n-Pr)), 1.84 (quint, J = 7.3 Hz, 2H, CH_2 (n-Pr)), 1.96 (app. br s, 2H, CH_2), 2.66 (app. br s, 2H, CH_2), 2.88 (t, J = 6.4 Hz, 2H, CH_2), 5.81 (t, J = 7.2 Hz, 1H, CH (vinyl)), 7.01 (dd, J = 1.2, 7.5 Hz, 1H, Ar), 7.05–7.18 (m, 6H, Ar), 7.35 (d, J = 7.6 Hz, 1H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$, 332K) δ 13.9 (CH_3), 22.6 (CH_2), 29.5 (CH_2), 31.3 (CH_2), 34.8 (CH_2), 35.2 (CH_2), 126.2 (CH), 126.3 (CH), 126.8 (CH), 127.1 (CH), 128.2 (CH), 128.4 (CH), 129.1 (CH), 130.5 (CH), 131.2 (CH), 140.3 (C), 140.5 (C), 140.9 (C), 143.2 (C), 143.8 (C); HRMS-EI m/z $[M]^+$ calcd for $C_{20}H_{22}$: 262.1722, found: 262.1721.

1.5.4. 12-Methylene-5,6,7,12-tetrahydrodibenzo[*a,d*]cyclooctene (2e') (Table 2, entry 4).



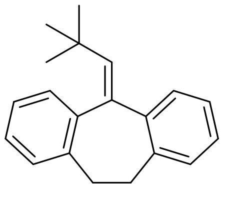
The title compound was synthesized using the same procedure described above. Colorless liquid: ^1H NMR (600 MHz, $CDCl_3$ 323K) δ 1.82 (quint, J = 6.3 Hz, 2H, CH_2), 2.62 (t, J = 6.3 Hz, 4H, CH_2), 5.47 (s, 2H, C=CH_2), 7.05 (dd, J = 2.0, 6.7 Hz, 2H, Ar), 7.17–7.23 (m, 4H, Ar), 7.49 (dd, J = 1.4, 7.2 Hz, 2H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$, 323K) δ 31.4 (CH_2), 32.1 ($2CH_2$), 118.8 (CH_2), 126.2 (2CH), 127.8 (2CH), 128.0 (2CH), 129.8 (2CH), 139.7 (2C), 141.7 (2C), 150.5 (C); HRMS-EI m/z $[M]^+$ calcd for $C_{17}H_{16}$: 220.1252, found: 220.1247.

1.5.5. 5-(Butylidene)-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (1d) (Table 2, entry 6).



To a mixture of 1-(pent-1-yn-1-yl)-2-phenethylbenzene (**7d**) (24.8 mg, 100 μmol) in CH_2Cl_2 (1 mL) at 0 °C was added TfOH (8.8 μL, 100 μmol). The mixture was stirred at 0 °C for 15 min, quenched with saturated aqueous $NaHCO_3$, and then extracted with ethyl acetate (3 × 1.0 mL). The combined organic layers were washed with brine and dried over Na_2SO_4, and evaporated. The residue was purified by silica gel column chromatography using ethyl acetate/hexane = 1/8 as an eluent to give 5-(butylidene)-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (**1d**) as a colorless liquid (23.9 mg, 96.2 μmol, 96%): ^1H NMR (600 MHz, $CDCl_3$) δ 0.88 (t, J = 7.4 Hz, 3H, CH_3 (n-Pr)), 1.43 (app. br s, 2H, CH_2 (n-Pr)), 2.06 (app. br s, 1H, CH_2), 2.11 (app. br s, 1H, CH_2), 2.77 (app. br s, 1H, CH_2), 2.95 (app. br s, 1H, CH_2), 3.31 (app. br s, 1H, CH_2), 3.40 (app. br s, 1H, CH_2), 5.86 (t, J = 7.4Hz, 1H, CH (vinyl)), 7.02–7.05 (m, 1H, Ar), 7.10–7.21 (m, 6H, Ar), 7.26–7.30 (m, 1H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$, 323K) δ 13.8 (CH_3), 23.0 (CH_2), 31.5 (CH_2), 32.1 (CH_2), 33.8 (CH_2), 125.6 (CH), 126.0 (CH), 126.9 (CH), 127.2 (CH), 127.9 (CH), 128.4 (CH), 128.6 (CH), 129.9 (CH), 132.2 (CH), 137.1 (C), 139.3 (C), 140.3 (C), 141.6 (C), 142.3 (C); HRMS-EI m/z $[M]^+$ calcd for $C_{19}H_{20}$: 248.1565, found: 248.1566.

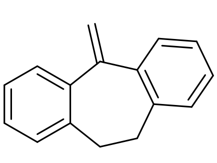
1.5.6. 5-(2,2-Dimethylpropylidene)-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (1c) (Table 2, entry 5).



The title compound was synthesized using the same procedure described above. Colorless liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 0.98 (s, 9H, CH_3 (t-Bu)), 2.72 (dt, J = 4.2, 13.6 Hz, 1H, CH_2), 2.93 (ddd, J = 4.1, 13.4, 17.3 Hz, 1H, CH_2), 3.30 (dt, J = 4.2, 17.3 Hz, 1H, CH_2), 3.52 (td, J = 3.9, 13.3 Hz, 1H, CH_2), 5.78 (s, 1H, CH (vinyl)), 6.93–7.01 (m, 1H, Ar), 7.07–7.28 (m, 7H, Ar); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 31.0 ($3CH_3$), 31.6 (CH_2), 33.7

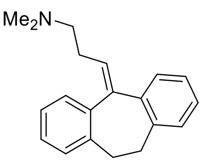
(CH_2), 33.8 (C), 125.3 (CH), 125.9 (CH), 126.7 (CH), 127.1 (CH), 127.3 (CH), 128.2 (CH), 128.3 (CH), 130.3 (CH), 136.2 (C), 138.7 (C), 139.9 (C), 141.5 (CH), 141.8 (C), 142.8 (C); HRMS-ESI *m/z* $[M+Na]^+$ calcd for $C_{20}H_{22}Na$: 285.1614, found: 285.1609.

1.5.7. 5-Methylene-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (1e') (Table 2, entry 7).



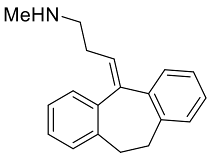
The title compound was synthesized using the same procedure described above. ^1H NMR and ^{13}C NMR spectra were identical to those in the literature.[4]

1.5.8. 3-(10,11-Dihydro-5*H*-dibenzo[*a,d*][7]annulen-5-ylidene)-*N,N*-dimethylpropan-1-amine (1a) (Table 2, entry 8).



To a mixture of *N,N*-dimethyl-4-(2-phenethylphenyl)but-3-yn-1-amine **(7a)** (13.8 mg, 49.7 μmol) in CH_2Cl_2 (0.5 mL) at 0 °Cwas added TfOH (21.9 μL, 250 μmol). The mixture was stirred at 0 °C for 10 min, quenched with saturated aqueous $NaHCO_3$, and extracted with ethyl acetate (3 × 1.0 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by silica gel column chromatography using chloroform/methanol = 1/1 to give 3-(10,11-dihydro-5*H*-dibenzo[*a,d*][7]annulen-5-ylidene)-*N,N*-dimethylpropan-1-amine (**1a**) as a colorless liquid (7.7 mg, 27.8 μmol, 56%): ^1H NMR (600 MHz, $CDCl_3$) δ 2.20 (s, 6H, CH_3 (NMe_2)), 2.28–2.46 (m, 4H, CH_2), 2.71–2.86 (m, 1H, CH_2), 2.91–3.07 (m, 1H, CH_2), 3.26–3.38 (m, 1H, CH_2), 3.38–3.51 (m, 1H, CH_2), 5.88 (t, *J* = 7.2 Hz, 1H, CH (vinyl)), 7.02–7.07 (m, 1H, Ar), 7.13–7.23 (m, 6H, Ar), 7.28–7.32 (m, 1H, Ar). ^1H NMR and ^{13}C NMR spectra were identical to those in the literature.[5]

1.5.9. 3-(10,11-Dihydro-5*H*-dibenzo[*a,d*][7]annulen-5-ylidene)-*N*-methylpropan-1-amine (1b) (Table 2, entry 9).



To a mixture of *N*-methyl-4-(2-phenethylphenyl)but-3-yn-1-amine (**7b**) (6.5 mg, 24.7 μmol) in CH_2Cl_2 (0.25 mL) at 0 °C was added TfOH (10.8 μL, 124 μmol). The mixture was then stirred at 0 °C for 10 min, quenched with saturated aqueous $NaHCO_3$, and then extracted with ethyl acetate (3 × 1.0 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by PTLC using chloroform/methanol = 1/1 as an eluent to give 3-(10,11-dihydro-5*H*-dibenzo[*a,d*][7]annulen-5-ylidene)-*N*-methylpropan-1-amine (**1b**) as a colorless liquid (4.4 mg, 16.7 μmol, 68%): IR (neat) 3417 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 2.02–2.16 (m, 1H, NH), 2.34 (q, *J* = 7.2 Hz, 2H, CH_2), 2.37 (s, 3H, CH_3 (NHMe)), 2.64–2.72 (m, 2H, CH_2), 2.74–2.86 (m, 1H, CH_2), 2.89–3.06 (m, 1H, CH_2), 3.27–3.46 (m, 2H, CH_2), 5.85 (t, *J* = 7.7 Hz, 1H, CH (vinyl)), 7.02–7.06 (m, 1H, Ar), 7.11–7.21 (m, 6H, Ar), 7.27–7.30 (m, 1H, Ar).

1.5.10. 3-(10,11-Dihydro-5*H*-dibenzo[*a,d*][7]annulen-5-ylidene)propan-1-ol (1f) (Table 2, entry 10).

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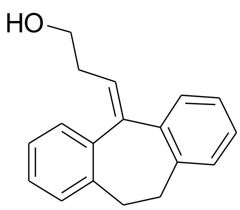
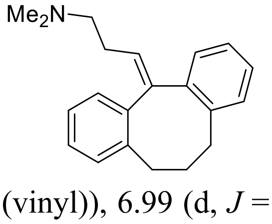
[4] G. A. Molander and E. D. Dowdy, *J. Org. Chem.*, 1999, **64**, 6515.

[5] S. Das, F. D. Bobbink, G. Laurenczy and P. J. Dyson, *Angew. Chem., Int. Ed.*, 2014, **53**, 12876.

The title compound was synthesized using the same procedure described above. Colorless solid: mp 81.5–81.8 °C; IR (KBr) 3394 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.30 (app. br s, 1H, OH), 2.36–2.46 (m, 2H, CH$_2$), 2.67–3.10 (m, 2H, CH$_2$), 3.20–3.52 (m, 2H, CH$_2$), 3.69 (app. br s, 2H, CH$_2$), 5.89 (t, J = 7.5 Hz, 1H, CH (vinyl)), 7.02–7.06 (m, 1H, Ar), 7.12–7.22 (m, 6H, Ar), 7.28–7.30 (m, 1H, Ar); ^{13}C NMR (125 MHz, CDCl$_3$) δ 32.0 (CH$_2$), 33.1 (CH$_2$), 33.7 (CH$_2$), 62.6 (CH$_2$), 125.8 (CH), 126.0 (CH), 127.2 (CH), 127.4 (CH), 127.5 (CH), 128.1 (CH), 128.3 (CH), 128.5 (CH), 130.0 (CH), 137.0 (C), 139.3 (C), 139.9 (C), 141.1 (C), 145.2 (C); HRMS-ESI m/z [M+Na]$^+$ calcd for C$_{18}$H$_{18}$ONa: 273.1250, found: 273.1252.

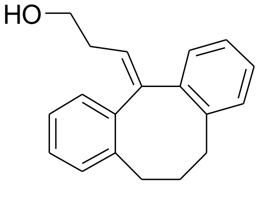


1.5.11. 3-(6,7-Dihydrodibenzo[*a,d*][8]annulen-12(5*H*)-ylidene)-*N,N*-dimethylpropan-1-amine (2f) (Table 2, entry 11).



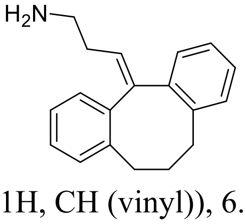
The title compound was synthesized using the same procedure described above. Yellow liquid: ^{1}H NMR (600 MHz, CDCl$_3$, 323K) δ 1.96 (app. br s, 2H, CH$_2$), 2.02 (q, J = 7.4 Hz, 2H CH$_2$), 2.15 (s, 6H, CH$_3$ (NMe$_2$)), 2.34 (t, J = 7.7 Hz, 2H, CH$_2$), 2.63 (app. br s, 2H, CH$_2$), 2.88 (t, J = 6.6 Hz, 2H, CH$_2$), 5.83 (t, J = 7.2 Hz, 1H, CH (vinyl)), 6.99 (d, J = 7.4 Hz, 1H, Ar), 7.04–7.17 (m, 6H, Ar), 7.35 (d, J = 7.4 Hz, 1H, Ar); ^{13}C NMR (150 MHz, CDCl$_3$, 323 K) δ 27.6 (CH$_2$), 29.6 (CH$_2$), 34.6 (CH$_2$), 34.9 (CH$_2$), 45.2 (2CH$_3$), 59.2 (CH$_2$), 126.2 (2CH), 126.9 (CH), 127.2 (CH), 128.2 (CH), 128.2 (CH), 128.8 (CH), 129.1 (CH), 130.6 (CH), 140.1 (C), 140.4 (C), 140.6 (C), 143.4 (C), 144.4 (C); HRMS-ESI m/z [M+H]$^+$ calcd for C$_{21}$H$_{26}$N: 292.2060, found: 292.2060.

1.5.12. 3-(6,7-Dihydrodibenzo[*a,d*][8]annulen-12(5H)-ylidene)propan-1-ol (2g) (Table 2, entry 12).



The title compound was synthesized using the same procedure described above. Colorless liquid: ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.18–1.25 (m, 1H, OH), 1.84–2.08 (m, 2H, CH$_2$), 2.15 (q, J = 6.8 Hz, 2H, CH$_2$), 2.54–2.75 (m, 2H, CH$_2$), 2.88 (t, J = 6.6 Hz, 2H, CH$_2$), 3.67 (t, J = 6.6 Hz, 2H, CH$_2$), 5.87 (t, J = 7.3 Hz, 1H, CH (vinyl)), 7.02 (dd, J = 1.3, 7.5 Hz, 1H, Ar), 7.06–7.19 (m, 6H, Ar), 7.37 (d, J = 7.2 Hz, 1H, Ar); ^{13}C NMR (150 MHz, CDCl$_3$, 322 K) δ 29.5 (CH$_2$), 33.0 (CH$_2$), 34.7 (CH$_2$), 35.1 (CH$_2$), 62.4 (CH$_2$), 126.3 (CH), 126.3 (CH), 126.9 (CH), 127.1 (CH), 127.4 (CH), 128.1 (CH), 128.3 (CH), 129.2 (CH), 130.6 (CH), 140.1 (C), 140.4 (C), 140.4 (C), 143.3 (C), 145.9 (C); HRMS-ESI m/z [M+H]$^+$ calcd for C$_{19}$H$_{21}$O: 265.1592, found: 265.1588.

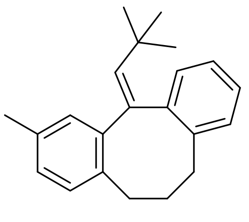
1.5.13. 3-(6,7-Dihydrodibenzo[*a,d*][8]annulen-12(5*H*)-ylidene)propan-1-amine (2h) (Table 2, entry 13).



The title compound was synthesized using the same procedure described above. Colorless liquid: IR (neat) 3502 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$, 322 K) δ 1.87 (app. br s, 2H, CH$_2$), 2.08 (q, J = 7.1 Hz, 2H, CH$_2$), 2.54 (app. br s, 2H, CH$_2$), 2.75 (t, J = 6.4 Hz, 2H, CH$_2$), 2.82 (app. br s, 2H, CH$_2$), 5.22 (app. br s, 2H, NH$_2$), 5.67 (t, J = 7.0 Hz, 1H, CH (vinyl)), 6.91 (d, J = 7.2 Hz, 1H, Ar), 6.93–6.97 (m, 1H, Ar), 6.99–7.08 (m, 5H, Ar), 7.29 (d, J = 7.5 Hz, 1H, Ar); ^{13}C NMR (150 MHz, CDCl$_3$, 322 K) δ 28.2 (CH$_2$), 29.6 (CH$_2$), 34.6 (CH$_2$), 34.9 (CH$_2$), 40.2

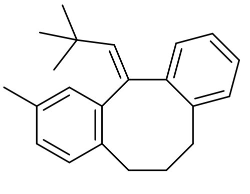
(CH_2), 124.3 (CH), 126.4 (CH), 126.6 (CH), 127.4 (CH), 127.7 (CH), 127.8 (CH), 128.1 (CH), 129.3 (CH), 130.7 (CH), 139.7 (C), 139.8 (C), 140.3 (C), 142.6 (C), 147.8 (C); HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{19}H_{22}N$: 264.1747, found: 264.1742.

1.5.14. (*E*)-12-(2,2-Dimethylpropylidene)-2-methyl-5,6,7,12-tetrahydrodibenzo[*a,d*]cyclooctene (*E*-2j) (Table 3, entry 7).



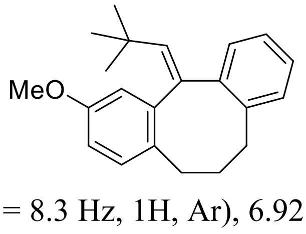
To a mixture of 1-(3,3-dimethylbut-1-yn-1-yl)-2- (3-(*p*-tolyl)propyl)benzene (**8l**) (29.0 mg, 100 μmol) in CH_2Cl_2 (1 mL) at 0 °C was added H_2SO_4 (9.8 μL, 100 μmol). The mixture was then stirred at 0 °C for 20 min, quenched with saturated aqueous $NaHCO_3$, and then extracted with ethyl acetate (3 × 1 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by silica gel column chromatography using ethyl acetate/hexane = 1/8 as an eluent to give ***E*-2j** as a colorless liquid (24.9 mg, 85.7 μmol, 86%): ^{1}H NMR (600 MHz, $CDCl_3$, 322 K) δ 0.96 (s, 9H, CH_3 (*t*-Bu)), 1.41–2.20 (m, 2H, CH_2), 2.25 (s, 3H, CH_3 (*p*–tol)), 2.57–3.29 (m, 4H, CH_2), 5.61 (s, 1H, CH (vinyl)), 6.81–6.87 (m, 2H, Ar), 6.96–7.01 (m, 1H, Ar), 7.02–7.07 (m, 3H, Ar), 7.10–7.14 (m, 1H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$, 322 K) δ 20.9 ($3CH_3$), 29.3 (CH_2), 30.7 (CH_3), 34.2 (C), 36.3 (CH_2), 37.3 (CH_2), 125.7 (CH), 126.8 (CH), 127.3 (CH), 128.9 (CH), 129.2 (CH), 129.6 (CH), 130.0 (CH), 135.6 (C), 137.1 (C), 139.4 (CH), 139.8 (C), 140.2 (C), 142.0 (C), 146.3 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{22}H_{26}$: 290.2035, found: 290.2035.

1.5.15. (*Z*)-12-(2,2-Dimethylpropylidene)-2-methyl-5,6,7,12-tetrahydro-dibenzo[*a,d*]cyclooctene (*Z*-2j) (Table 3, entry 6).



The title compound was synthesized using the same procedure described above. Colorless solid: mp 49.7–50.2 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (s, 9H, CH_3 (*t*-Bu)), 1.49–2.22 (m, 2H, CH_2), 2.25 (s, 3H, CH_3 (*p*–tol)), 2.52–3.35 (m, 4H, CH_2), 5.60 (s, 1H, CH (vinyl)), 6.87 (d, *J* = 7.4 Hz, 1H, Ar), 6.90 (d, *J* = 7.5, 1H, Ar), 6.93 (s, 1H, Ar), 6.98 (dd, *J* = 1.3, 7.3 Hz, 1H, Ar), 7.04 (ddd, *J* = 1.5, 7.2, 7.5 Hz, 1H, Ar), 7.10 (ddd, *J* = 1.5, 7.2, 7.5 Hz, 1H, Ar), 7.22 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$, 341 K) δ 20.7 ($3CH_3$), 28.8 (CH_2), 30.4 (CH_3), 33.9 (C), 36.5 (CH_2), 36.6 (CH_2), 125.9 (CH), 126.4 (CH), 127.2 (CH), 128.3 (CH), 129.3 (CH), 129.3 (CH), 129.7 (CH), 134.8 (C), 136.8 (C), 139.2 (CH), 139.6 (C), 140.0 (C), 141.5 (C), 146.3 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{22}H_{26}$: 290.2035, found: 290.2031.

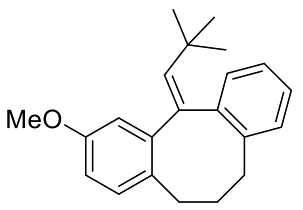
1.5.16. (*Z*)-12-(2,2-Dimethylpropylidene)-2-methoxy-5,6,7,12-tetrahydrodibenzo[*a,d*]cyclooctene (*Z*-2i) (Table 3, entry 2).



The title compound was synthesized using the same procedure described above. Colorless liquid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.92 (s, 9H, CH_3 (*t*-Bu)), 1.29–2.38 (m, 2H, CH_2), 2.44–3.22 (m, 4H, CH_2 (Bn)), 3.67 (s, 3H, OMe), 5.52 (s, 1H, CH (vinyl)), 6.54 (dd, *J* = 2.7, 8.4 Hz, 1H, Ar), 6.63 (d, *J* = 2.4 Hz, 1H, Ar), 6.86 (d, *J* = 8.3 Hz, 1H, Ar), 6.92 (dd, *J* = 1.3, 7.6 Hz, 1H, Ar), 6.98 (td, *J* = 1.4, 7.4 Hz, 1H, Ar), 7.03 (td, *J* = 1.3, 7.4 Hz, 1H, Ar), 7.14 (d, *J* = 7.2 Hz, 1H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$) δ 29.1 (C), 30.4 ($3CH_3$), 33.9 (CH_2), 36.4 (CH_2), 36.5 (CH_2), 55.0 (CH_3), 111.5 (CH), 114.6 (CH), 125.9 (CH), 126.4 (CH), 128.4 (CH), 129.7

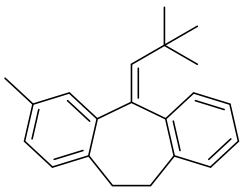
(CH), 130.3 (CH), 132.4 (C), 139.2 (CH), 139.3 (C), 140.1 (C), 142.8 (C), 146.0 (C), 157.4 (C); HRMS-EI *m/z* [M]$^+$ calcd for $C_{22}H_{26}O$: 306.1984, found: 306.1982.

1.5.17. (*E*)-12-(2,2-Dimethylpropylidene)-2-methoxy-5,6,7,12-tetrahydro-dibenzo[*a,d*]cyclooctene (*E*-2i) (Table 3, entry 4).



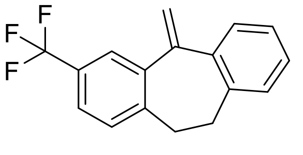
The title compound was synthesized using the same procedure described above. Yellow liquid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.98 (s, 9H, CH_3 (*t*-Bu)), 2.00–2.41 (m, 1H, CH_2), 2.41–3.40 (m, 5H, CH_2), 3.79 (s, 3H, OMe), 5.65 (s, 1H, CH (vinyl)), 6.62 (dd, *J* = 2.9, 8.5 Hz, 1H, Ar), 6.82 (s, 1H, Ar), 6.94 (d, *J* = 8.2 Hz, 1H, Ar), 7.10 (m, 4H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$, 323 K) δ 29.2 (C), 30.4 ($3CH_3$), 33.9 (CH_2), 35.7 (CH_2), 37.1 (CH_2), 55.1 (CH_3), 111.1 (CH), 114.6 (CH), 125.5 (CH), 126.7 (CH), 128.7 (CH), 129.4 (CH), 130.7 (CH), 132.3 (C), 139.3 (C), 139.4 (CH), 140.1 (C), 141.5 (C), 147.3 (C), 157.8 (C); HRMS-EI *m/z* [M]$^+$ calcd for $C_{22}H_{26}O$: 306.1984, found: 306.1982.

1.5.18. (*E*)-5-(2,2-Dimethylpropylidene)-10,11-dihydro-3-methyl-5*H*-dibenzo[*a,d*]cycloheptene (*E*-1g) (Table 3, entry 9).



The title compound was synthesized using the same procedure described above. Colorless liquid: mp 82.6–83.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (s, 9H, CH_3 (*t*-Bu)), 2.29 (s, 3H, CH_3 (*p*-tol)), 2.70 (dt, *J* = 4.4, 13.6 Hz, 1H, CH_2), 2.88 (ddd, *J* = 4.3, 13.2, 17.1 Hz, 1H, CH_2), 3.25 (dt, *J* = 4.4, 17.1 Hz, 1H, CH_2), 3.49 (td, *J* = 4.3, 13.6 Hz, 1H, CH_2), 5.77 (s, 1H, CH (vinyl)), 6.86 (d, *J* = 8.1 Hz, 1H, Ar), 6.91 (dd, *J* = 1.7, 7.8 Hz, 1H, Ar), 7.04–7.21 (m, 5H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8 (CH_3), 31.1 ($3CH_3$), 31.7 (CH_2), 33.2 (CH_2), 33.8 (C), 125.3 (CH), 127.1 (CH), 127.2 (CH), 127.5 (CH), 128.1 (CH), 128.8 (CH), 130.3 (CH), 133.1 (C), 135.3 (C), 138.8 (C), 140.0 (C), 141.2 (CH), 141.9 (C), 142.5 (C); HRMS-EI *m/z* [M]$^+$ calcd for $C_{21}H_{24}$: 276.1878, found: 276.1881.

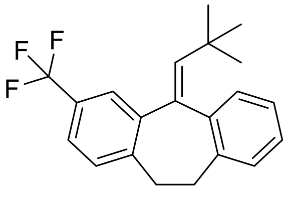
1.5.19. 10,11-Dihydro-5-methylene-3-(trifluoromethyl)-5*H*-dibenzo[*a,d*]cycloheptene (1h') (Table 3, entry 10).



The title compound was synthesized using the same procedure described above. Colorless liquid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.15–3.19 (m, 2H, CH_2), 3.19–3.22 (m, 2H, CH_2), 5.47 (d, *J* = 1.2 Hz, 1H, C=CH_2), 5.51 (d, *J* = 1.2 Hz, 1H, C=CH_2), 7.14 (d, *J* = 7.1 Hz, 1H, Ar), 7.19–7.26 (m, 3H, Ar), 7.37 (dd, *J* = 1.4, 7.4 Hz, 1H, Ar), 7.46 (d, *J* = 8.5 Hz, 1H, Ar), 7.61 (s, 1H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$) δ 32.8 (CH_2), 33.1 (CH_2), 118.7 (CH_2), 124.2 (q, ^1J = 272.0 Hz, CF_3), 124.3 (q, ^3J = 4.1 Hz, CH), 124.9 (q, ^3J = 4.1 Hz, CH), 126.5 (CH), 128.0 (CH), 128.3 (CH), 128.6 (q, ^2J = 20.9 Hz, C), 129.0 (CH), 129.3 (CH), 137.8 (C), 140.2 (C), 141.8 (C), 142.4 (C), 150.6 (C); HRMS-EI *m/z* [M]$^+$ calcd for $C_{17}H_{13}F_3$: 274.0969, found: 274.0965.

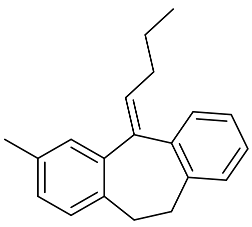
1.5.20. (*E*)-5-(2,2-Dimethylpropylidene)-10,11-dihydro-3-(trifluoromethyl)-5*H*-dibenzo[*a,d*]cycloheptene (*E*-1h) (Table 3, entry 10).

Light yellow liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (s, 9H, CH_3 (*t*-Bu)), 2.75 (dt, *J* = 4.3, 13.8 Hz, 1H,



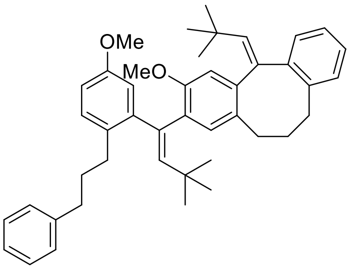
CH_2), 2.96 (td, J = 4.3, 15.6 Hz, 1H, CH_2), 3.34 (dd, J = 4.3, 17.3 Hz, 1H, CH_2), 3.52 (td, J = 4.3, 13.8 Hz, 1H, CH_2), 5.81 (s, 1H, CH (vinyl)), 7.07 (d, J = 8.1 Hz, 1H, Ar), 7.12–7.20 (m, 4H, Ar), 7.32 (dd, J = 1.5, 8.1 Hz, 1H, Ar), 7.48 (s, 1H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$) δ 30.9 (3CH_3), 31.2 (CH_2), 33.7 (CH_2), 34.0 (C), 123.1 (q, ^3J = 3.8 Hz, CH), 124.3 (q, ^1J = 271.7 Hz, CF_3), 125.1 (q, ^3J = 3.3 Hz, CH), 125.6 (CH), 127.3 (CH), 127.7 (CH), 128.1 (q, ^2J = 32.4 Hz, C), 128.3 (CH), 130.8 (CH), 138.3 (C), 138.8 (C), 141.1 (C), 142.3 (C), 142.7 (CH), 143.2 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{21}H_{21}F_3$: 330.1595, found: 330.1598.

1.5.21. (*E*)-5-Butylidene-10,11-dihydro-3-methyl-5*H*-dibenzo[*a,d*]cycloheptene (*E*-1i) (Table 3, entry 14).



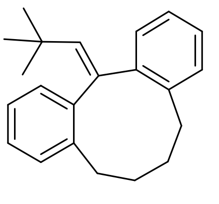
The title compound was synthesized using the same procedure described above. Colorless liquid: ^{1}H NMR (600 MHz, $CDCl_3$, 324 K) δ 0.92 (t, J = 7.5 Hz, 3H, CH_3 (*n*-Pr)), 1.44–1.51 (m, 2H, CH_2 (*n*-Pr)), 2.12 (app. br s, 2H, CH_2 (*n*-Pr)), 2.33 (s, 3H, CH_3), 2.60–3.61 (m, 4H, CH_2), 5.87 (t, J = 7.7Hz, 1H, CH (vinyl)), 6.92–6.99 (m, 2H, Ar), 7.11–7.23 (m, 5H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$, 324 K) δ 13.6 (CH_3), 20.6 (CH_3), 22.8 (CH_2), 31.3 (CH_2), 32.1 (CH_2), 33.2 (CH_2), 125.4 (CH), 127.0 (CH), 127.5 (CH), 127.8 (CH), 128.2 (CH), 128.9 (CH), 129.7 (CH), 131.6 (CH), 133.9 (C), 135.2 (C), 139.2 (C), 140.3 (C), 141.4 (C), 142.5 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{20}H_{22}$: 262.1722, found: 262.1725.

1.5.22. (*Z*)-12-(2,2-Dimethylpropylidene)-2-methoxy-3-((*Z*)-1-(5-methoxy-2-(3-phenylpropyl)-phenyl)-3,3-dimethylbut-1-en-1-yl)-5,6,7,12-tetrahydrodibenzo[*a,d*]cyclooctane (10) (Table 3, entry 1).



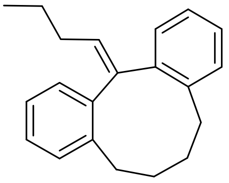
Colorless liquid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.91 (s, 9H, CH_3 (*t*-Bu)), 0.94 (s, 9H, CH_3 (*t*-Bu)), 1.36–1.49 (m, 1H, CH_2), 1.60–1.73 (m, 2H, CH_2), 1.99–2.34 (m, 1H, CH_2), 2.36–2.42 (m, 2H, CH_2), 2.42–2.50 (m, 2H, CH_2), 2.52–3.38 (m, 4H, CH_2), 3.68 (s, 3H, OMe), 3.83 (s, 3H, OMe), 5.59 (s, 1H, CH (vinyl)), 5.82 (s, 1H, CH (vinyl)), 6.61 (s, 1H, Ar), 6.70–6.75 (m, 1H, Ar), 6.75 (dd, J = 2.9, 8.5 Hz, 1H, Ar), 6.93 (s, 1H, Ar), 6.96–7.01 (m, 2H, Ar), 7.04–7.09 (m, 3H, Ar), 7.11 (t, J = 7.3 Hz, 1H, Ar), 7.15 (t, J = 7.3 Hz, 1H, Ar), 7.18–7.26 (m, 3H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$, 322 K) δ 29.1 (2C), 30.6 (3CH_3), 30.9 (3CH_3), 31.9 (CH_2), 32.0 (CH_2), 34.1 (CH_2), 34.2 (CH_2), 36.1 (CH_2), 36.4 (CH_2), 55.4 (CH_3), 55.9 (CH_3), 112.5 (CH), 113.1 (CH), 117.9 (CH), 125.5 (CH), 126.1 (CH), 126.6 (CH), 128.2 (C), 128.2 (2CH), 128.4 (C), 128.4 (2CH), 128.5 (CH), 129.0 (CH), 130.0 (CH), 132.0 (C), 132.0 (CH), 133.1 (C), 139.7 (C), 139.8 (C), 139.8 (C), 140.4 (C), 141.4 (C), 142.6 (C), 143.3 (2CH), 155.0 (C), 156.5 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{44}H_{52}O_2$: 612.3967, found: 612.3970.

1.5.23. 13-(2,2-Dimethylpropylidene)-6,7,8,13-tetrahydro-5*H*-dibenzo[*a,d*]cyclononene (3a) (Table 4, entry 1).



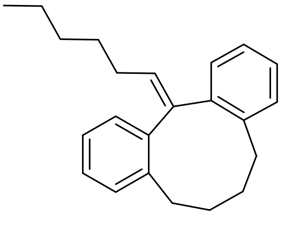
To a mixture of 1-(3,3-dimethylbut-1-yn-1-yl)-2-(4-phenylbutyl)benzene **(9a)** (29.2 mg, 101 μmol) in CH_2Cl_2 (1 mL) at 0 °C was added TfOH (8.8 μL, 100 μmol). The mixture was stirred at 0 °C for 10 min, quenched with saturated aqueous $NaHCO_3$, and then extracted with ethyl acetate (3 × 1 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and evaporated. The residue was purified by silica gel column chromatography using hexane as an eluent to give **3a** as a colorless liquid (12.4 mg, 42.7 μmol, 43%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.94 (s, 10H, CH_3 (*t*-Bu), CH_2), 1.34–1.45 (m, 1H, CH_2), 1.71–1.81 (m, 2H, CH_2), 2.46–2.56 (m, 2H, CH_2), 3.11 (dt, *J* = 5.3, 13.3 Hz, 1H, CH_2), 3.37–3.54 (m, 1H, CH_2), 5.51 (s, 1H, CH (vinyl)), 7.01–7.15 (m, 6H, Ar), 7.24–7.30 (m, 2H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$) δ 27.5 (CH_2), 29.3 (CH_2), 30.4 (CH_2), 30.6 ($3CH_3$), 30.9 (CH_2), 34.5 (C), 125.5 (CH), 125.5 (CH), 126.9 (CH), 127.1 (CH), 128.9 (CH), 129.2 (CH), 129.7 (CH), 129.8 (CH), 137.0 (C), 139.7 (C), 141.4 (C), 141.8 (C), 142.2 (CH), 145.8 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{22}H_{26}$: 290.2035, found: 290.2031.

1.5.24. 13-Butylidene-6,7,8,13-tetrahydro-5*H*-dibenzo[*a,d*]cyclononene (3b) (Table 4, entry 3).



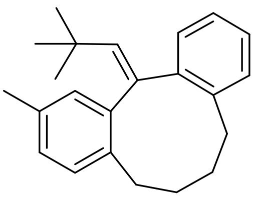
The title compound was synthesized using the same procedure described above. Colorless liquid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.4 Hz, 3H, CH_3 (*n*-Pr)), 1.43 (sext, *J* = 7.4 Hz, 2H, CH_2 (*n*-Pr)), 1.44–1.86 (m, 4H, CH_2), 1.93 (q, *J* = 6.6 Hz, 2H, CH_2 (*n*-Pr)), 2.10–3.46 (m, 4H, CH_2), 5.70 (t, *J* = 7.3 Hz, 1H, CH (vinyl)), 7.03 (dd, *J* = 1.8, 6.9 Hz, 1H, Ar), 7.08 (dd, *J* = 1.9, 7.6 Hz, 1H, Ar), 7.10–7.18 (m, 5H, Ar), 7.33 (dd, *J* = 1.9, 6.8 Hz, 1H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$) δ 13.9 (CH_3), 22.4 (CH_2), 28.7 (CH_2), 29.2 (CH_2), 30.8 (CH_2), 31.1 (CH_2), 31.7 (CH_2), 125.6 (CH), 125.8 (CH), 126.9 (CH), 127.0 (CH), 128.7 (CH), 129.0 (CH), 129.2 (CH), 129.4 (CH), 132.3 (CH), 140.5 (C), 141.0 (C), 141.1 (2C), 144.0 (C); HRMS-EI *m/z* $[M]^+$ calcd for $C_{21}H_{24}$: 276.1878, found: 276.1877.

1.5.25. 13-Hexylidene-6,7,8,13-tetrahydro-5*H*-dibenzo[*a,d*]cyclononene (3c) (Table 4, entry 4).



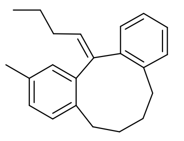
The title compound was synthesized using the same procedure described above. Colorless liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (t, *J* = 7.6 Hz, 3H, CH_3), 1.22–1.26 (m, 6H, CH_2), 1.37–1.44 (m, 2H, CH_2), 1.44–1.70 (m, 2H, CH_2), 1.95 (ap q, *J* = 7.7 Hz, 2H, CH_2), 2.20–3.20 (m, 4H, CH_2), 5.78 (t, *J* = 7.2 Hz, 1H, CH (vinyl)), 7.03 (dd, *J* = 1.7, 7.6 Hz, 1H, Ar), 7.07–7.09 (m, 1H, Ar), 7.11–7.18 (m, 5H, Ar), 7.33 (dd, *J* = 1.7, 7.6 Hz, 1H, Ar); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.0 (CH_3), 22.5 (CH_2), 28.7 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 30.8 (CH_2), 31.5 (CH_2), 31.7 (CH_2), 125.6 (CH), 125.8 (CH), 126.9 (CH), 127.0 (CH), 128.7 (CH), 129.0 (CH), 129.2 (CH), 129.4 (CH), 132.5 (CH), 140.5 (C), 140.8 (C), 141.1 (C), 141.2 (C), 144.0 (C); HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{23}H_{29}$: 305.2264, found: 305.2271.

1.5.26. (*E*)- and (*Z*)-13-(2,2-Dimethylpropylidene)-2-methyl-6,7,8,13-tetrahydro-5*H*-dibenzo[*a,d*]-cyclononene (3d) (Table 4, entry 5).



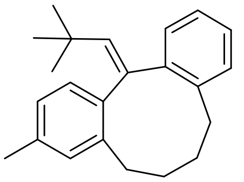
The title compound was obtained as a mixture of (*E*)- and (*Z*)-isomers (major:minor = 52:48) by the same procedure described above. Yellow liquid: ^{1}H NMR (500 MHz, $CDCl_3$) (mixture) δ 0.92–0.95 (m, 20H, CH_3 (*t*-Bu), CH_2), 1.33–1.43 (m, 2H, CH_2), 1.69–1.81 (m, 4H, CH_2), 2.26 (s, 3H, CH_3 (*p*–tol)), 2.30 (s, 3H, CH_3 (*p*–tol)), 2.45–2.53 (m, 4H, CH_2), 3.02–3.13 (m, 2H, CH_2), 3.32–3.49 (m, 2H, CH_2), 5.48 (s, 1H, CH (vinyl)), 5.48 (s, 1H, CH (vinyl)), 6.89–6.93 (m, 3H, Ar), 6.96 (d, *J* = 7.6 Hz, 1H, Ar), 7.02–7.14 (m, 8H, Ar), 7.25–7.31 (m, 2H, Ar); ^{13}C NMR (150 MHz, CDCl$_3$) (mixture) δ 21.0 (CH$_3$), 21.1 (CH$_3$), 27.2 (CH$_2$), 27.5 (CH$_2$), 28.6 (CH$_2$), 29.1 (CH$_2$), 30.0 (CH$_2$), 30.2 (CH$_2$), 30.3 (CH$_2$), 30.4 (6CH$_3$), 30.7 (CH$_2$), 34.3 (C), 34.3 (C), 125.2 (CH), 125.3 (CH), 126.6 (CH), 126.8 (CH), 127.5 (CH), 127.5 (CH), 128.5 (CH), 128.7 (CH), 129.0 (CH), 129.4 (2CH), 129.5 (CH), 129.7 (CH), 130.2 (CH), 134.5 (C), 134.6 (C), 136.3 (C), 136.8 (C), 136.9 (C), 138.5 (C), 139.7 (C), 140.9 (C), 141.2 (C), 141.7 (C), 141.8 (CH), 141.8 (CH), 145.3 (C), 145.7 (C); HRMS-EI *m/z* [M]$^+$ calcd for C$_{23}$H$_{28}$: 304.2191, found: 304.2182.

1.5.27. (*E*)- and (*Z*)-13-Butylidene-2-methyl-6,7,8,13-tetrahydro-5*H*-dibenzo[*a,d*]cyclononene (3e) (Table 4, entry 6).



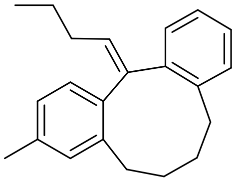
The title compound was obtained as a mixture of (*E*)- and (*Z*)-isomers (major:minor = 74:26) by the same procedure described above. Colorless liquid: ^{1}H NMR (500 MHz, CDCl$_3$) (major) δ 0.89 (t, 3H, J = 1.7, 7.6 Hz, CH$_3$), 1.40–1.46 (m, 2H, CH$_2$), 1.52–1.57 (m, 4H, CH$_2$), 1.89–1.97 (m, 2H, CH$_2$), 2.26 (s, 3H, CH$_3$), 2.30–3.20 (m, 4H, CH$_2$), 5.69 (t, J = 6.5 Hz, 1H, vinyl), 6.87 (br s, 1H, Ar), 6.96 (dd, J = 1.4, 7.5 Hz, 1H, Ar), 7.01–7.03 (m, 2H, Ar), 7.12–7.17 (m, 2H, Ar), 7.34–7.31 (dd, J = 1.6, 7.4 Hz, 1H, Ar); ^{13}C NMR (150 MHz, CDCl$_3$) (major) δ 13.9 (CH$_3$), 21.0 (CH$_3$), 22.4 (CH$_2$), 28.9 (CH$_2$), 29.1 (CH$_2$), 30.9 (CH$_2$), 31.09 (CH$_2$), 31.13 (CH$_2$) 125.6 (CH), 126.8 (CH), 127.7 (CH), 128.9 (CH), 129.2 (CH), 129.3 (CH), 129.4 (CH), 132.1 (CH), 135.1 (C), 137.9 (C), 140.2 (C), 141.1 (C), 141.3 (C), 144.1 (C); HRMS-ESI *m/z* [M+Na]$^+$ calcd for C$_{22}$H$_{26}$Na: 313.1927, found: 313.1932.

1.5.28. (*E*)- and (*Z*)-13-(2,2-Dimethylpropylidene)-3-methyl-6,7,8,13-tetrahydro-5*H*-dibenzo[*a,d*]-cyclononene (3f) (Table 4, entry 7).



The title compound was obtained as a mixture of (*E*)- and (*Z*)-isomers (major:minor = 51:49) by the same procedure described above. Colorless liquid: ^{1}H NMR (500 MHz, CDCl$_3$) (mixture) δ 0.89–1.01 (m, 20H, CH$_3$ (*t*-Bu), CH$_2$), 1.32–1.46 (m, 2H, CH$_2$), 1.69–1.82 (m, 4H, CH$_2$), 2.26 (s, 3H, CH$_3$), 2.28 (s, 3H, CH$_3$), 2.42–2.56 (m, 4H, CH$_2$), 3.02–3.16 (m, 2H, CH$_2$), 3.33–3.52 (m, 2H, CH$_2$), 5.50 (s, 2H, CH (vinyl)), 6.85–6.96 (m, 4H, Ar), 7.01–7.19 (m, 8H, Ar), 7.21–7.26 (m, 2H, Ar); ^{13}C NMR (125 MHz, CDCl$_3$) (mixture) δ 21.2 (3CH$_3$), 21.3 (3CH$_3$), 27.5 (CH$_2$), 27.6 (CH$_2$), 29.3 (CH$_2$), 29.3 (CH$_2$), 30.3 (CH$_2$), 30.4 (CH$_2$), 30.7 (CH$_3$), 30.7 (CH$_3$), 31.0 (CH$_2$), 31.0 (CH$_2$), 34.5 (2C), 125.5 (CH), 125.6 (CH), 126.2 (CH), 126.3 (CH), 126.8 (CH), 127.0 (CH), 128.9 (CH), 129.1 (2CH), 129.6 (CH), 129.7 (CH), 129.8 (CH), 129.8 (CH), 130.4 (CH), 136.4 (C), 136.6 (C), 137.0 (C), 137.2 (C), 138.4 (C), 139.6 (C), 139.7 (C), 141.6 (2C), 141.7 (C), 142.1 (CH), 142.2 (CH), 143.1 (C), 146.1 (C); HRMS-ESI *m/z* [M+H]$^+$ calcd for C$_{23}$H$_{29}$: 305.2264, found: 305.2261.

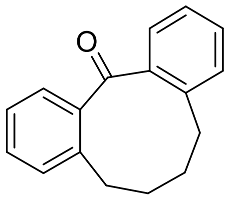
1.5.29. (*E*)- and (*Z*)-13-Butylidene-3-methyl-6,7,8,13-tetrahydro-5*H*-dibenzo[*a,d*]cyclononene (3g) (Table 4, entry 8).



The title compound was obtained as a mixture of (*E*)- and (*Z*)-isomers (major:minor = 51:49) by the same procedure described above. Colorless liquid: ^{1}H NMR (500 MHz, CDCl$_3$) (mixture) δ 0.87 (t, J = 7.3 Hz, 3H, CH$_3$), 0.88 (t, J = 7.3 Hz, 3H, CH$_3$), 1.38–1.46 (m, 4H, CH$_2$), 1.52–1.57 (m, 8H, CH$_2$), 1.89–1.97 (m, 4H, CH$_2$), 2.28 (s, 3H, CH$_3$), 2.29 (s, 3H, CH$_3$), 2.30–3.20 (m, 8H, CH$_2$), 5.68 (t, J = 7.0 Hz, 1H, vinyl), 5.69 (t, J = 7.0 Hz, 1H, vinyl), 6.85 (br s, 1H, Ar), 6.93–6.97 (m, 4H, Ar), 7.01–7.03 (m, 1H, Ar), 7.06 (app d, J = 7.6 Hz, 1H, Ar), 7.10–7.18 (m, 5H, Ar), 7.23 (d, J = 7.6 Hz, 1H, Ar), 7.29–7.31 (m, 1H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$) (mixture) δ 13.90 (CH_3), 13.92 (CH_3), 21.0 (CH_3), 21.1 (CH_3), 22.4 ($2CH_2$), 28.8 ($2CH_2$), 29.2 ($2CH_2$), 30.9 (CH_2), 31.1 (CH_2), 31.3 ($2CH_2$), 31.7 (CH_2), 31.8 (CH_2), 125.6 (CH), 125.8 (CH), 126.3 (CH), 126.5 (CH), 126.8 (CH), 126.9 (CH), 128.6 (CH), 128.7 (CH), 129.0 (CH), 129.2 (2CH), 129.4 (CH), 129.8 (CH), 130.3 (CH), 132.0 (CH), 132.2 (CH), 136.4 (2C), 137.5 (C), 140.7 (C), 140.93 (C), 140.94 (C), 140.97 (C), 140.99 (C), 141.06 (C), 141.08 (C), 141.2 (C), 144.2 (C); HRMS-ESI m/z $[M+H]^+$ calcd for $C_{22}H_{27}$: 291.2107, found: 291.2115.

1.6. Preparation of 5,6,7,8-tetrahydro-13*H*-dibenzo[*a,d*][9]annulen-13-one (6)

1.6.1. 5,6,7,8-Tetrahydro-13*H*-dibenzo[*a,d*][9]annulen-13-one (6) (eqn (3)).



To a stirred mixture of 13-butylidene-6,7,8,13-tetrahydro-5*H*-dibenzo[*a,d*]cyclononene (**3b**) (95.7 mg, 350 μmol), $RuCl_3$ (24.2 mg, 92.6 μmol, 26 mol%), CH_3CN (5.0 mL) and distilled water (3.0 mL) at room temperature was added a mixture of Oxone (903 mg, 1.47 mmol) and $NaHCO_3$ (378 mg, 4.52 mmol) in portions over a period of 10 min. The mixture was stirred for 2 h, quenched with saturated aqueous NaS_2O_3, and then extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, dried over Na_2SO_4. Then the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using ethyl acetate/hexane = 1/8 as an eluent to give 5,6,7,8-tetrahydro-13*H*-dibenzo[*a,d*][9]annulen-13-one (**6**) as a colorless liquid (50.7 mg, 215 μmol, 61%): IR (neat) 1666 cm^{-1} (lit.[6] 1655 cm^{-1}); ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.73 (app. br s, 4H, CH_2), 2.68 (app. br s, 4H, CH_2), 7.19 (d, J = 7.6 Hz, 2H, Ar), 7.30 (d, J = 7.6 Hz, 2H, Ar), 7.39 (td, J = 1.1, 7.6 Hz, 2H, Ar), 7.48 (d, J = 7.6 Hz, 2H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$) δ 27.0 ($2CH_2$), 32.9 ($2CH_2$), 126.1 (2CH), 126.6 (2CH), 130.6 (2CH), 130.9 (2CH), 141.1 (2C), 141.4 (2C), 203.4 (C=O); HRMS-ESI m/z $[M+Na]^+$ calcd for $C_{17}H_{16}ONa$: 259.1093, found: 259.1089.

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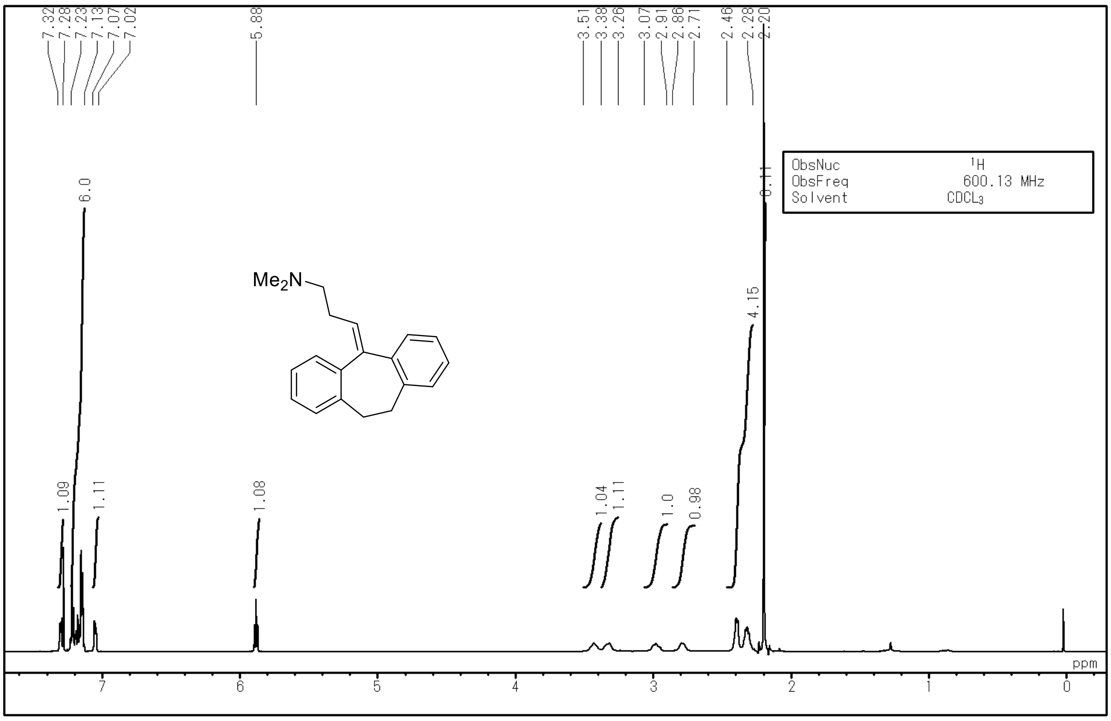
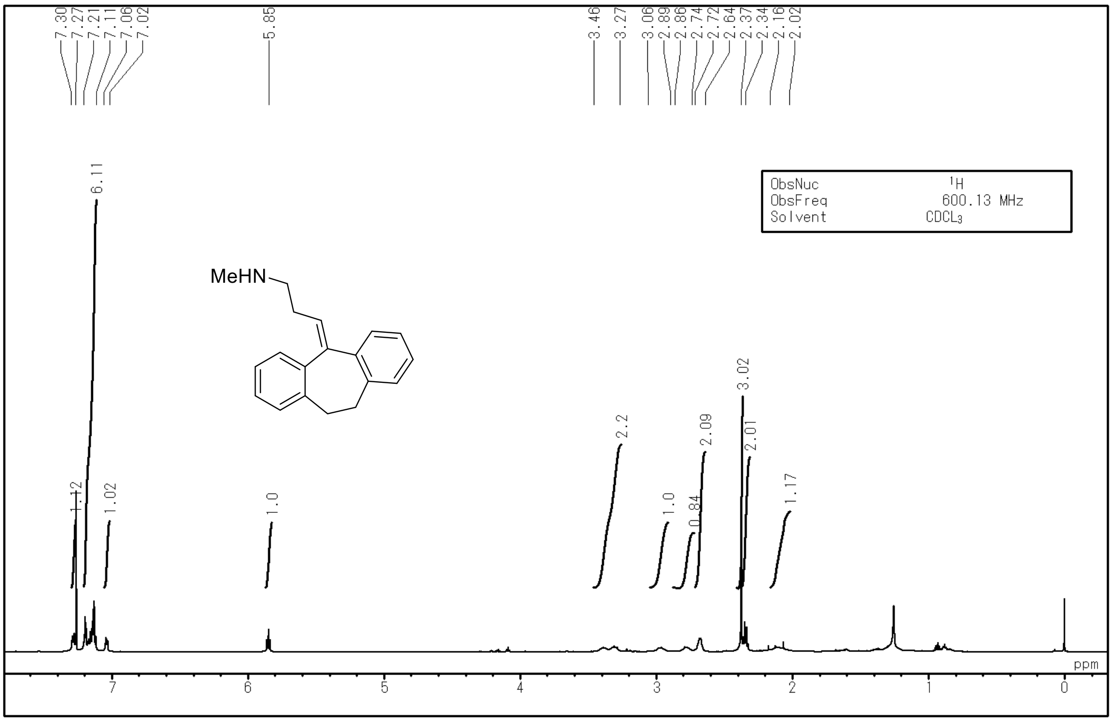
[6] P. Caubere, M. S. Mourad, G. Guillaumet, *Tetrahedron* , 1973, **29**, 1851.

2. NMR spectra

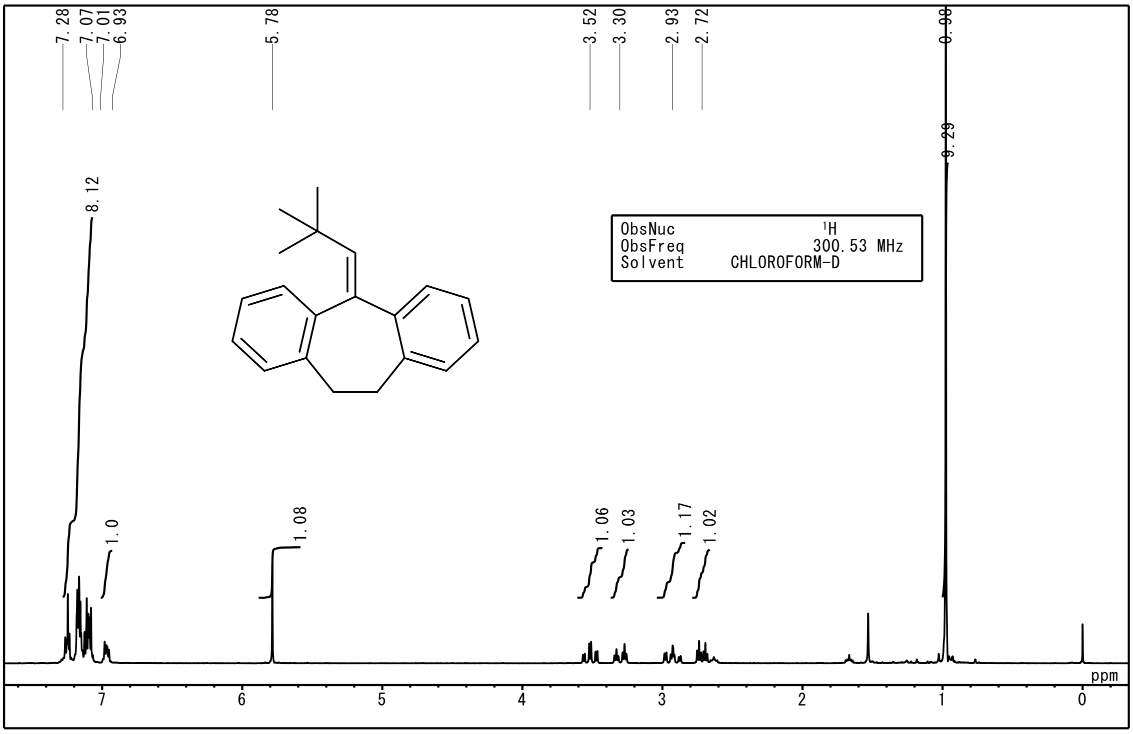
3-(10,11-Dihydro-5*H*-dibenzo[*a,d*][7]annulen-5-ylidene)-*N,N*-dimethylpropan-1-amine (1a).

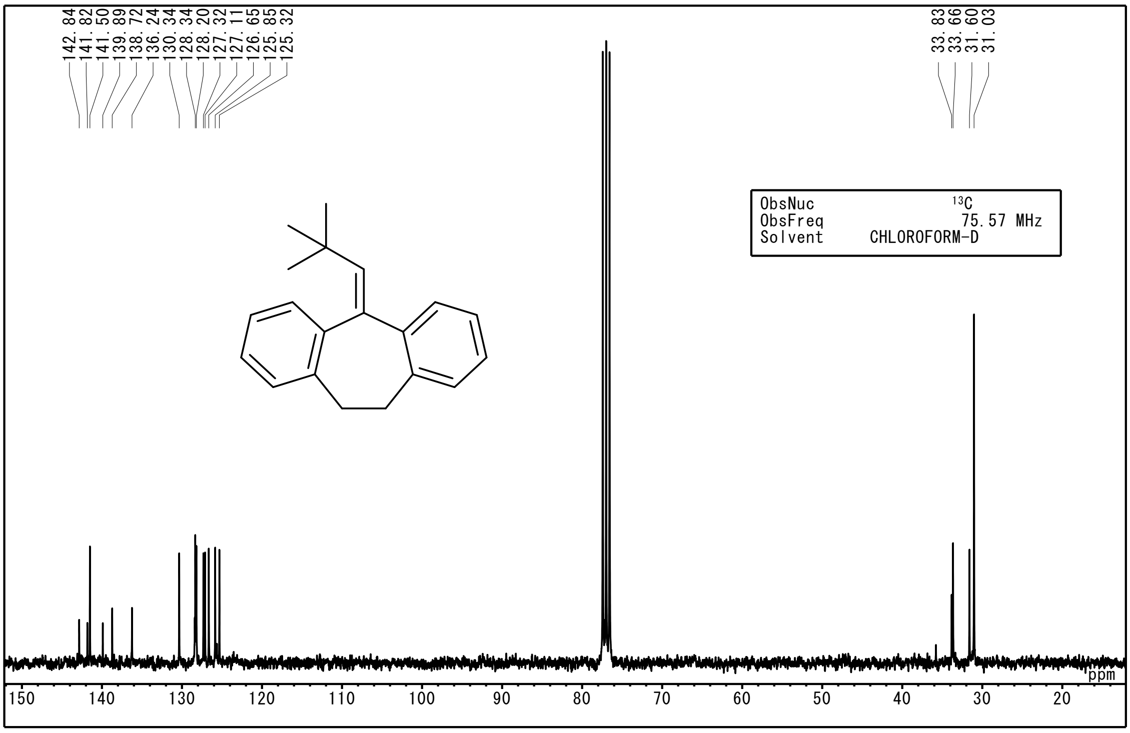


3-(10,11-Dihydro-5*H*-dibenzo[*a,d*][7]annulen-5-ylidene)-*N*-methylpropan-1-amine (1b).

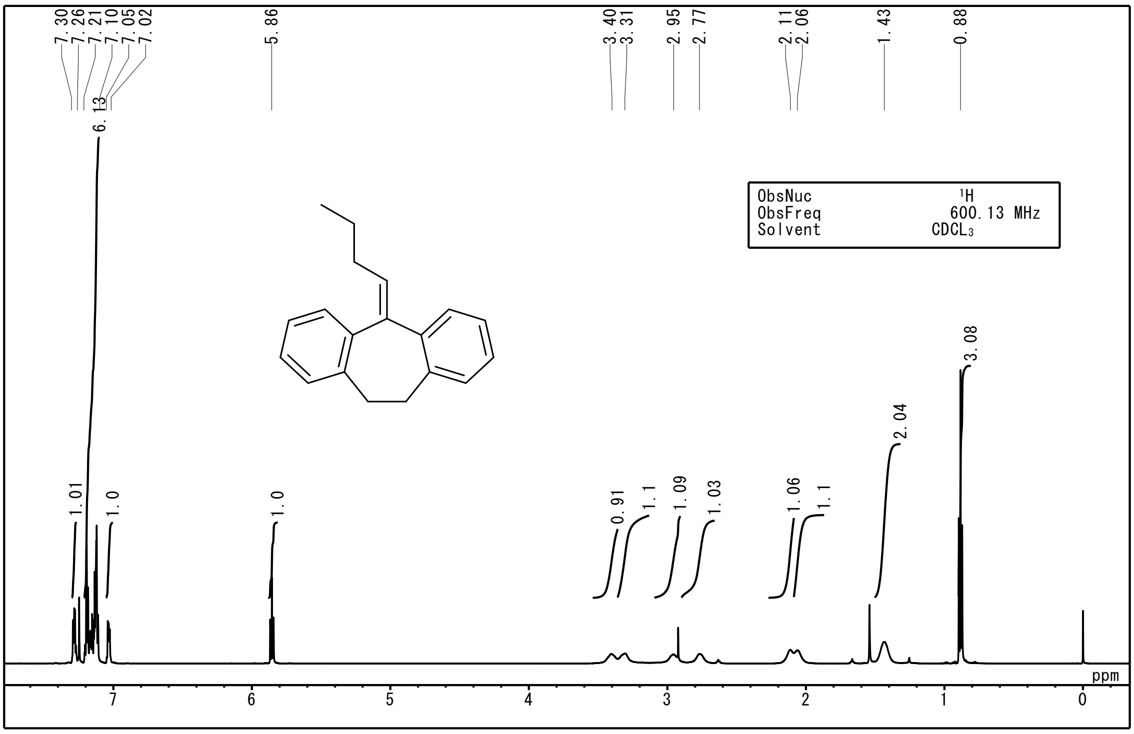


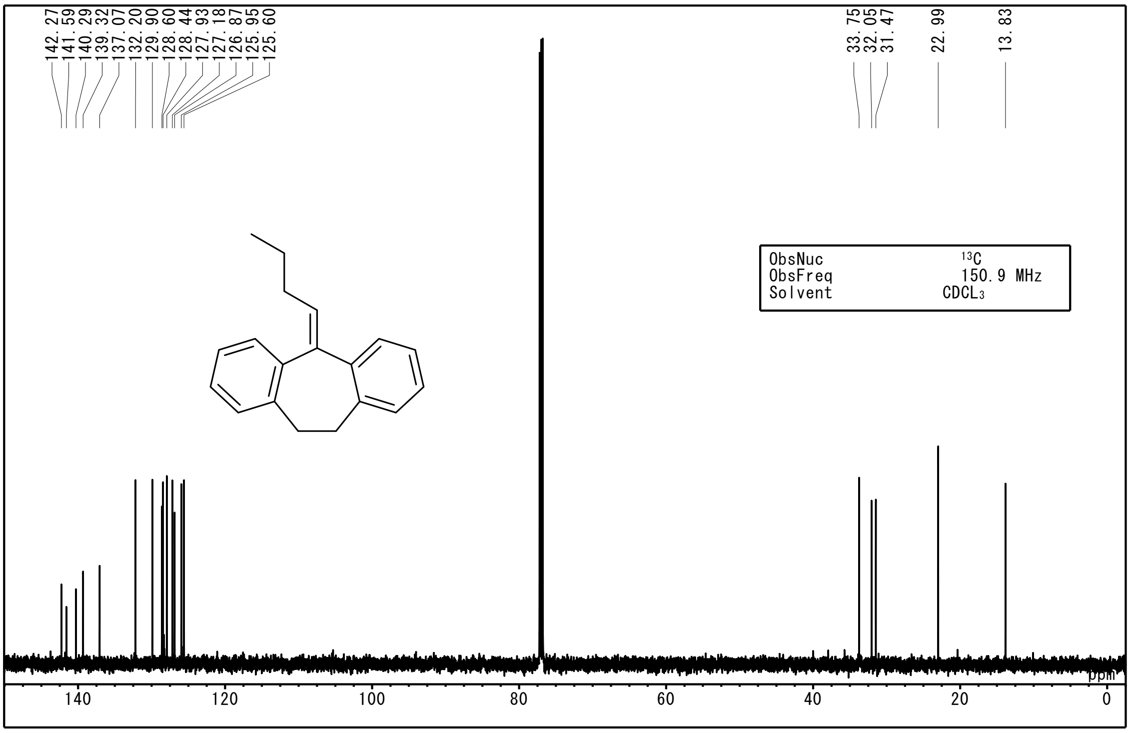
5-(2,2-Dimethylpropylidene)-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (1c).



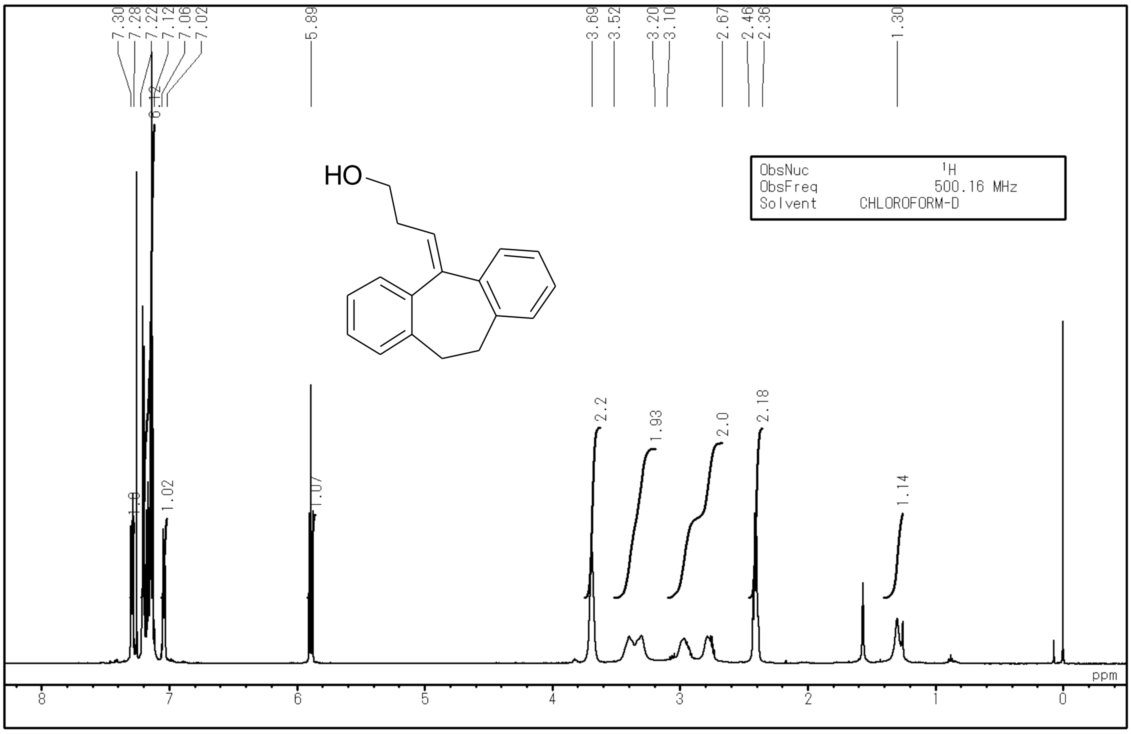


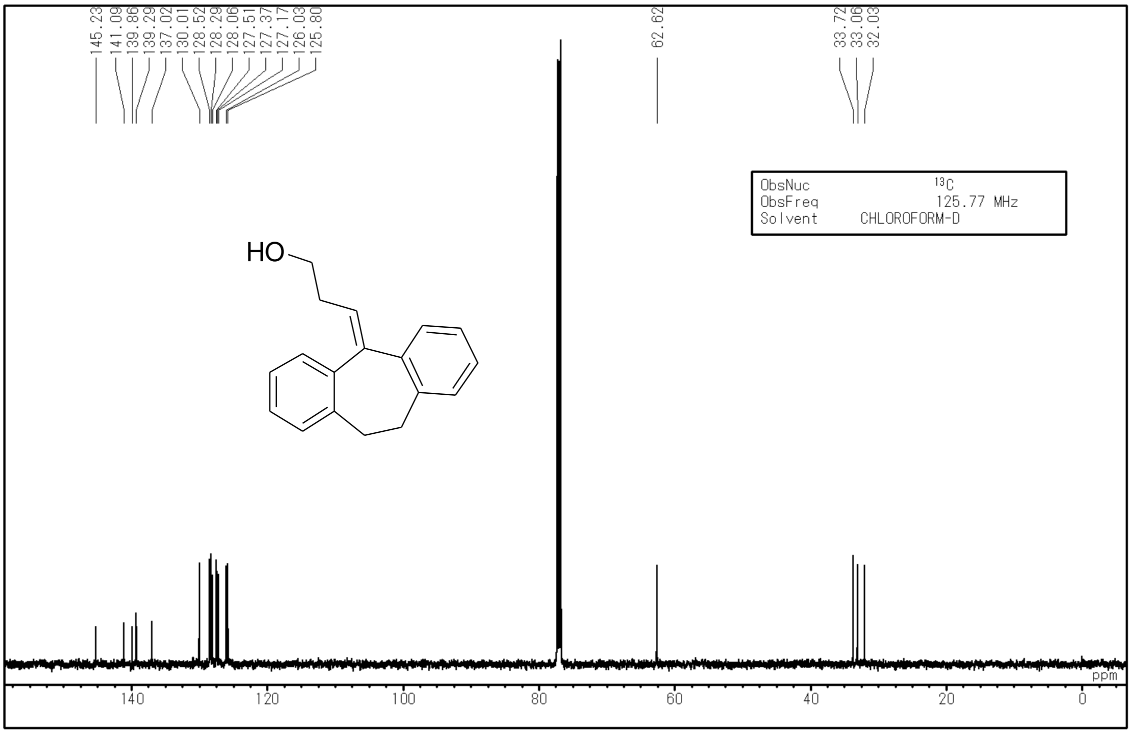
5-(Butylidene)-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (1d).



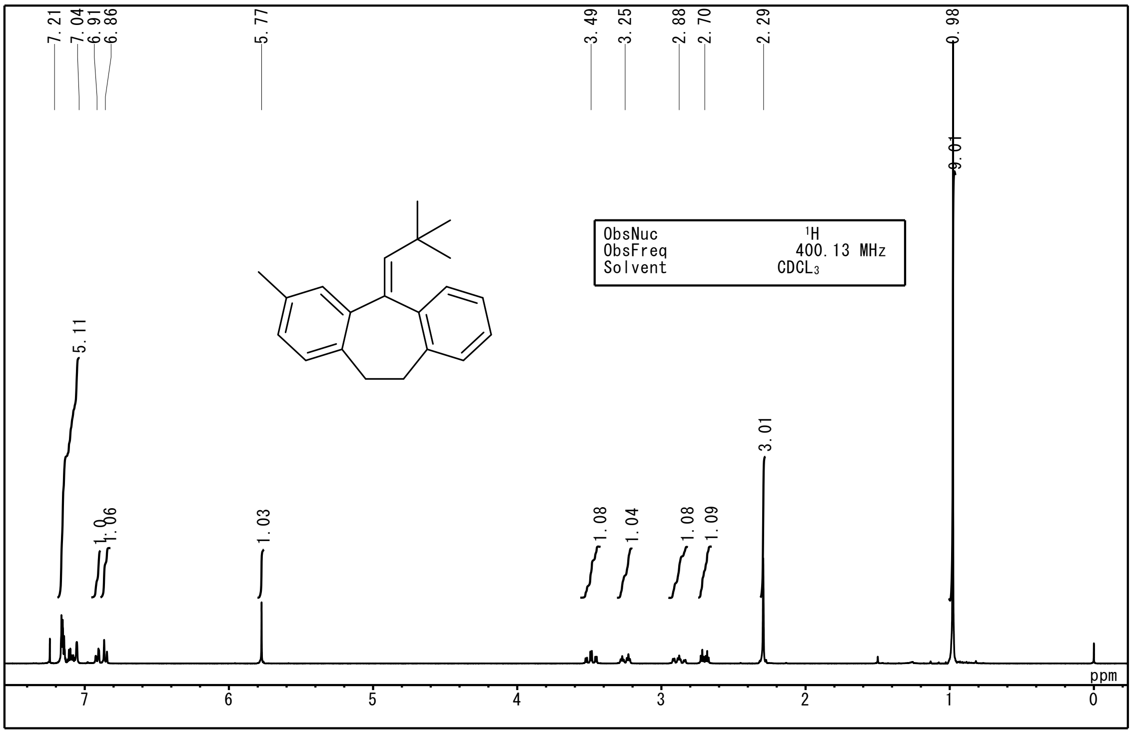


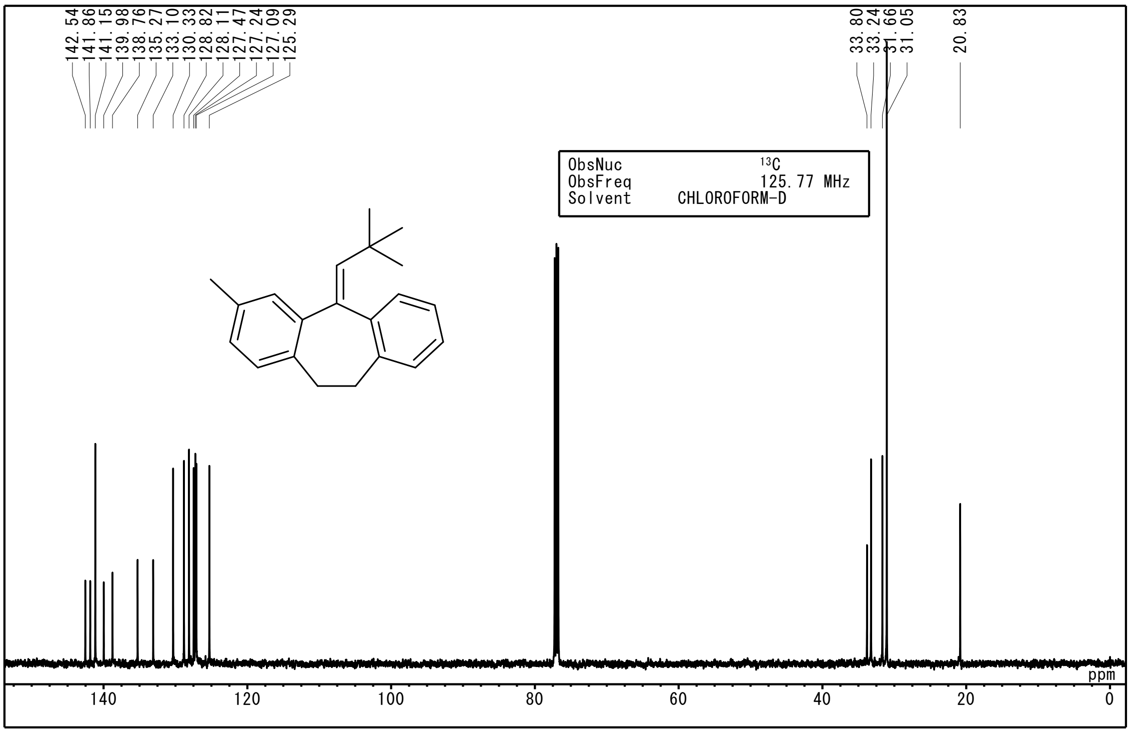
3-(10,11-Dihydro-5*H*-dibenzo[*a,d*][7]annulen-5-ylidene)propan-1-ol (1f).



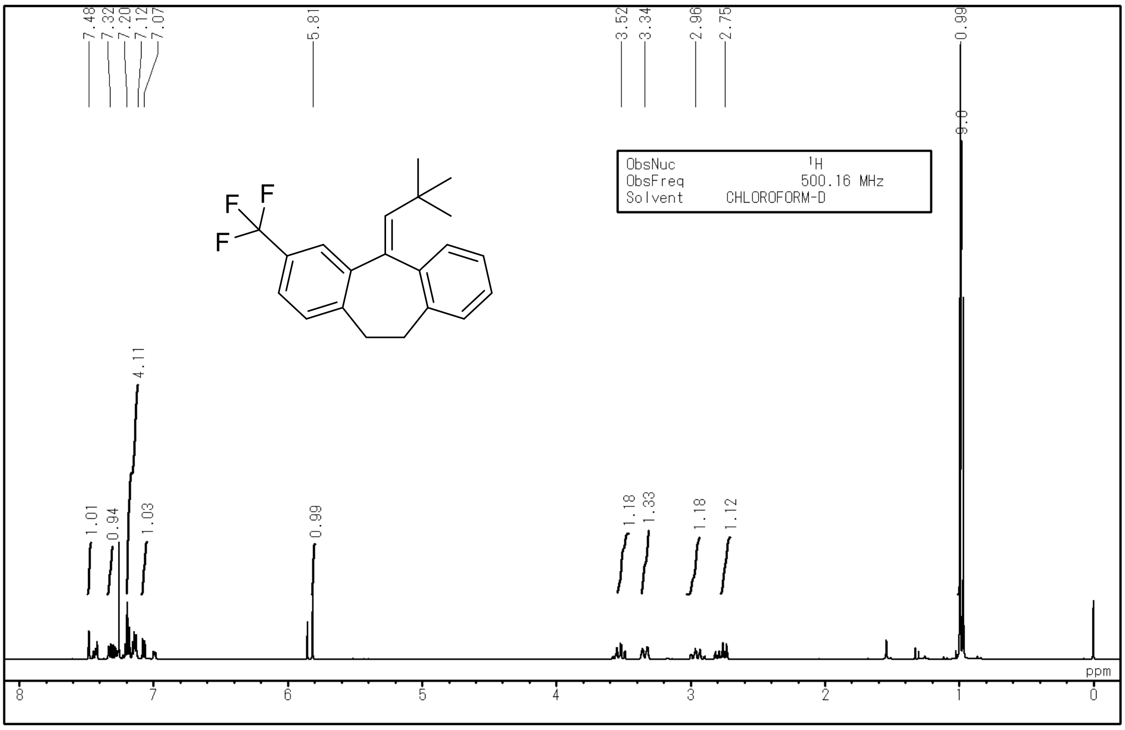


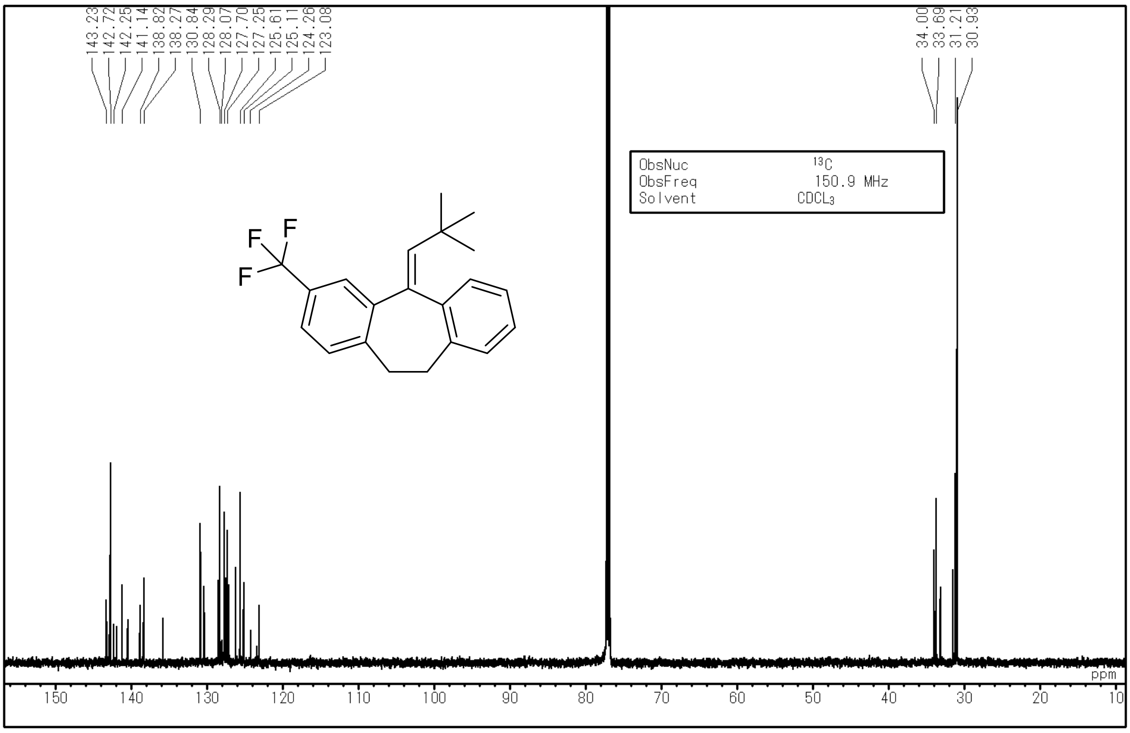
(*E*)-5-(2,2-Dimethylpropylidene)-10,11-dihydro-3-methyl-5*H*-dibenzo[*a,d*]cycloheptene (*E*-1g).



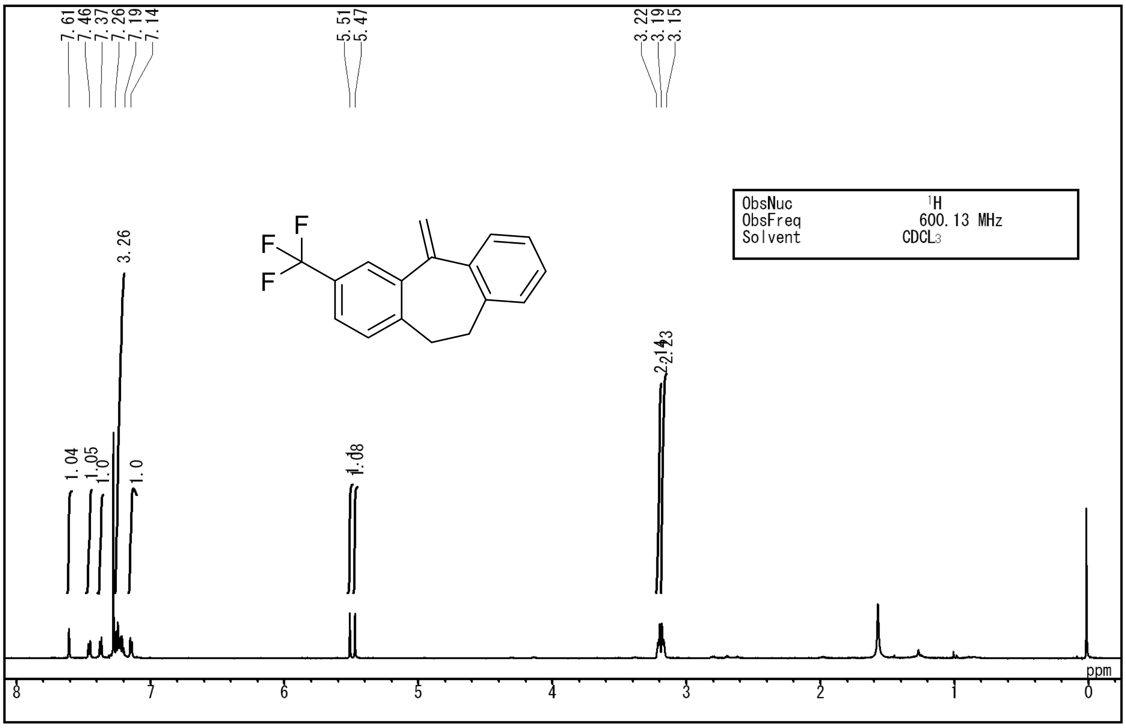


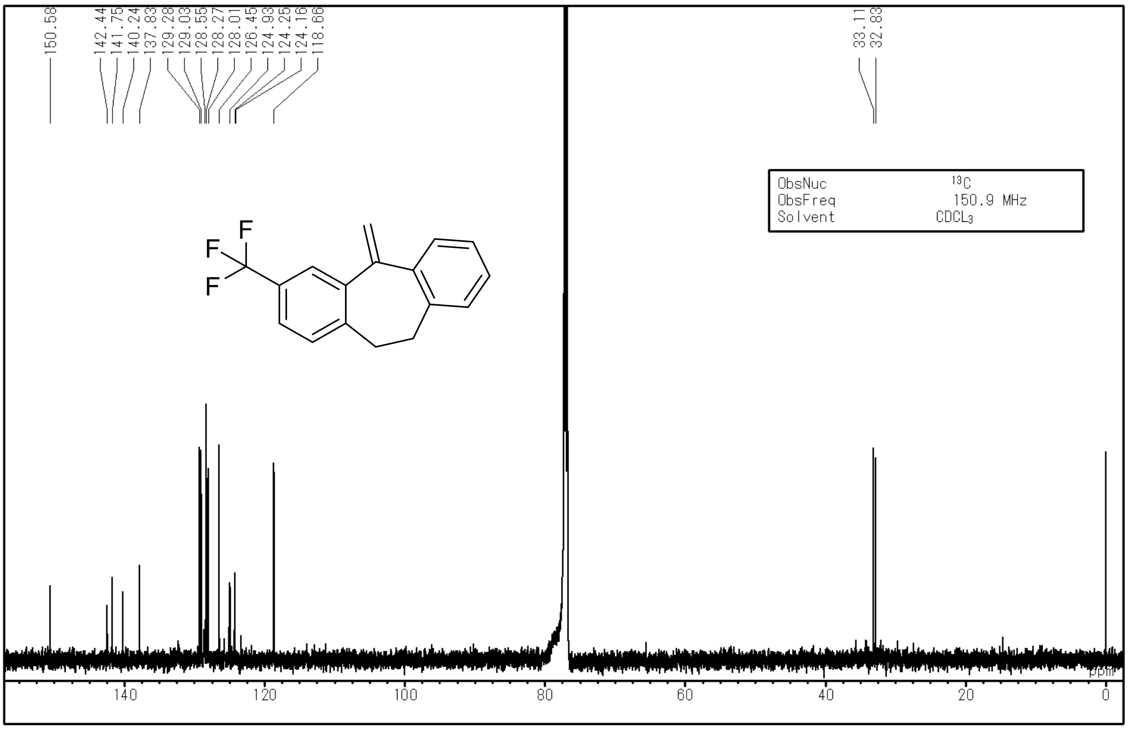
(*E*)-5-(2,2-Dimethylpropylidene)-10,11-dihydro-3-(trifluoromethyl)-5*H*-dibenzo[*a*, *d*]cycloheptene (*E*-1h).



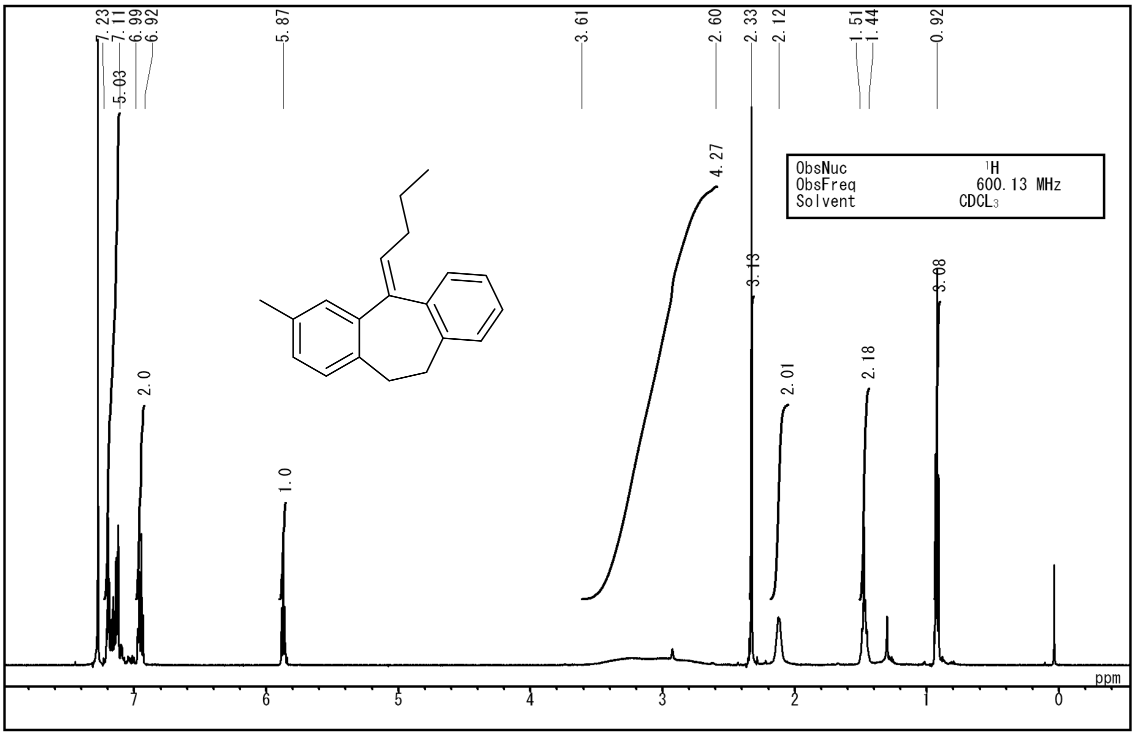


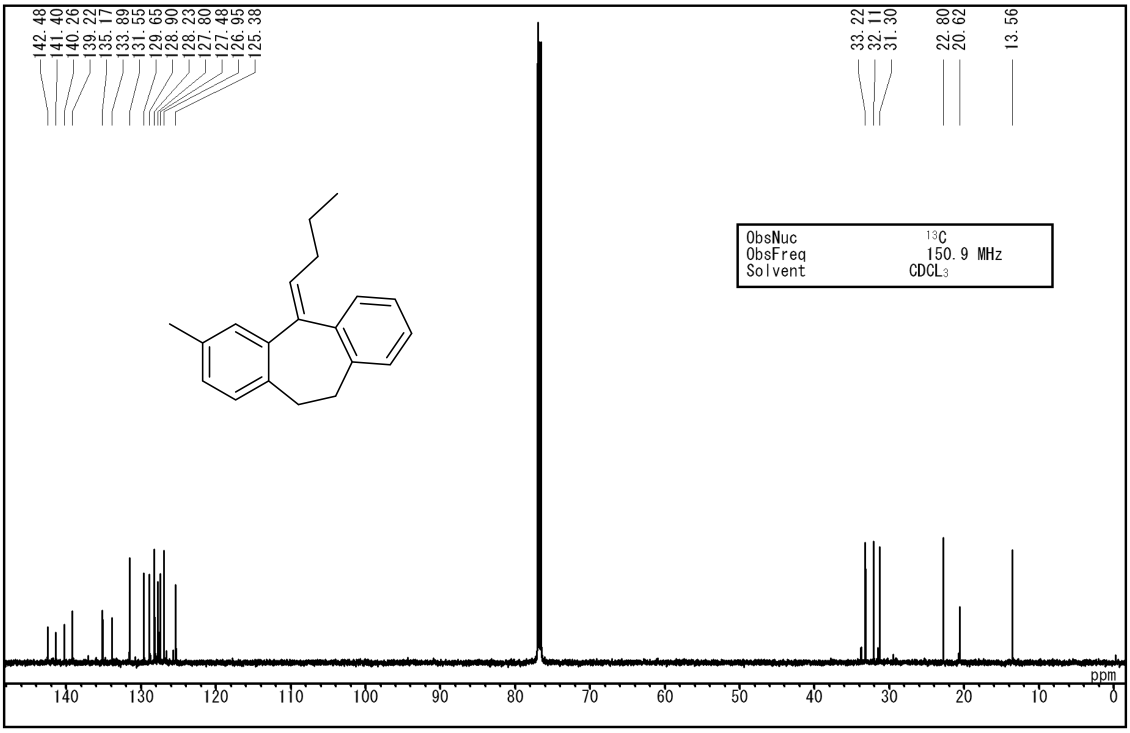
10,11-Dihydro-5-methylene-3-(trifluoromethyl)-5*H*-dibenzo[*a,d*]cycloheptene (1h').



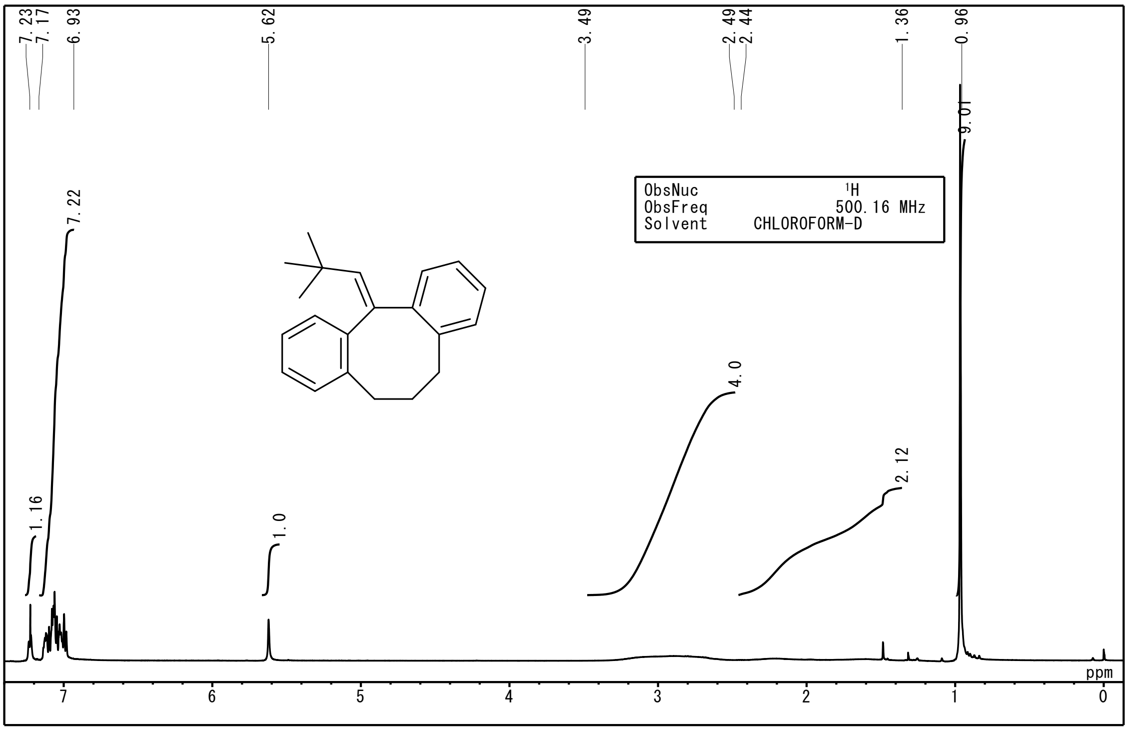


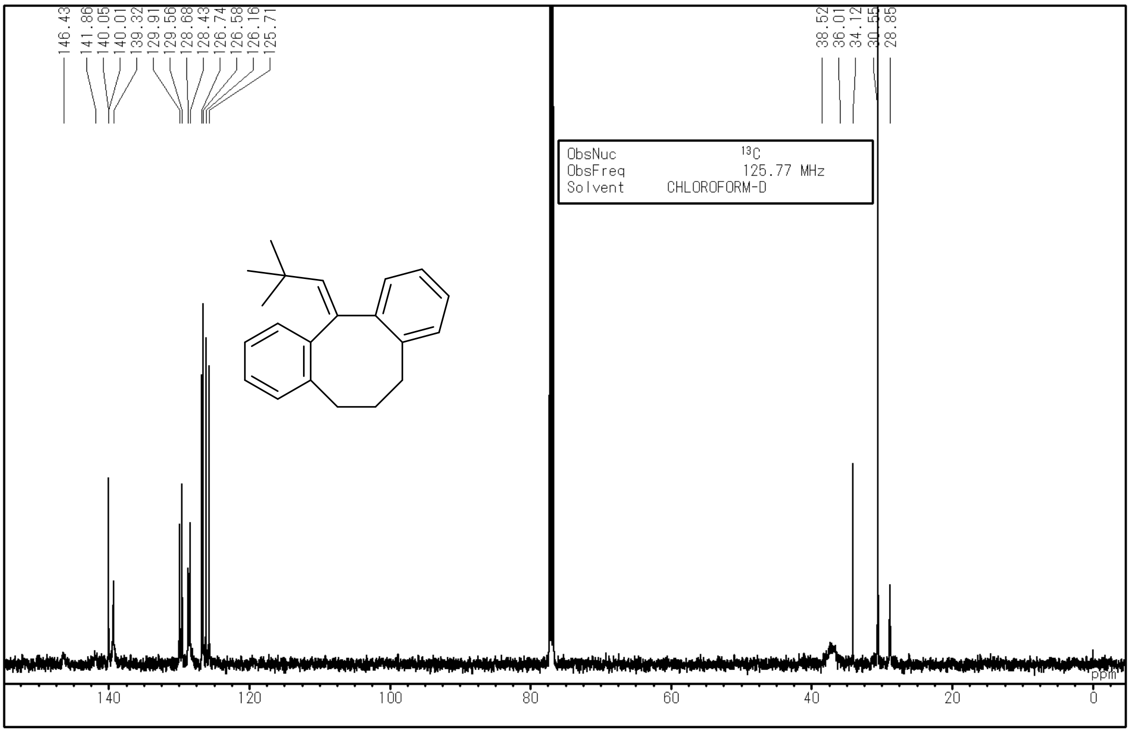
(*E*)-5-Butylidene-10,11-dihydro-3-methyl-5*H*-dibenzo[*a,d*]cycloheptene (*E*-1i).



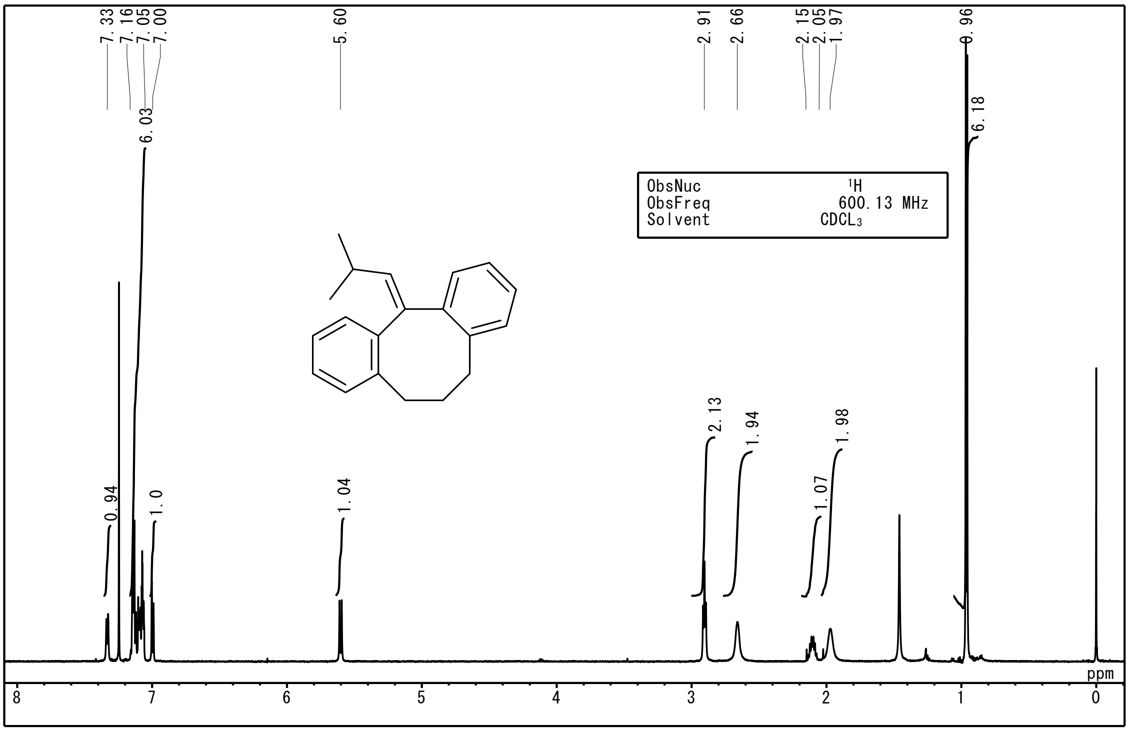


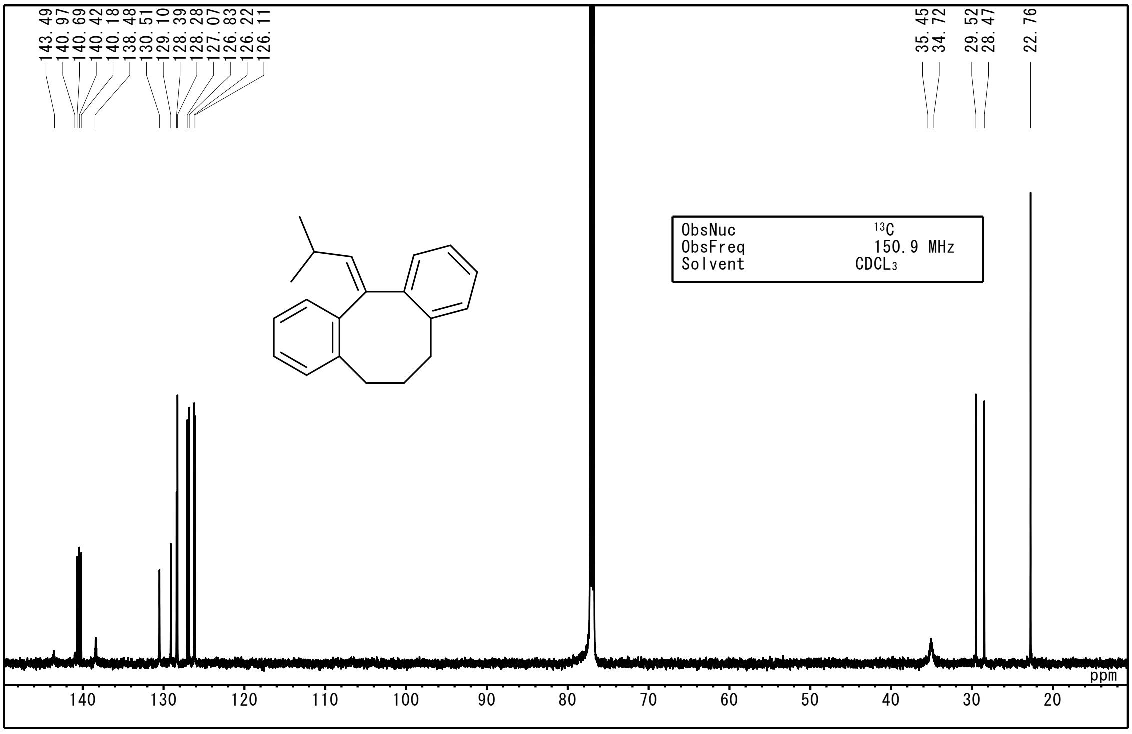
12-(2,2-Dimethylpropylidene)-5,6,7,12-tetrahydro-dibenzo[*a*,*d*]cyclooctene (2a).



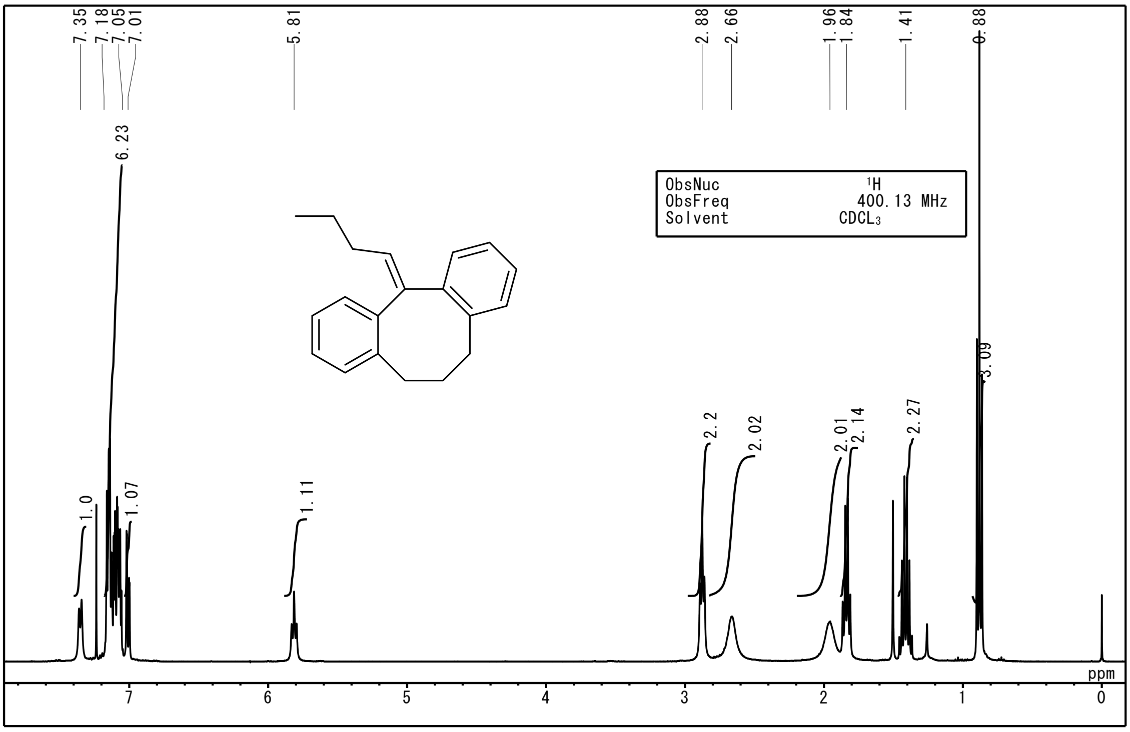


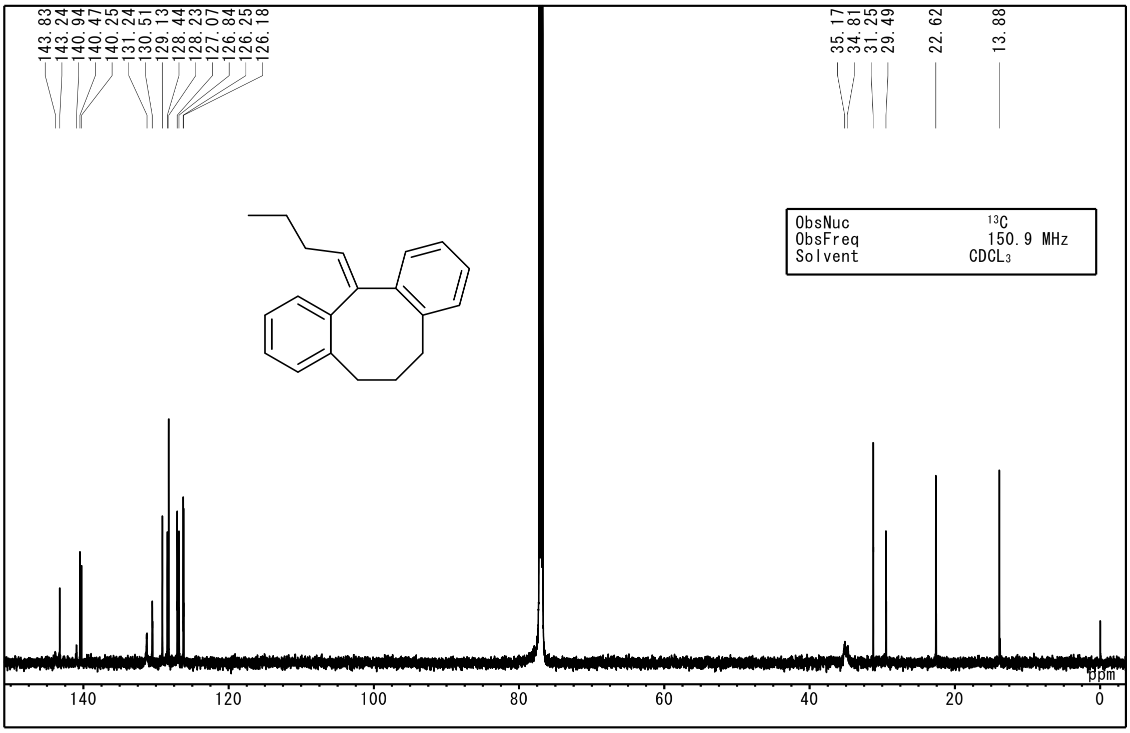
5,6,7,12-Tetrahydro-12-(2-methylpropylidene)-dibenzo[*a,d*]cyclooctene (2b).



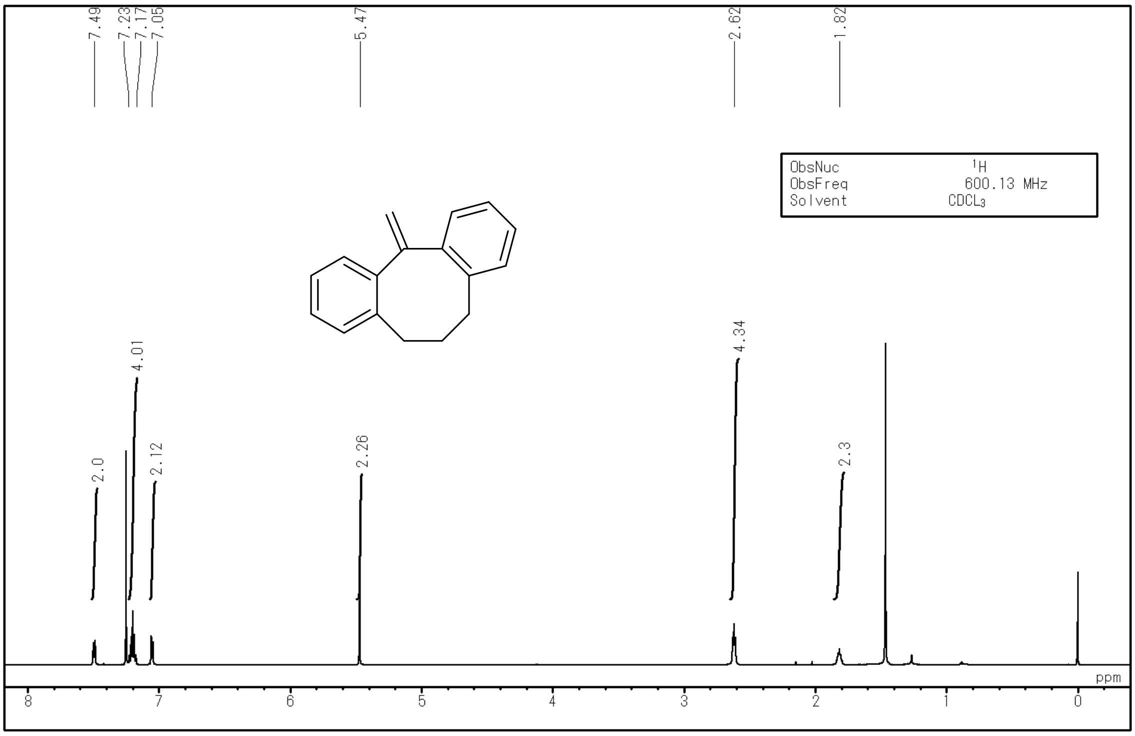


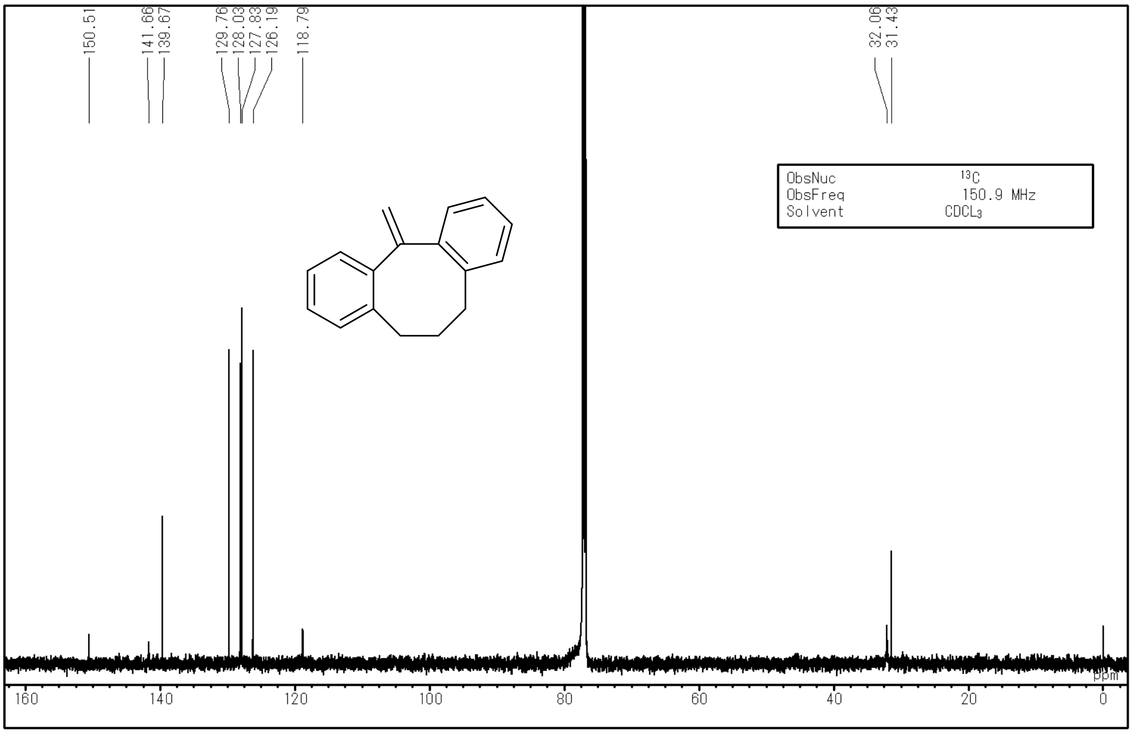
12-Butylidene-5,6,7,12-tetrahydrodibenzo[*a,d*]cyclooctene (2c).



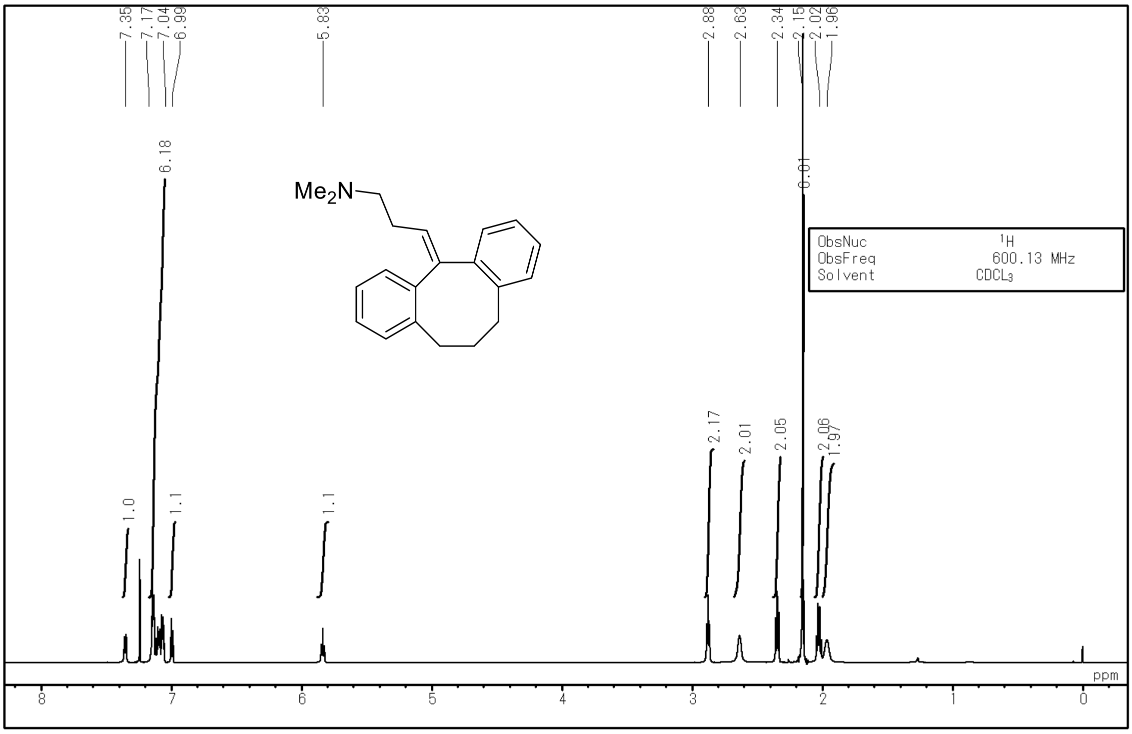


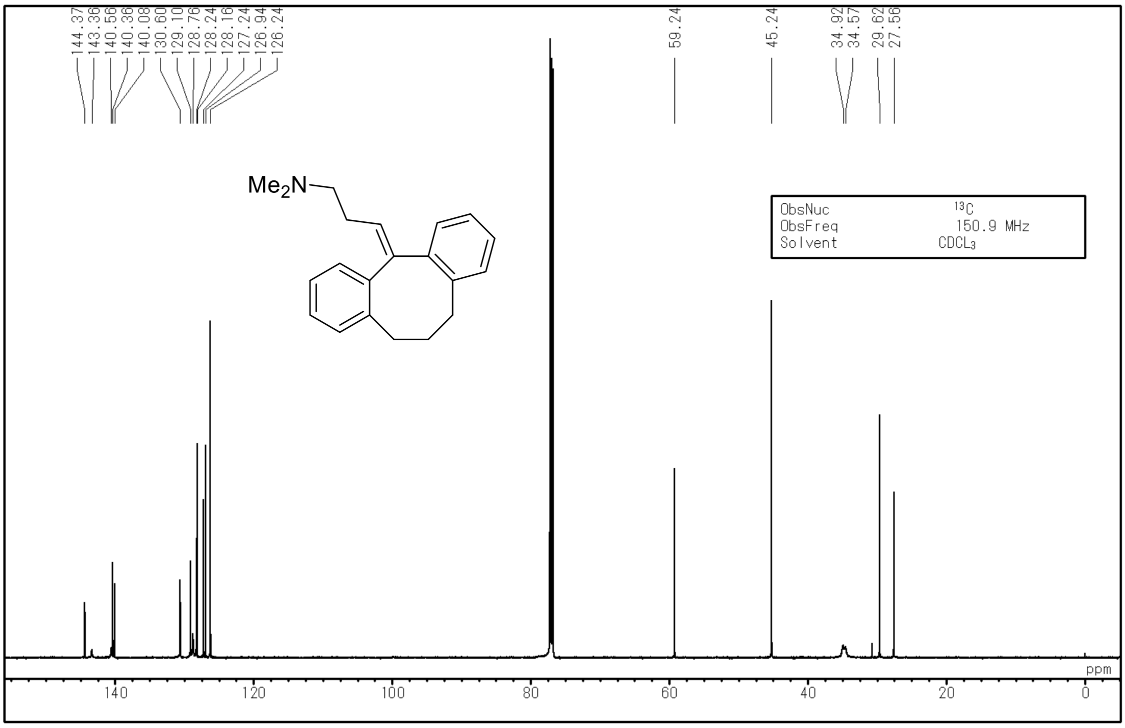
12-Methylene-5,6,7,12-tetrahydrodibenzo[*a,d*]cyclooctene (2e’).



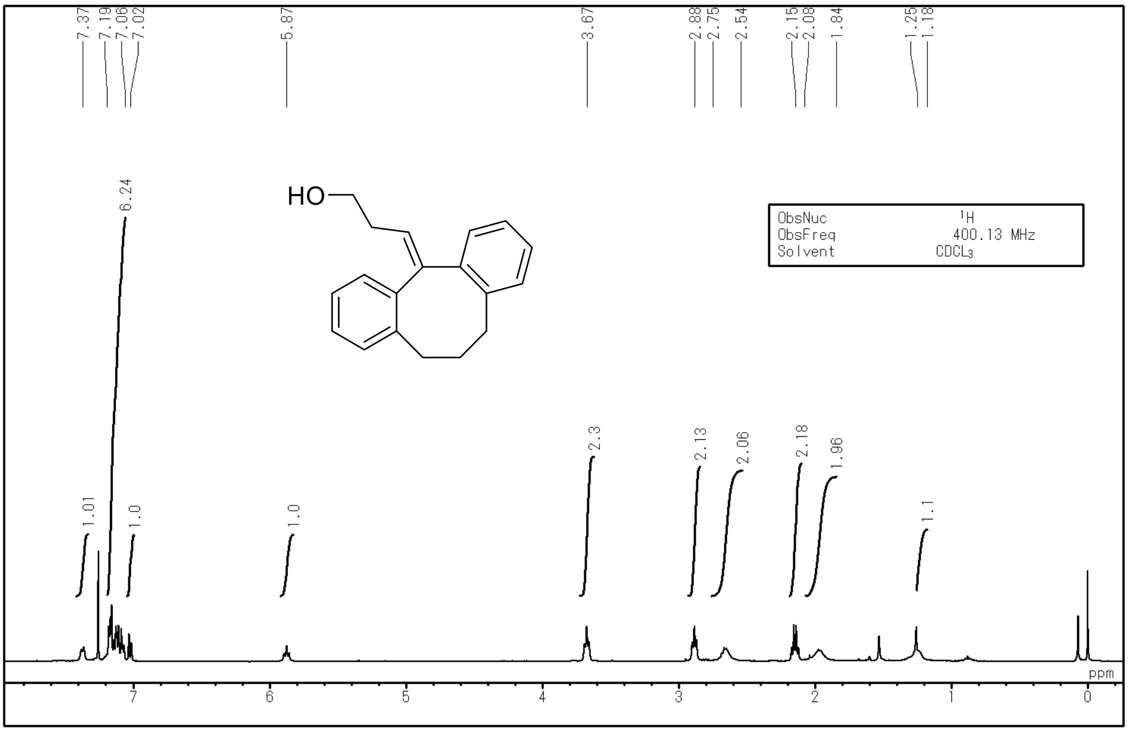


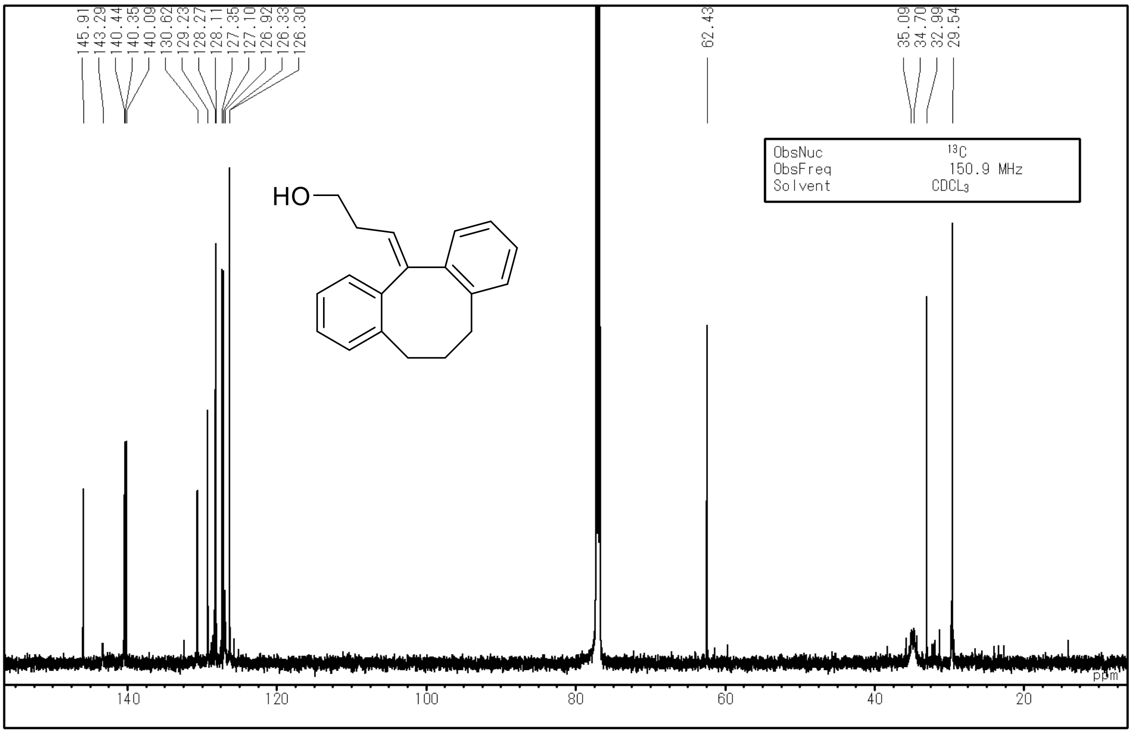
3-(6,7-Dihydrodibenzo[*a,d*][8]annulen-12(5*H*)-ylidene)-*N,N*-dimethylpropan-1-amine (2f).



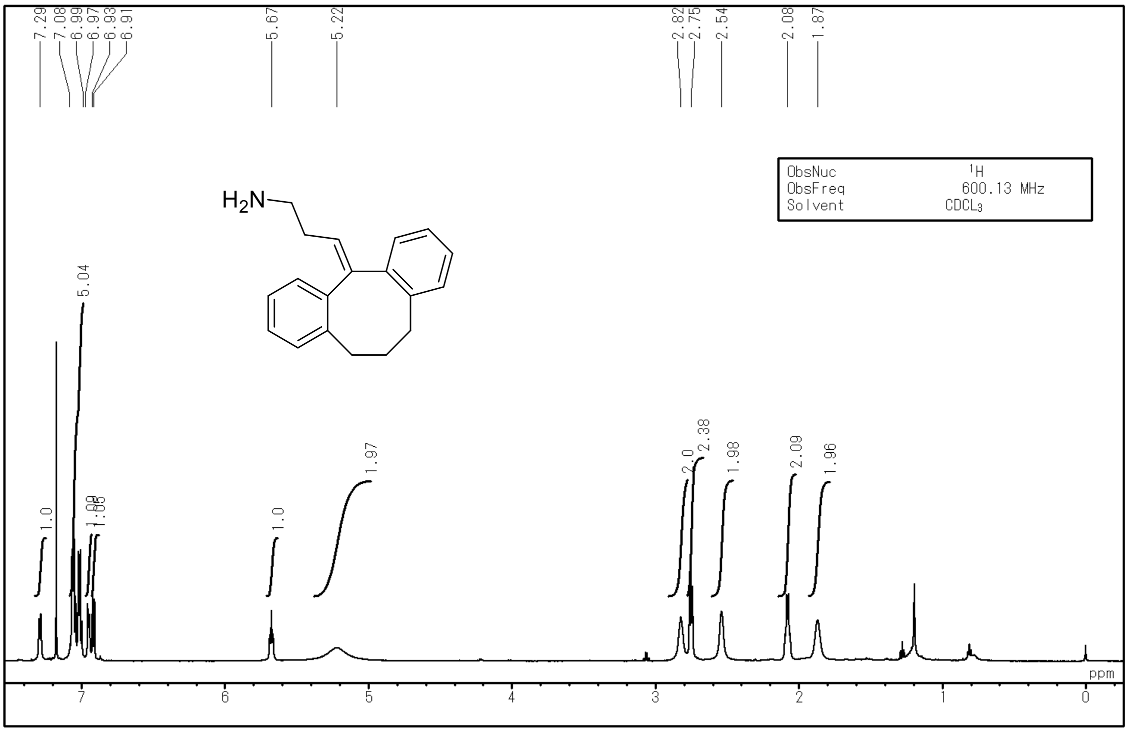


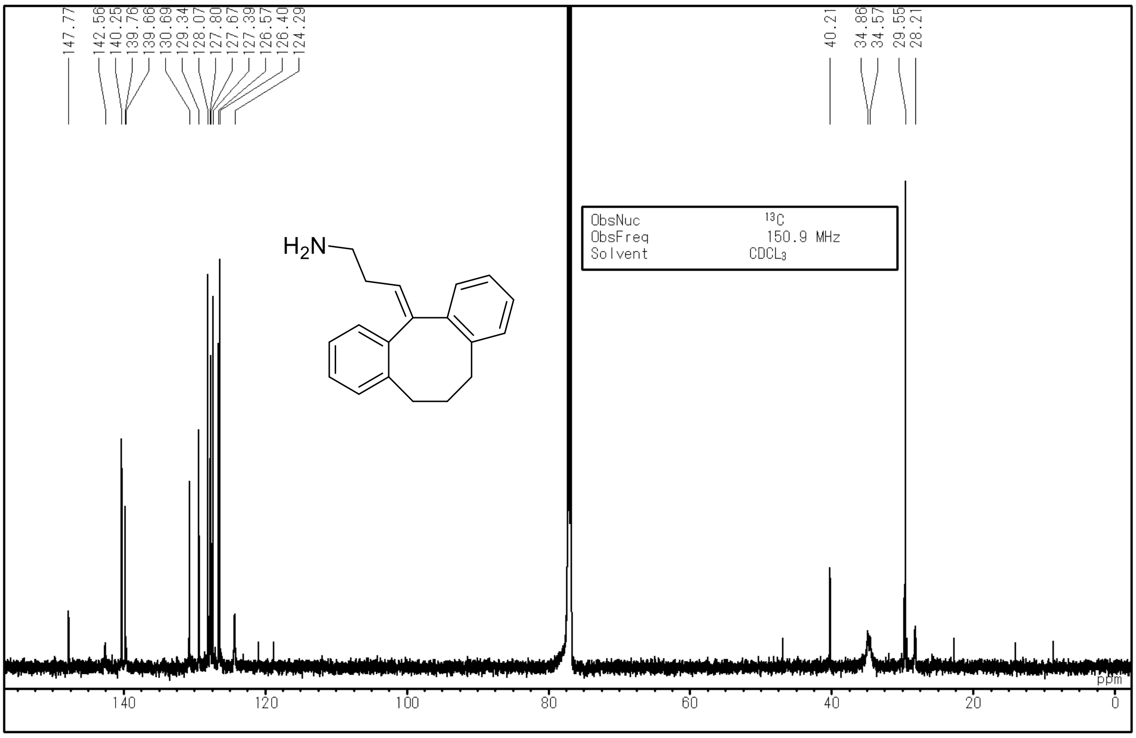
3-(6,7-Dihydrodibenzo[*a,d*][8]annulen-12(5*H*)-ylidene)propan-1-ol (2g).



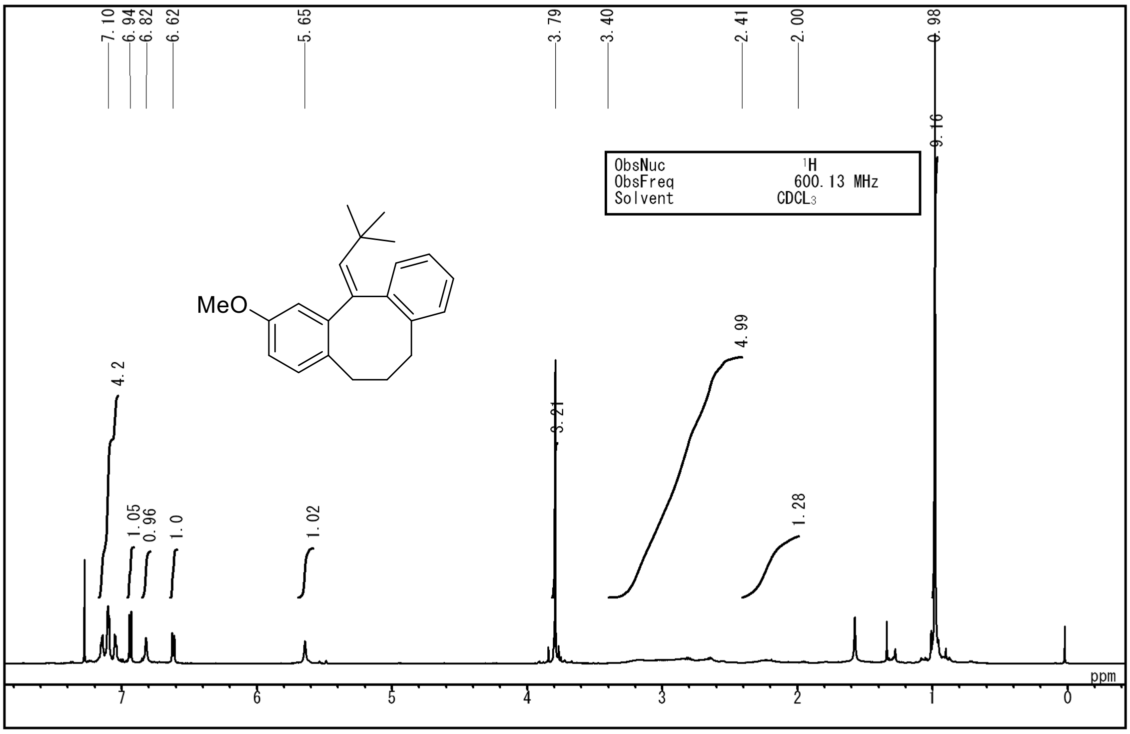


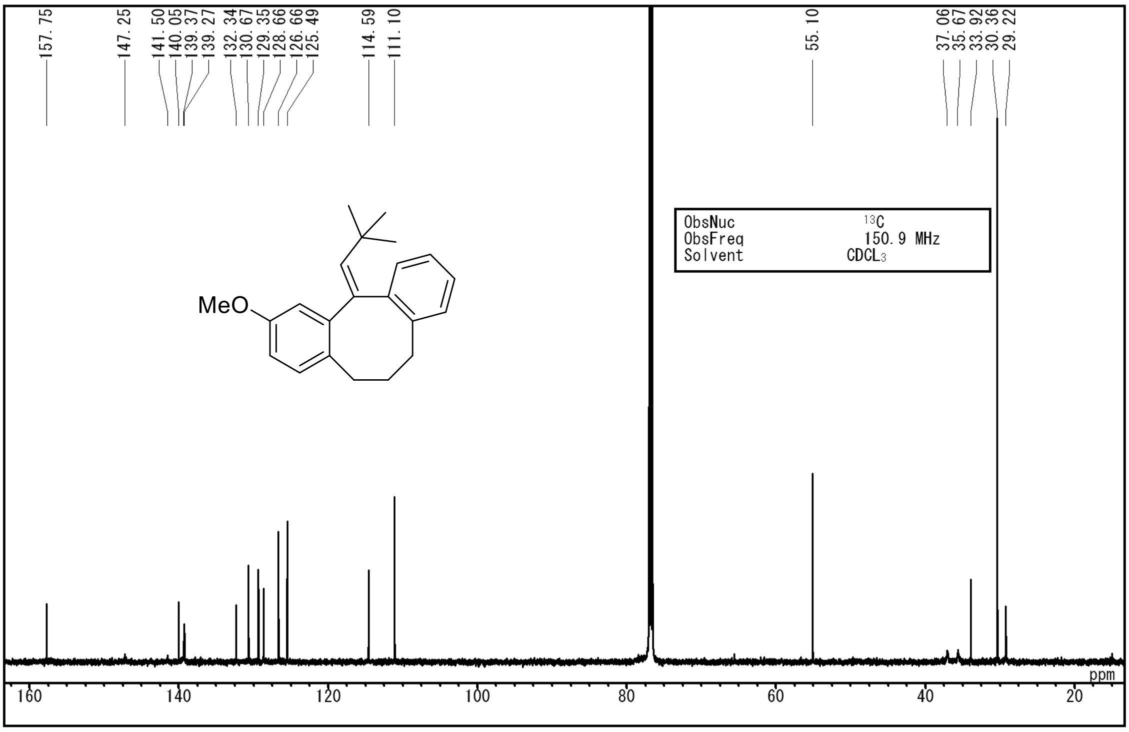
3-(6,7-Dihydrodibenzo[*a,d*][8]annulen-12(5*H*)-ylidene)propan-1-amine (2h).



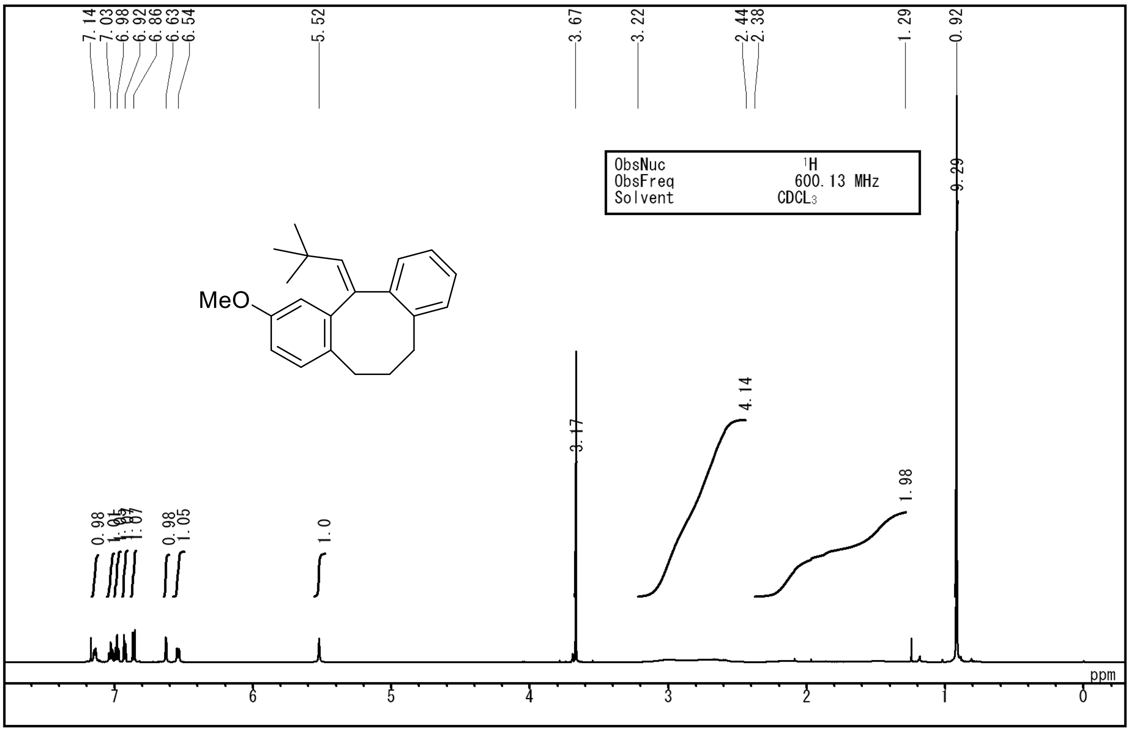


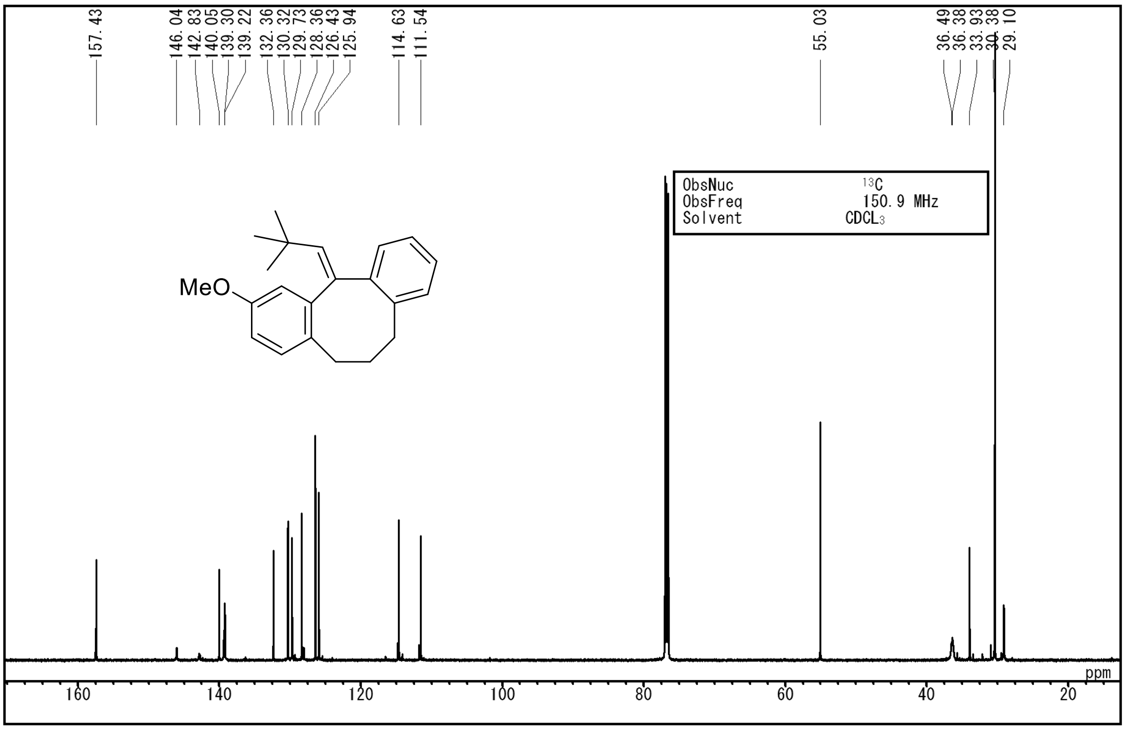
(*E*)-12-(2,2-Dimethylpropylidene)-2-methoxy-5,6,7,12-tetrahydro-dibenzo[*a,d*]-cyclooctene (*E*-2i).



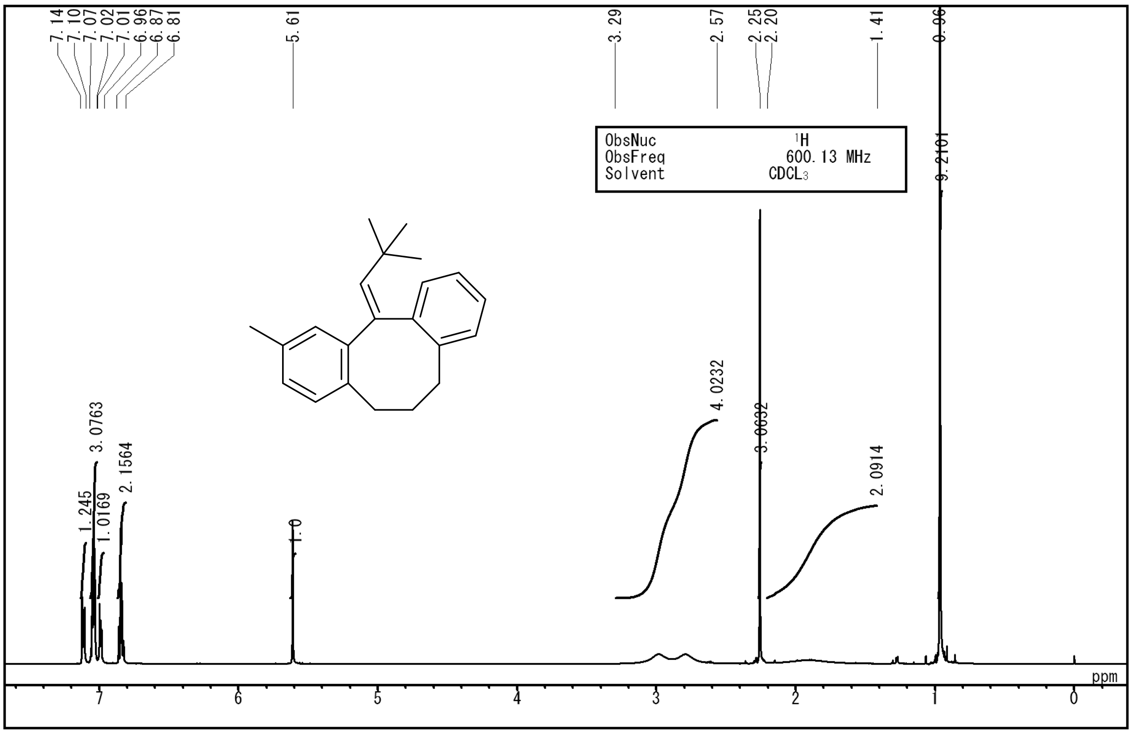


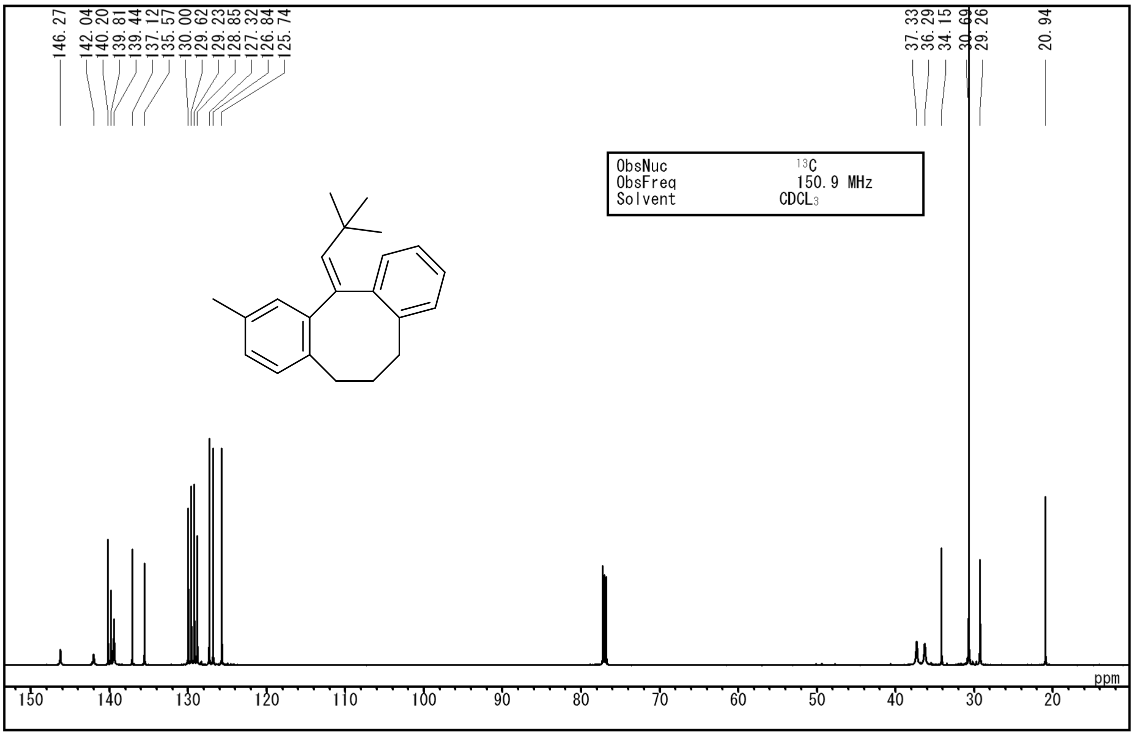
(*Z*)-12-(2,2-Dimethylpropylidene)-2-methoxy-5,6,7,12-tetrahydro-dibenzo[*a,d*]-cyclooctene (*Z*-2i).



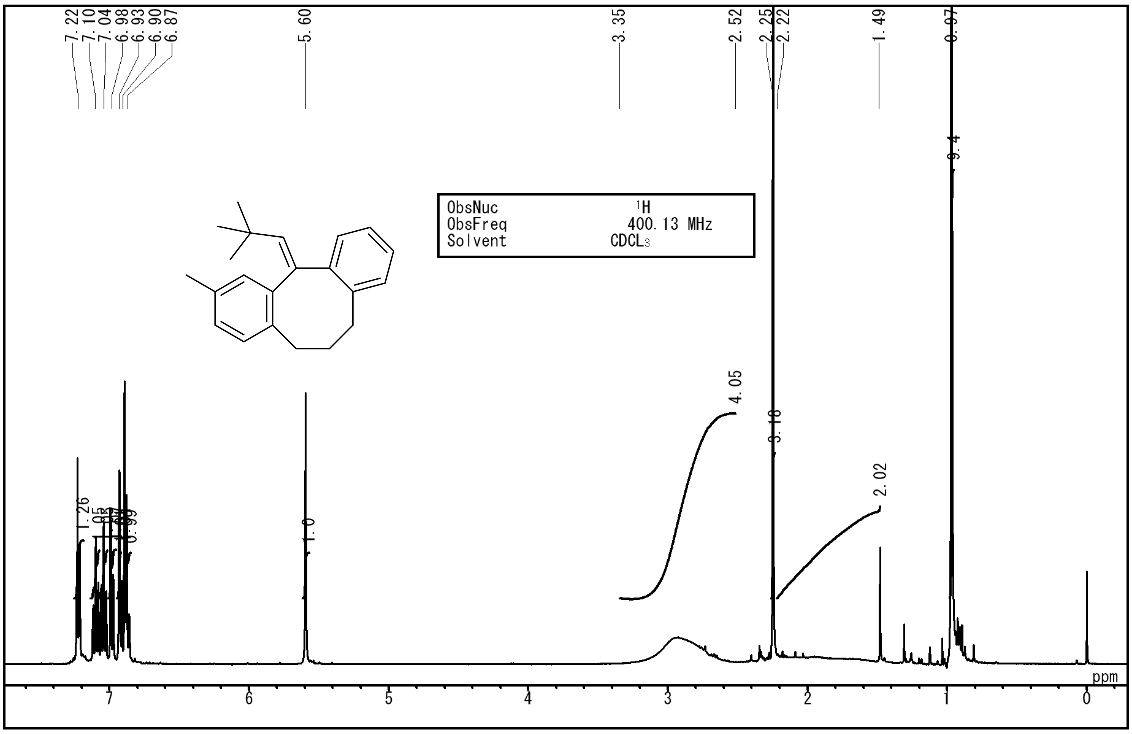


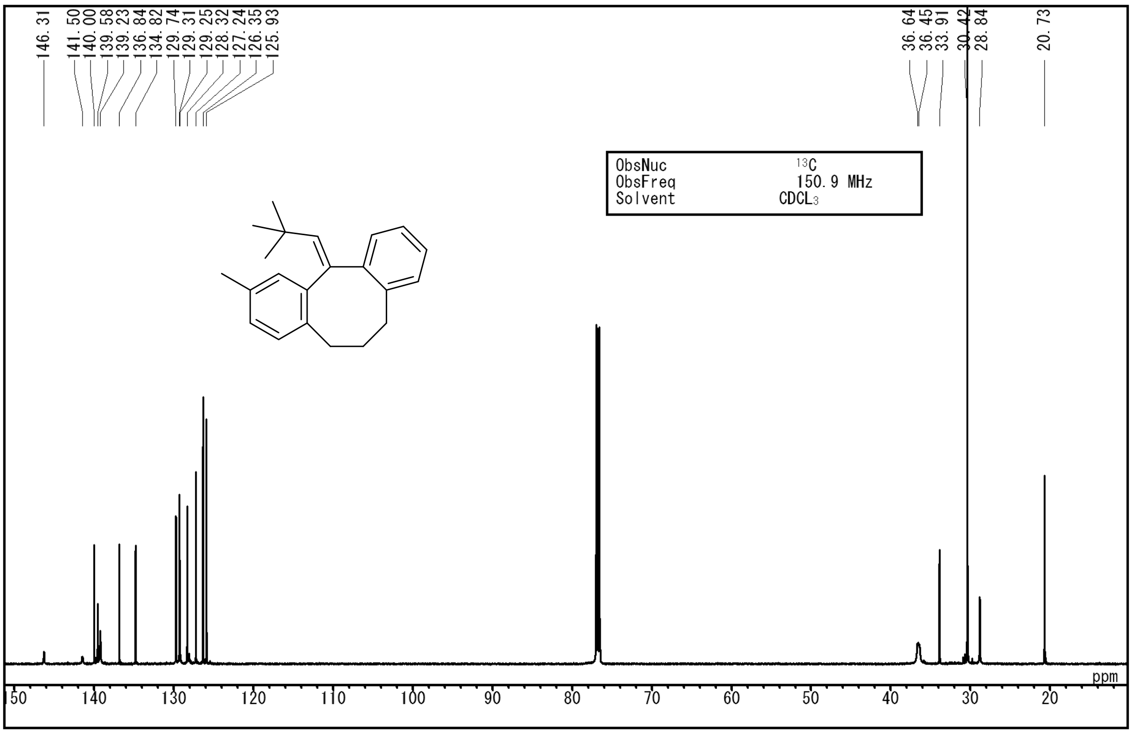
(*E*)-12-(2,2-Dimethylpropylidene)-2-methyl-5,6,7,12-tetrahydrodibenzo[*a,d*]-cyclooctene (*E*-2j).



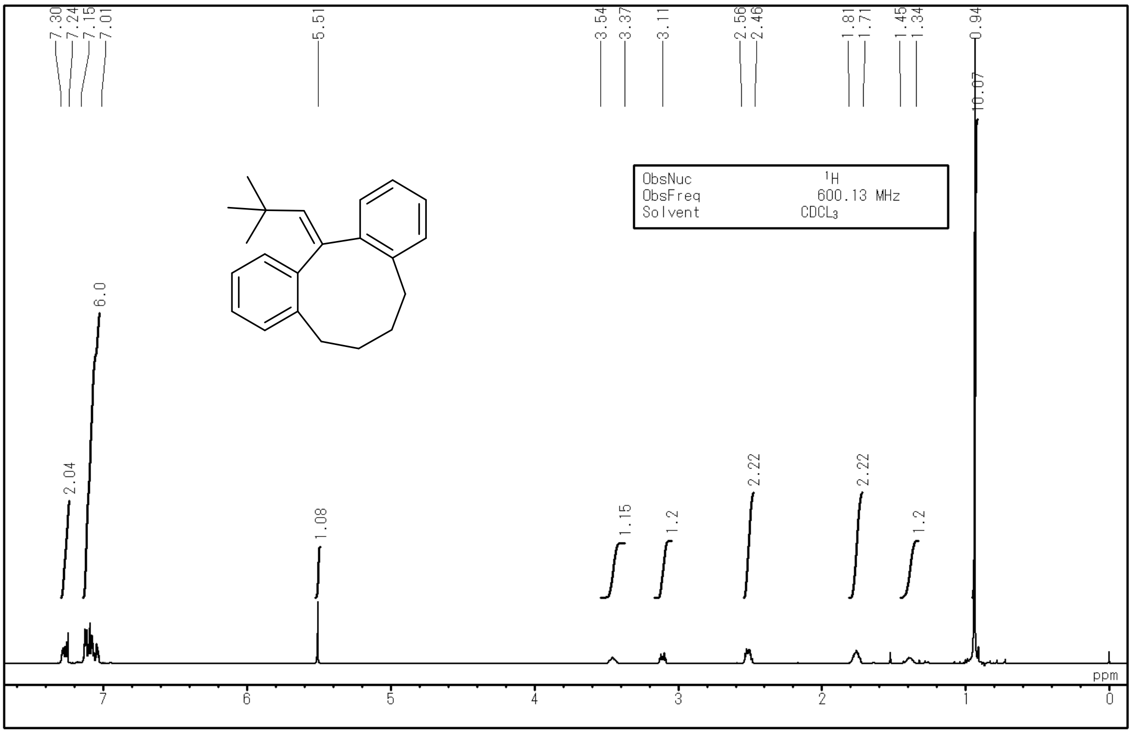


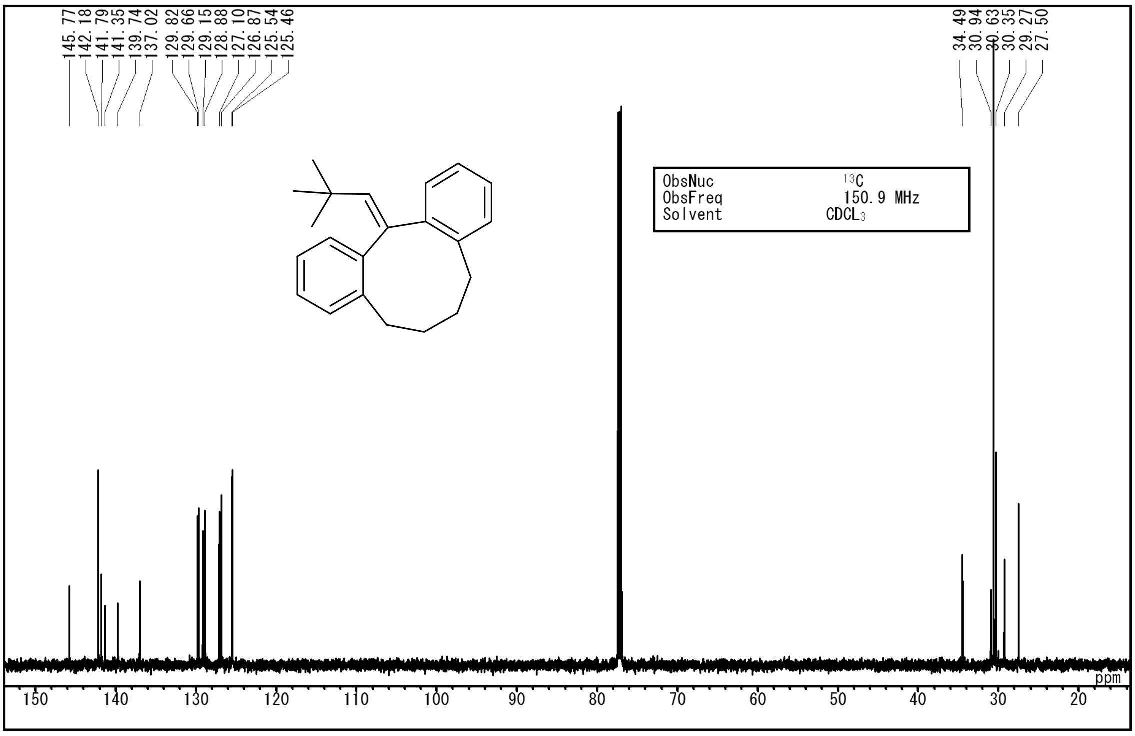
(*Z*)-12-(2,2-Dimethylpropylidene)-2-methyl-5,6,7,12-tetrahydro-dibenzo[*a,d*]-cyclooctene (*Z*-2j).



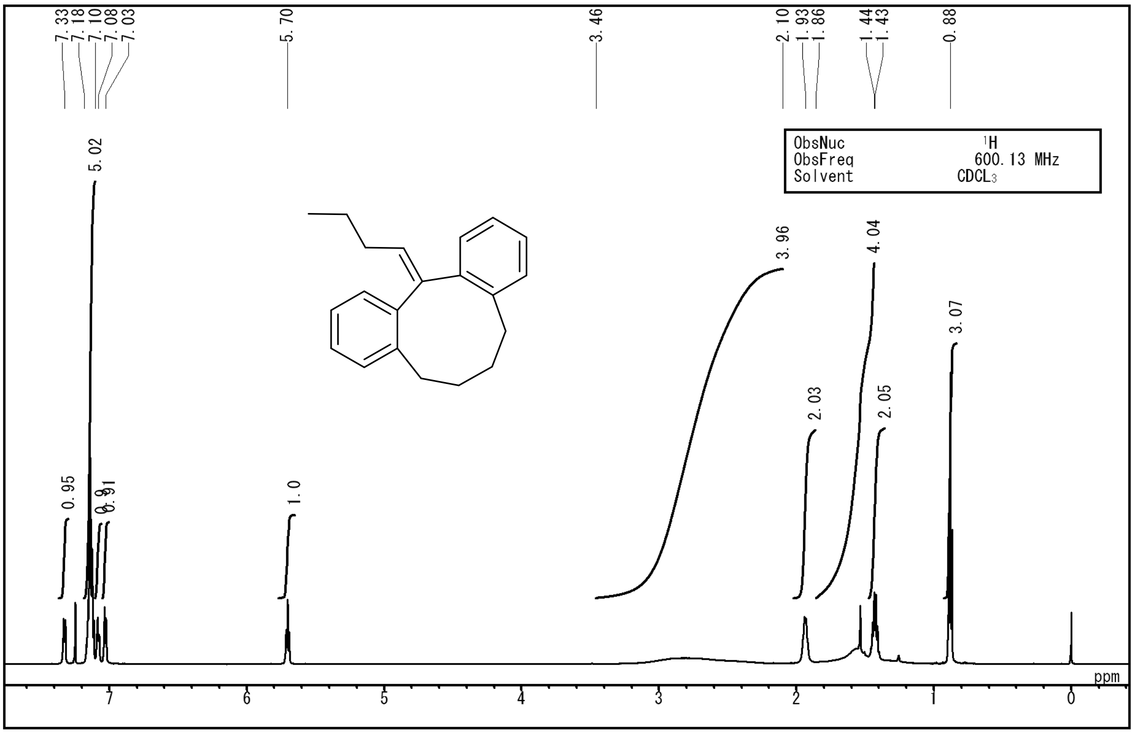


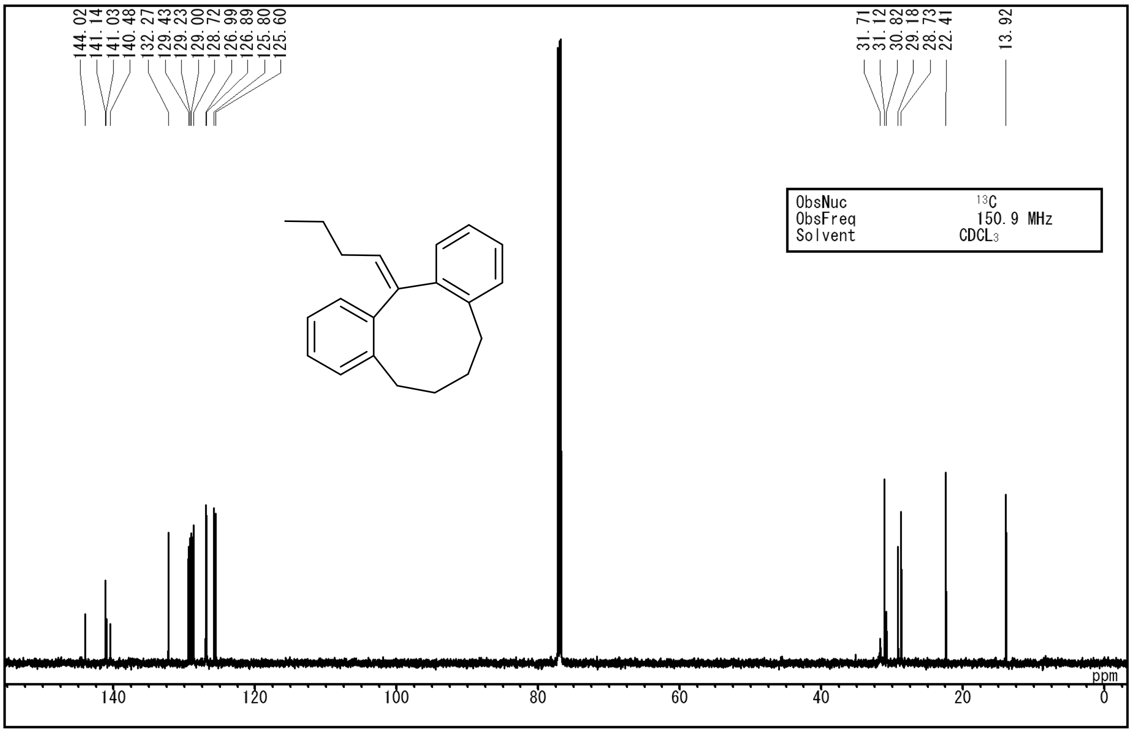
13-(2,2-Dimethylpropylidene)-6,7,8,13-tetrahydro-5*H*-dibenzo[*a,d*]cyclononene (3a).



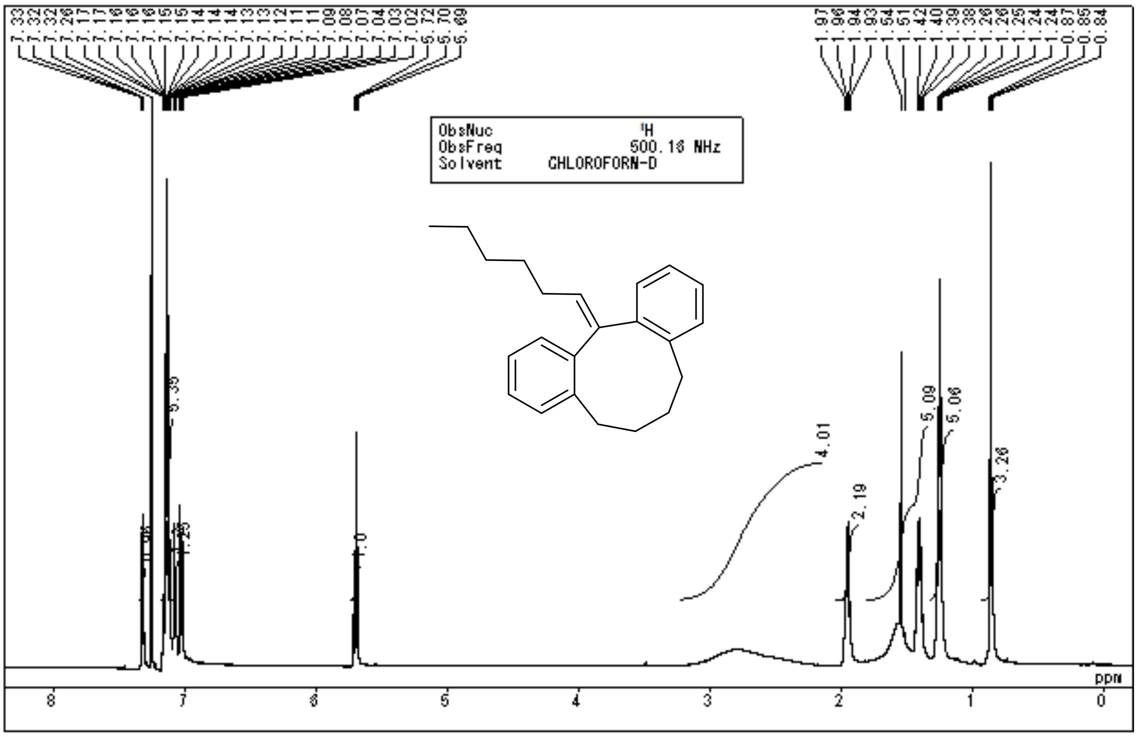


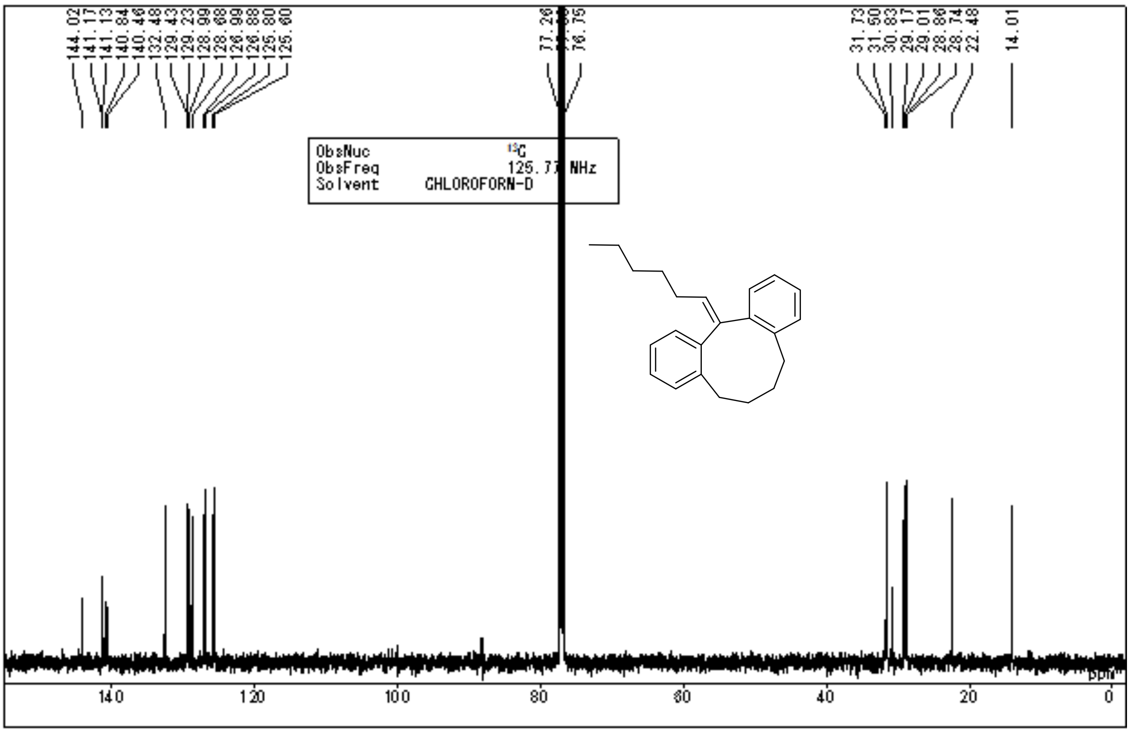
13-Butylidene-6,7,8,13-tetrahydro-5*H*-dibenzo[*a,d*]cyclononene (3b).



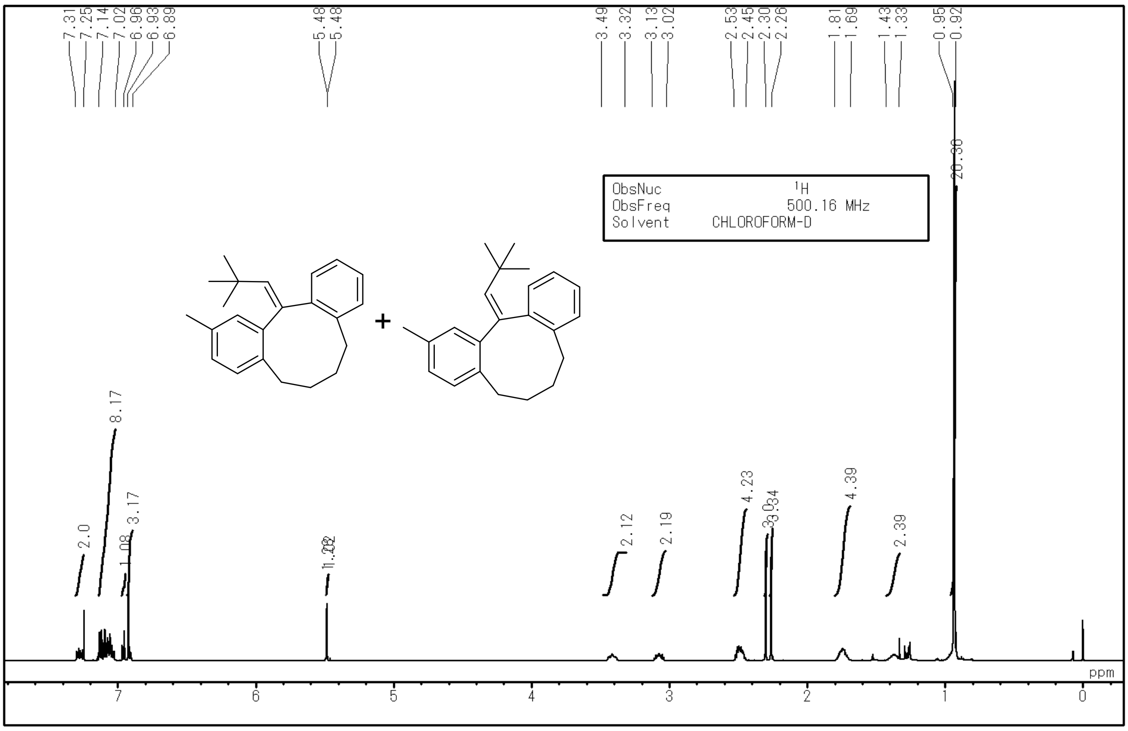


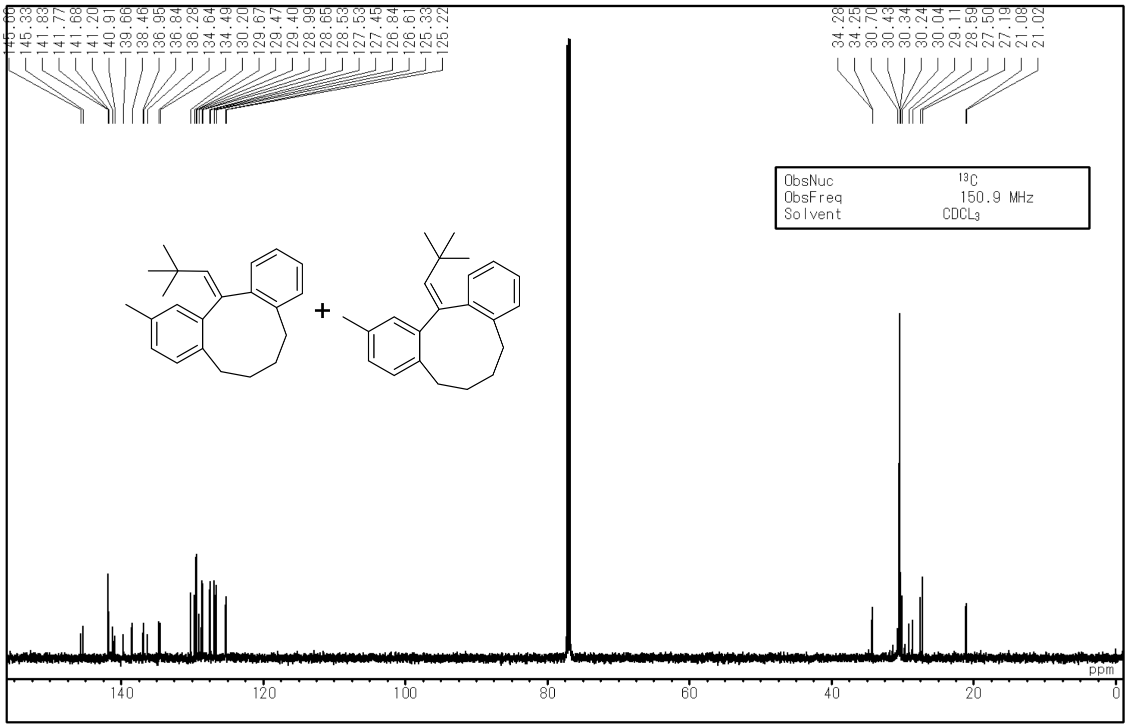
13-Hexylidene-6,7,8,13-tetrahydro-5*H*-dibenzo[*a,d*]cyclononene (3c).



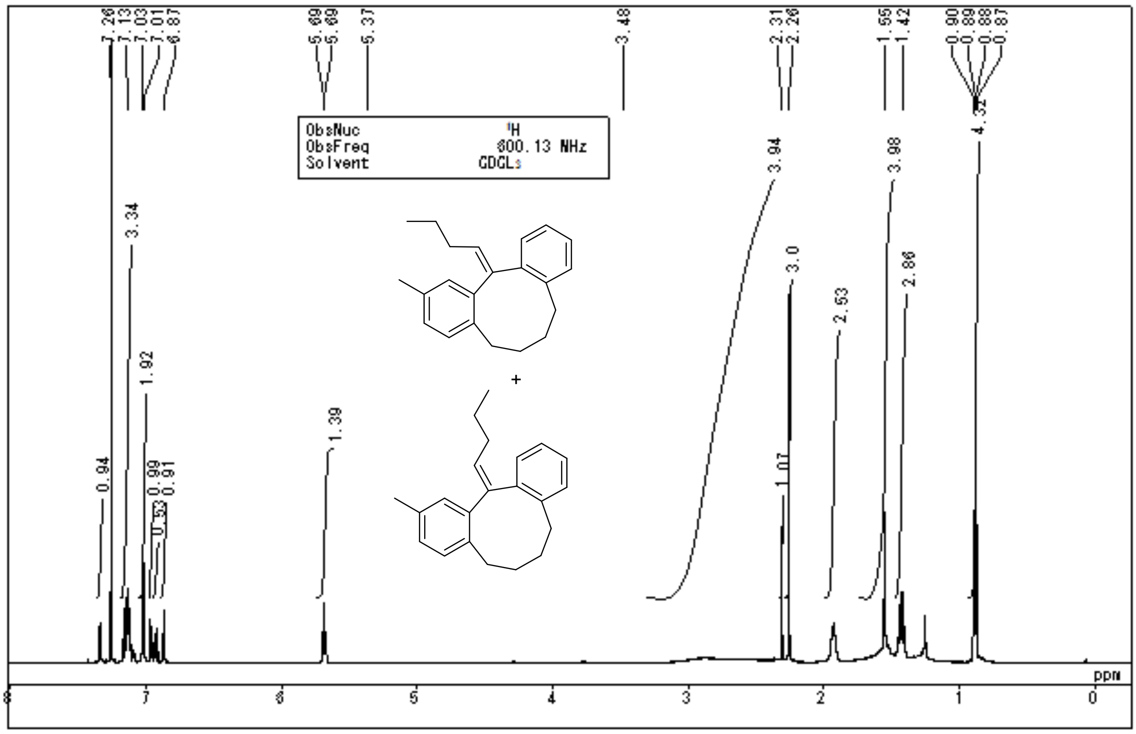


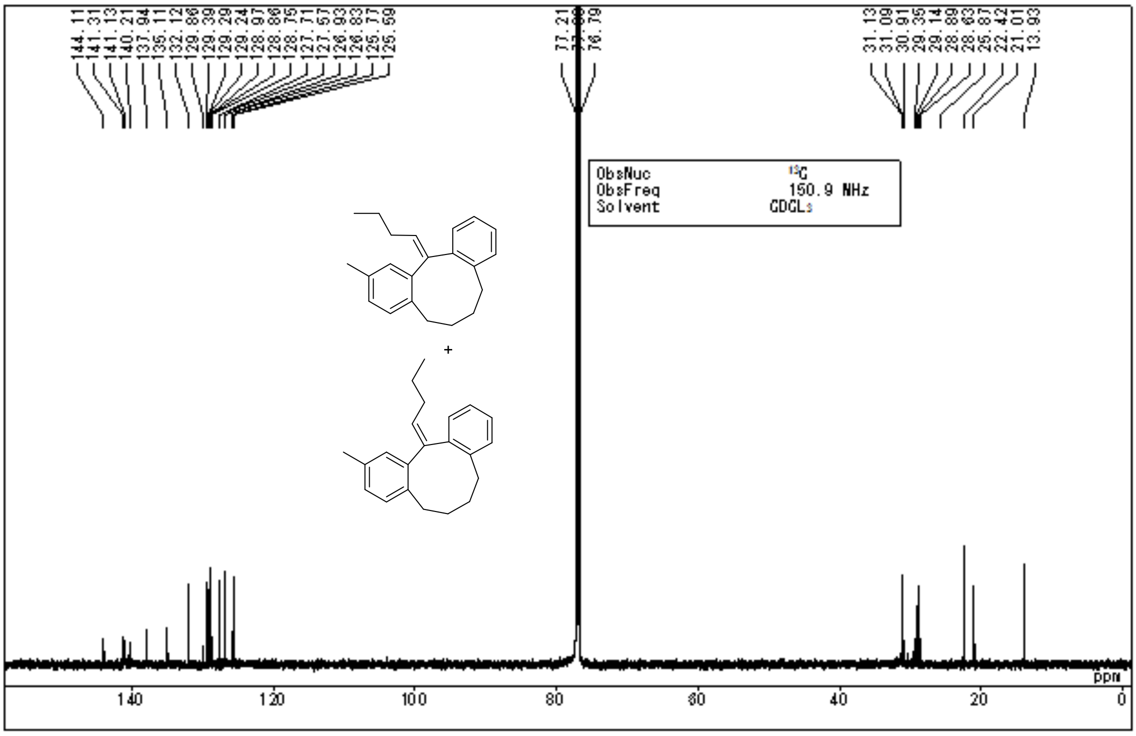
(*E*)- and (*Z*)-13-(2,2-Dimethylpropylidene)-2-methyl-6,7,8,13-tetrahydro-5*H*-dibenzo[*a,d*]cyclononene (3d).



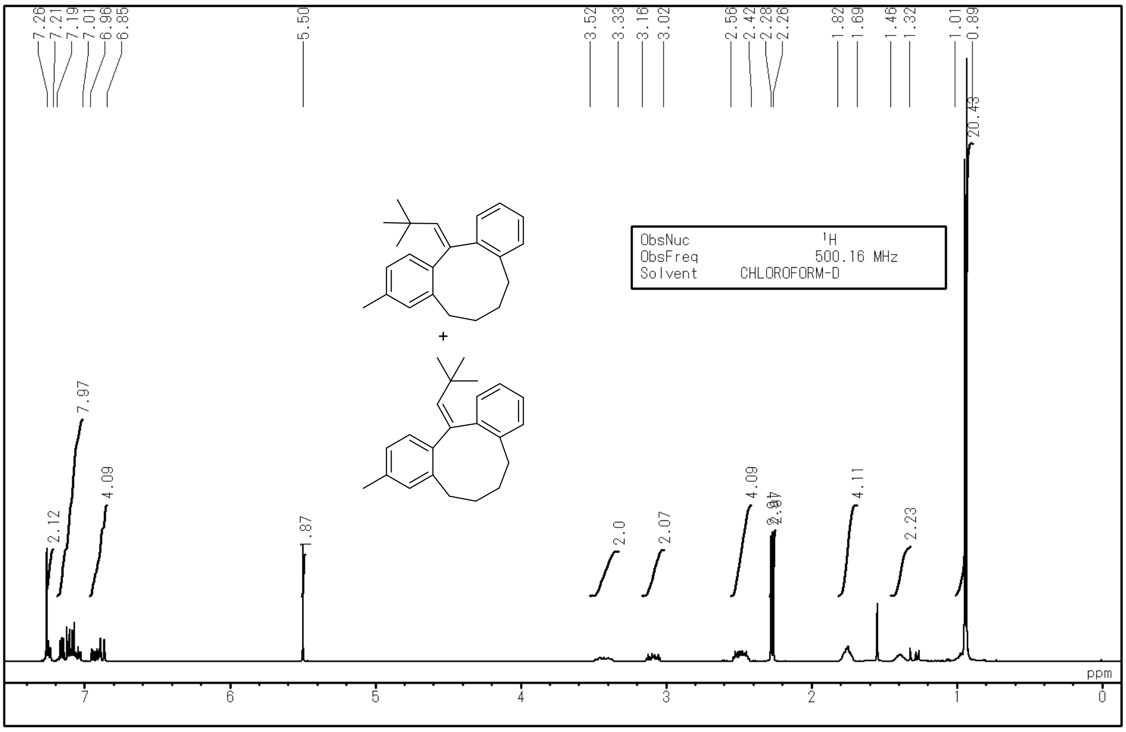


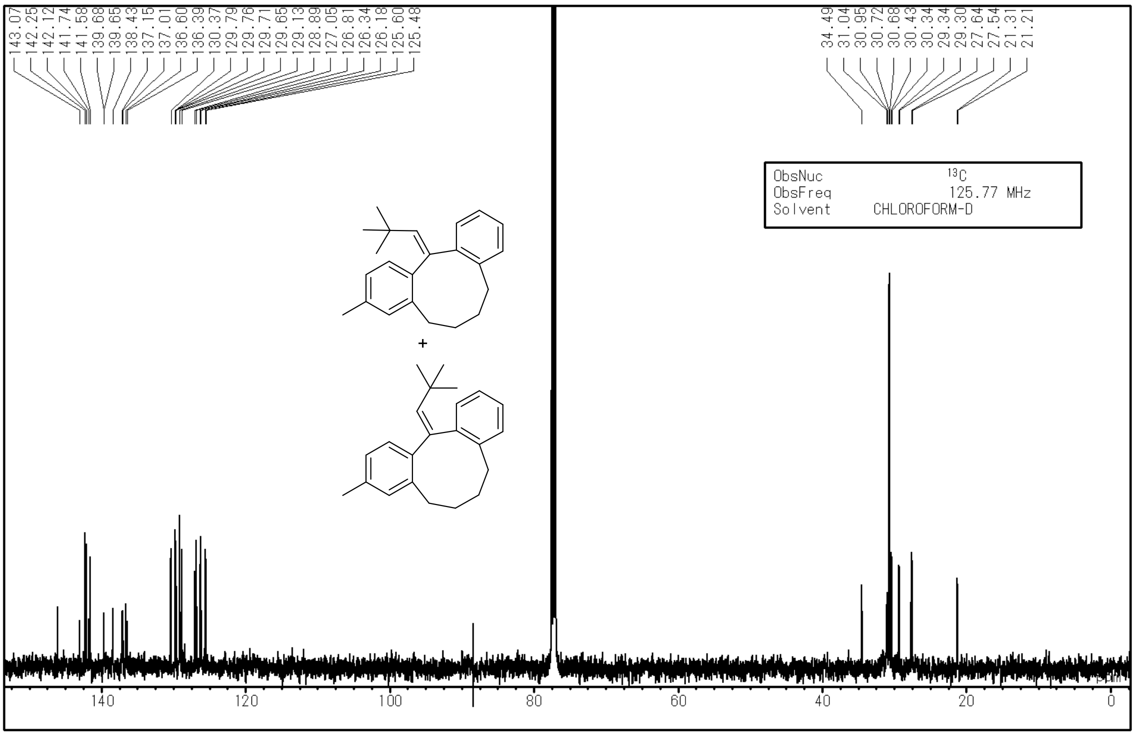
(*E*)- and (*Z*)-13-Butylidene-2-methyl-6,7,8,13-tetrahydro-5*H*-dibenzo[*a,d*]-cyclononene (3e).



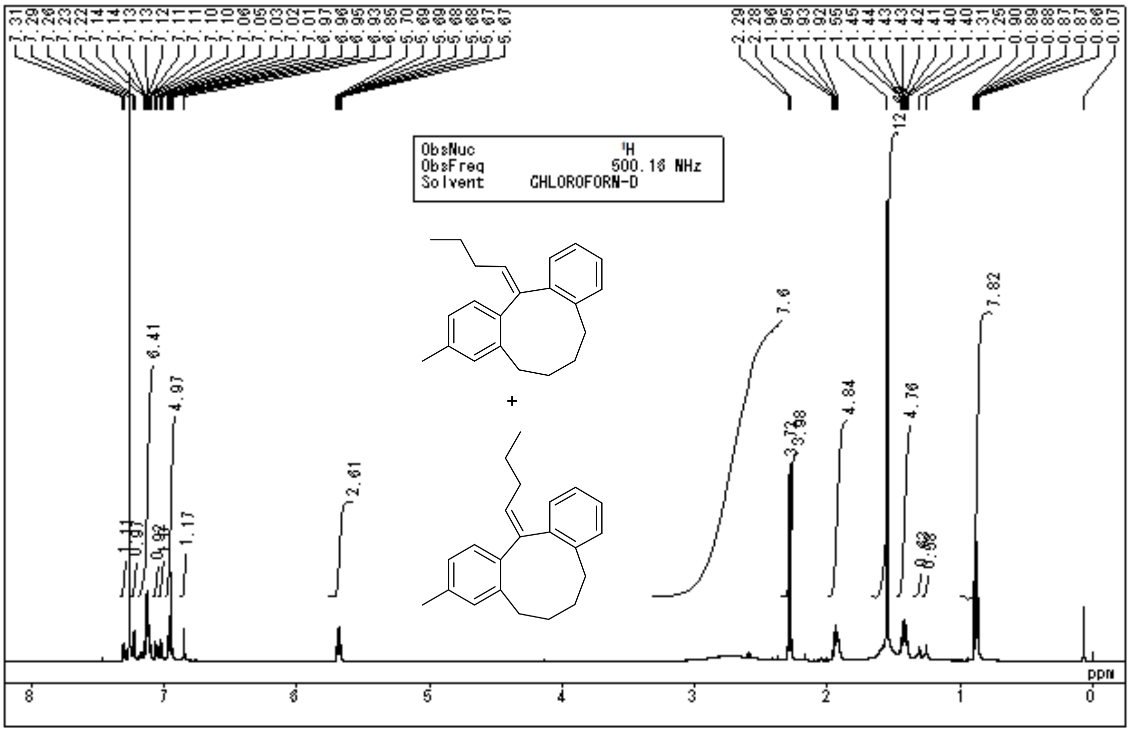


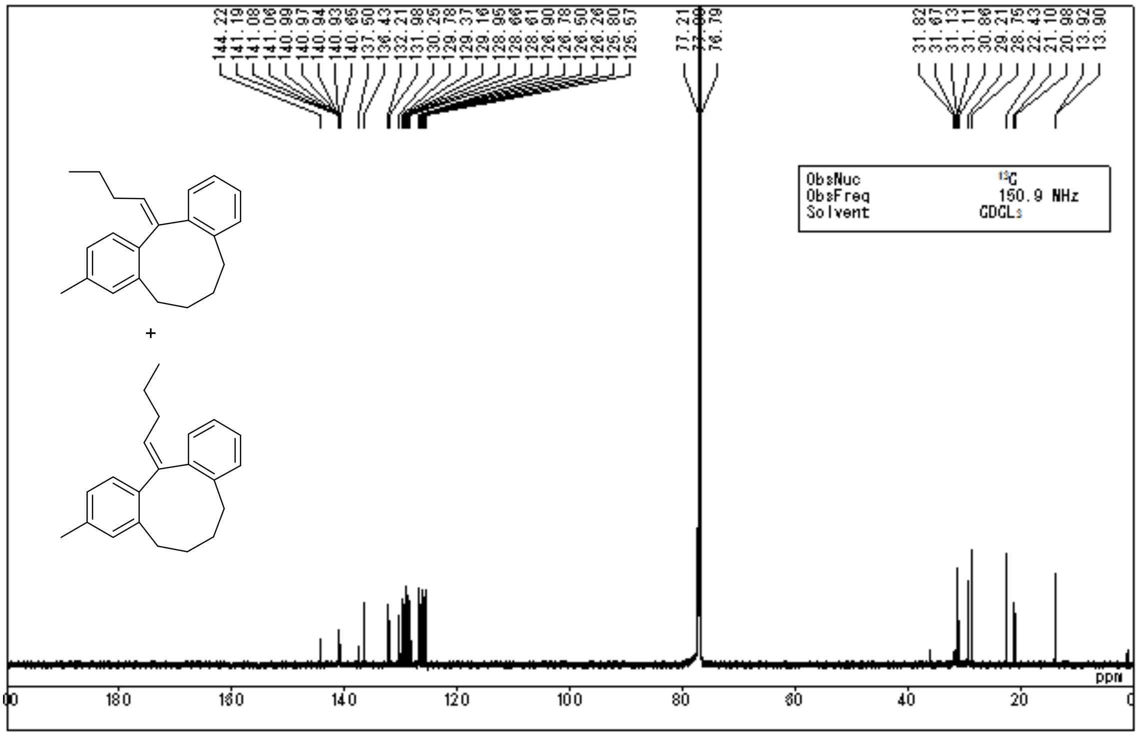
(*E*)- and (*Z*)-13-(2,2-Dimethylpropylidene)-3-methyl-6,7,8,13-tetrahydro-5*H*-dibenzo[*a*,*d*]cyclononene (3f).



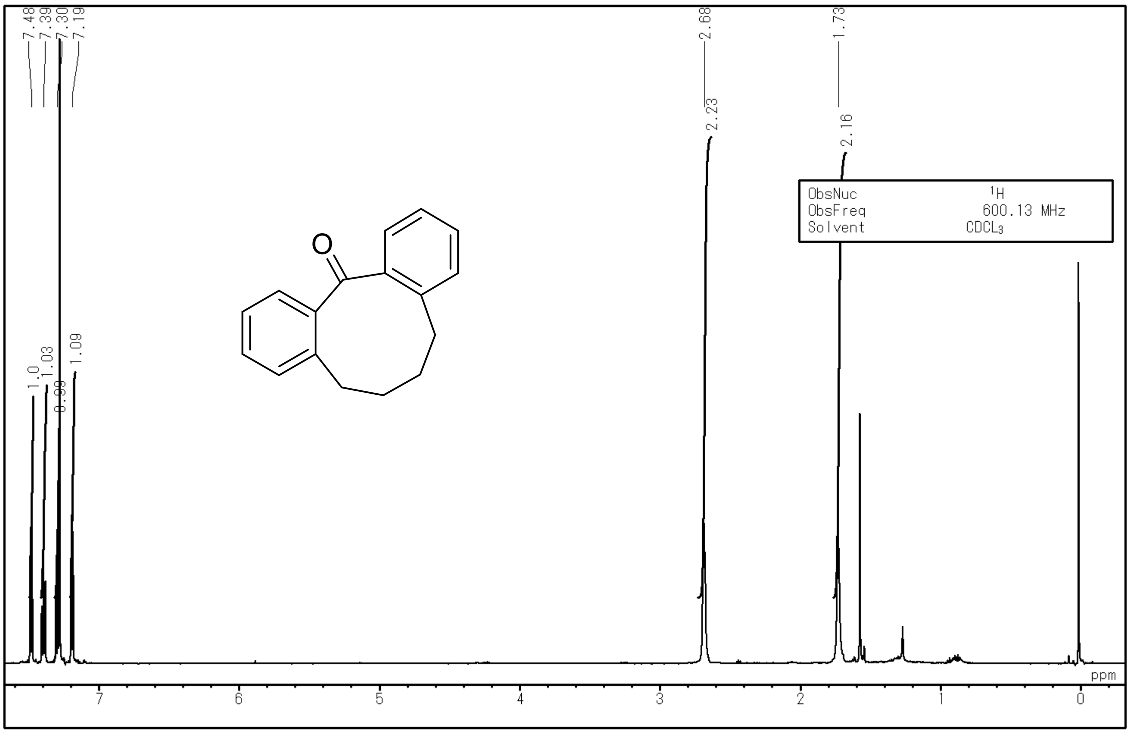


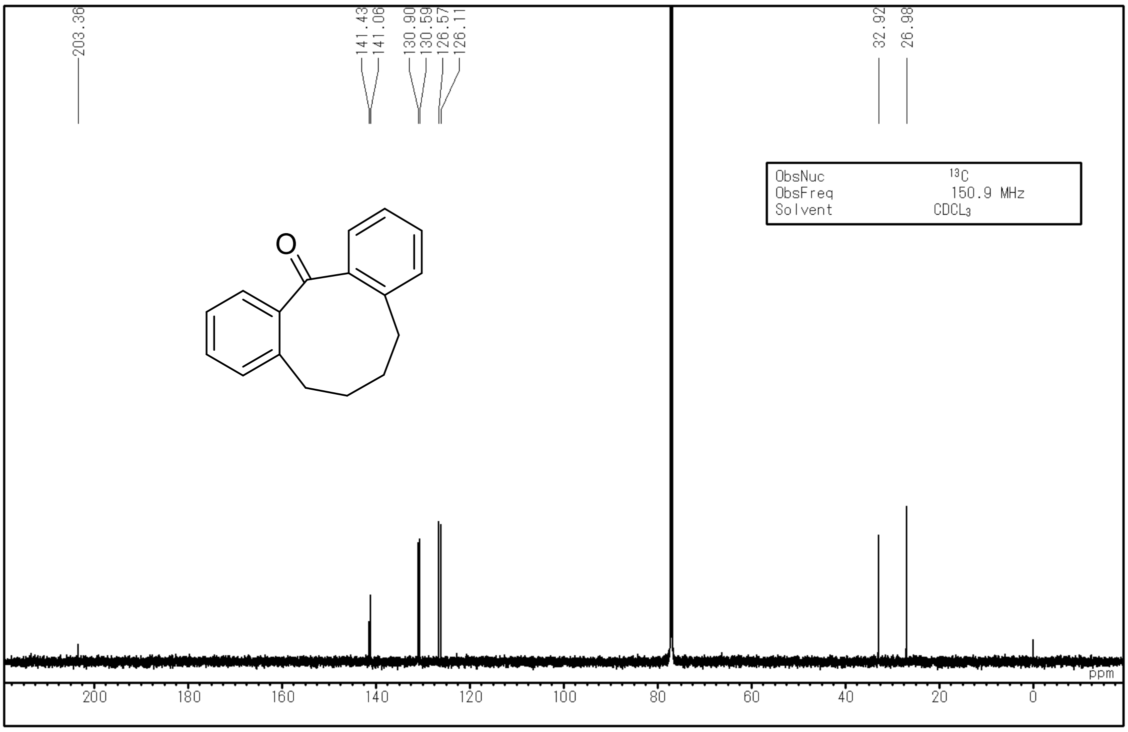
(*E*)- and (*Z*)-13-Butylidene-3-methyl-6,7,8,13-tetrahydro-5*H*-dibenzo[*a,d*]-cyclononene (3g).



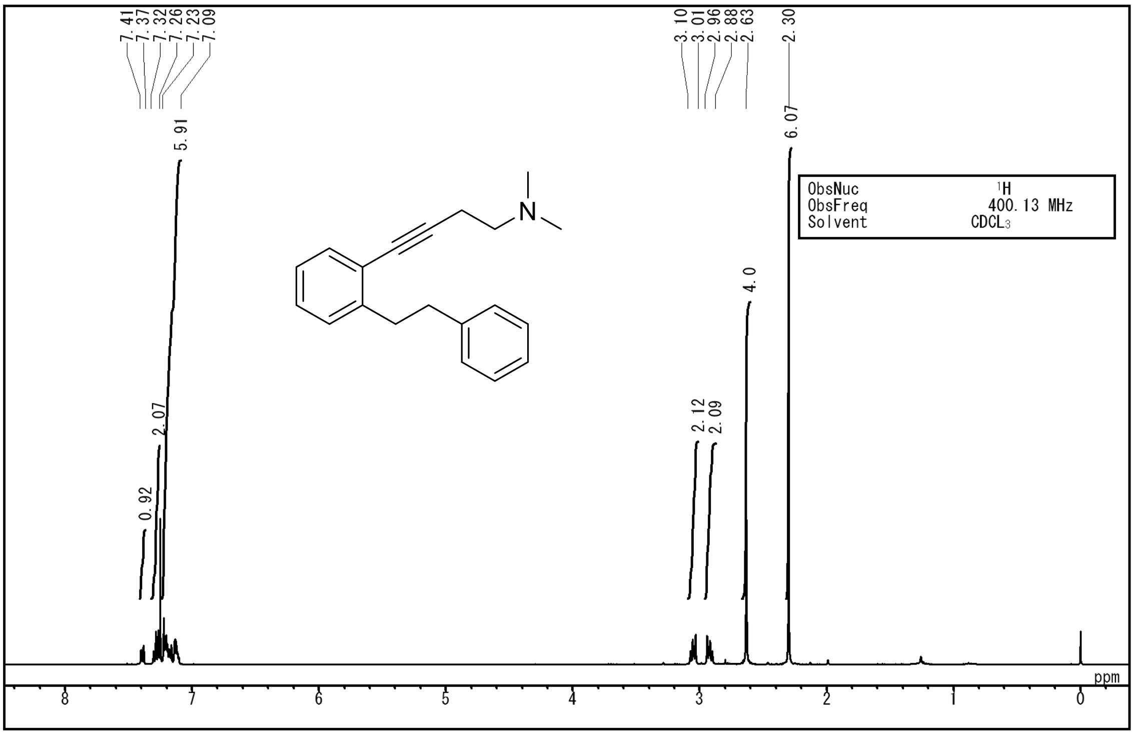


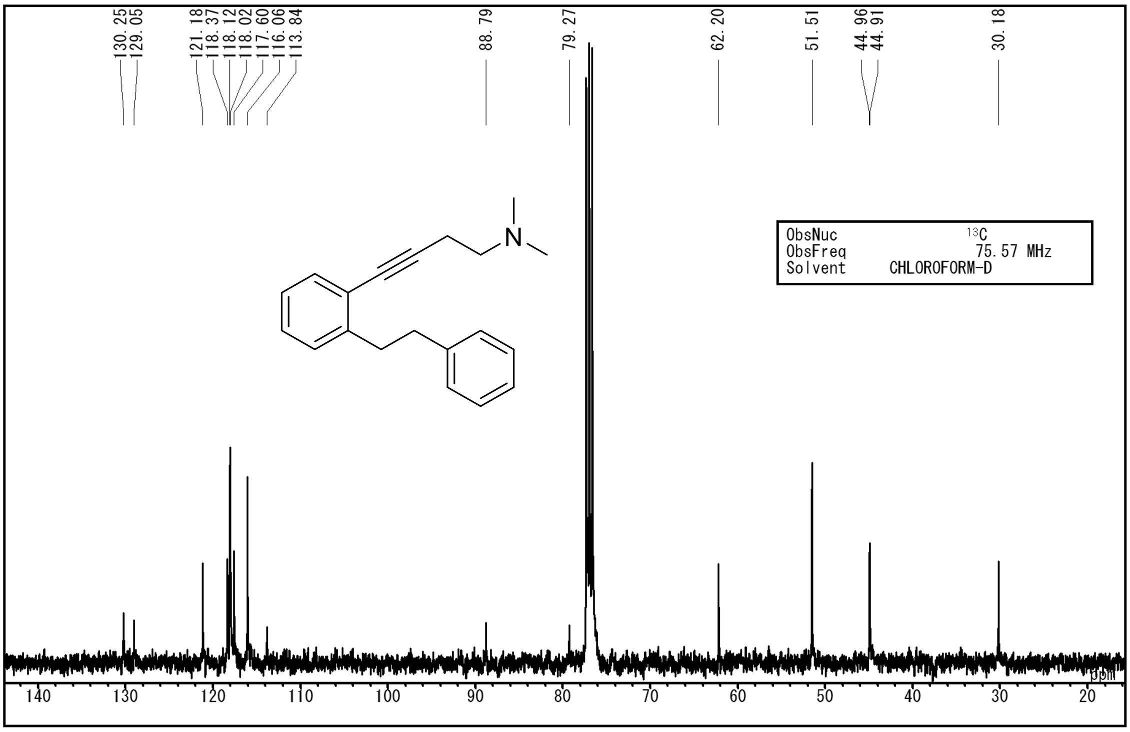
5,6,7,8-Tetrahydro-13*H*-dibenzo[*a,d*][9]annulen-13-one (6).



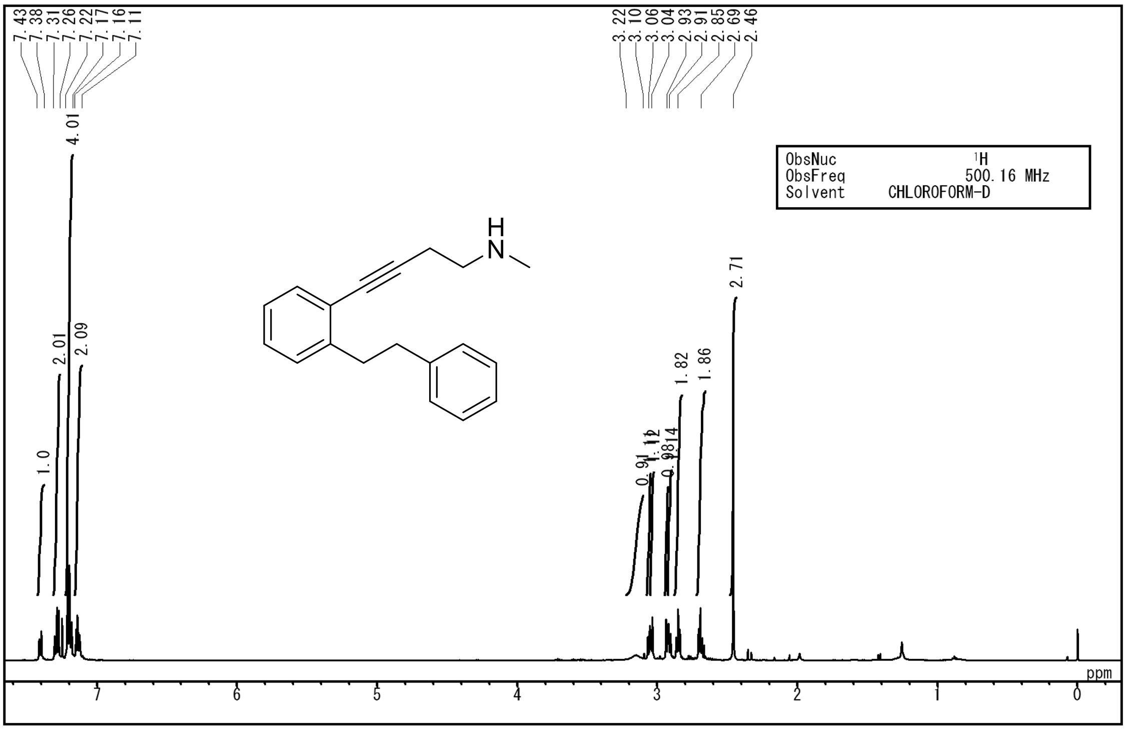


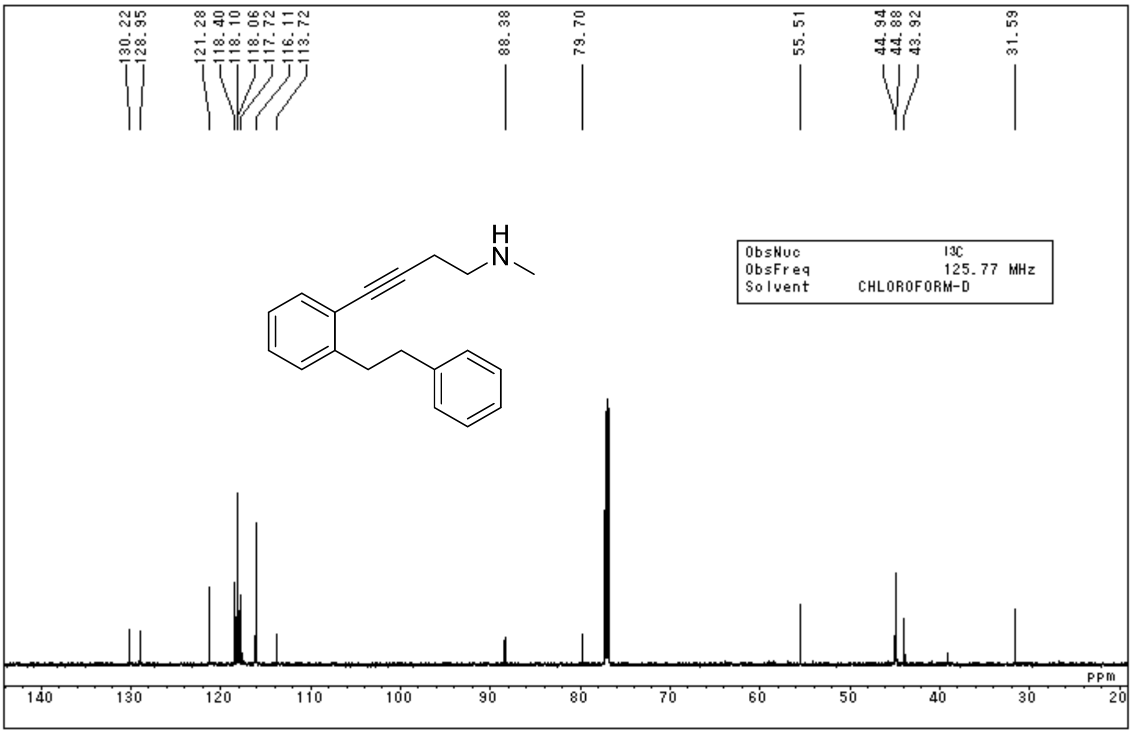
N,*N*-Dimethyl-4-(2-phenethylphenyl)but-3-yn-1-amine (7a).



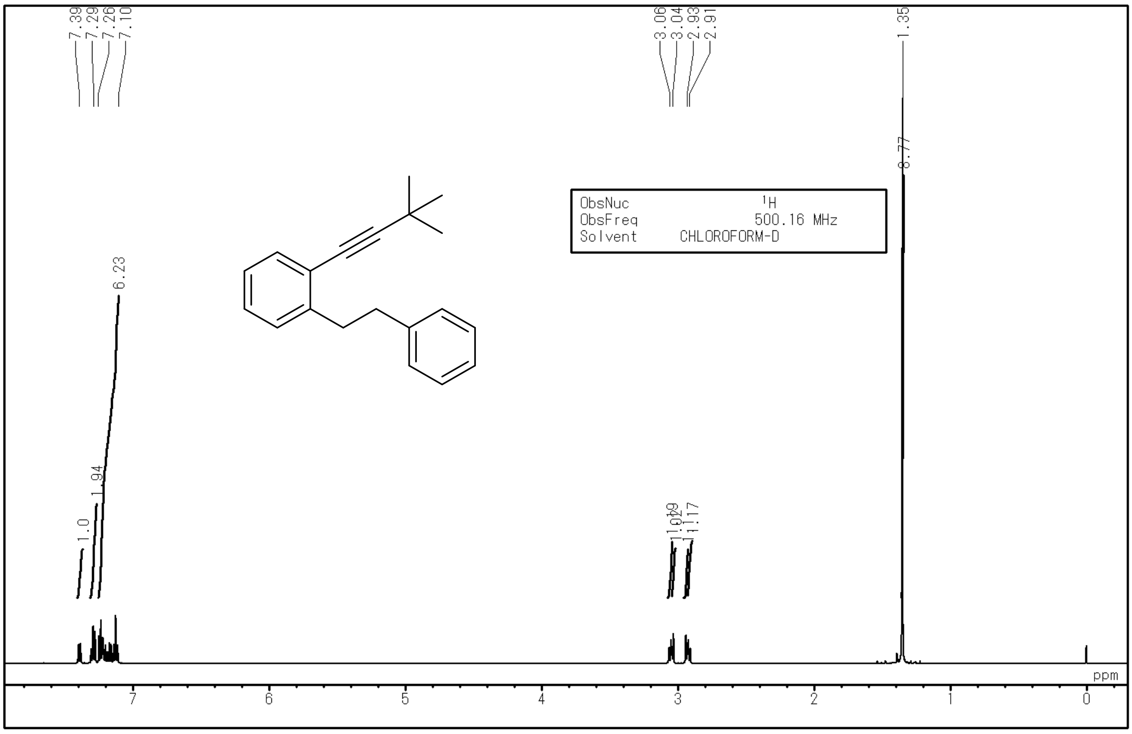


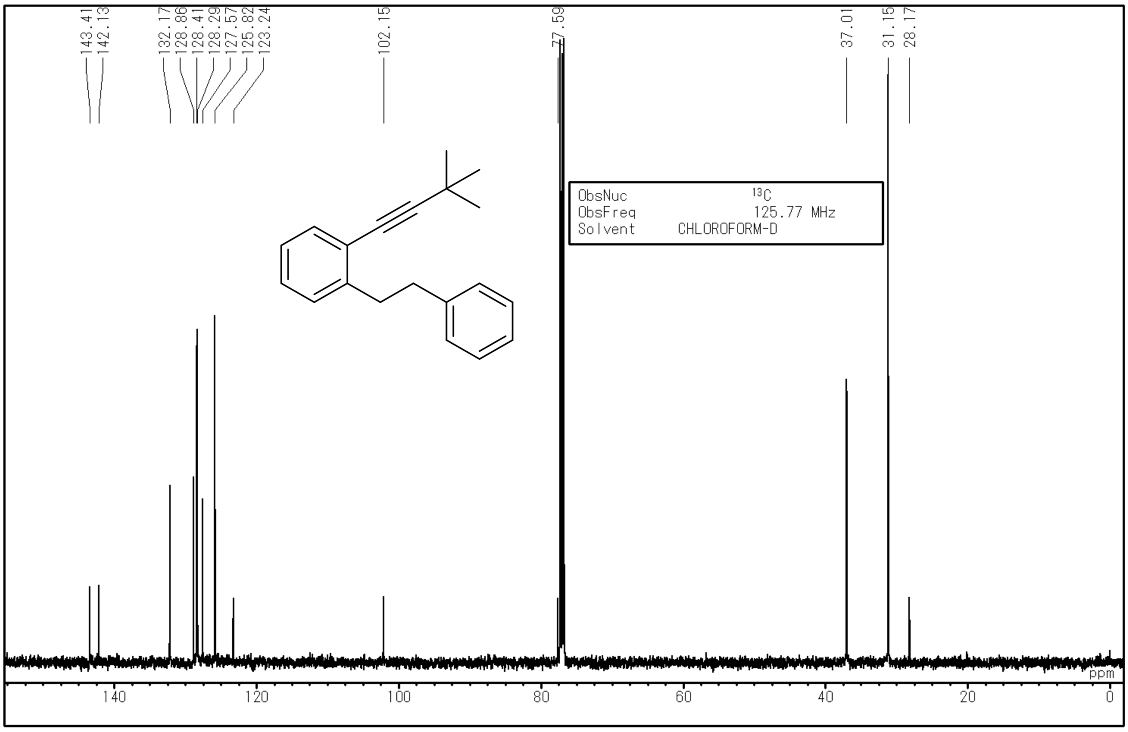
***N*-Methyl-4-(2-phenethylphenyl)but-3-yn-1-amine (7b).**



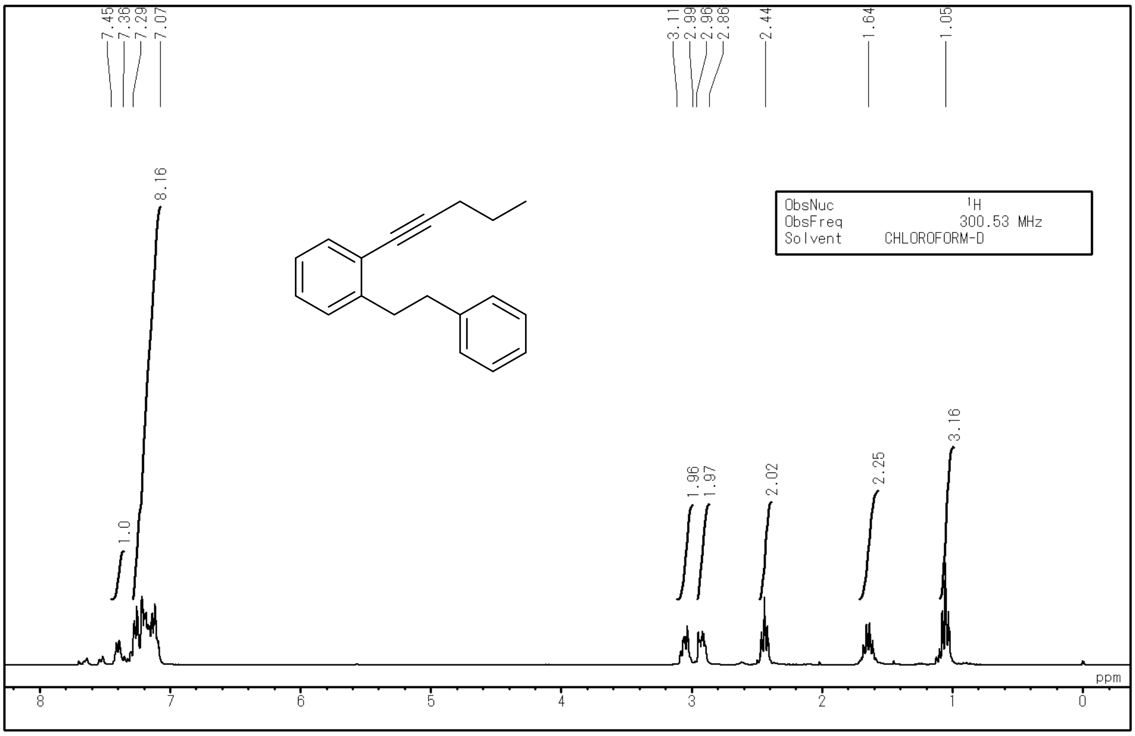


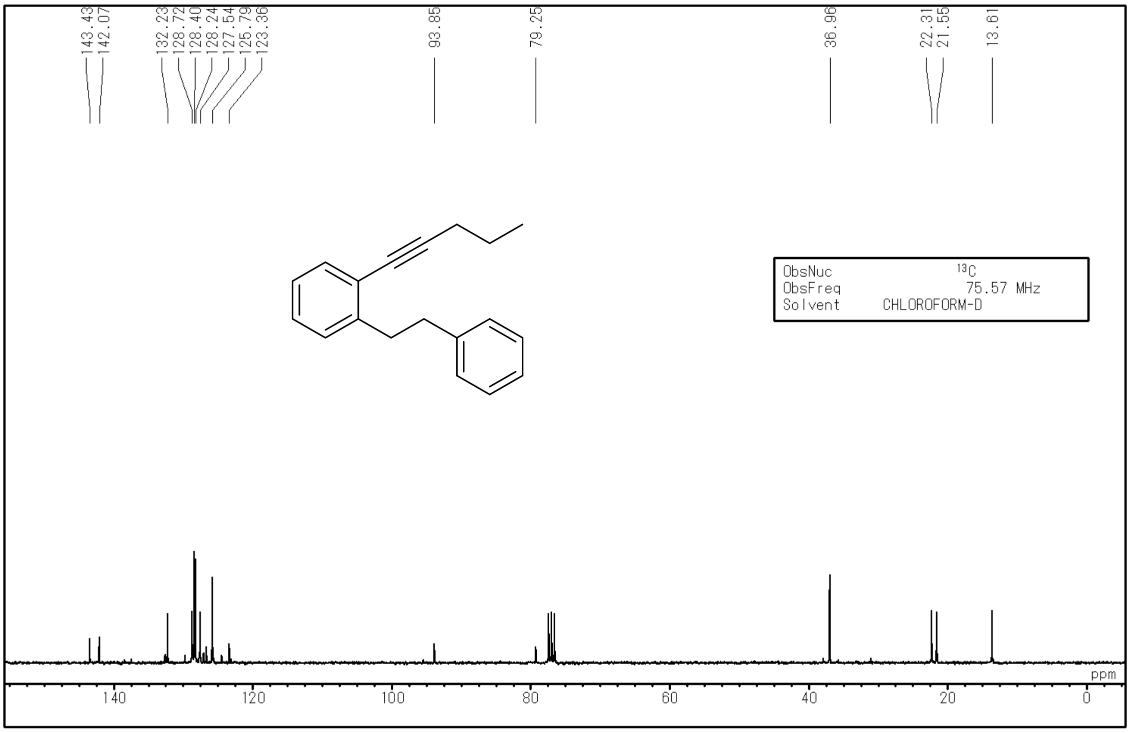
1-(3,3-Dimethylbut-1-yn-1-yl)-2-phenethylbenzene (7c).



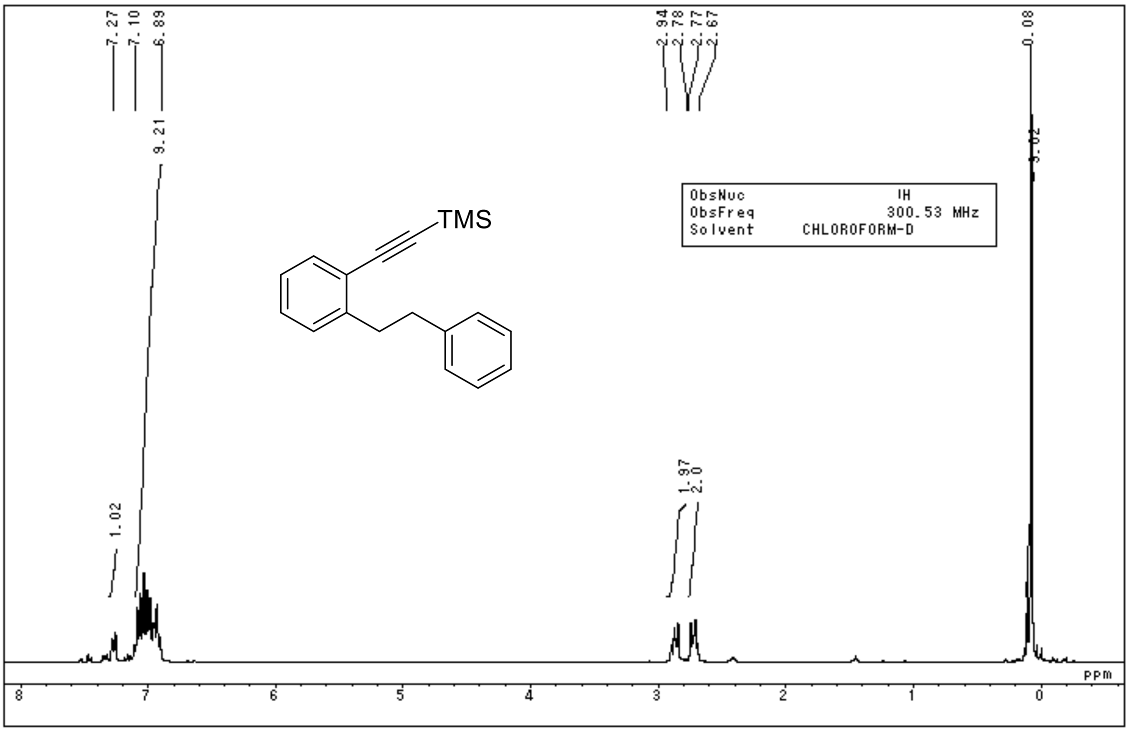


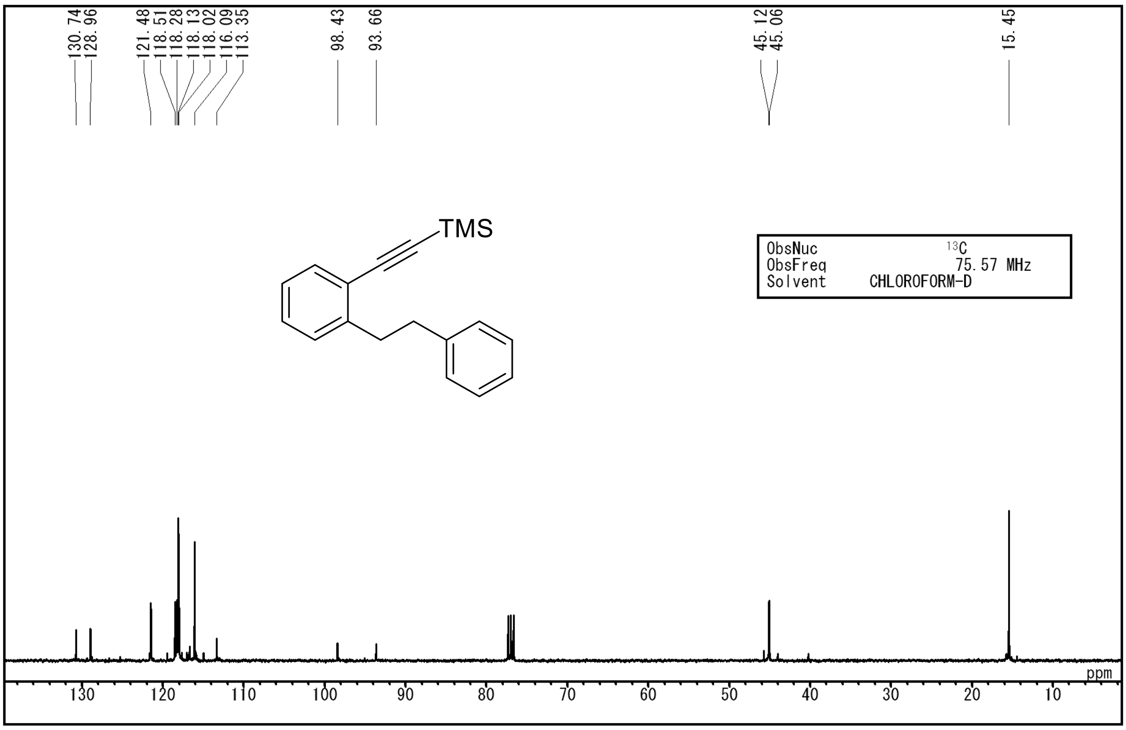
1-(Pent-1-yn-1-yl)-2-phenethylbenzene (7d).



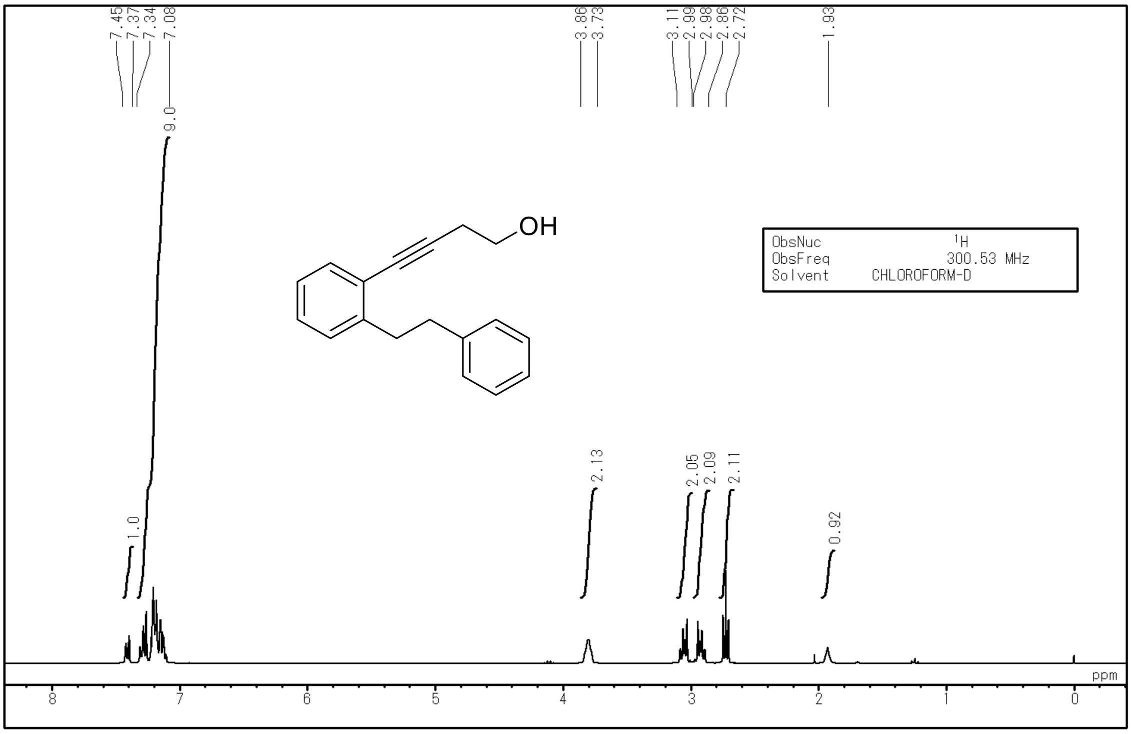


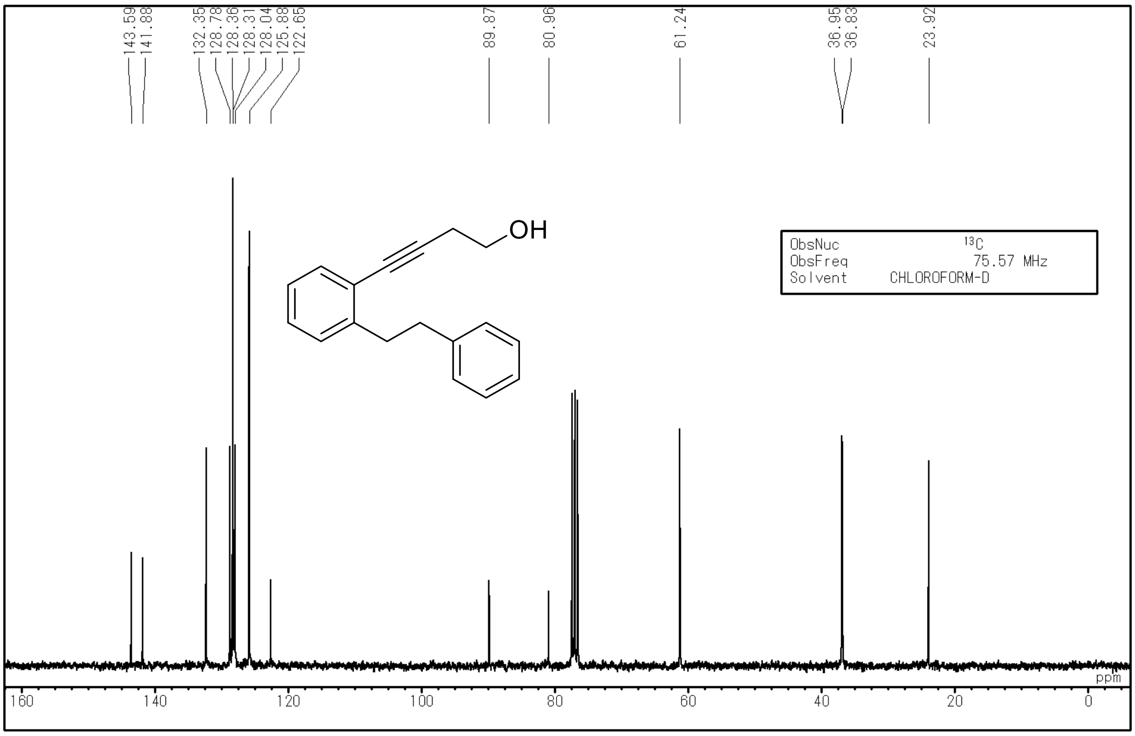
Trimethyl((2-phenethylphenyl)ethynyl)silane (7e).



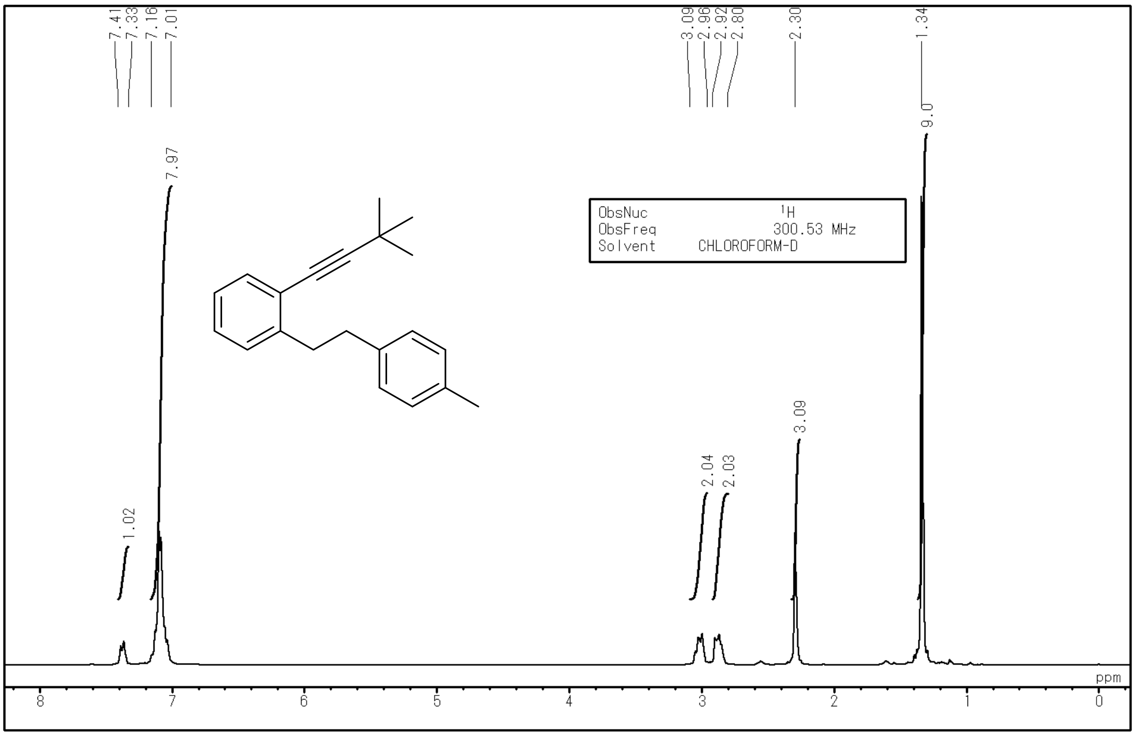


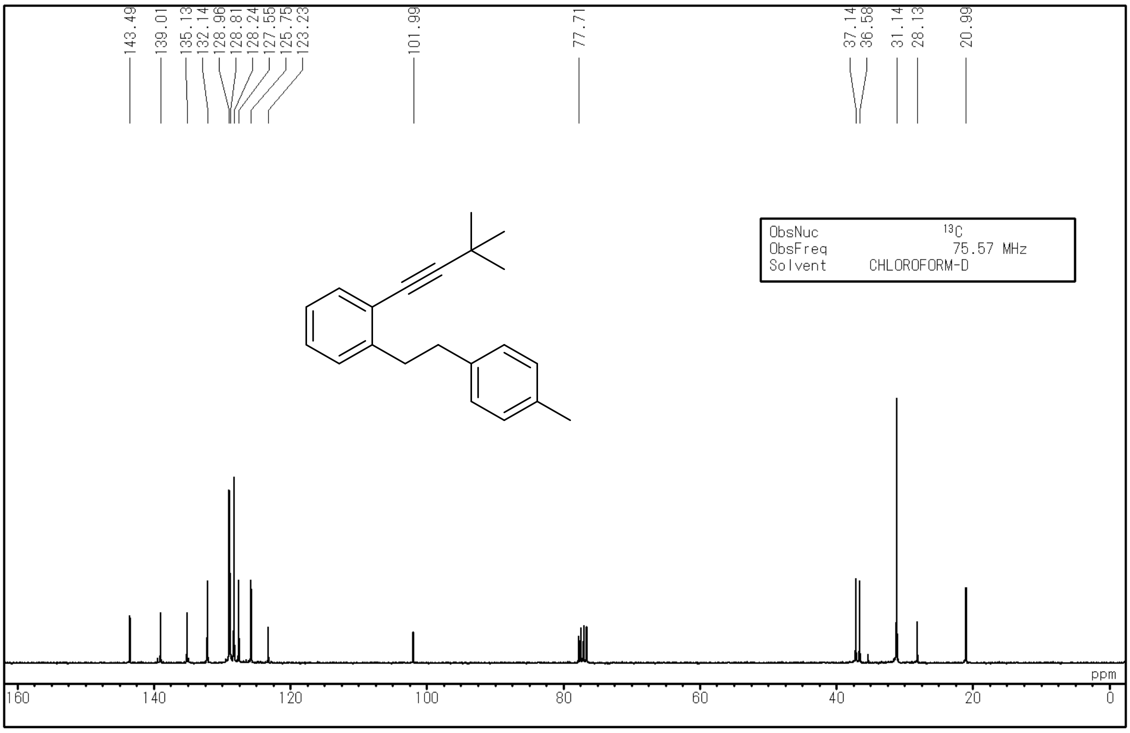
4-(2-Phenethylphenyl)but-3-yn-1-ol (7f).



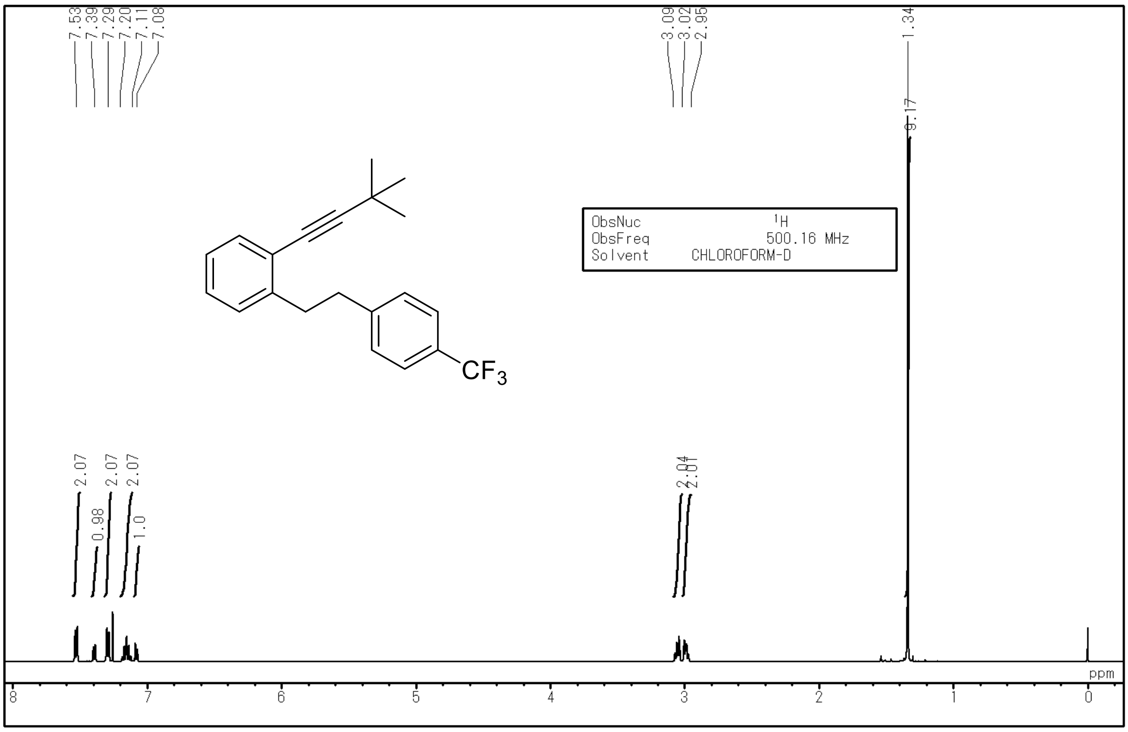


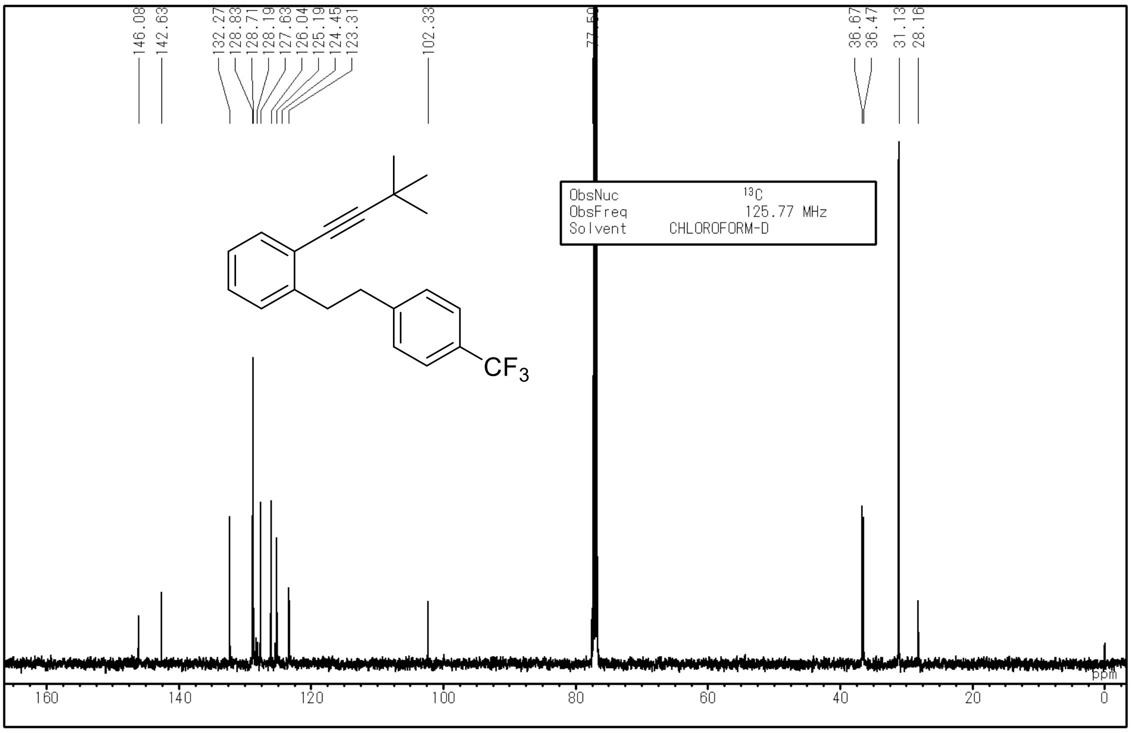
1-(3,3-Dimethylbut-1-yn-1-yl)-2-(4-methylphenethyl)benzene (7g).



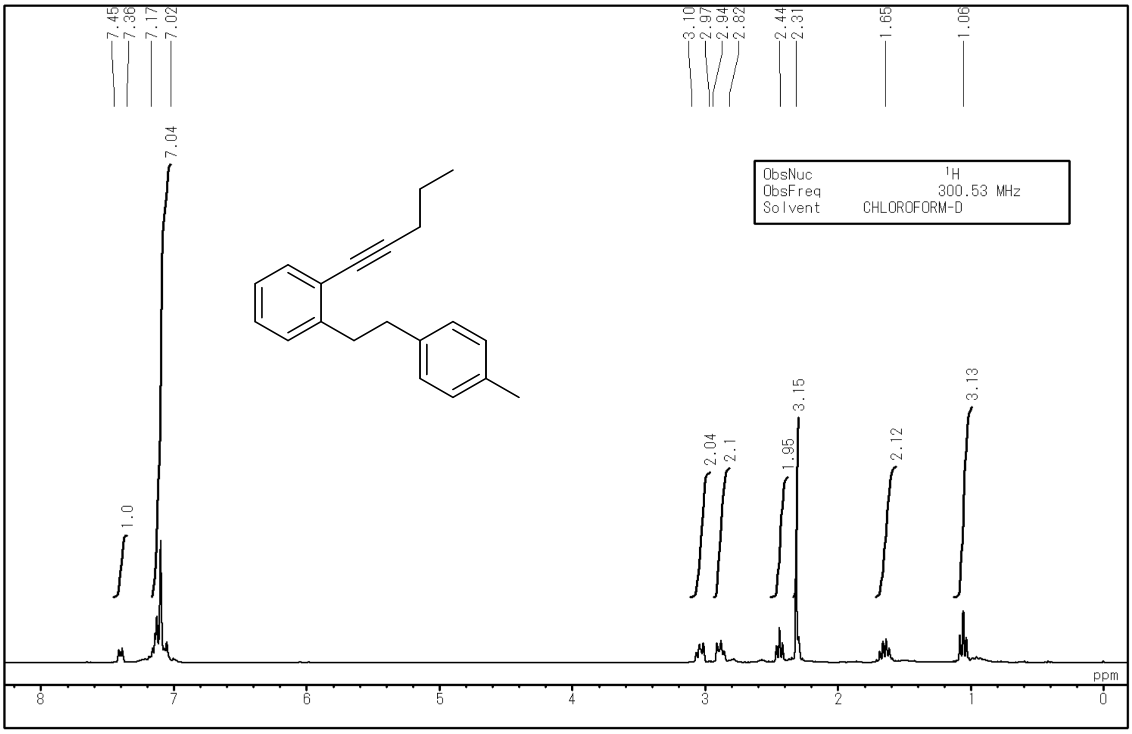


1-(3,3-Dimethylbut-1-yn-1-yl)-2-(4-(trifluoromethyl)phenethyl)benzene (7h).

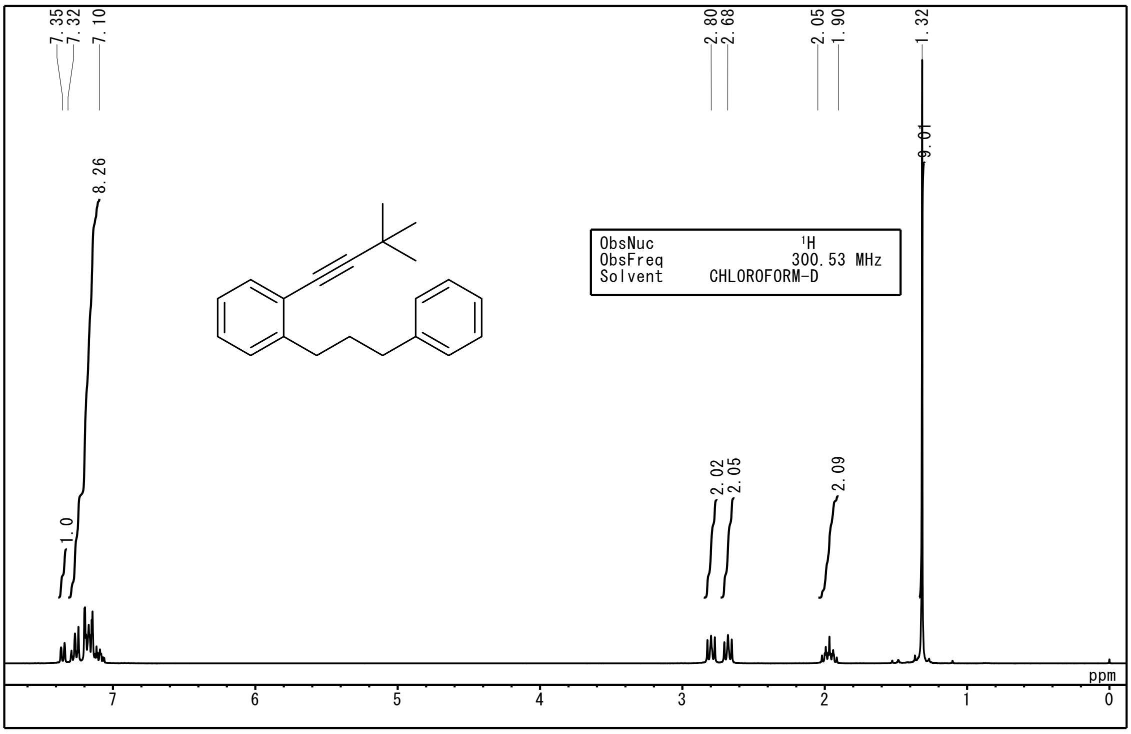


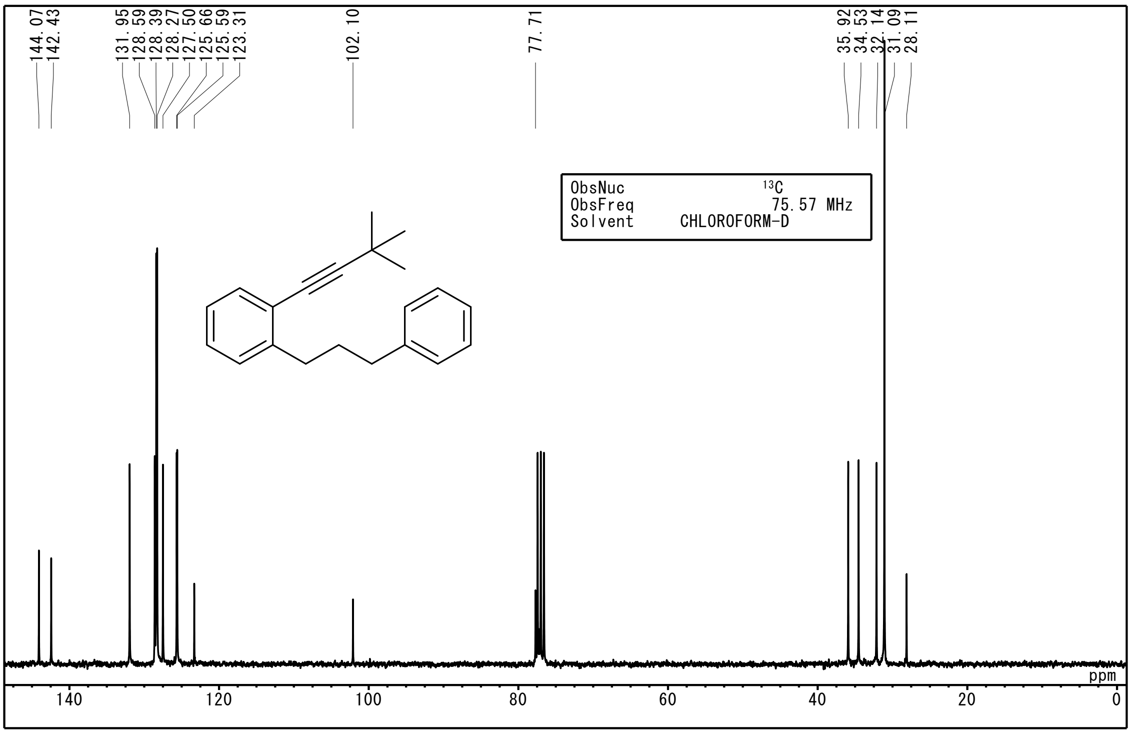


1-(4-Methylphenethyl)-2-(pent-1-yn-1-yl)benzene (7i).

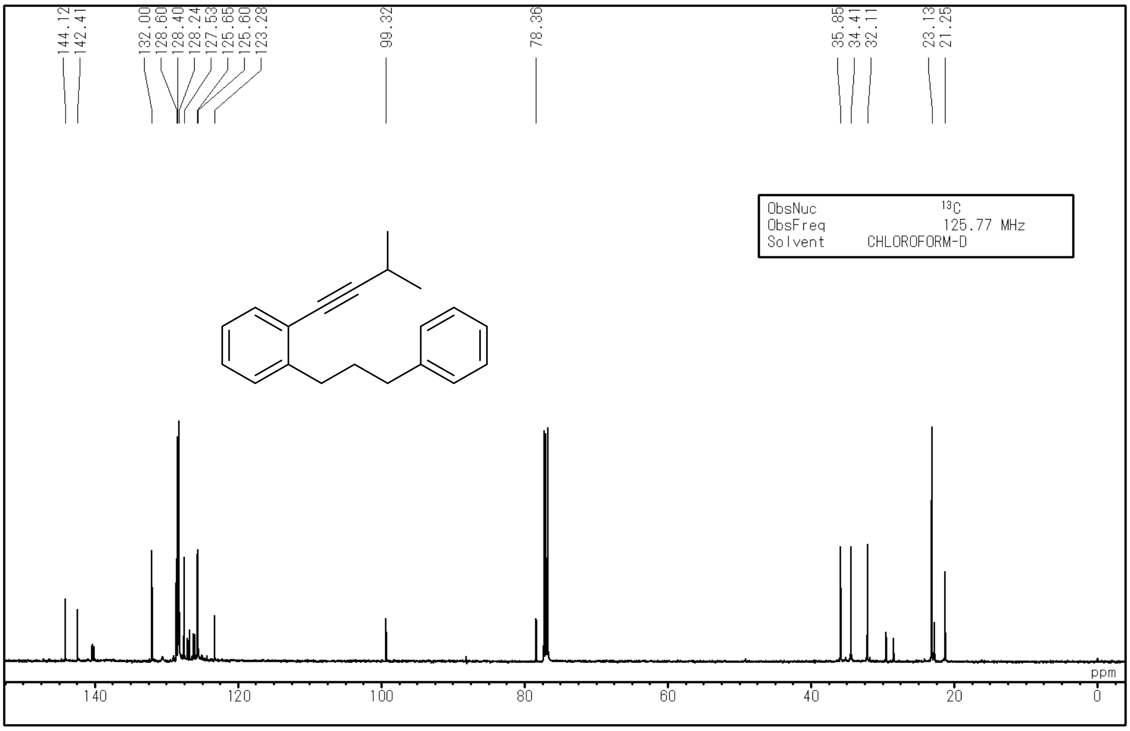


1-(3,3-Dimethylbut-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8a).

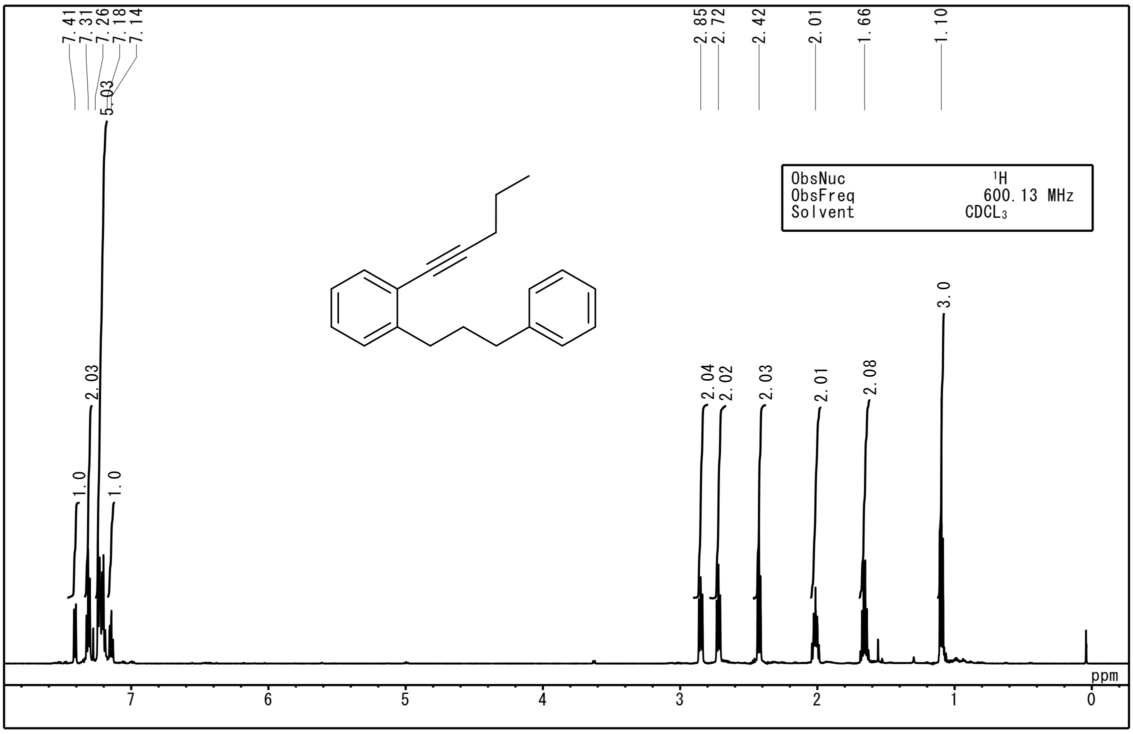


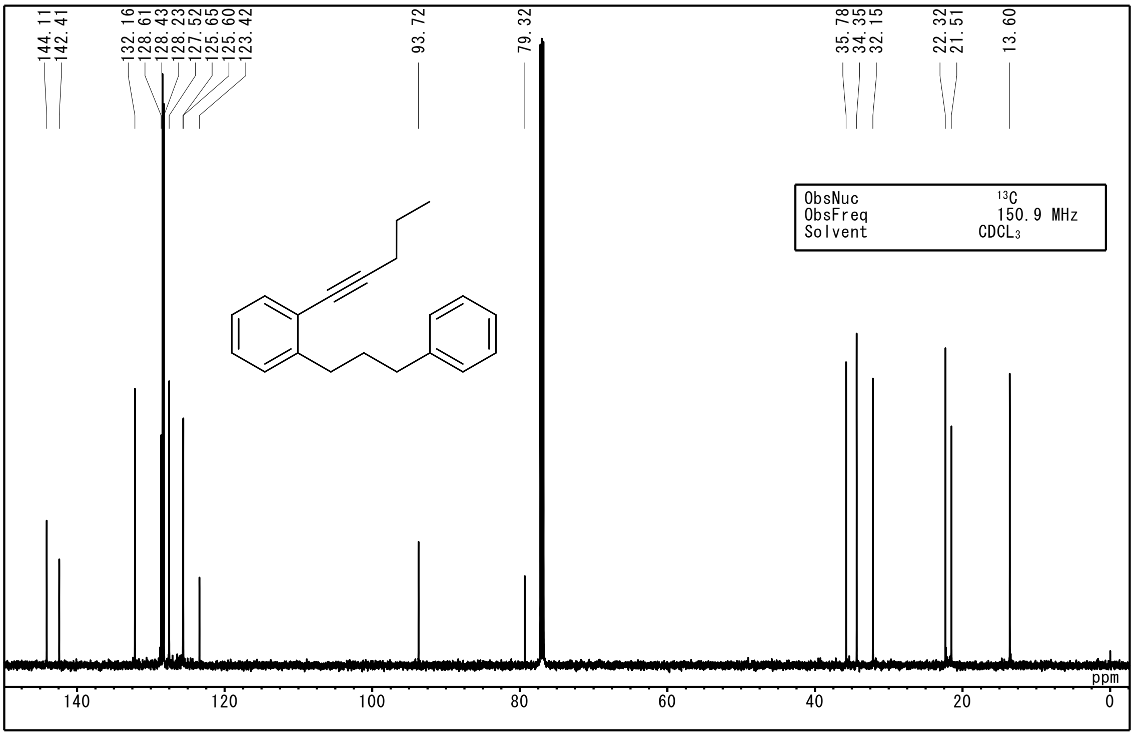


1-(3-Methylbut-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8b).

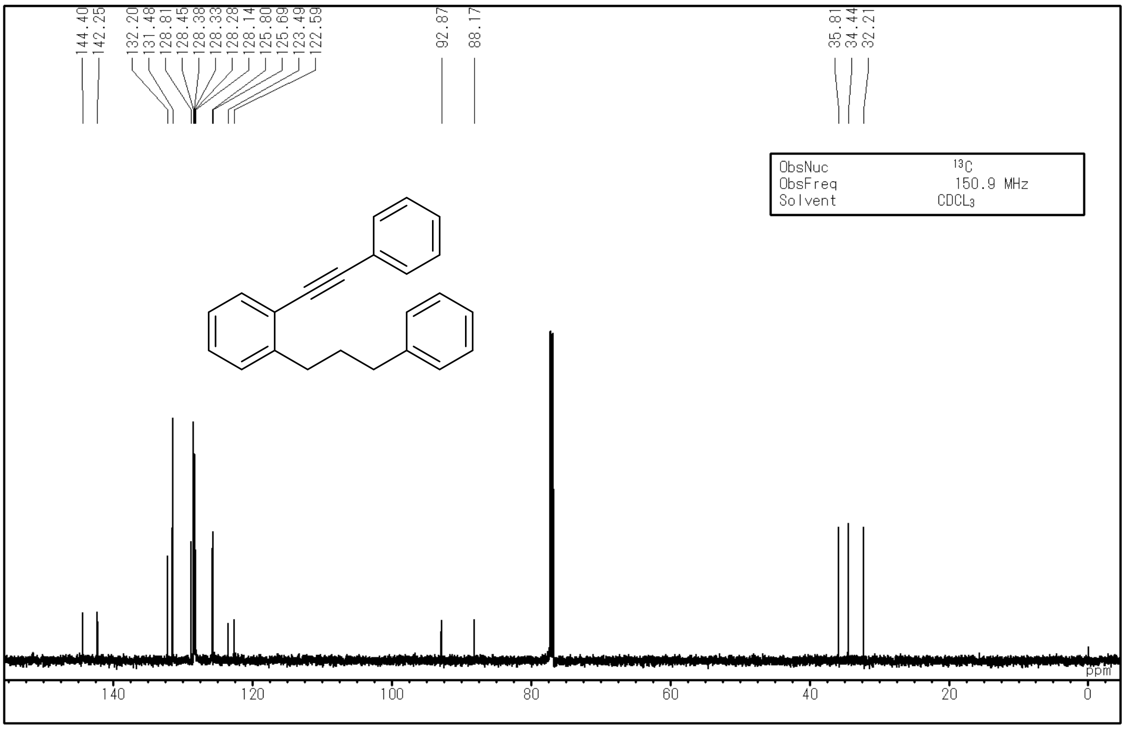


1-(Pent-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8c).

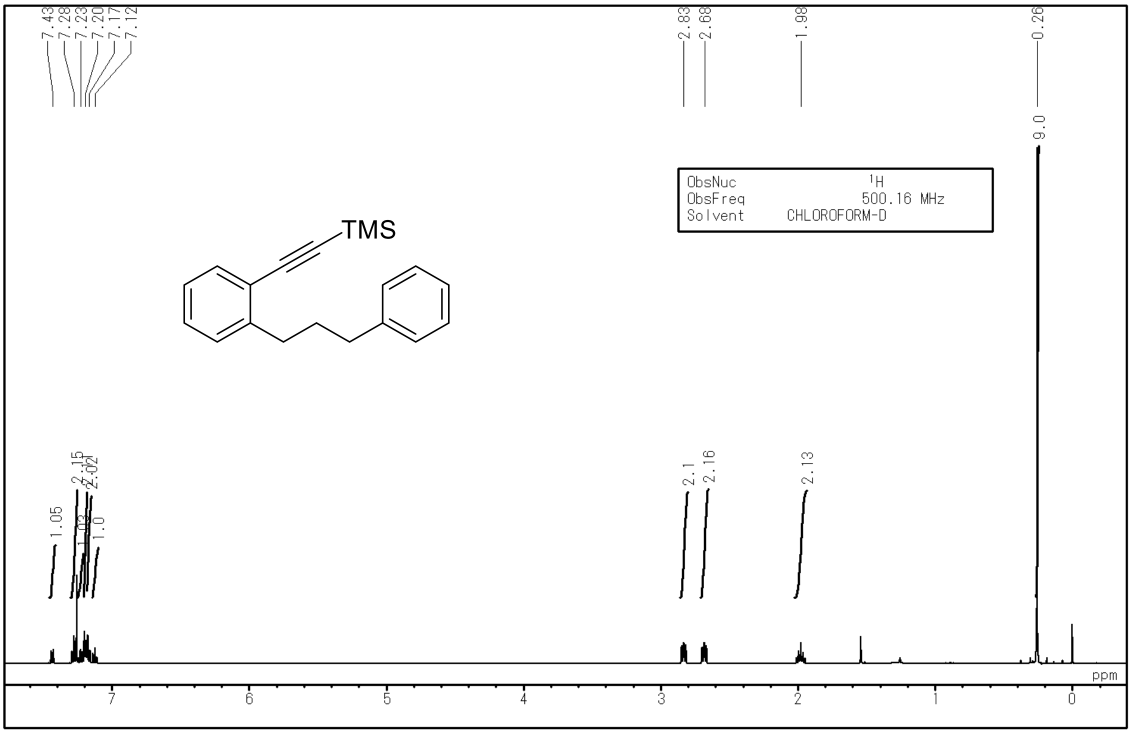


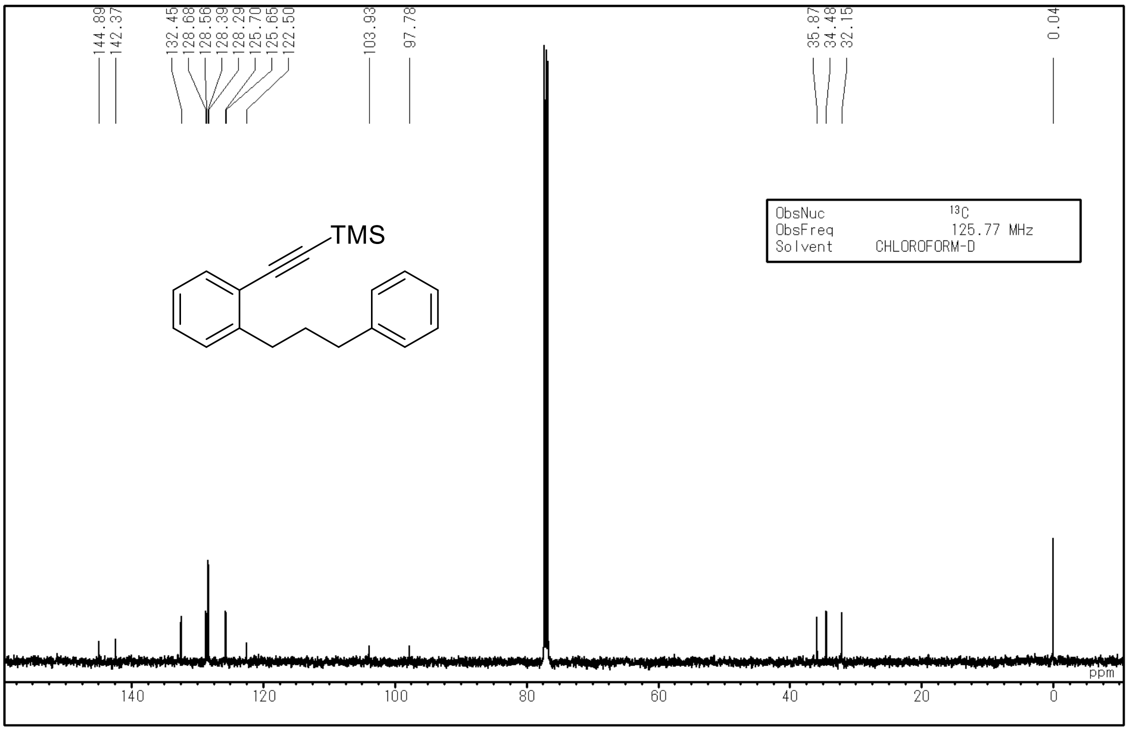


1-(Phenylethynyl)-2-(3-phenylpropyl)benzene (8d).

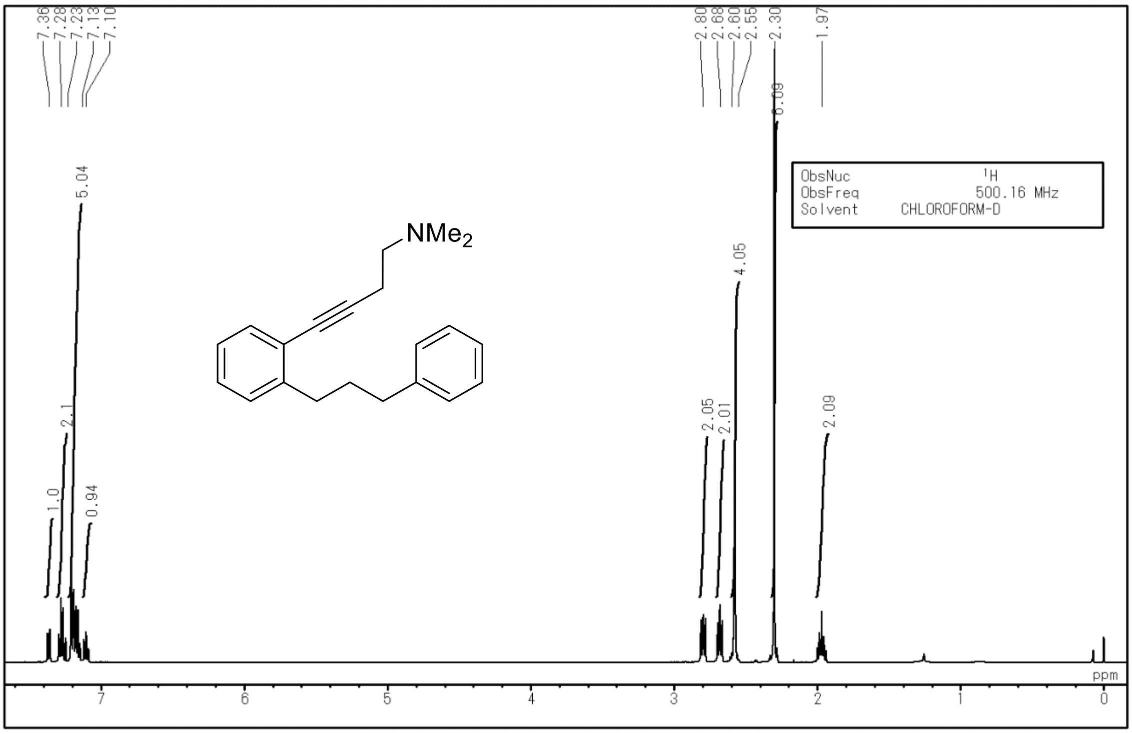


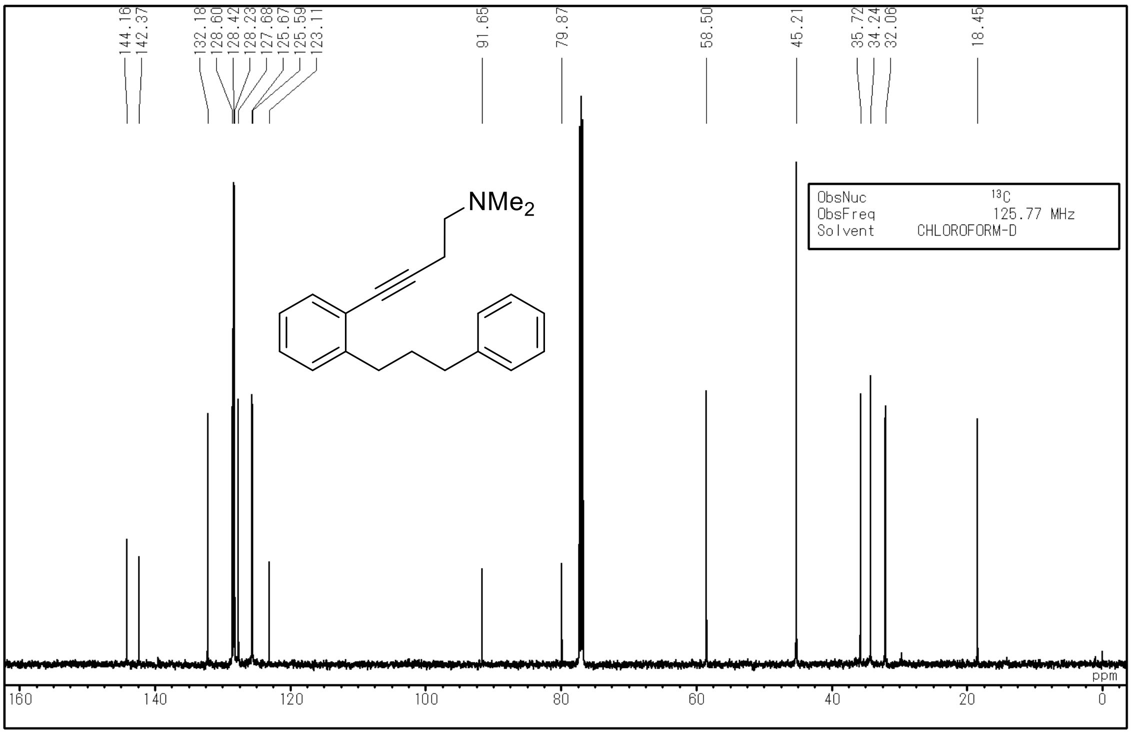
Trimethyl((2-(3-phenylpropyl)phenyl)ethynyl)silane (8e).



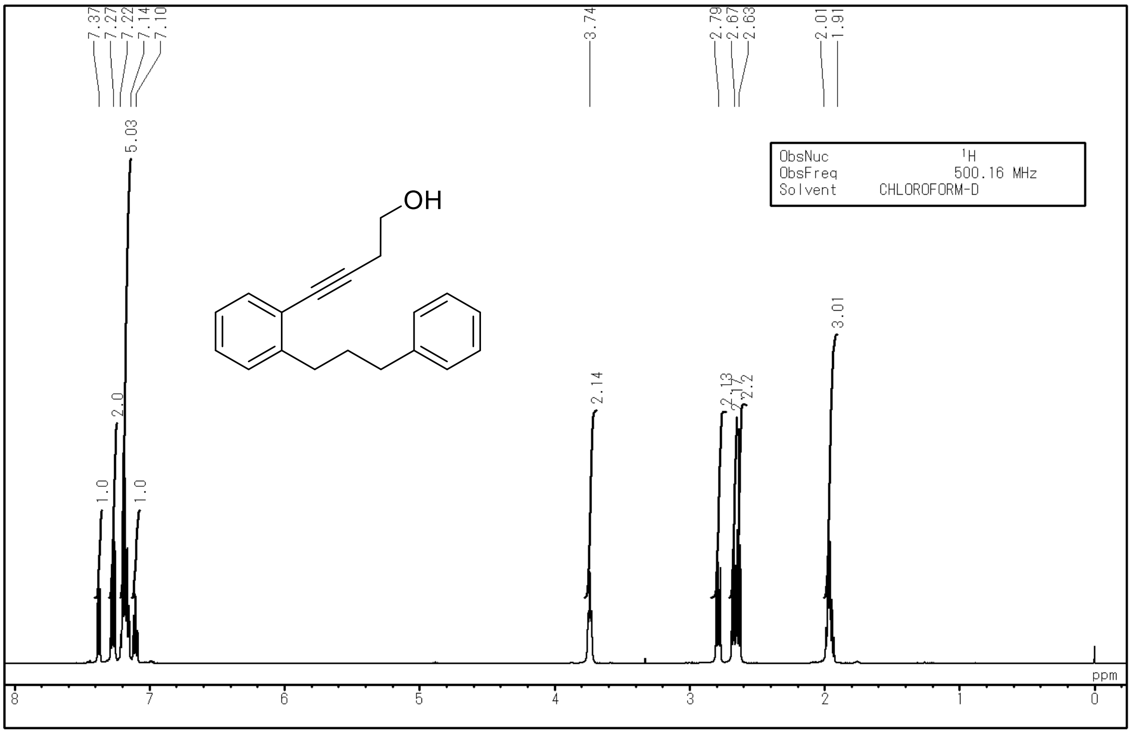


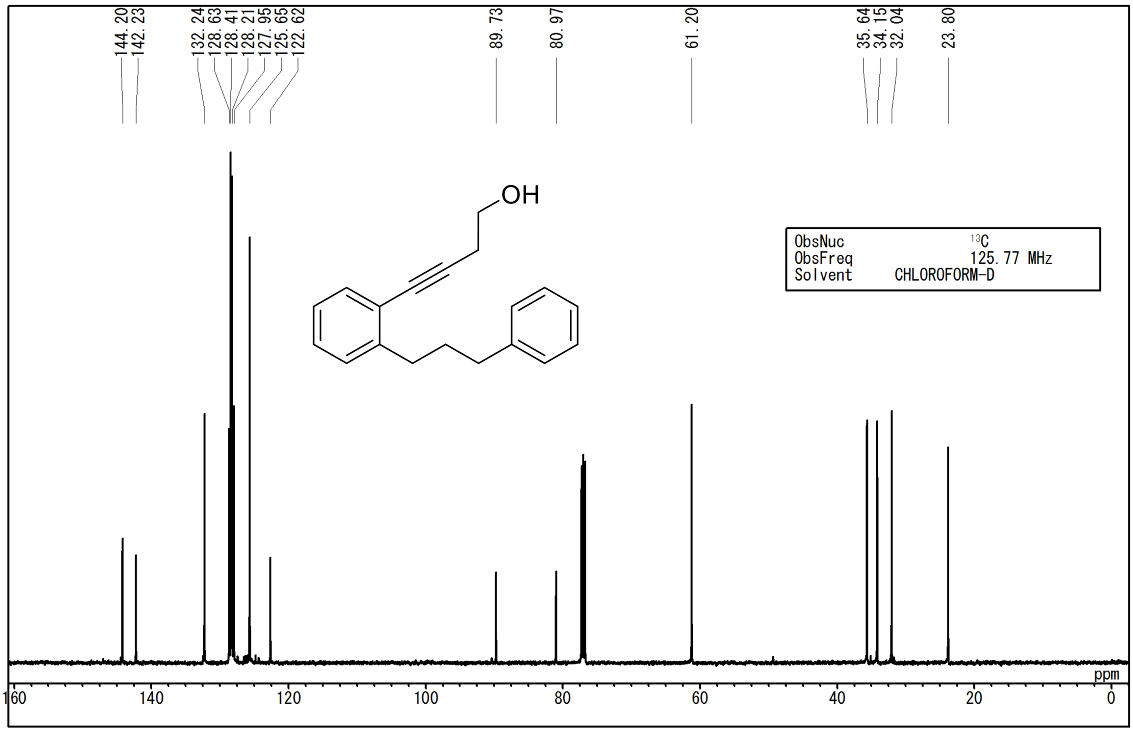
_N,N_-Dimethyl-4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-amine (8f).



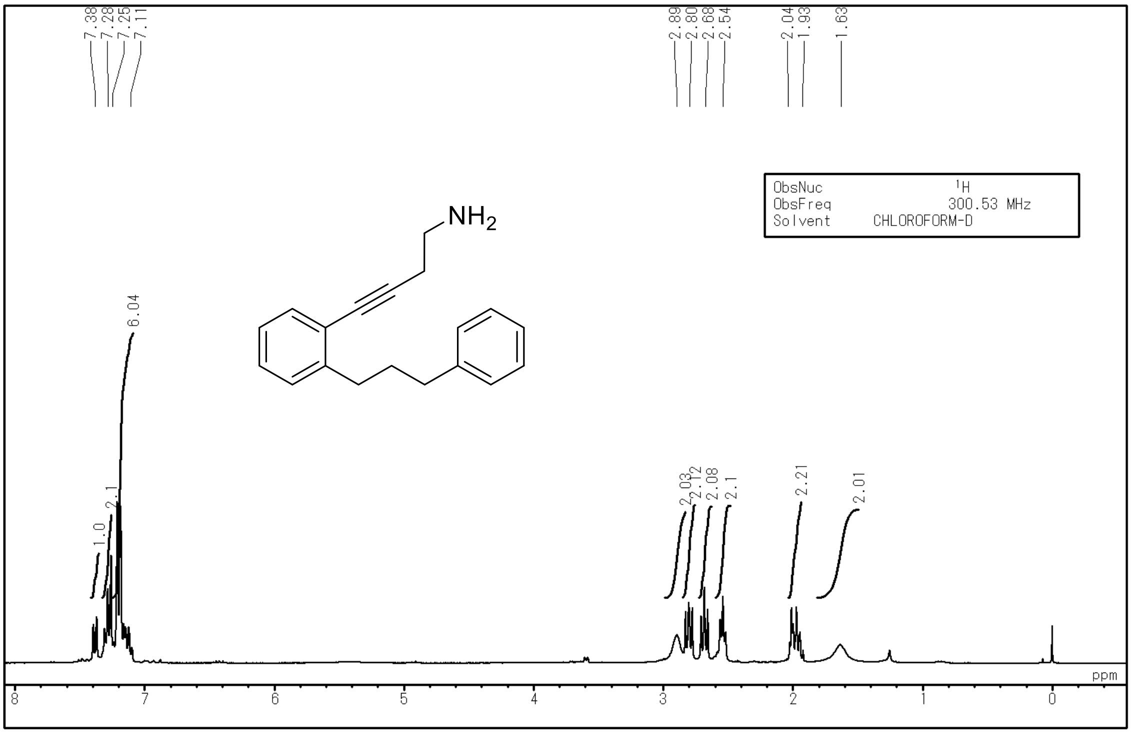


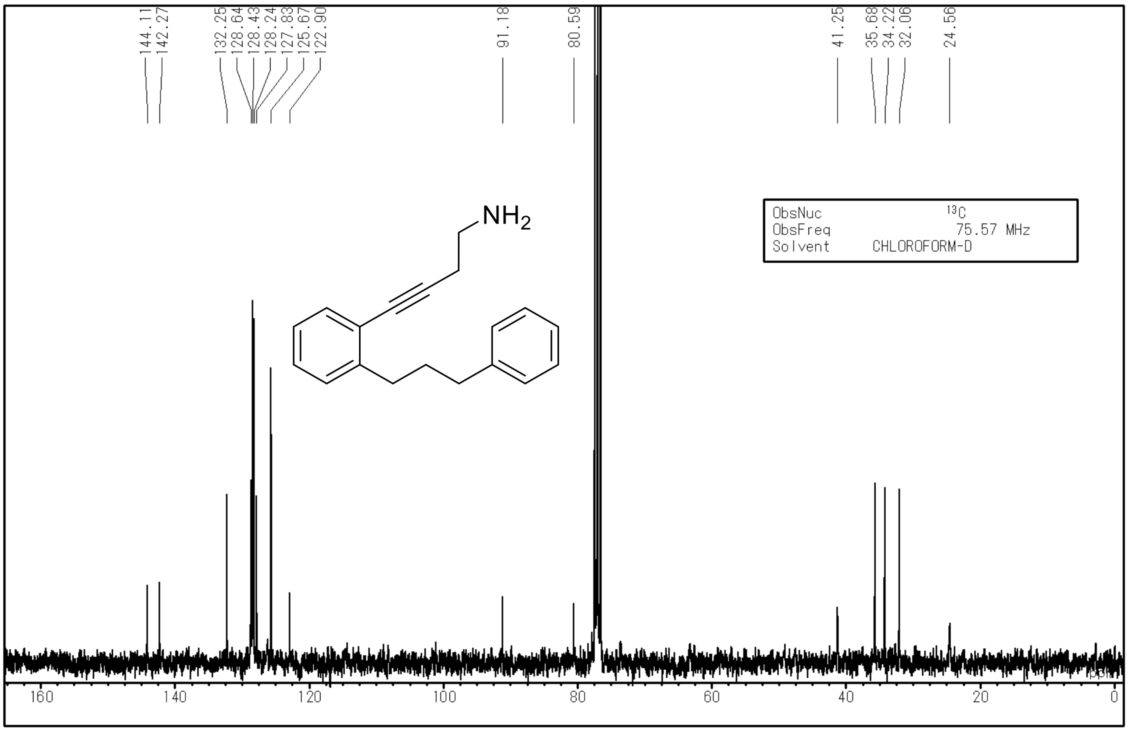
4-(2-(3-Phenylpropyl)phenyl)but-3-yn-1-ol (8g).



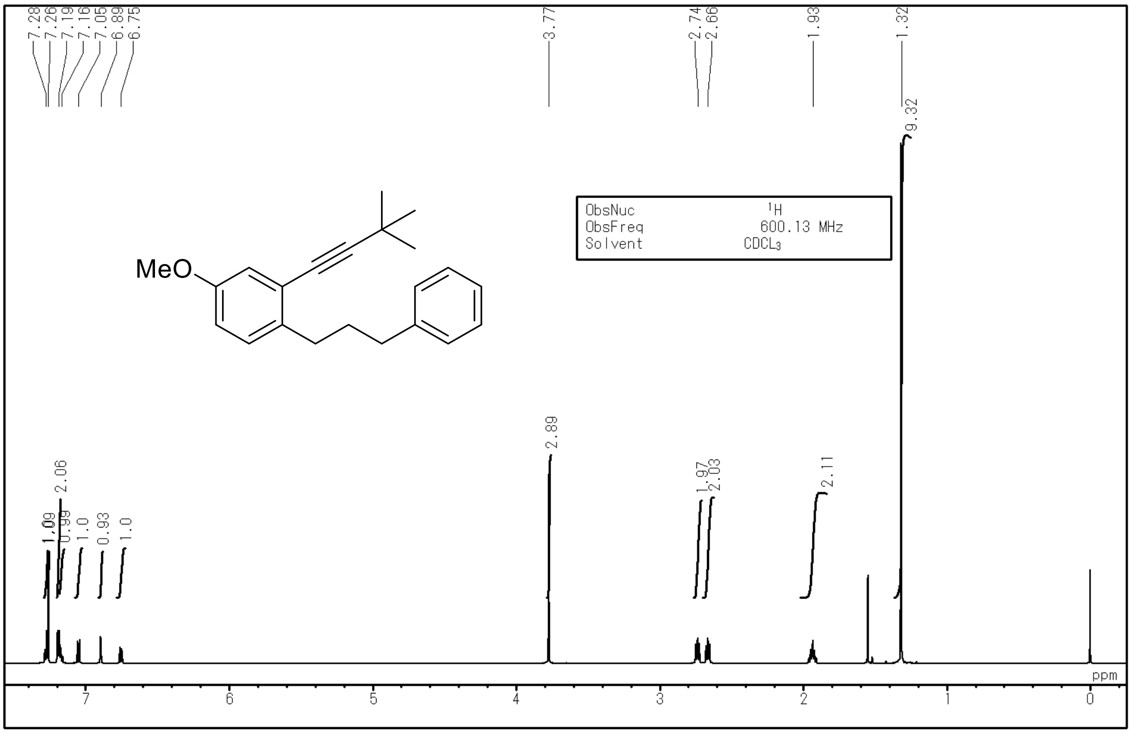


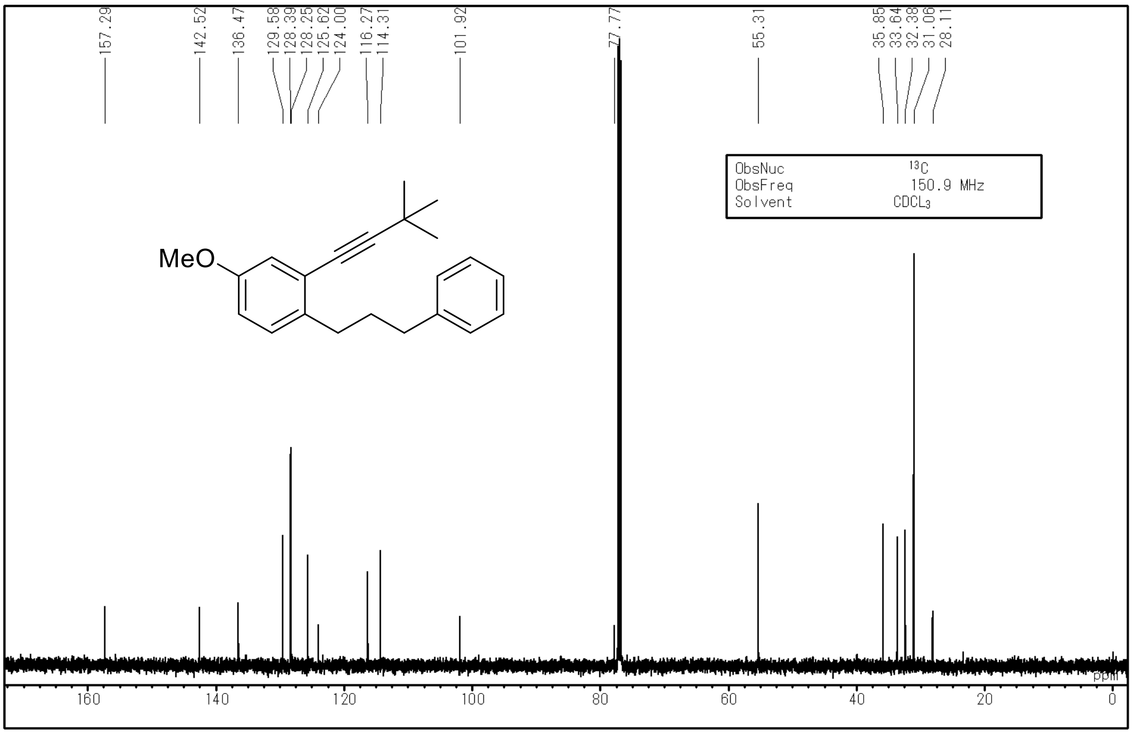
4-(2-(3-Phenylpropyl)phenyl)but-3-yn-1-amine (8h).



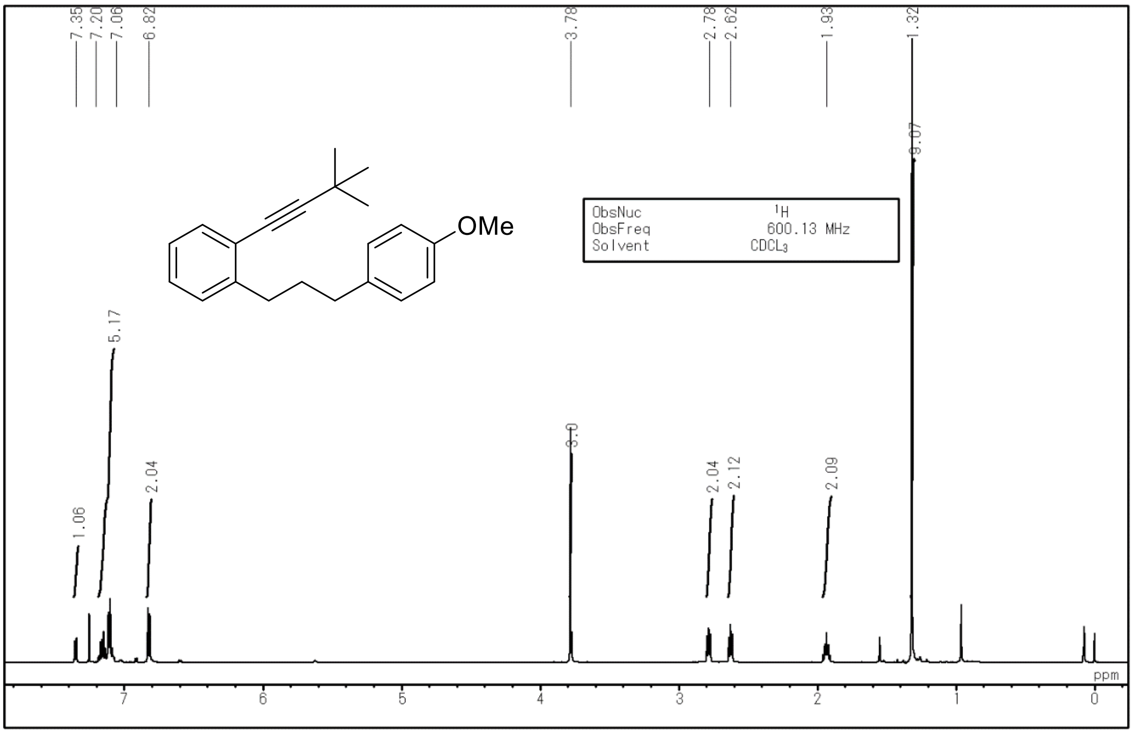


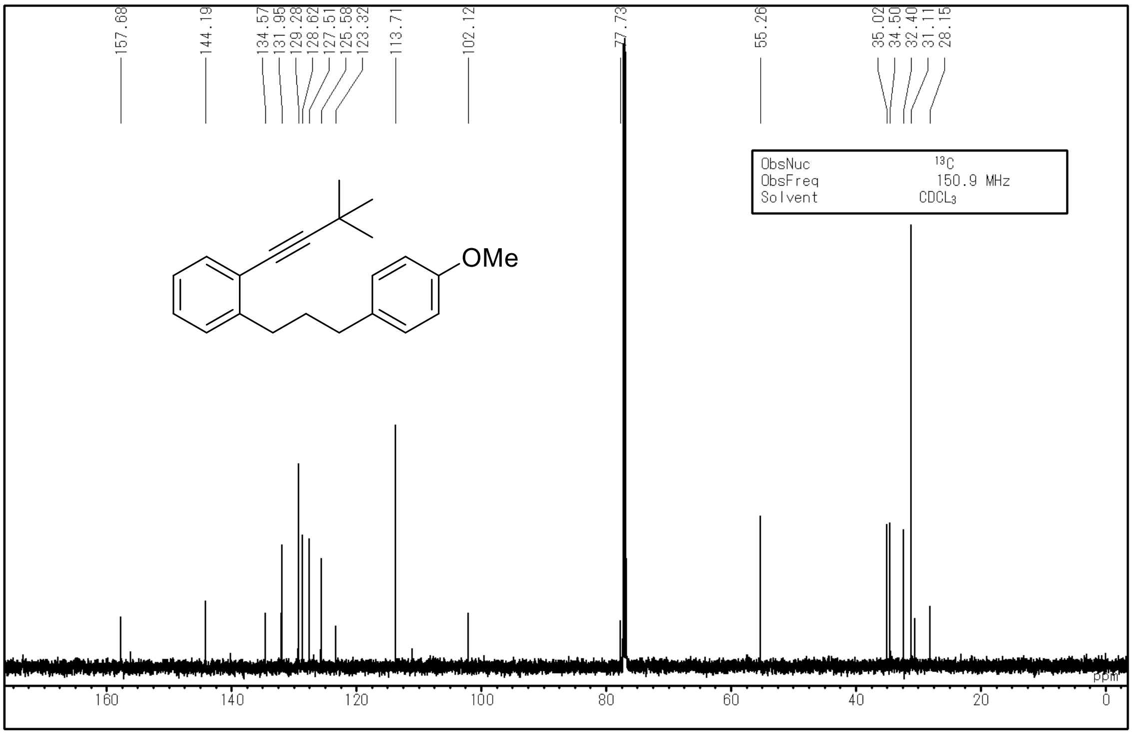
2-(3,3-Dimethylbut-1-yn-1-yl)-4-methoxy-1-(3-phenylpropyl)benzene (8i).



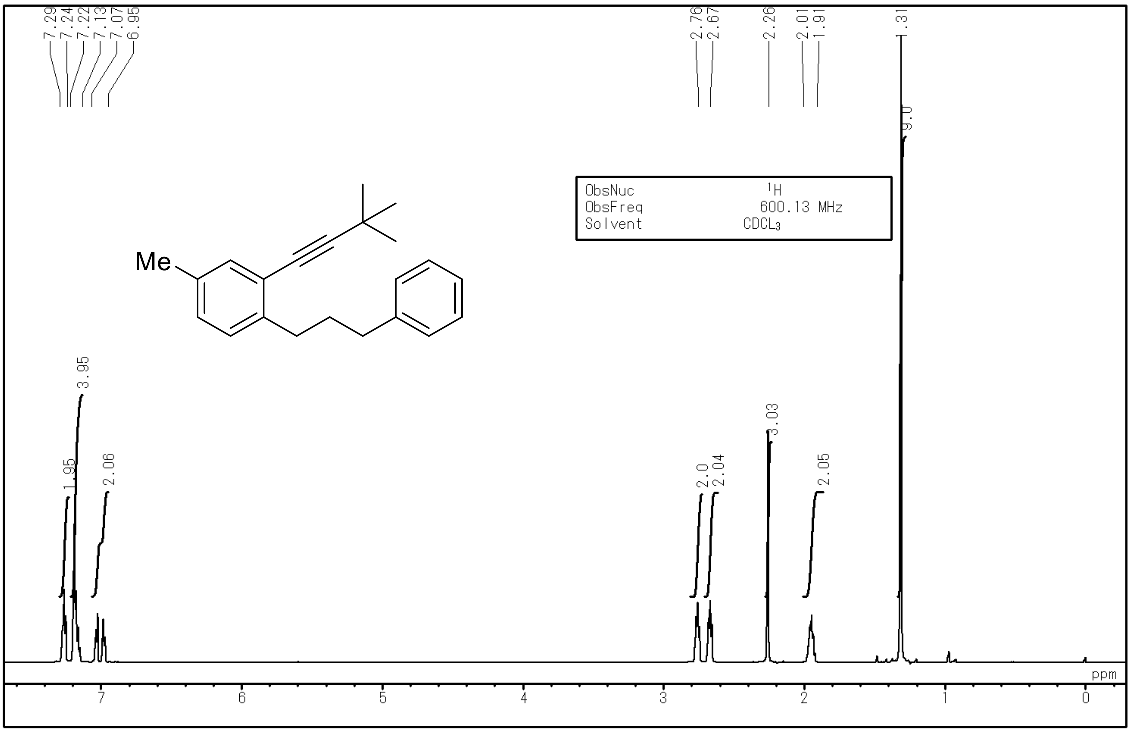


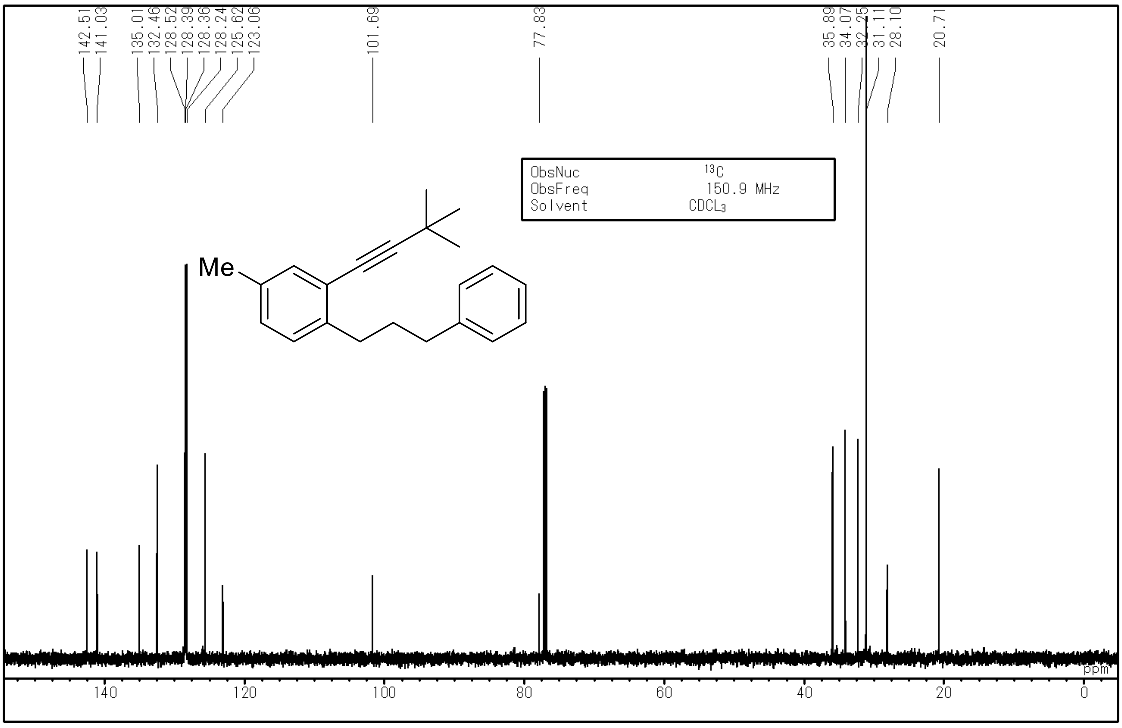
1-(3,3-Dimethylbut-1-yn-1-yl)-2-(3-(4-methoxyphenyl)propyl)benzene (8j).



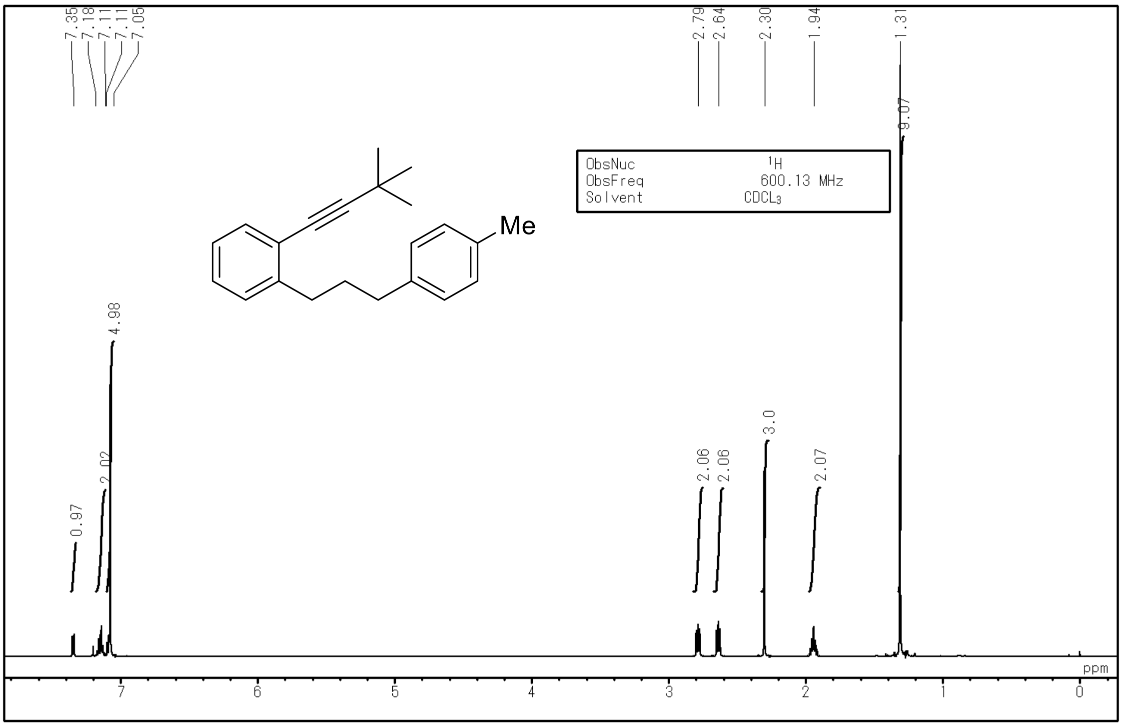


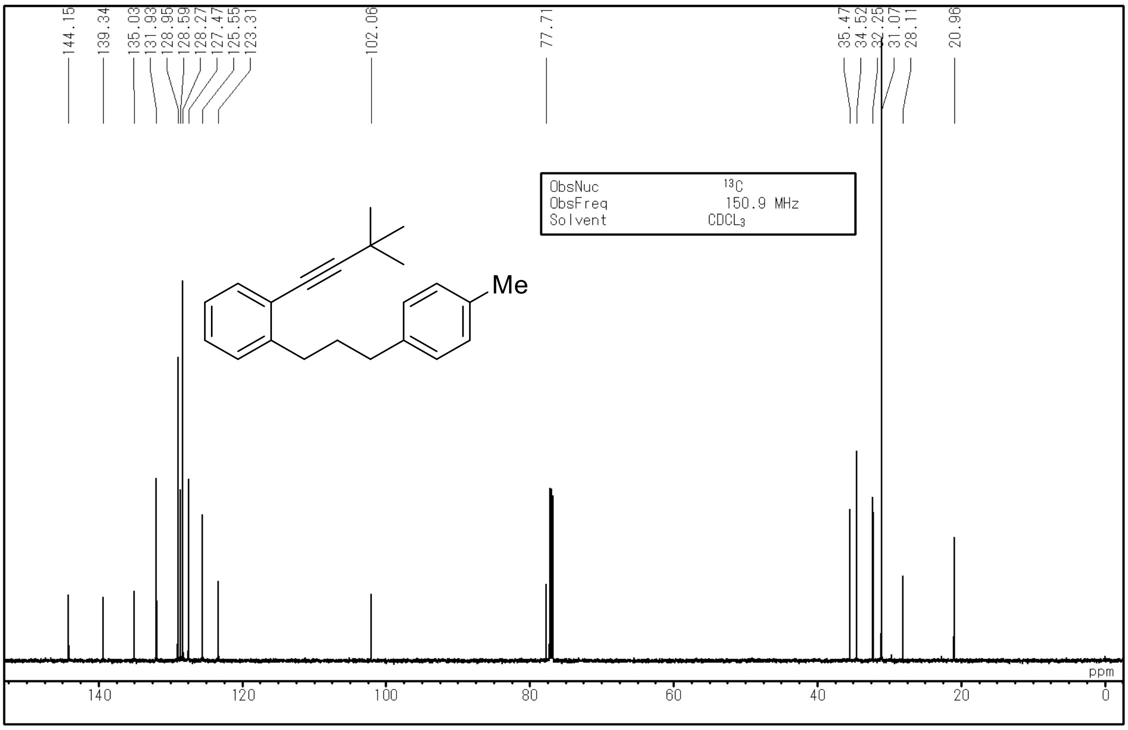
2-(3,3-Dimethylbut-1-yn-1-yl)-4-methyl-1-(3-phenylpropyl)benzene (8k).



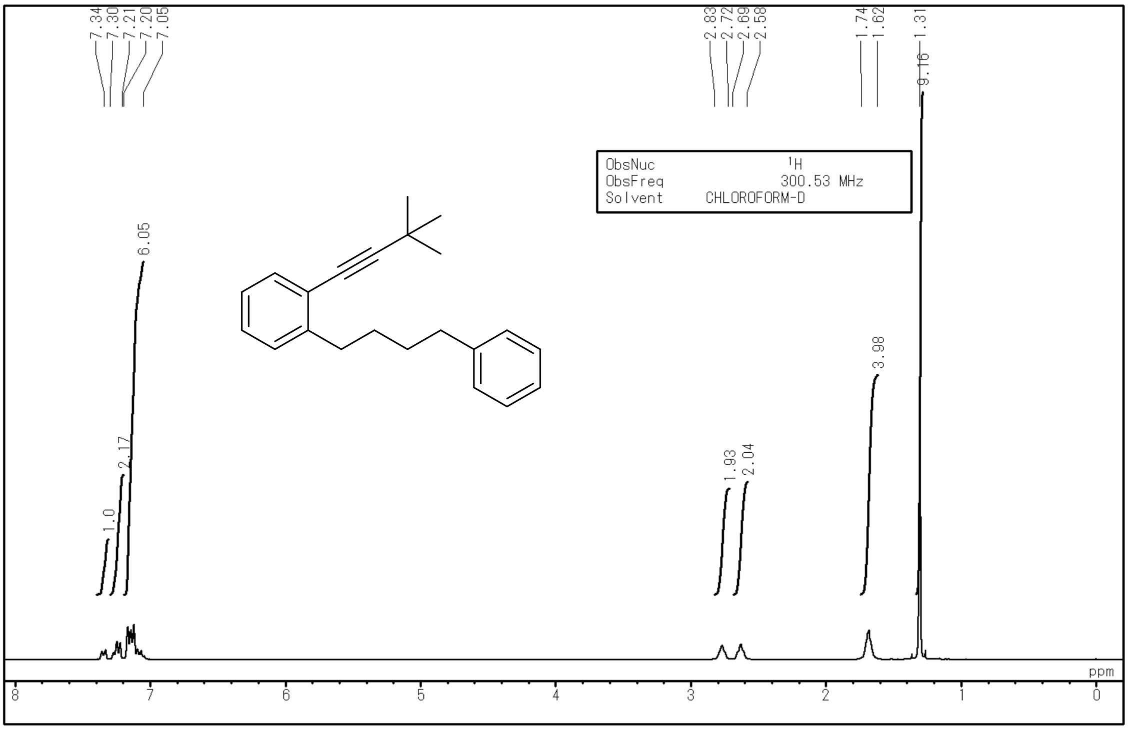


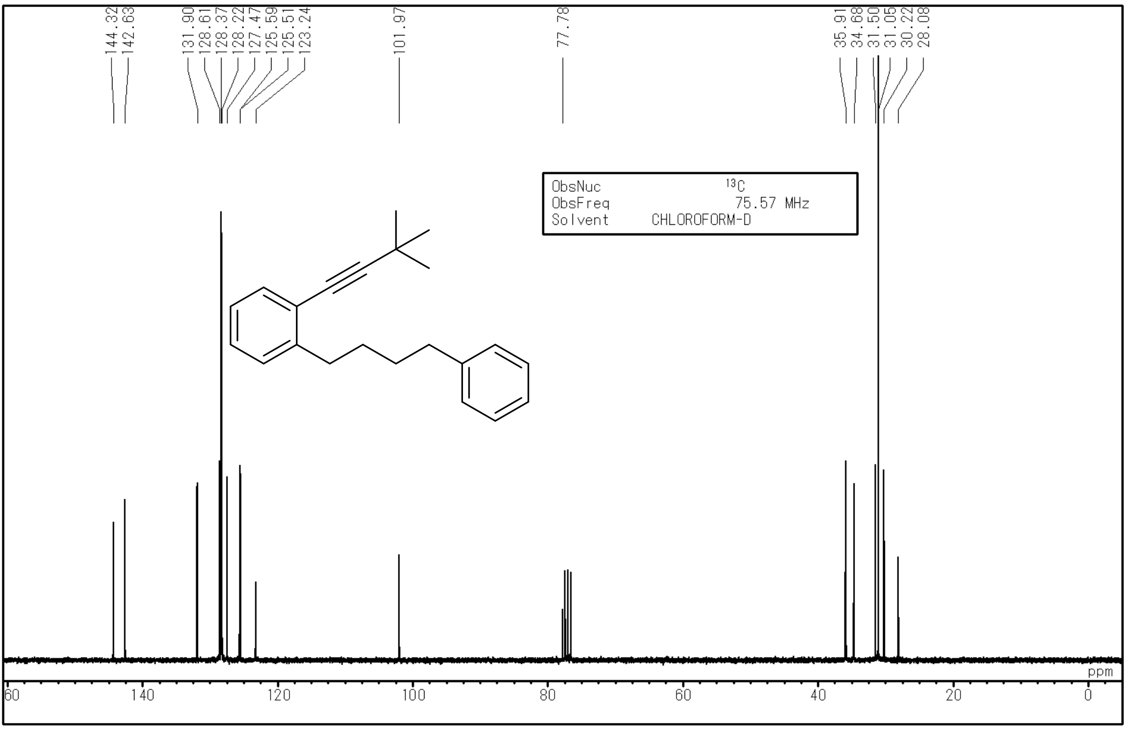
1-(3,3-Dimethylbut-1-yn-1-yl)-2-(3-(*p*-tolyl)propyl)benzene (8l).



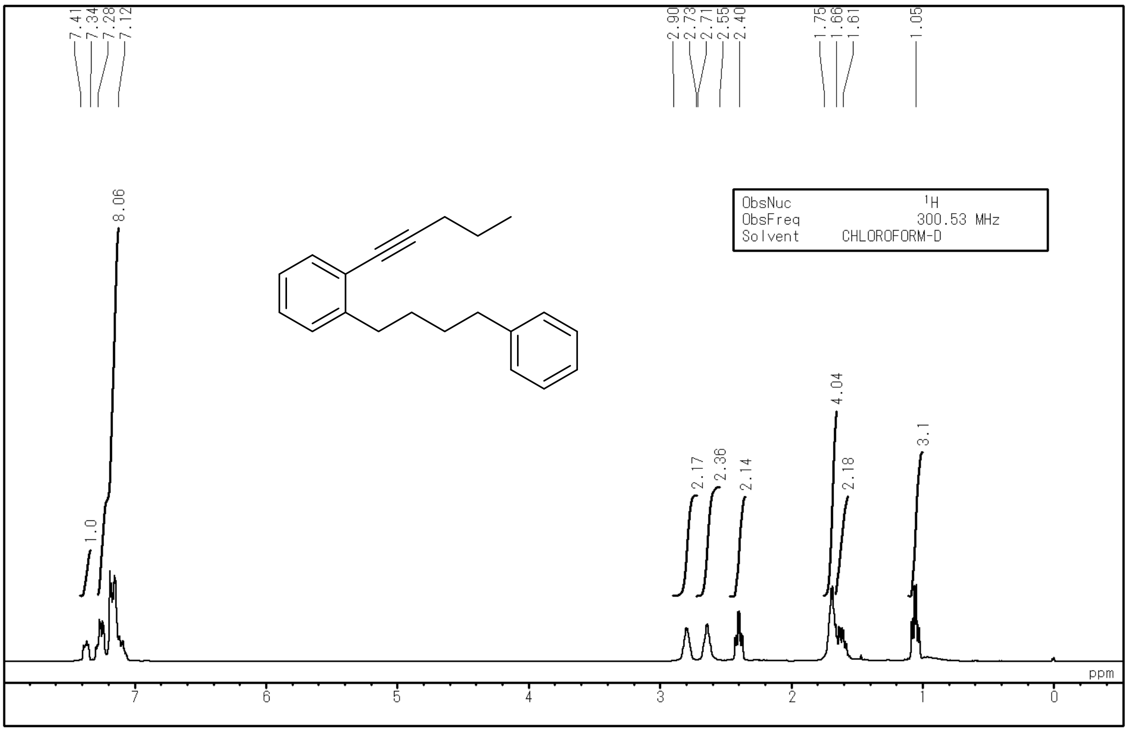


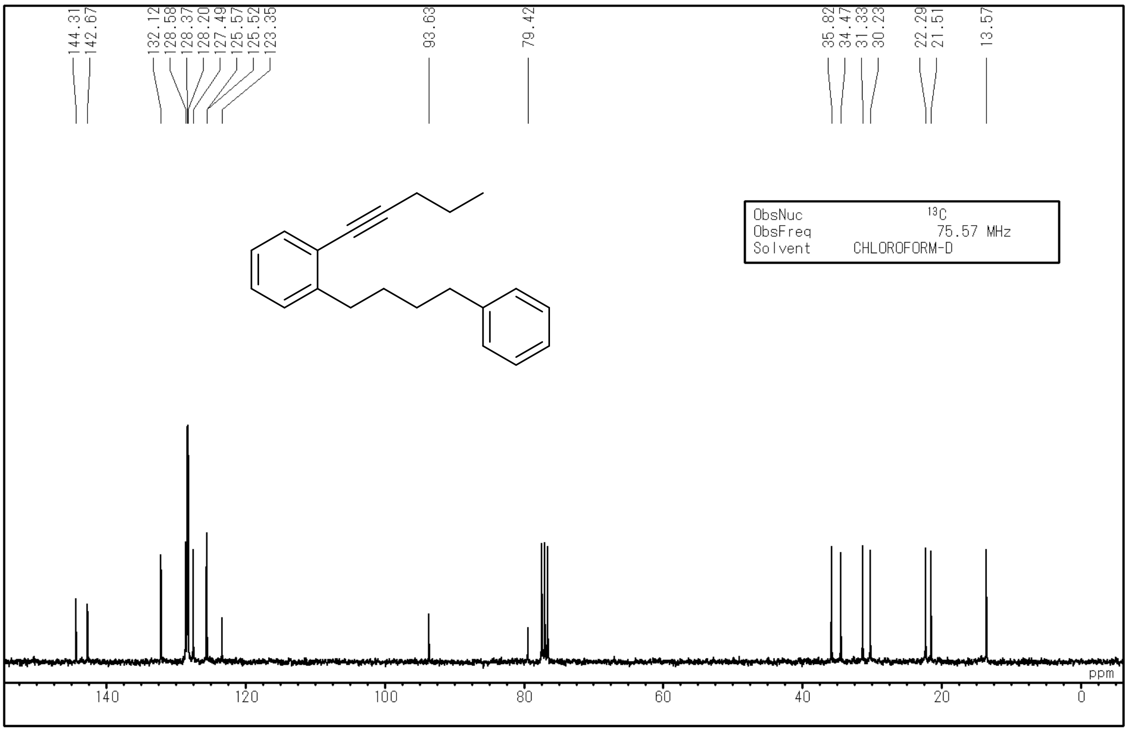
1-(3,3-Dimethylbut-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9a).



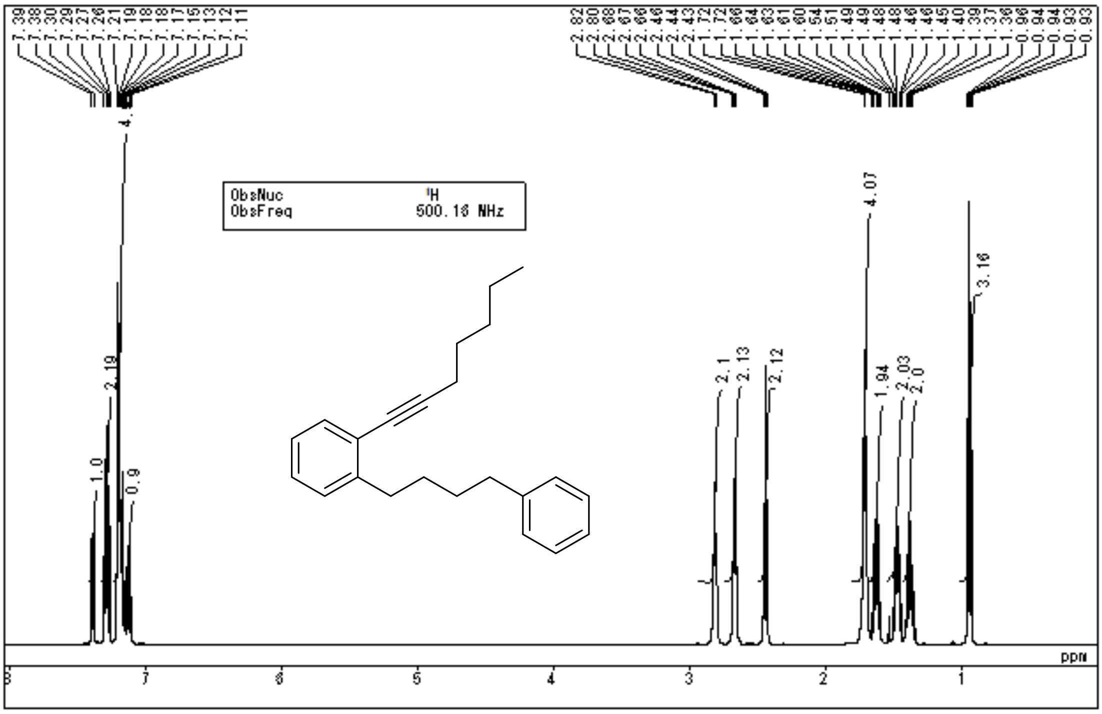


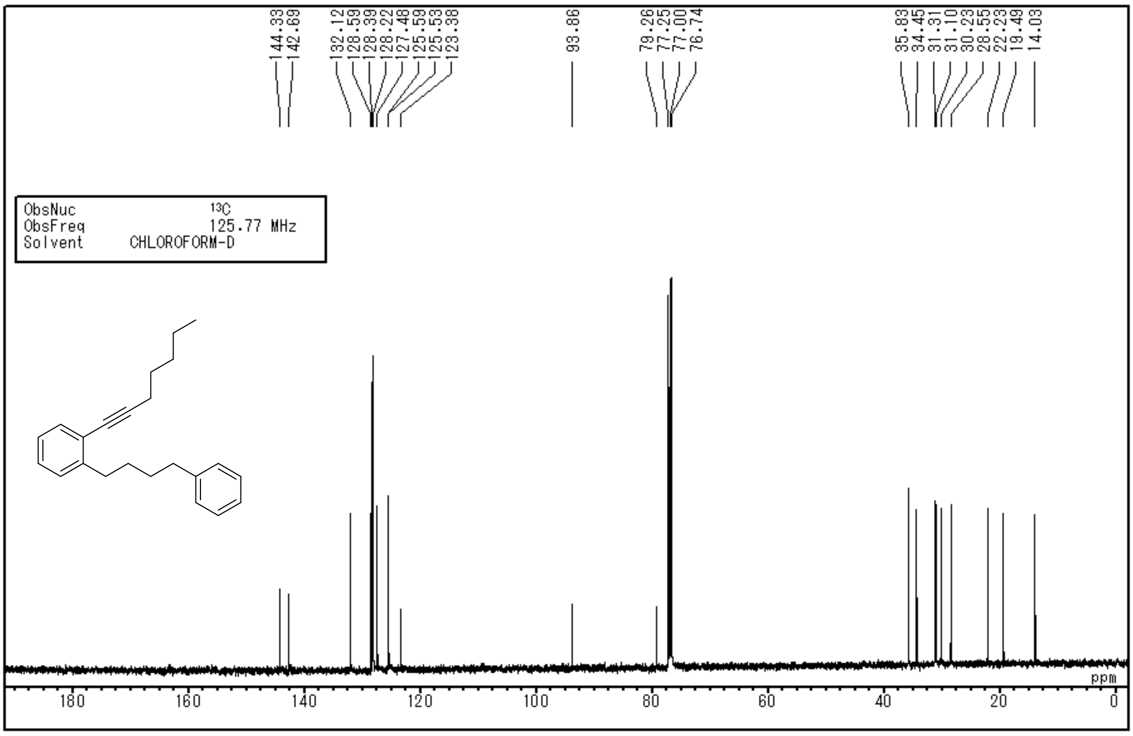
1-(Pent-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9b).



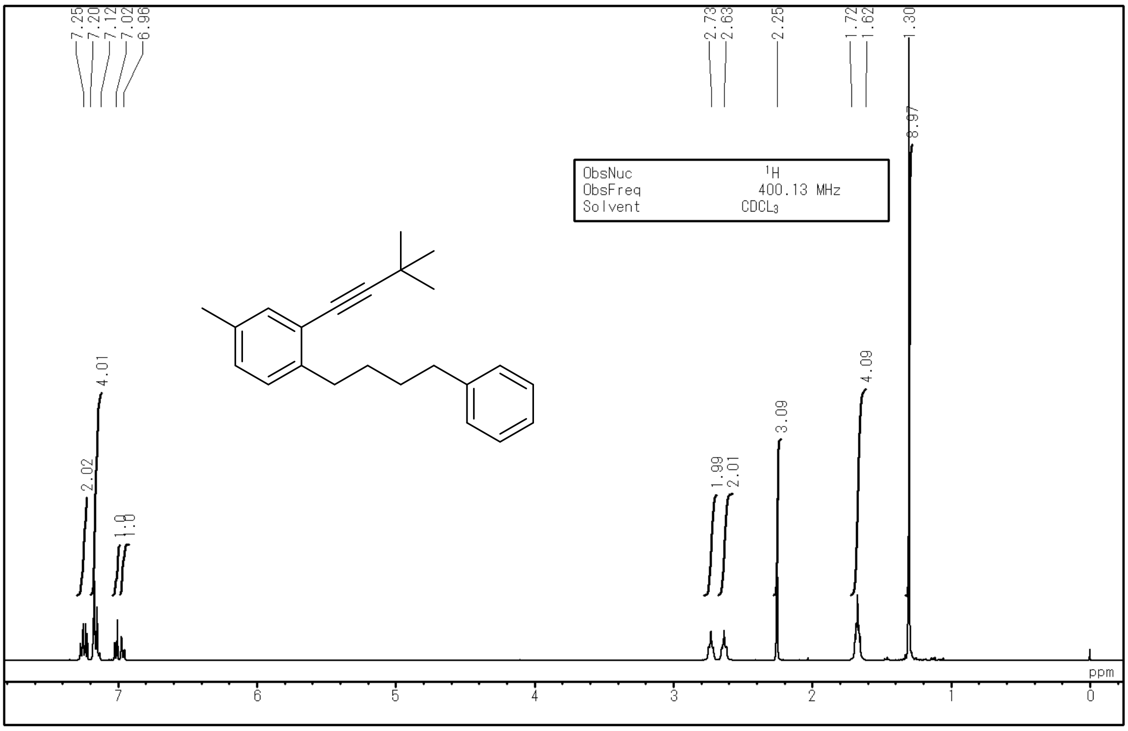


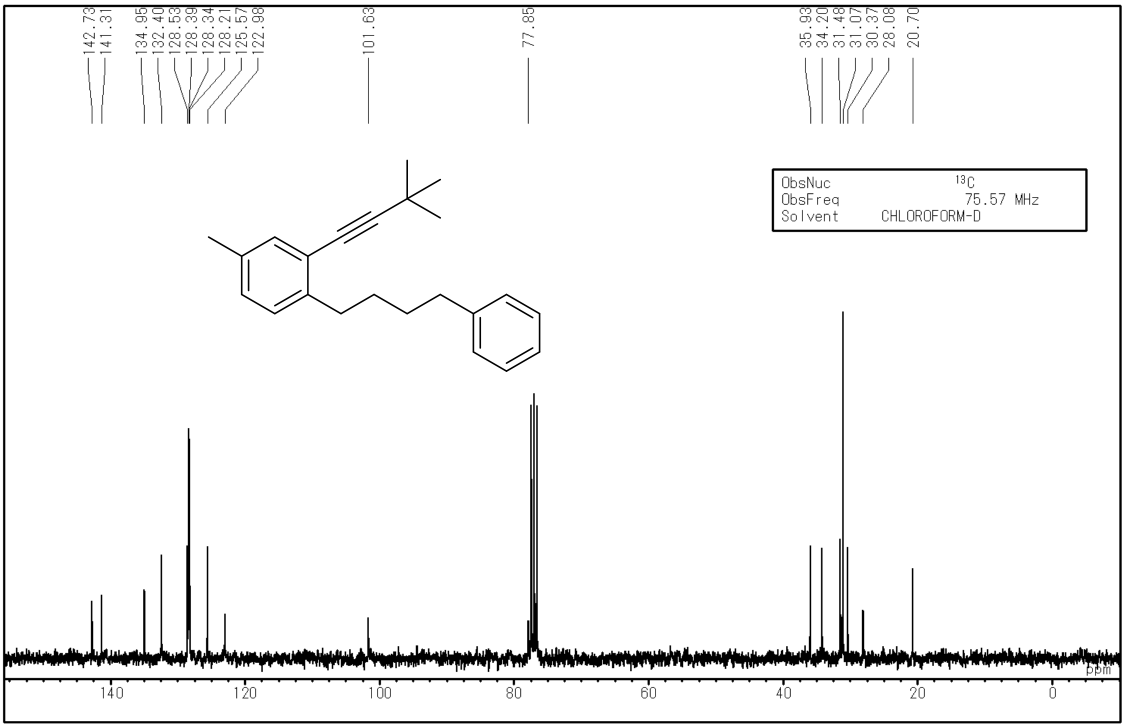
1-(Hept-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9c).



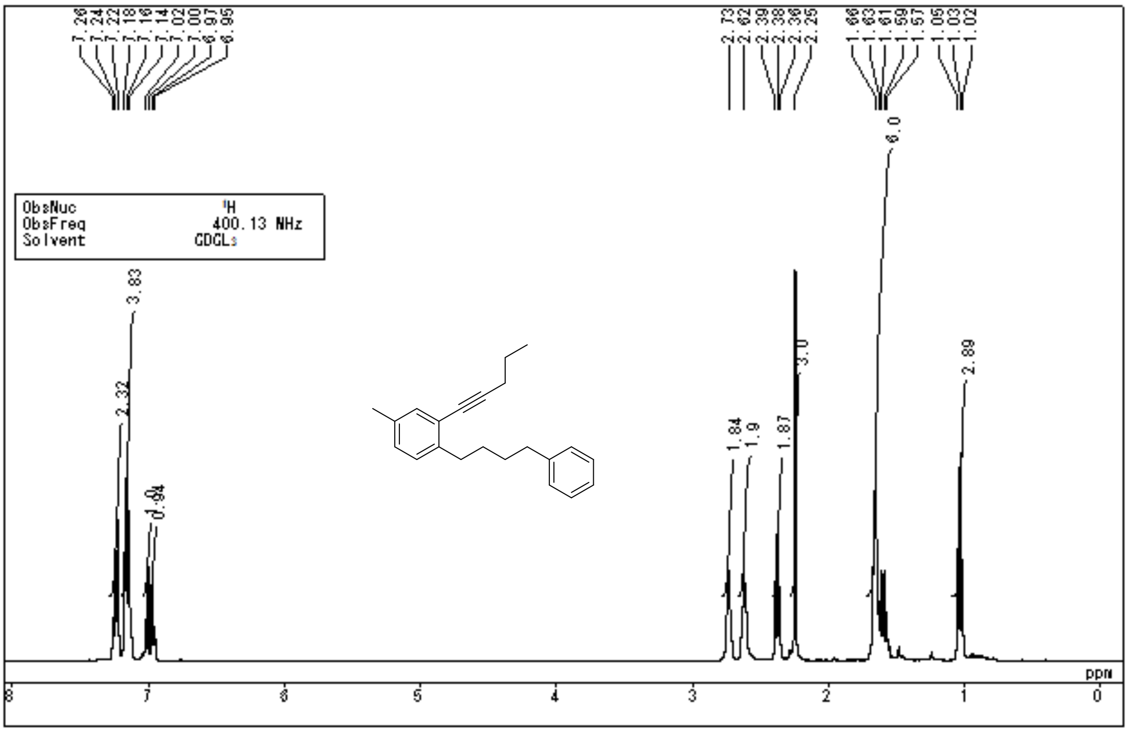


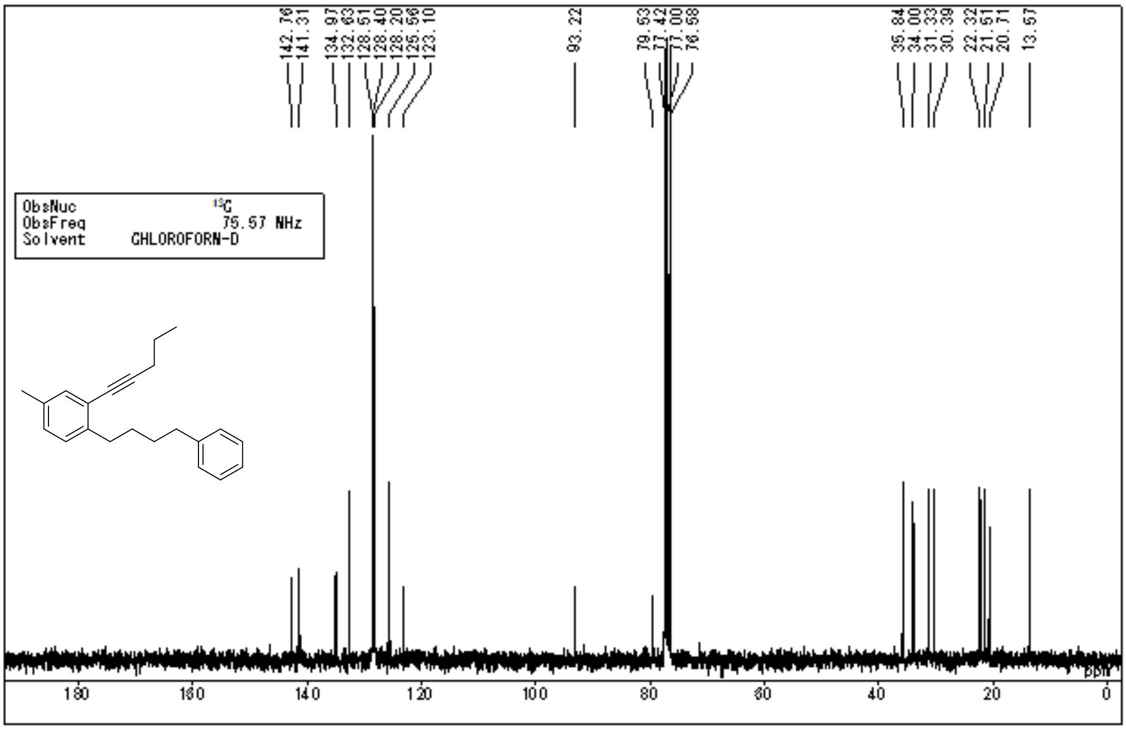
2-(3,3-Dimethylbut-1-yn-1-yl)-4-methyl-1-(4-phenylbutyl)benzene (9d).



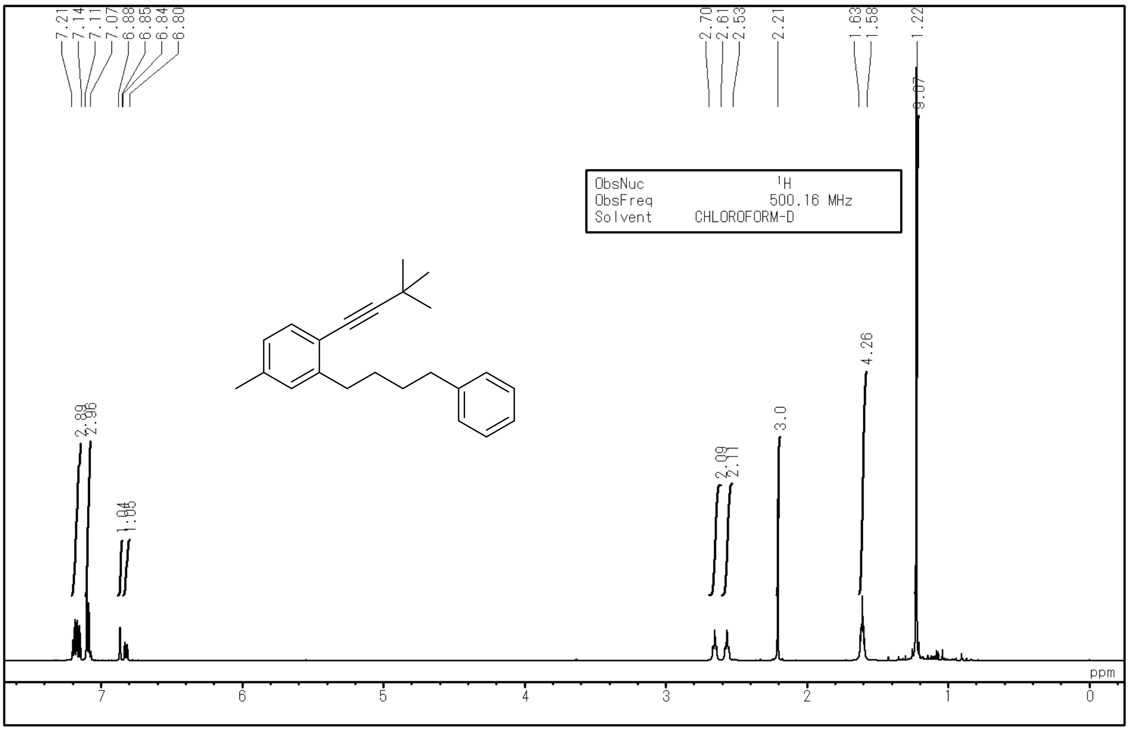


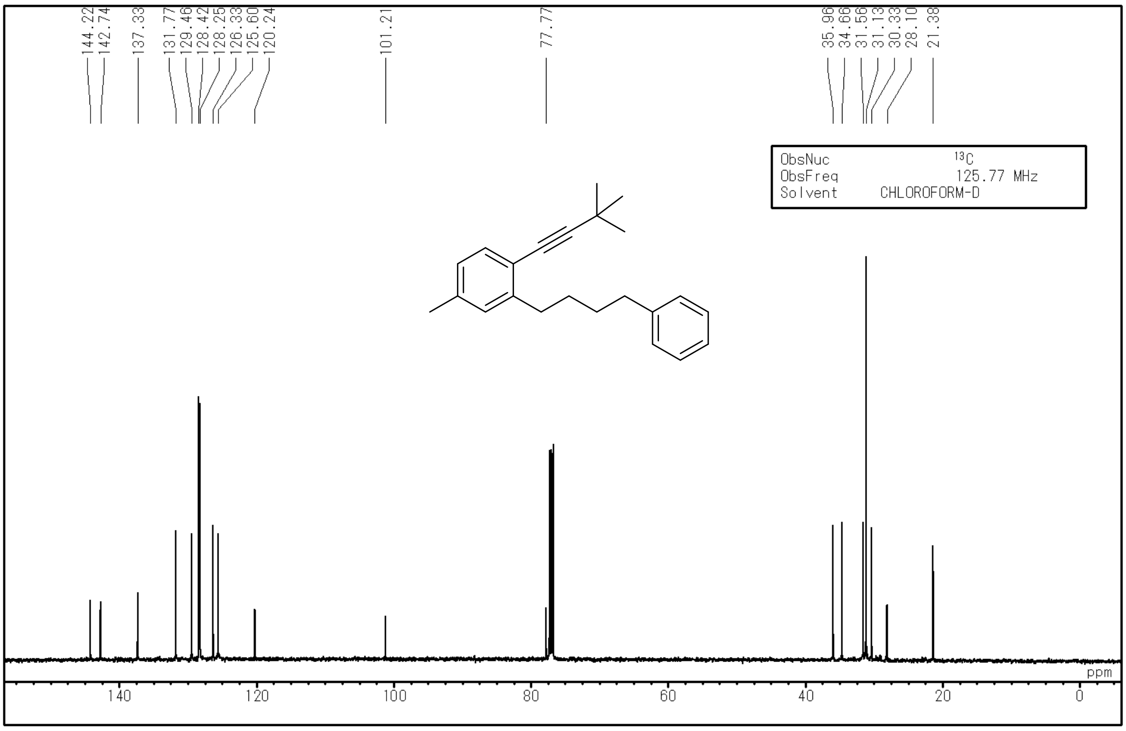
4-Methyl-2-(pent-1-yn-1-yl)-1-(4-phenylbutyl)benzene (9e).



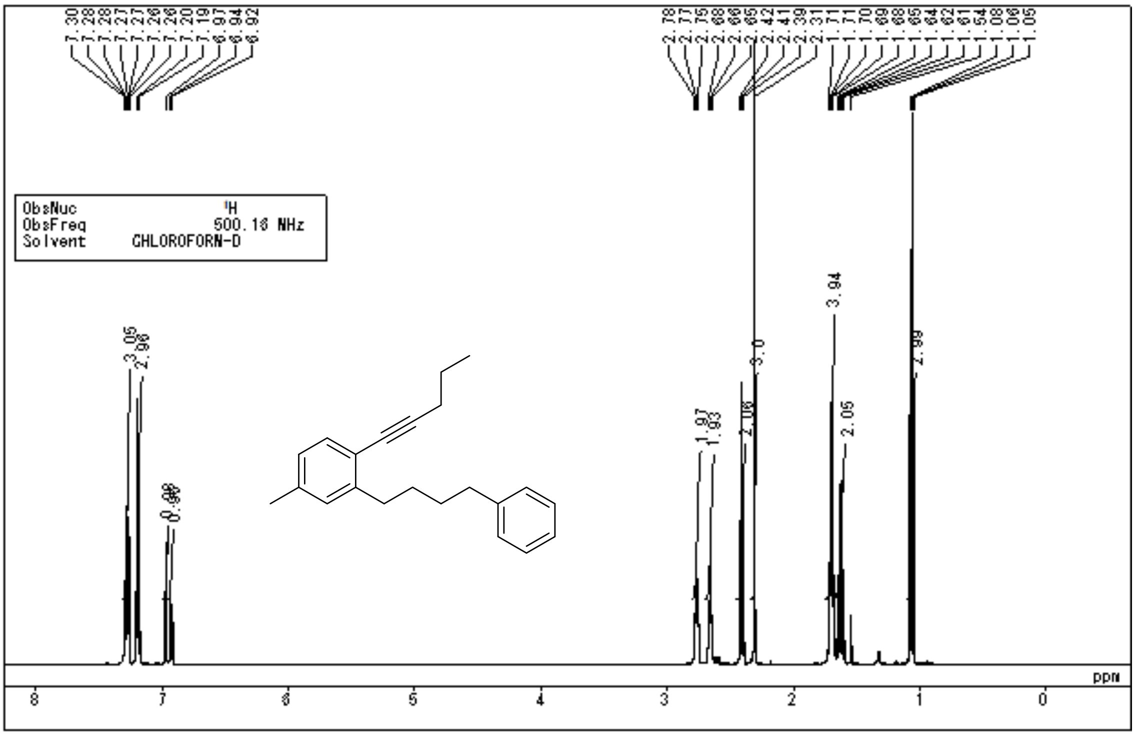


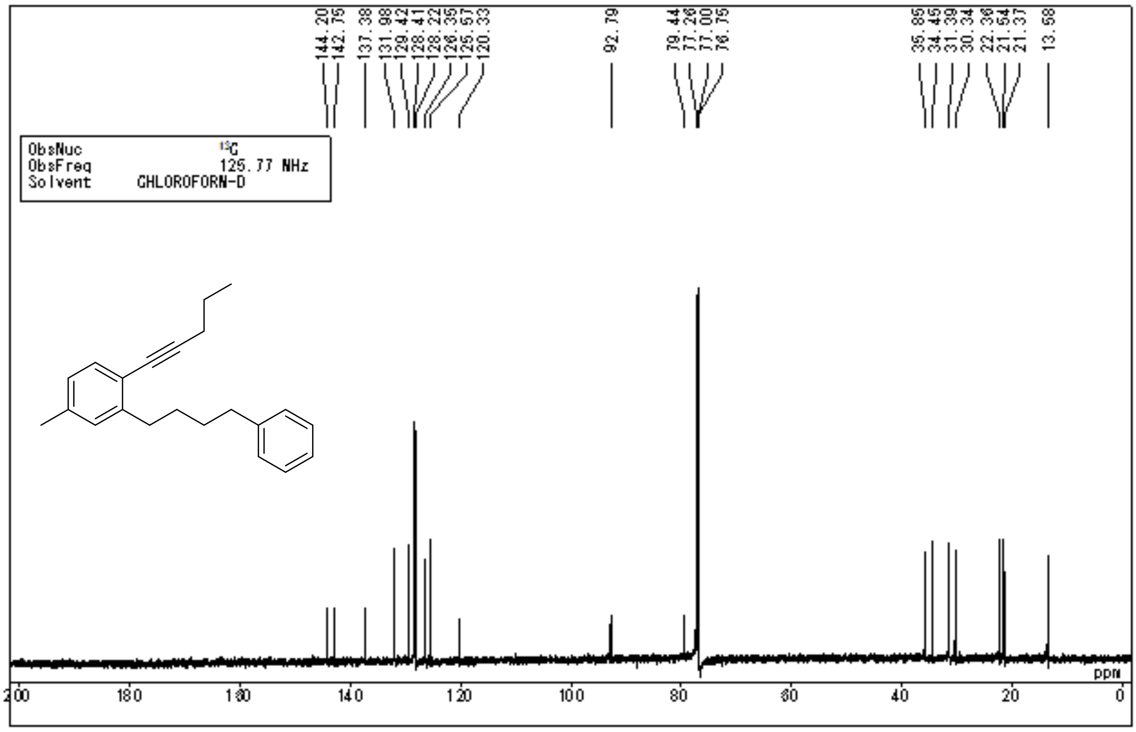
1-(3,3-Dimethylbut-1-yn-1-yl)-4-methyl-2-(4-phenylbutyl)benzene (9f).





4-Methyl-1-(pent-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9g).





(*Z*)-12-(2,2-Dimethylpropylidene)-2-methoxy-3-((*Z*)-1-(5-methoxy-2-(3-phenylpropyl)phenyl)-3,3-dimethylbut-1-en-1-yl)-5,6,7,12-tetrahydrodibenzo[*a,d*]cyclooctane (10).