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Hypervalent-iodine (Ⅲ) Oxidation of Hydrazones to Diazo Compounds and One-pot Nickel (Ⅱ)-catalyzed Cyclopropanation

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General

Alkenes **2a**, **2b**, **2g**-**2j**, **2m** and norbornene were used as received from commercially available sources, or synthesized according to literature.[1] Iodosobenzene was freshly synthesized and dried according to literature.[2] Petroleum ether refers to the fraction boiling in the 60-90 °C range. Column chromatography was performed with Silica Gel (200-300 mesh). ^{1}H and ^{13}C spectra were recorded at 500.0 MHz and 125.0 MHz on a Bruker DRX 500 spectrometer in $CDCl_3$ and tetramethylsilane (TMS) was used as a reference. Melting points were measured on a Yamato melting point apparatus Model MP-21 and were uncorrected. GC-MS were performed on an ISQ Trace 1300 (electrospray ionization: EI). For thin-layer chromatography (TLC), Sorbent silica gel XHL TLC plates (130815) were used. High resolution mass spectra (EI) were obtained using Waters Micromass GCT Premier (electron energy: 70 eV).

General procedure for the synthesis of *N*-unsubstituted hydrazones[3]

The corresponding ketone (10 mmol) was added to a solution of hydrazine hydrate (80% solution in water, 66 mmol, 4.0 mL), and *p*-toluenesulfonic acid (0.4 mmol, 0.078g) in absolute alcohol (5.0 mL). The mixture was heated at 75 °C until the starting carbonyl compound was completely consumed (monitored by TLC). The reaction mixture was cooled to room temperature, kept stirring and ice-cold water was added dropwise until the mass became completely thickened. The precipitate was filtered and washed with cold water (3×10 mL) and dried in air.

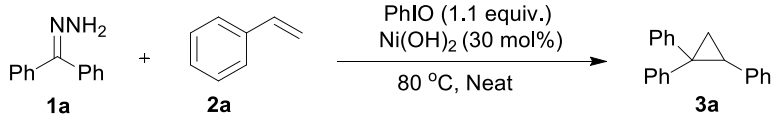
General procedure for the one-pot cyclopropanation of alkenes with hydrazones

A screwed tube was charged with the corresponding hydrazone (0.5 mmol), $Ni(OH)_2$ (30 mol%, 0.014g) and alkene (4.0 equiv.). For solid alkenes, chloroform (0.2 mL) was used as solvent. Magnetic stirrer with oil bath was used and pre-heated to 80 °C. The screwed tube was then put to the oil bath and at the same time iodosobenzene (1.1 eq., 0.121g) was added. The reaction was stirred at 80 °C until total disappearing of the red-violet color which indicated the completion of the reaction. The reaction mixture was purified by column chromatography using petroleum ether or petroleum ether/ ethyl acetate as eluent.

Influence of alkenes equivalents

A screwed tube was charged with benzophenone hydrazone (0.5 mmol), $Ni(OH)_2$ (30 mol%, 0.014g) and styrene (x equiv.). The reaction was stirred at 80 °C until total disappearing of the red-violet color which indicated the completion of the reaction. The yield was determined by 1H-NMR using CH_2I_2 as internal standard.

Table S1. Yield of cyclopropane with different equivalents of styrene



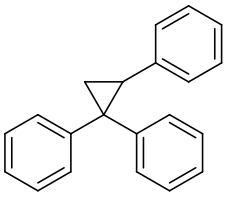
Entry	Styrene (equiv.)	Yield (%)[a]
1	2	55
2	3	68
3	4	74 (72[b])
4	5	71

[a] The yield was determined by 1H-NMR using CH_2I_2 as internal standard.

[b] Isolated yield.

Spectroscopic data of products

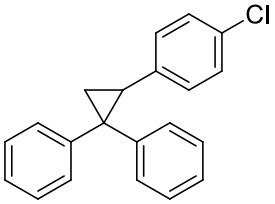
1. Cyclopropane-1,1,2-triyltribenzene (3a)[4]



White solid; **m.p.** 51-52 °C (Lit[5] m.p. 51-52 °C); $\mathbf{R_f}$ = 0.39 (petroleum ether); Yield: 72%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35-6.90 (comp, 15H), 2.89 (dd, *J* = 9.0 Hz, *J* = 6.5 Hz, 1H), 2.02 (dd, *J* =6.5 Hz, *J* = 5.5 Hz, 1H), 1.84 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 1H).

2. (2-(4-Chlorophenyl)cyclopropane-1,1-diyl)dibenzene (3b)[4]

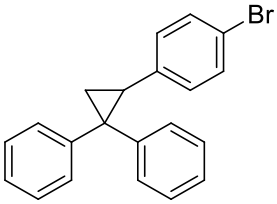


Colorless oil; $\mathbf{R_f}$ = 0.38 (petroleum ether); Yield: 73%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28-6.77 (comp, 14H), 2.82 (dd, *J* = 9.0 Hz, *J* = 6.5 Hz, 1H), 1.94 (dd, *J* = 6.5, *J* = 5.5 Hz, 1H), 1.83 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.7, 139.9, 137.5, 131.4, 131.2, 129.2, 128.5, 128.2, 127.8, 127.4, 126.5, 126.1, 39.6, 31.9, 21.2.

3. (2-(4-Bromophenyl)cyclopropane-1,1-diyl)dibenzene (3c)[4]

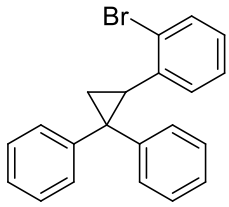


Colorless oil; $\mathbf{R_f}$ = 0.37 (petroleum ether); Yield: 74%.

^{1}H NMR (500 MHz, $CDCl_3$): δ =7.34-7.15 (comp, 12H), 6.78 (d, *J* = 8.5 Hz, 2H) 2.86 (dd, *J* = 9.0 Hz, *J* = 6.5 Hz, 1H), 2.01-1.98 (m, 1H), 1.88 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.7, 139.9, 138.0, 131.2, 130.8, 129.7, 128.5, 128.2, 127.4, 126.6, 126.2, 119.5, 39.6, 32.0, 21.3.

4. (2-(2-Bromophenyl)cyclopropane-1,1-diyl)dibenzene (3d)



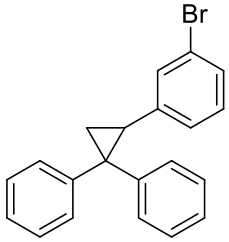
White solid; **m.p.** 104-105 °C; $\mathbf{R_f}$ = 0.39 (petroleum ether); Yield: 67%.

^{1}H NMR (500 MHz, $CDCl_3$): δ =7.56-6.59 (comp, 14H), 3.23 (dd, *J* = 9.0 Hz, *J* = 6.5 Hz, 1H), 2.16-2.14 (m, 1H), 1.72 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.6, 141.4, 139.8, 131.3, 131.1, 129.2, 128.7, 128.5, 128.2, 127.5, 126.6, 126.3, 126.2, 121.9, 39.8, 31.9, 21.1.

HRMS (EI, 70 eV): m/z (M^+) calcd for $C_{21}H_{17}Br$: 348.0514, found 348.0511.

5. (2-(3-Bromophenyl)cyclopropane-1,1-diyl)dibenzene (3e)



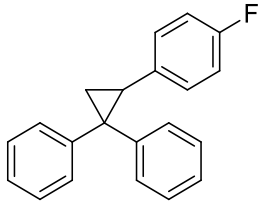
White solid; **m.p.** 91-92 °C; $\mathbf{R_f}$ = 0.40 (petroleum ether); Yield: 71%.

^{1}H NMR (500 MHz, $CDCl_3$): δ =7.35-6.94 (comp, 13H), 6.74 (d, *J* = 7.5 Hz, 1H), 2.85 (dd, *J* = 9.0 Hz, *J* = 6.5 Hz, 1H), 2.01-1.99 (m, 1H), 1.86 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.6, 141.4, 139.8, 131.3, 131.1, 129.2, 128.7, 128.5, 128.2, 127.5, 126.6, 126.3, 126.2, 121.9, 39.8, 31.9, 21.1.

HRMS (EI, 70 eV): m/z (M^+) calcd for $C_{21}H_{17}Br$: 348.0513, found 348.0511.

6. (2-(4-Fluorophenyl)cyclopropane-1,1-diyl)dibenzene (3f)[4]

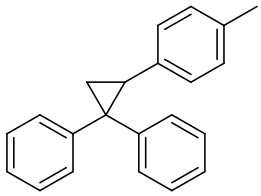


Colorless oil; $\mathbf{R_f}$ = 0.40 (petroleum ether); Yield: 74%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.36-7.13 (comp, 14H), 2.90 (dd, *J* = 9.0 Hz, *J* = 6.5 Hz, 1H), 2.01-1.98 (m, 1H), 1.86 (dd, *J* = 9.0 Hz, *J* = 5.5Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.2 (d, *J* = 242.5 Hz), 146.9, 140.1, 134.5, 131.2, 129.3 (d, *J* = 7.5 Hz), 128.5, 128.1, 127.5, 126.4, 126.1, 114.6 (d, *J* = 7.5 Hz), 39.2, 31.7, 21.0.

7. (2-(*p*-Tolyl)cyclopropane-1,1-diyl)dibenzene (3g)[4]

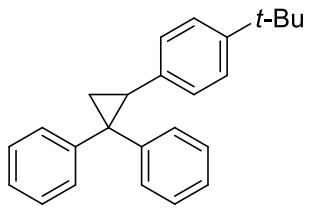


Colorless oil; $\mathbf{R_f}$ = 0.39 (petroleum ether); Yield: 73%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37-7.13 (comp, 10H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 2.89 (dd, *J* = 9.0 Hz, *J* = 6.5 Hz, 1H), 2.30 (s, 3H), 2.01 (dd, *J* = 6.5 Hz, *J* = 5.5 Hz, 1H), 1.86 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.3, 140.5, 135.7, 135.1, 131.3, 128.5, 128.4, 128.0, 127.9, 127.5, 126.3, 125.9, 39.2, 32.3, 21.1, 21.1.

8. (2-(4-(*tert*-Butyl)phenyl)cyclopropane-1,1-diyl)dibenzene (3h)[4]



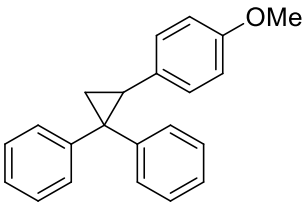
Light yellow solid; **m.p.** 84-85 °C; $\mathbf{R_f}$ = 0.41 (petroleum ether); Yield: 70%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31-7.09 (comp, 12H), 6.79 (d, *J* = 8.5 Hz, 2H), 2.81 (dd, *J* = 9.0 Hz, *J* = 6.5 Hz, 1H), 1.93 (dd, *J* = 6.5, *J* = 5.5 Hz, 1H), 1.82 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 1H), 1.25 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.4, 147.2, 140.4, 135.7, 131.3, 128.3, 127.9, 127.6, 127.4, 126.2, 125.8, 124.5, 39.1, 34.3, 32.1, 31.3, 21.2.

HRMS (EI, 70 eV): m/z (M^+) calcd for $C_{25}H_{26}$: 326.2035, found 326.2029.

9. (2-(4-Methoxyphenyl)cyclopropane-1,1-diyl)dibenzene (3i)[4]

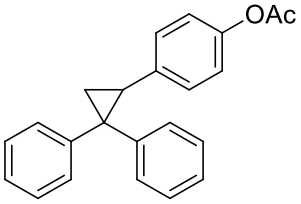


Light yellow solid; **m.p.** 114-115 °C; **R_f** = 0.55 (petroleum ether/ ethyl acetate = 10:1); Yield: 63%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28-7.07 (comp, 10H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.65 (d, *J* = 8.5 Hz, 2H), 3.72 (s, 3H), 2.81 (dd, *J* = 9.0 Hz, *J* = 6.5 Hz, 1H), 1.92-1.90 (m, 1H), 1.79 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.6, 147.2, 140.4, 131.3, 130.8, 128.9, 128.3, 128.0, 127.4, 126.2, 125.8, 113.2, 55.2, 38.8, 31.9, 21.0.

10. 4-(2,2-Diphenylcyclopropyl)phenyl acetate (3j)



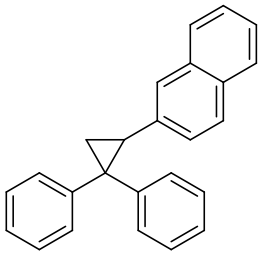
Light yellow solid; **m.p.** 84-85 °C; **R_f** = 0.29 (petroleum ether/ethyl acetate = 10:1); Yield: 68%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34-6.88 (comp, 14H), 2.91-2.89 (m, 1H), 2.27 (s, 3H), 2.00-1.99 (m, 1H), 1.89-1.86 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.5, 148.7, 146.9, 140.1, 136.5, 131.3, 128.8, 128.5, 128.1, 127.5, 126.5, 126.1, 120.8, 39.4, 31.9, 21.3, 21.2.

HRMS (EI, 70 eV): m/z (M^+) calcd for $C_{23}H_{20}O_2$: 326.1463, found 326.1461.

11. 2-(2,2-Diphenylcyclopropyl)naphthalene (3k)



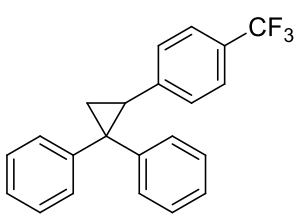
Colorless oil; **R_f** = 0.22 (petroleum ether); Yield: 72%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73-6.94 (comp, 17H), 3.03 (dd, *J* = 9.0 Hz, *J* = 6.5 Hz, 1H), 2.14-2.12 (m, 1H), 1.92 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.0, 140.2, 136.5, 133.2, 131.9, 131.2, 128.4, 128.0, 127.5, 127.0, 126.5, 126.3, 126.9, 125.8, 125.1, 39.6, 32.8, 21.3.

HRMS (EI, 70 eV): m/z (M^+) calcd for $C_{25}H_{20}$: 320.1565, found 320.1569.

12. (2-(4-(Trifluoromethyl)phenyl)cyclopropane-1,1-diyl)dibenzene (3l)[4]

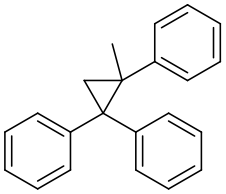


Colorless oil; **R_f** = 0.39 (petroleum ether); Yield: 42%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 9.0 Hz, 4H), 7.20-7.08 (comp, 6H), 6.93 (d, *J* = 8.0 Hz, 2H), 2.88 (dd, *J* = 9.0 Hz, *J* = 6.5 Hz, 1H), 2.02-2.00 (m, 1H), 1.89 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.4, 143.2, 139.6, 131.1, 128.5, 128.2, 128.0, 127.3, 126.6, 126.2, 124.3 (q, *J* = 270 Hz), 124.5.

13. (2-Methylcyclopropane-1,1,2-triyl)tribenzene (3m)[4]

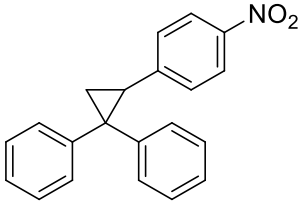


White solid; **m.p.** 70-71 °C; $\mathbf{R_f}$ = 0.34 (petroleum ether); Yield: 46%.

^{1}H NMR (500 MHz, $CDCl_3$): δ =7.53-6.88 (comp, 15H), 2.21 (d, *J* = 5.5 Hz, 2H), 1.55 (d, *J* = 5.5 Hz, 2H), 1.36 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ =143.7, 143.2, 143.1, 130.3, 129.6, 128.5, 128.4, 127.8, 127.5, 126.2, 125.6, 125.3, 42.9, 32.8, 26.2, 25.0.

14. (2-(4-Nitrophenyl)cyclopropane-1,1-diyl)dibenzene (3n)



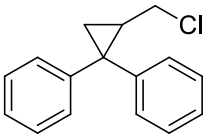
Light yellow solid; **m.p.** 103-104 °C; $\mathbf{R_f}$ = 0.41 (petroleum ether/ethyl acetate = 10:1); Yield: 81%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.95-6.94 (comp, 14H), 2.93 (dd, *J* = 9.0 Hz, *J* = 6.5 Hz, 1H), 2.08 (dd, *J* = 6.5 Hz, *J* = 5.5 Hz, 1H), 1.96 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.4, 146.0, 139.1, 131.0, 128.6, 128.4, 128.3, 127.3, 126.9, 126.4, 122.9, 41.2, 32.3, 22.1.

HRMS (EI, 70 eV): m/z (M^+) calcd for $C_{21}H_{17}NO_2$: 315.1259, found 315.1255.

15. (2-(Chloromethyl)cyclopropane-1,1-diyl)dibenzene (3o)[5]

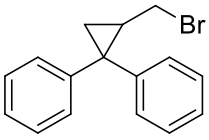


White Oil; $\mathbf{R_f}$ = 0.46 (petroleum ether); Yield: 67%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44-7.17 (comp, 10H), 3.38 (dd, *J* = 11.0 Hz, *J* = 7.5 Hz, 1H), 3.31 (dd, *J* = 11.0 Hz, *J* = 7.5 Hz, 1H), 2.14-2.08 (m, 1H), 1.46-1.42 (comp, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.8, 140.2, 130.5, 128.6, 128.5, 128.0, 127.1, 126.3, 43.7, 33.0, 27.9, 20.0.

16. (2-(Bromomethyl)cyclopropane-1,1-diyl)dibenzene (3p)[6]

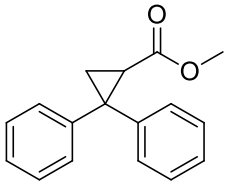


Colorless oil; $\mathbf{R_f}$ = 0.45 (petroleum ether); Yield: 51%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40-7.12 (comp, 10H), 3.20-3.12 (m, 1H), 2.16-2.11 (m, 1H), 1.46-1.42 (m, 1H), 1.40-1.37 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.7, 138.9, 129.5, 127.5, 127.4, 126.9, 126.1, 125.3, 38.5, 34.6, 27.3, 20.1.

17. Methyl 2,2-diphenylcyclopropanecarboxylate (3q)[7]

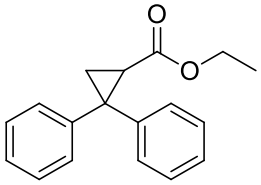


Colorless oil; $\mathbf{R_f}$ = 0.36 (petroleum ether/ ethyl acetate=20:1); Yield: 80%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40-7.38 (comp, 2H), 7.34-7.27 (comp, 6H), 7.26-7.21 (comp, 2H), 3.53 (s, 3H), 2.60 (dd, *J* = 8.0 Hz, 6.0 Hz, 1H), 2.22 (dd, *J* = 6.0 Hz, 5.0 Hz, 1H), 1.66 (dd, *J* = 8.0 Hz, 5.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.30, 144.95, 140.40, 129.81, 128.65, 128.51, 127.79, 127.18, 126.74, 51.86, 40.12, 29.01, 20.34.

18. Ethyl 2,2-diphenylcyclopropanecarboxylate (3r)[8]



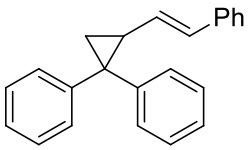
Colorless oil; $\mathbf{R_f}$ = 0.38 (petroleum ether/ ethyl acetate=20:1); Yield: 79%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43-7.42 (comp, 2H), 7.36-7.31 (comp, 6H), 7.29-7.22 (comp, 2H), 4.04-3.95 (comp, 2H), 2.62 (dd, *J* =

8.0 Hz, 6.0 Hz, 1H), 2.25 (dd, *J* = 6.0 Hz, 5.0 Hz, 1H), 1.66 (dd, *J* = 8.0 Hz, 5.0 Hz, 1H), 1.09 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.81, 145.03, 140.42, 129.92, 128.60, 128.43, 127.74, 127.11, 126.66, 60.60, 39.97, 29.20, 20.27, 14.17.

19. (*E*)-(2-styrylcyclopropane-1,1-diyl)dibenzene (3s)[9]

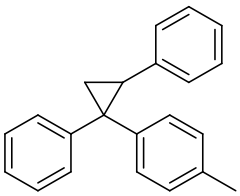


White solid; **m.p.** 60-61 °C (Lit[9] m.p. 60-61 °C); **R_f** = 0.27 (petroleum ether); Yield: 91%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.30-7.24 (comp, 7H), 7.22-7.14 (comp, 4H), 6.61 (d, *J* = 16.0 Hz, 1H), 5.52 (dd, *J* = 16.0 Hz, 10.0 Hz, 1H), 2.46 (dd, J = 15.0 Hz, 9.0 Hz, 1H), 1.78 (dd, *J* = 9.0 Hz, 5.0 Hz, 1H), 1.64 (t, *J* = 5.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.60, 140.47, 136.81, 130.78, 130.16, 128.30, 127.58, 127.49, 126.27, 125.82, 125.01, 124.90, 36.75, 30.28, 22.06.

20. (1-(*p*-Tolyl)cyclopropane-1,2-diyl)dibenzene (mixture of diasteromers 1.1:1) (3t)



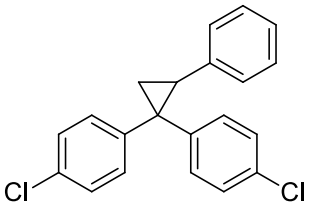
White solid; **m.p.** 56-57 °C ; **R_f** = 0.36 (petroleum ether); Yield: 76%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39-6.95 (comp, 29.4H), 2.95-2.91 (comp, 2.1H), 2.40 (s, 3.3H), 2.31 (s, 3H), 2.07-2.03 (comp, 2.1H), 1.90-1.86 (comp, 2.1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.4, 144.3, 140.6, 139.0, 138.9, 137.3, 135.8, 135.6, 131.2, 131.1, 129.2, 128.8, 128.5, 128.1, 128.1, 127.8, 127.5, 126.3, 125.9, 125.7, 39.2, 39.1, 32.6, 32.4, 21.2, 21.1, 21.1, 20.9.

HRMS (EI, 70 eV): m/z (M^+) calcd for $C_{22}H_{20}$: 284.1565, found 284.1560.

21. 4,4'-(2-Phenylcyclopropane-1,1-diyl)bis(chlorobenzene) (3u)[10]

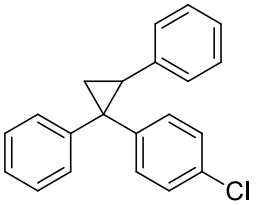


Colorless oil; **R_f** = 0.41 (petroleum ether); Yield: 80%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29-6.90 (comp, 13H), 2.88 (dd, *J* = 9.0 Hz, *J* = 7.0 Hz, 1H), 1.99 (dd, *J* = 7.0 Hz, *J* = 5.5 Hz, 1H), 1.88 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.0, 138.5, 137.9, 132.4, 132.0, 128.8, 128.6, 128.4, 128.0, 126.1, 38.1, 32.6, 20.8.

22. (1-(4-Chlorophenyl)cyclopropane-1,2-diyl)dibenzene (mixture of diasteromers 1:1) (3v)



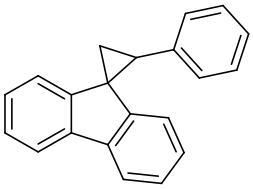
Colorless oil; **R_f** = 0.37 (petroleum ether); Yield: 75%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31-6.88 (comp, 28H), 2.88 (dd, *J* = 9.0 Hz, *J* = 7.0 Hz, 1H), 2.83 (dd, *J* = 9.0 Hz, *J* = 7.0 Hz, 1H), 2.01 (dd, *J* = 7.0 Hz, *J* = 5.5 Hz, 1H), 1.96 (dd, *J* = 7.0 Hz, *J* = 5.5 Hz, 1H), 1.82 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 1H), 1.78 (dd, *J* = 9.0 Hz, *J* = 5.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.5, 145.6, 139.8, 139.0, 138.3, 138.2, 132.5, 132.1, 131.7, 131.1, 128.8, 128.5, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.4, 126.5, 126.2, 125.9, 125.8, 38.8, 38.6, 32.5, 32.4, 20.9, 20.7.

HRMS (EI, 70 eV): m/z (M^+) calcd for $C_{21}H_{17}Cl$: 304.1019, found 304.1018.

23. 2-Phenylspiro[cyclopropane-1,9'-fluorene] (3w)[11]

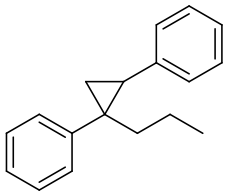


White Solid; **m.p.** 125-126 °C (Lit[11] m.p. 127-128 °C); $\mathbf{R_f}$ = 0.30 (petroleum ether); Yield: 84%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 7.0 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.40-6.91 (comp, 11H), 6.16 (d, *J* = 7.5 Hz, 1H), 3.38 (t, *J* = 8.0 Hz, 1H), 2.22 (d, *J* = 8.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.4, 144.3, 140.5, 139.7, 137.2, 130.2, 128.2, 126.9, 126.9, 126.1, 126.0, 125.8, 121.7, 119.8, 119.7, 118.6, 35.7, 35.1, 22.4.

24. (1-Propylcyclopropane-1,2-diyl)dibenzene (mixture of diasteromers 1.1:1) (3x)



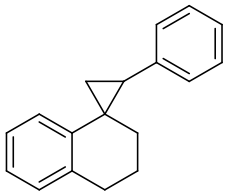
Colorless oil; $\mathbf{R_f}$ = 0.65 (petroleum ether); Yield: 86%.

^{1}H NMR (500 MHz, $CDCl_3$): δ =7.44 (d, *J* = 7.5 Hz, 1H), 7.38-7.00 (comp, 16.8H), 6.75 (d, *J* = 7.0 Hz, 2H), 2.39-2.36 (m, 1H), 2.25-2.22 (m, 1H), 1.98-1.92 (m, 1H), 1.58-1.53 (m, 1H), 1.49-1.29 (comp, 10.5H), 0.92-0.89 (comp, 3.3H), 0.72-0.68 (comp, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.4, 140.6, 140.0, 139.2, 131.0, 129.2, 129.0, 128.3, 128.1, 127.7, 127.5, 126.0, 125.9, 125.0, 45.5, 37.0, 36.2, 33.0, 30.5, 30.1, 20.3, 20.2, 19.0, 16.2, 14.2.

HRMS (EI, 70 eV): m/z (M^+) calcd for $C_{18}H_{20}$: 236.1565, found 236.1562.

25. 2-Phenyl-3',4'-dihydro-2'H-spiro[cyclopropane-1,1'-naphthalene] (mixture of diasteromers 2:1) (3y)



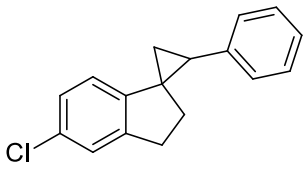
White solid; **m.p.** 68-69 °C ; $\mathbf{R_f}$ = 0.52 (petroleum ether); Yield: 76%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39-6.96 (comp, 25H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.33 (d, *J* = 8.0 Hz, 1H), 3.02-2.87 (comp, 6H), 2.57 (t, *J* = 8.0 Hz, 2H), 2.35-2.27 (comp, 4H), 1.80 (t, *J* = 6.0 Hz, 1H), 1.77-1.36 (comp, 14H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.1, 138.5, 138.3, 138.2, 137.6, 136.9, 130.1, 129.2, 128.9, 128.4, 128.1, 127.8, 126.3, 126.1, 125.8, 124.9, 124.5, 122.0, 36.8, 35.8, 35.7, 30.8, 30.5, 29.1, 27.9, 25.9, 22.8, 21.8, 21.1, 18.2.

HRMS (EI, 70 eV): m/z (M^+) calcd for $C_{18}H_{18}$: 234.1409, found 234.1414.

26. 5'-Chloro-2-phenyl-2',3'-dihydrospiro[cyclopropane-1,1'-indene] (mixture of diasteromers 1.5: 1) (3z)



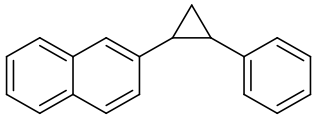
Colorless oil; $\mathbf{R_f}$ = 0.60 (petroleum ether); Yield: 70%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37-6.75 (comp, 19H), 5.89 (d, *J* = 8.0 Hz, 1H), 3.18-3.11 (m, 1H), 3.05-2.86 (comp, 4H), 2.60 (t, *J* = 8.0 Hz, 1H), 2.46-2.38 (comp, 2.5H), 2.24-2.19 (m, 1H), 2.02-1.97 (comp, 1.5H), 1.89-1.83 (comp, 1.5H), 1.52 (d, *J* = 7.0 Hz, 3H), 1.49 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.8, 146.8, 145.6, 142.9, 139.0, 137.9, 131.6, 131.3, 130.1, 128.3, 128.1, 126.7, 126.3, 126.1, 125.6, 124.6, 124.2, 122.2, 119.6, 37.2, 34.9, 33.7, 33.4, 33.2, 30.8, 30.4, 29.3, 20.5, 18.8.

HRMS (EI, 70 eV): m/z (M^+) calcd for $C_{17}H_{15}$: 254.0862, found 254.0868.

27. 2-(2-Phenylcyclopropyl)naphthalene (mixture of diasteromers 2.8:1) (3aa)[12]

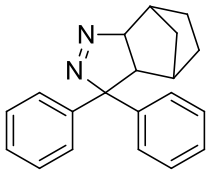


White solid; **m.p.** 77-78 °C (lit[12] pure trans isomer m.p. 79.5-80 °C); $\mathbf{R_f}$ = 0.39 (petroleum ether); Yield: 88%.

^{1}H NMR (500 MHz, $CDCl_3$): δ =7.90-7.07 (comp, 45.6H), 2.72-2.64 (comp, 2H), 2.45-2.35 comp, 5.6H), 1.70-1.59 (comp, 7.6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.6, 140.1, 138.4, 136.3, 135.0, 133.7, 133.4, 132.8, 132.2, 132.0, 130.7, 129.1, 128.6, 128.3, 128.2, 127.9, 127.8, 127.6, 127.6, 127.5, 127.2, 127.1, 126.3, 126.1, 126.0, 125.8, 125.3, 125.1, 124.8, 124.0, 28.5, 28.3, 24.8, 24.7, 18.3, 11.8.

28. 3,3-Diphenyl-3a,4,5,6,7,7a-hexahydro-3H-4,7-methanoindazole (4)[13]

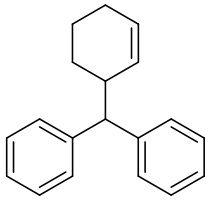


White solid; **m.p.** 154-156 °C (dec) (Lit[13] m.p. 154-156°C); $\mathbf{R_f}$ = 0.55 (petroleum ether/ ethyl acetate=10:1); Yield: 89%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.37-7.20 (comp, 10H), 4.95 (d, *J* = 6.5 Hz, 1H), 2.99 (d, *J* = 9.0 Hz, 1H), 2.56 (d, *J* = 6.5 Hz, 1H), 1.68-1.57 (comp, 2H), 1.48-1.36 (comp, 2H), 1.23-1.20 (m, 1H), 0.72 (d, *J* = 10.5 Hz, 1H), 0.57 (d, *J* = 10.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.5, 142.0, 128.5, 128.0, 127.9, 127.6, 127.2, 126.9, 103.0, 99.9, 48.3, 38.7, 38.3, 32.4, 29.0, 26.0.

29. (Cyclohex-2-en-1-ylmethylene)dibenzene (5)[14]

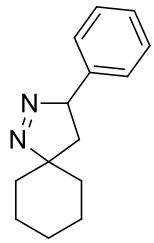


Colorless Oil; $\mathbf{R_f}$ =0.63 (petroleum ether); Yield: 47%.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34-7.14 (comp, 10H), 5.70-5.66 (m, 1H), 5.48-5.45 (m, 1H), 3.61 (d, *J* = 15Hz, 1H), 2.02-1.98 (comp, 2H), 1.77-1.70 (m, 1H), 1.64-1.59 (m, 1H), 1.56-1.48 (m, 1H), 1.24-1.17 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.2, 143.9, 130.1, 128.5, 128.5, 128.4, 128.2, 128.0, 58.2, 38.9, 28.3, 25.5, 21.5.

30. 3-Phenyl-1,2-diazaspiro[4.5]dec-1-ene (6)



Colorless oil; $\mathbf{R_f}$ = 0.30 (petroleum ether/ethyl acetate=9:1); Yield: 43%. Easy decompose to unknown complex in chloroform or long time exposure at 50 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41-7.25 (comp, 5H), 5.45 (t, *J* = 9.0 Hz, 1H), 2.32-2.28 (m, 1H), 2.20-2.16 (m, 1H), 2.00-1.88 (comp, 3H), 1.72-1.68 (m, 1H), 1.61-1.32 (comp, 4H), 1.28-1.32 (m, 1H), 0.91-0.86 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.9, 128.9, 127.7, 127.3, 94.4, 90.3, 37.9, 36.3, 33.2, 25.5, 23.7, 23.3.

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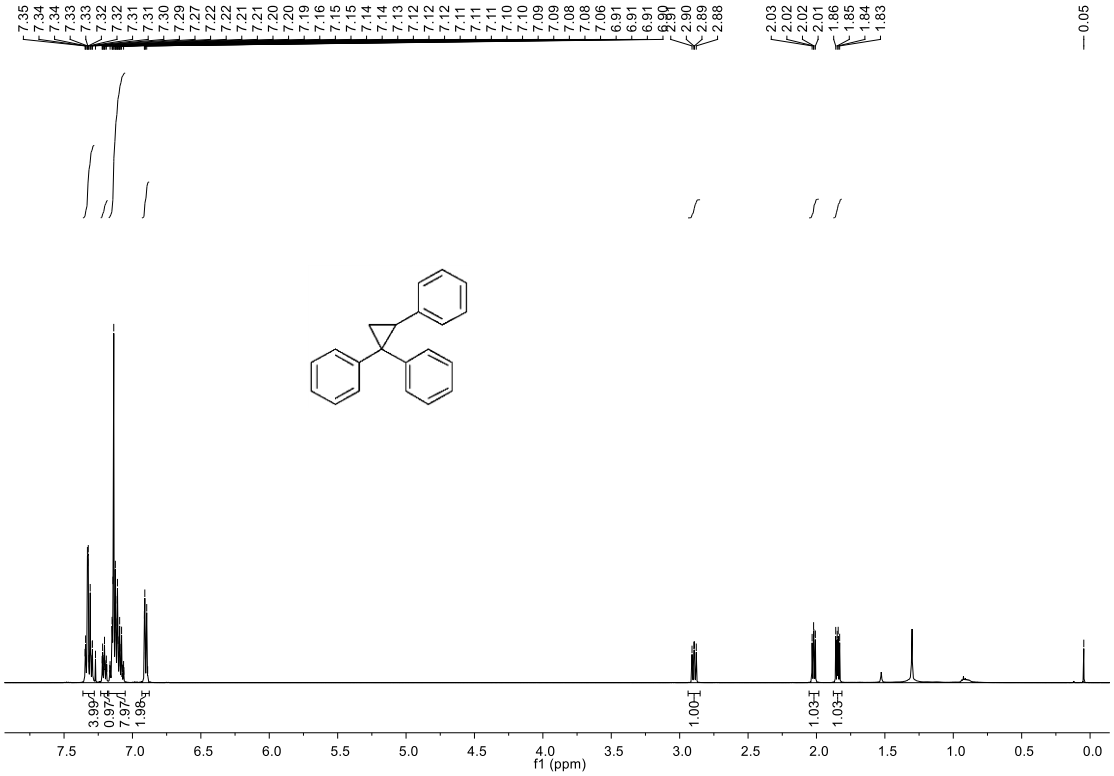
Copies of ^{1}H, ^{13}C spectra

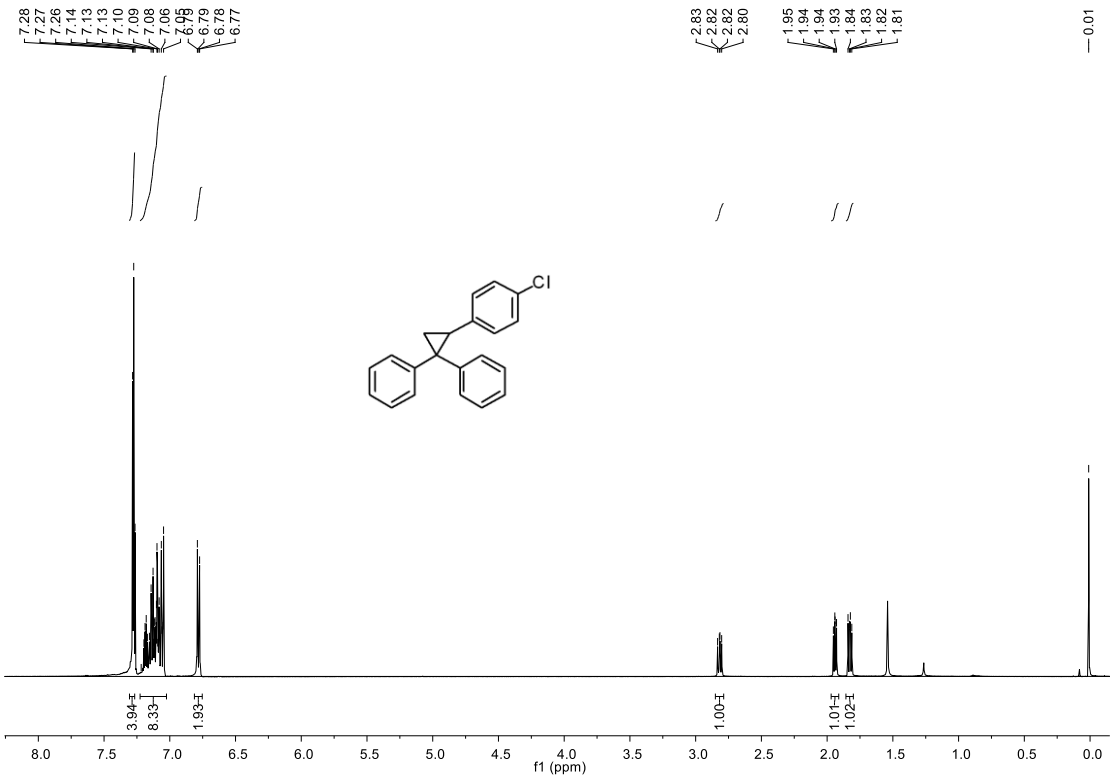
1. Cyclopropane-1,1,2-triyltribenzene (3a)

^{1}H NMR (500 MHz, $CDCl_3$)

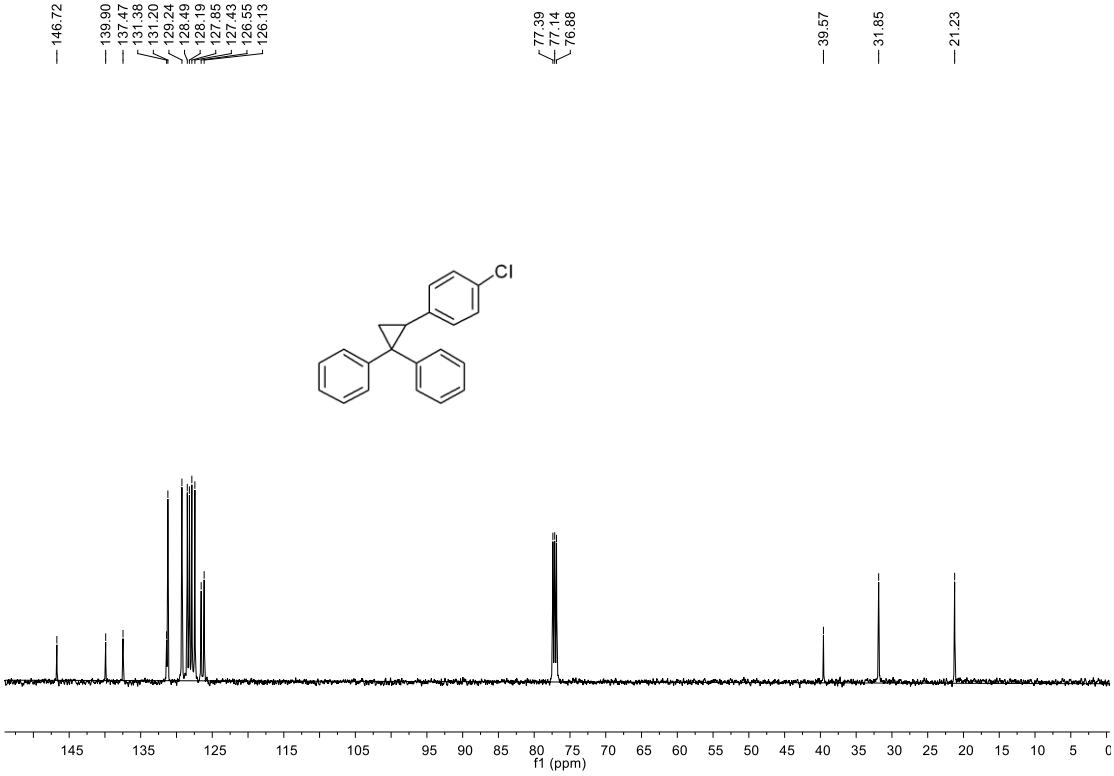


2. (2-(4-Chlorophenyl)cyclopropane-1,1-diyl)dibenzene (3b)

^{1}H NMR (500 MHz, $CDCl_3$)

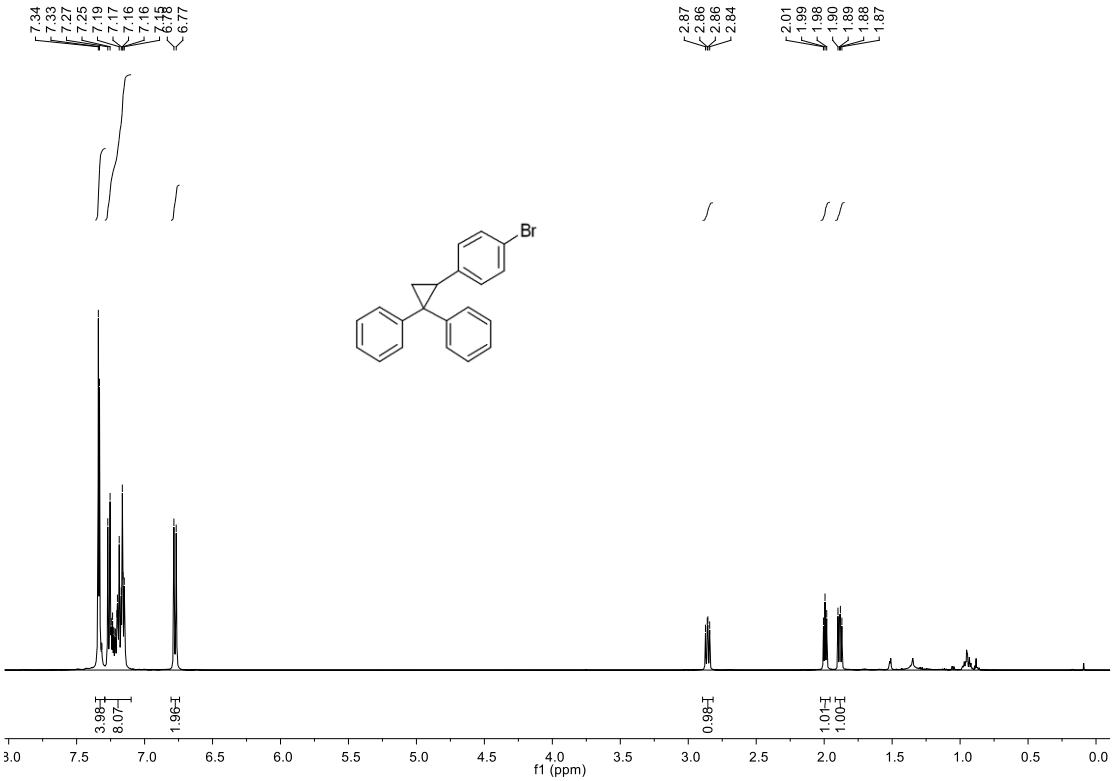


^{13}C NMR (125 MHz, $CDCl_3$)

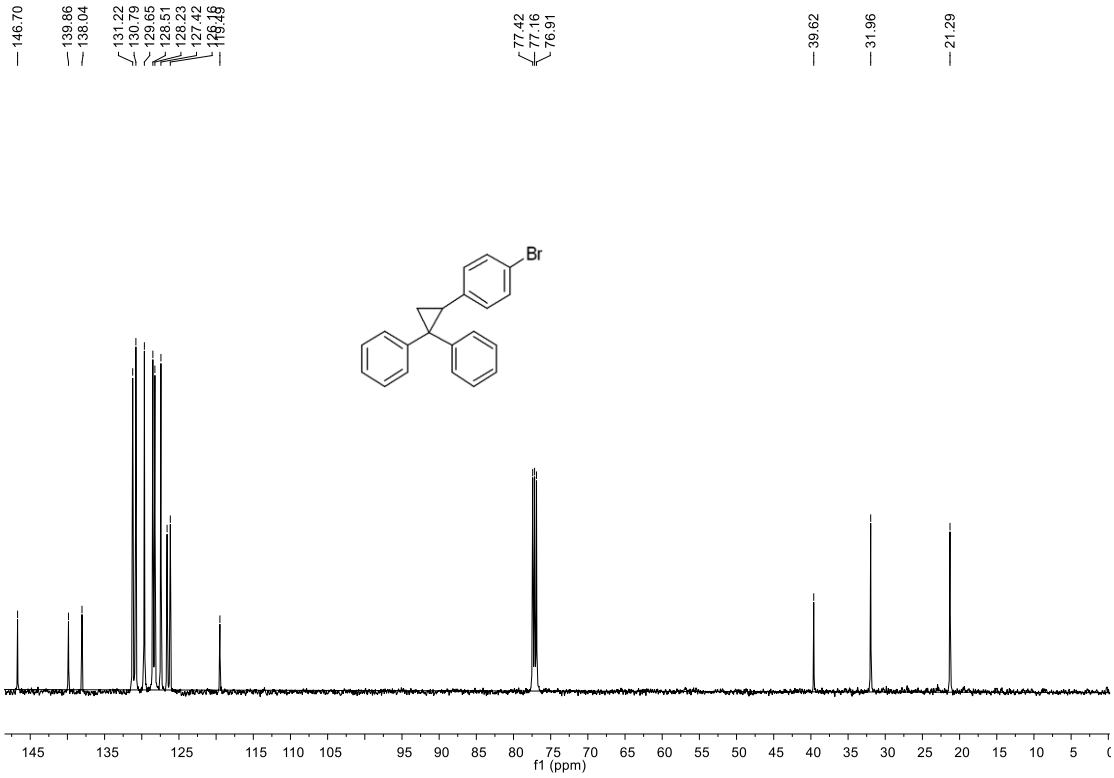


3. (2-(4-Bromophenyl)cyclopropane-1,1-diyl)dibenzene (3c)

^{1}H NMR (500 MHz, $CDCl_3$)

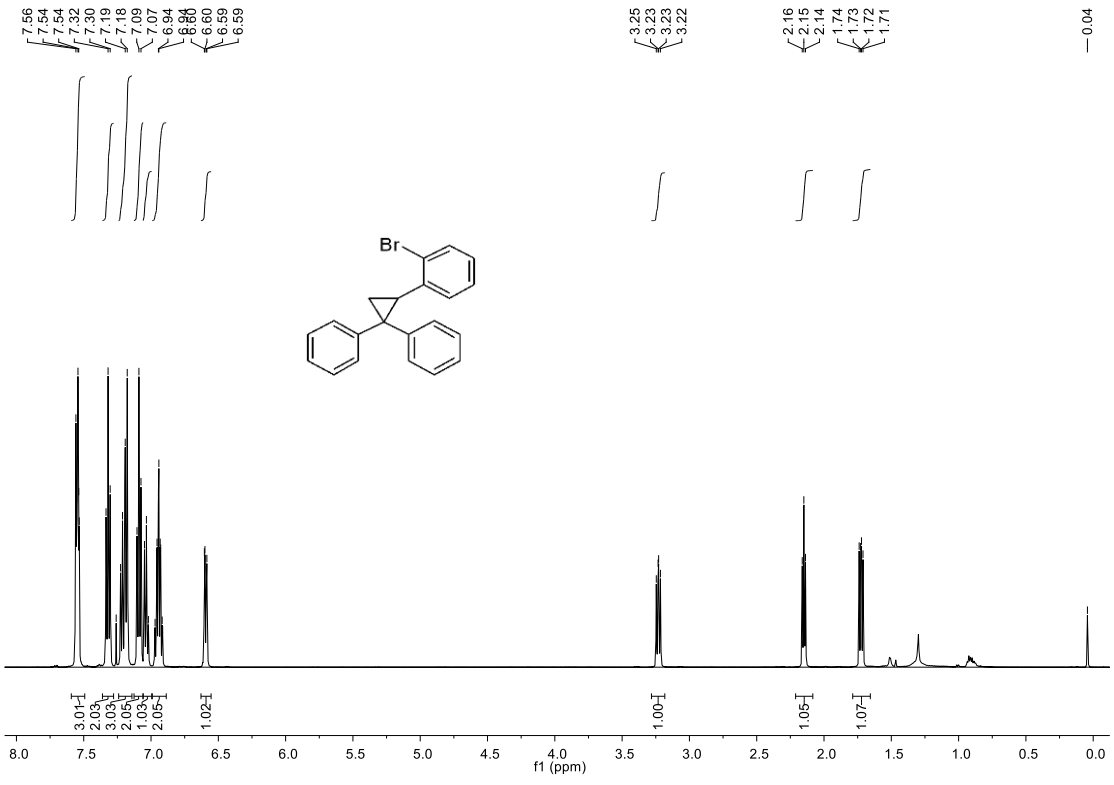


^{13}C NMR (125 MHz, $CDCl_3$)

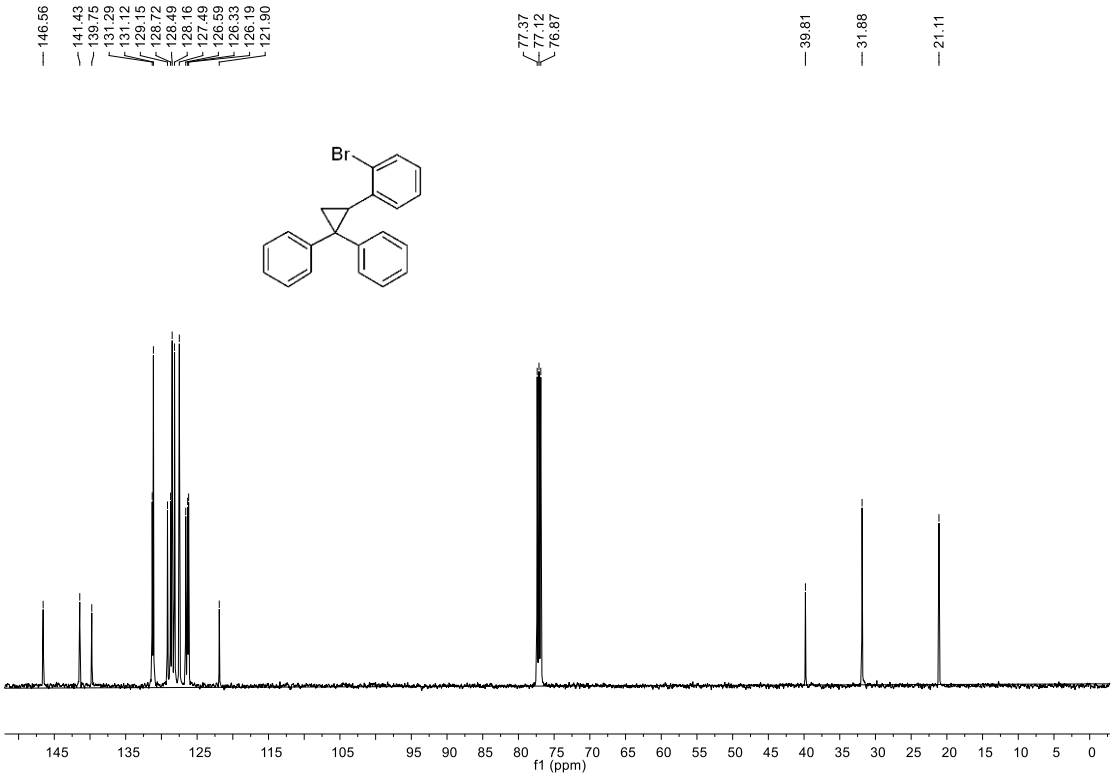


4. (2-(2-Bromophenyl)cyclopropane-1,1-diyl)dibenzene (3d)

^{1}H NMR (500 MHz, $CDCl_3$)

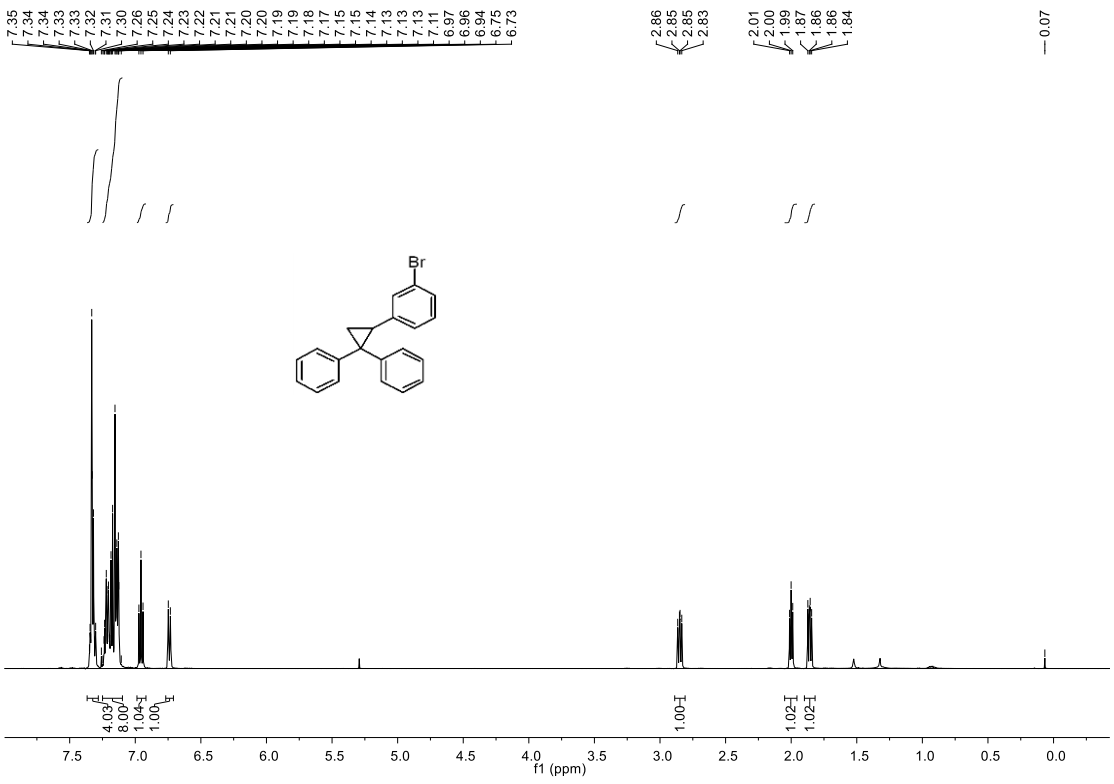


^{13}C NMR (125 MHz, $CDCl_3$)

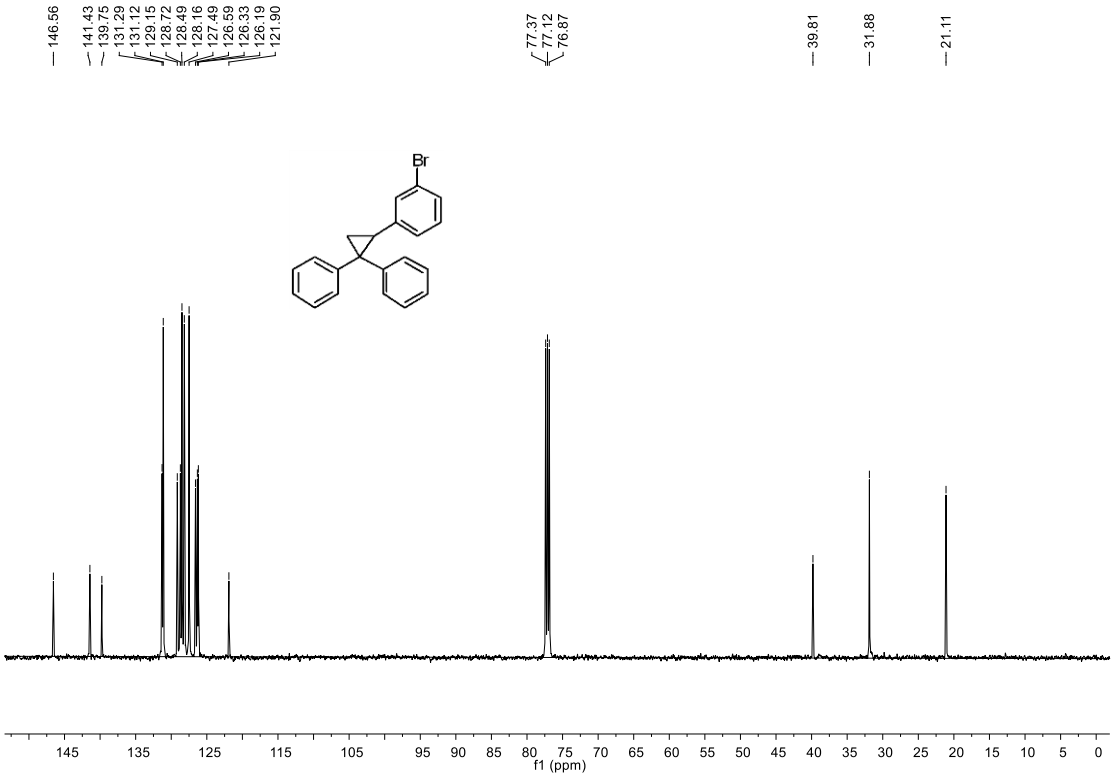


5. (2-(3-Bromophenyl)cyclopropane-1,1-diyl)dibenzene (3e)

^{1}H NMR (500 MHz, $CDCl_3$)

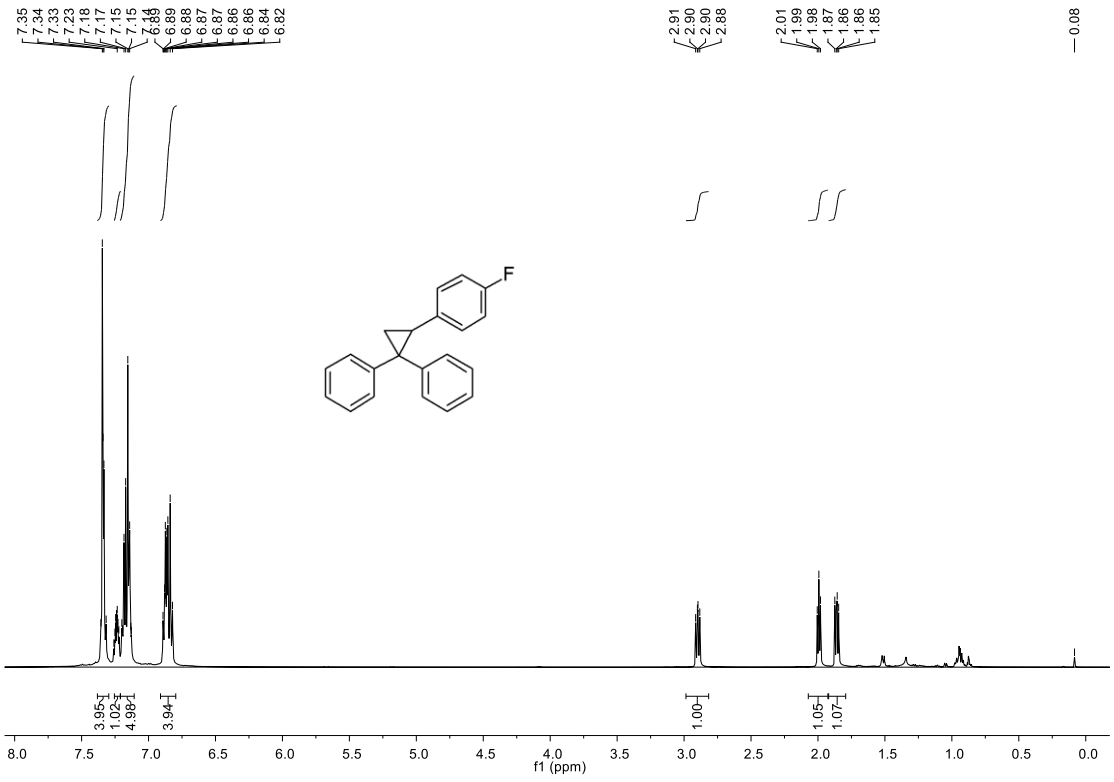


^{13}C NMR (125 MHz, $CDCl_3$)

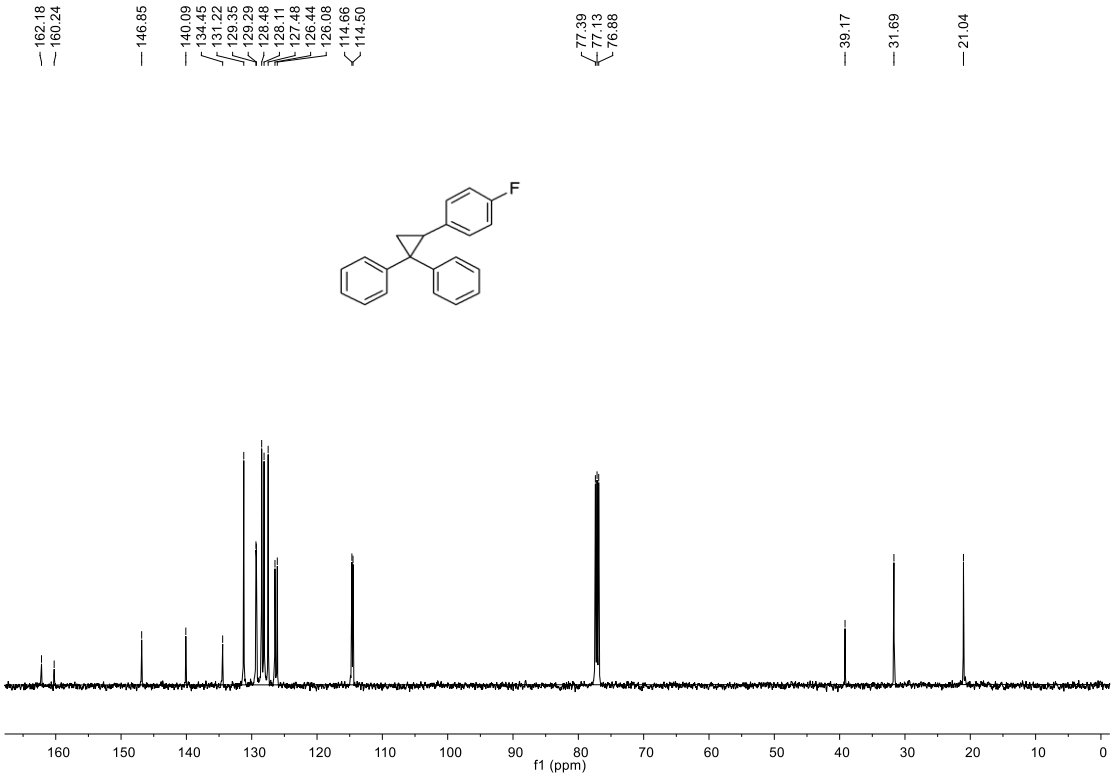


6. (2-(4-Fluorophenyl)cyclopropane-1,1-diyl)dibenzene (3f)

^{1}H NMR (500 MHz, $CDCl_3$)

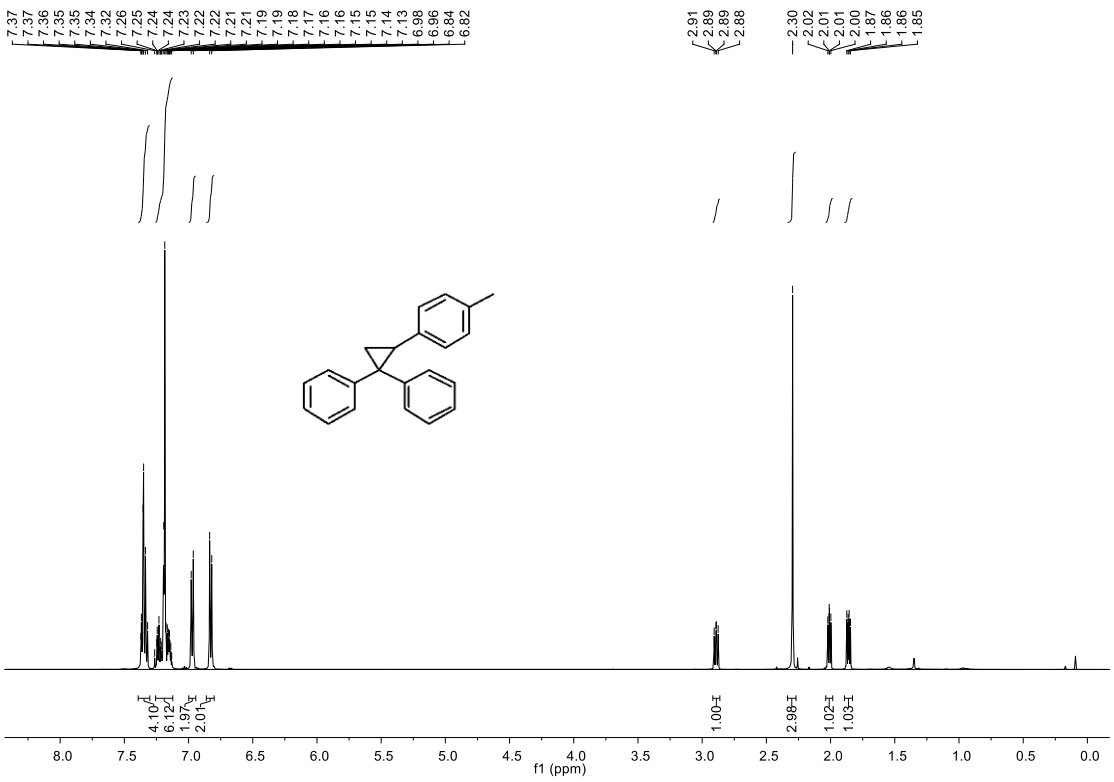


^{13}C NMR (125 MHz, $CDCl_3$)

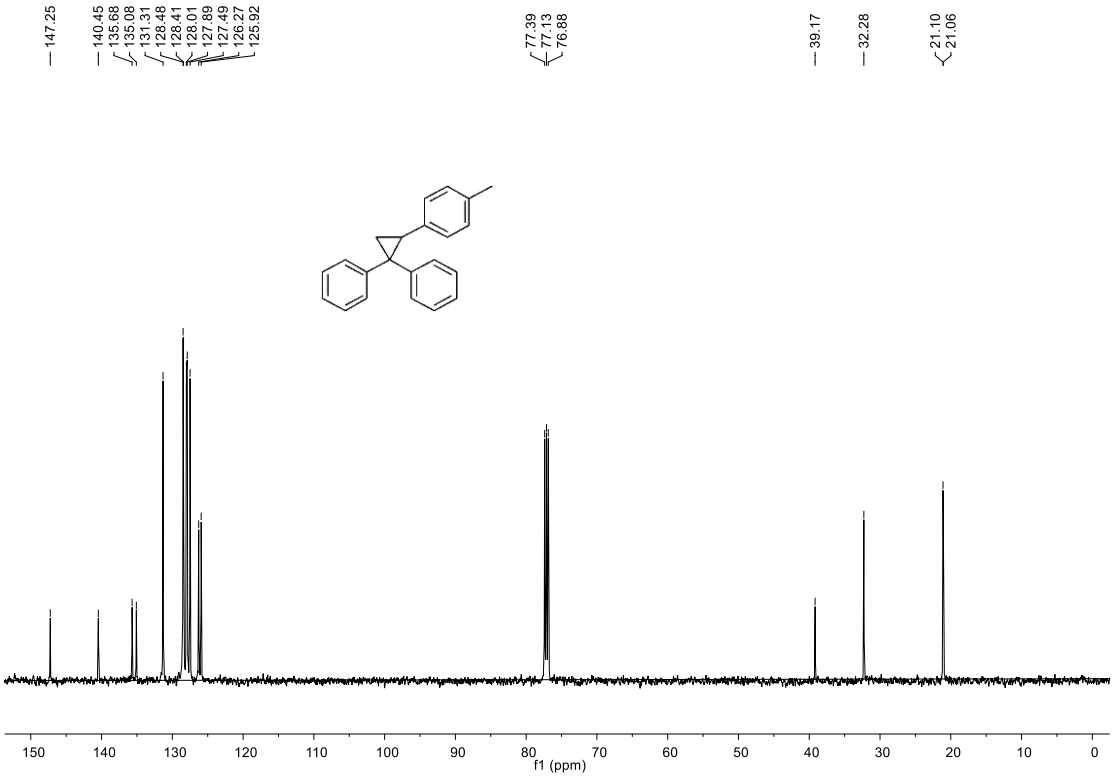


7. (2-(*p*-Tolyl)cyclopropane-1,1-diyl)dibenzene (3g)

^{1}H NMR (500 MHz, $CDCl_3$)

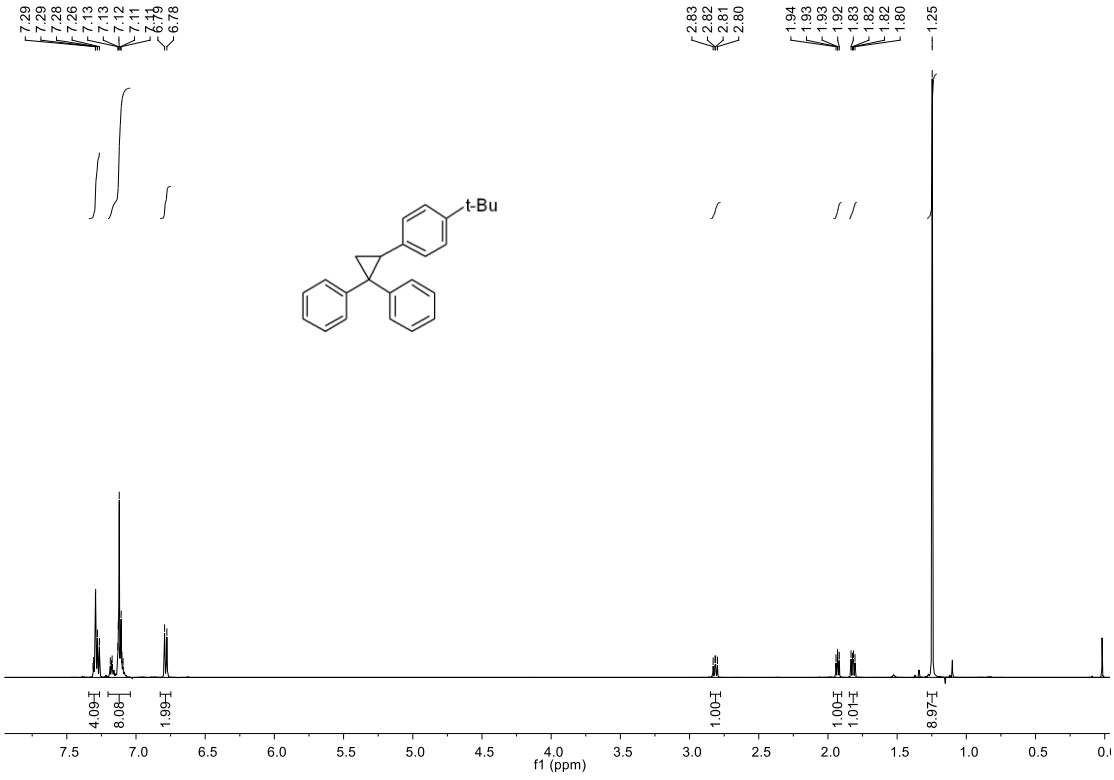


^{13}C NMR (125 MHz, $CDCl_3$)

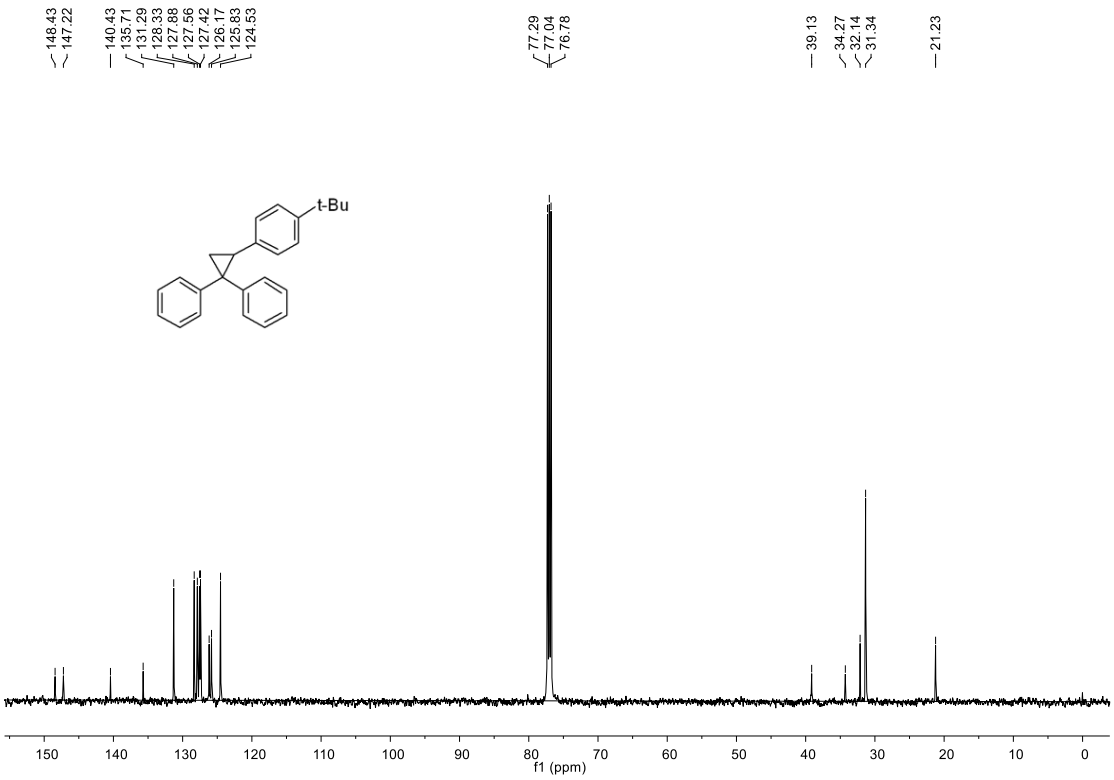


8. (2-(4-(*tert*-Butyl)phenyl)cyclopropane-1,1-diyl)dibenzene (3h)

^{1}H NMR (500 MHz, $CDCl_3$)

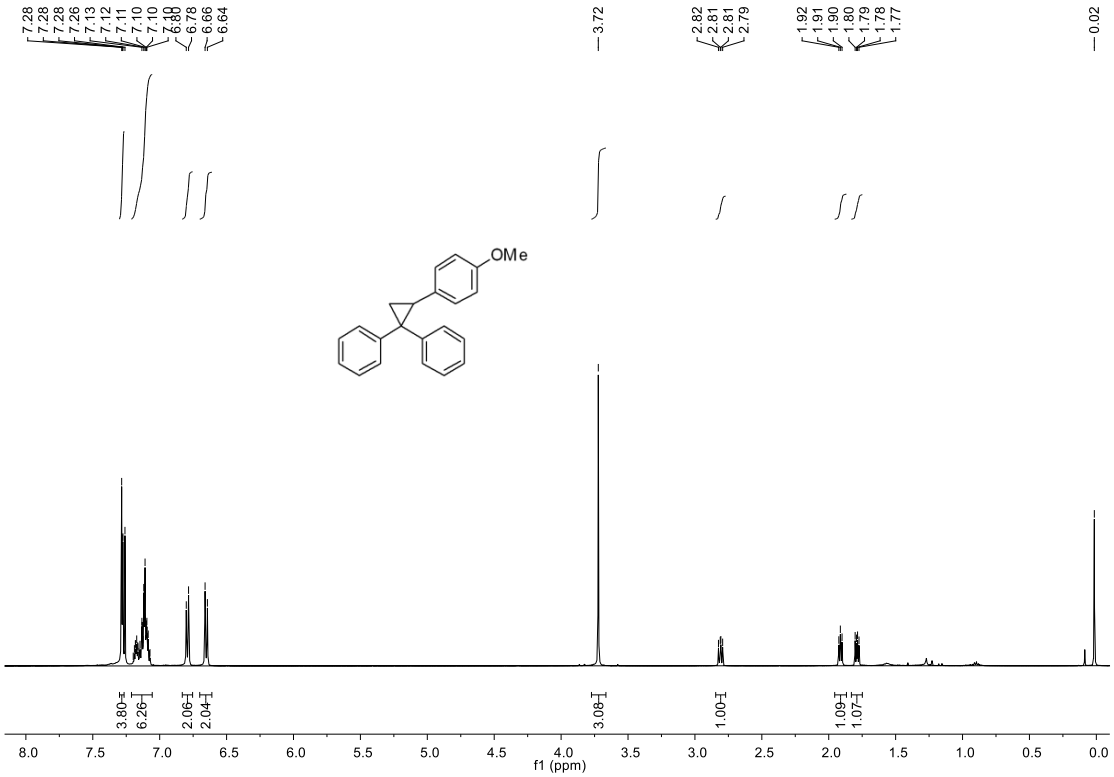


^{13}C NMR (125 MHz, $CDCl_3$)

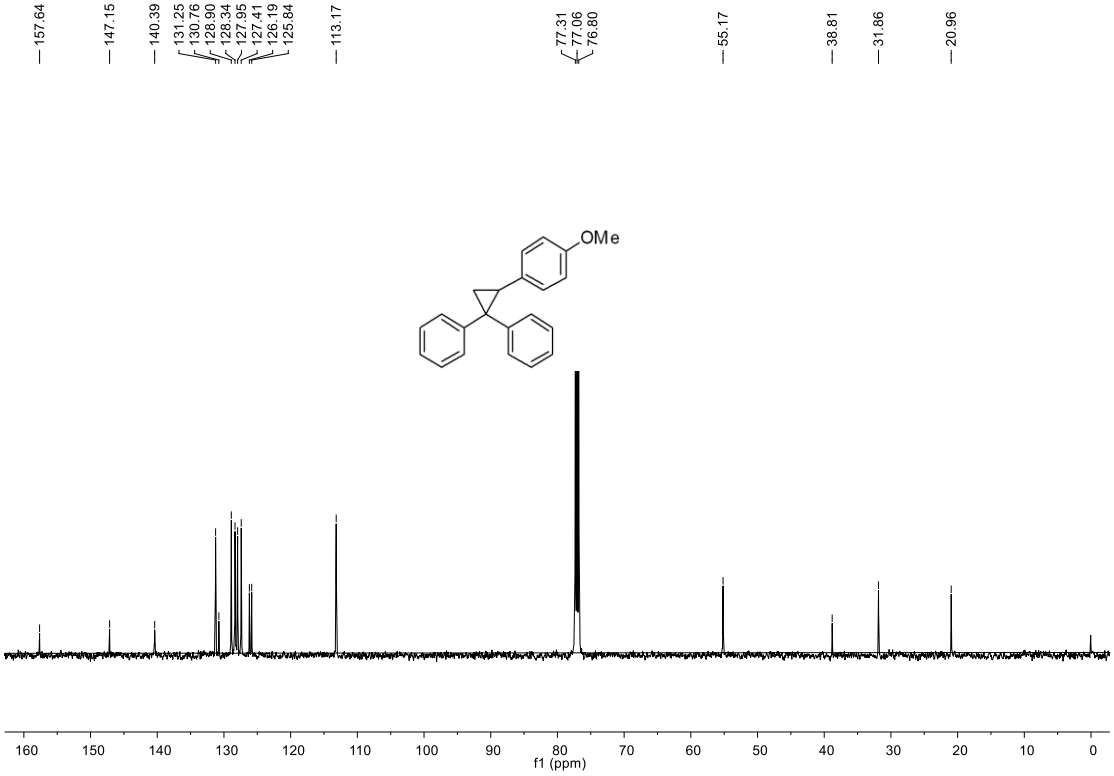


9. (2-(4-Methoxyphenyl)cyclopropane-1,1-diyl)dibenzene (3i)

^{1}H NMR (500 MHz, $CDCl_3$)

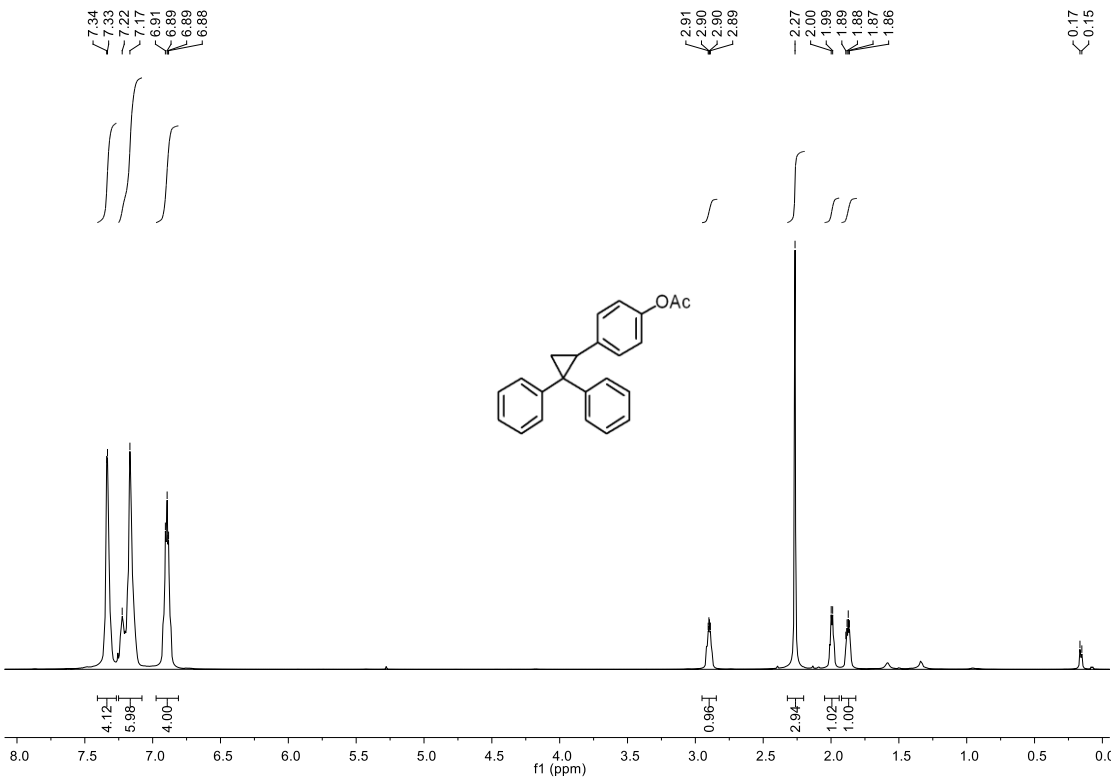


^{13}C NMR (125 MHz, $CDCl_3$)

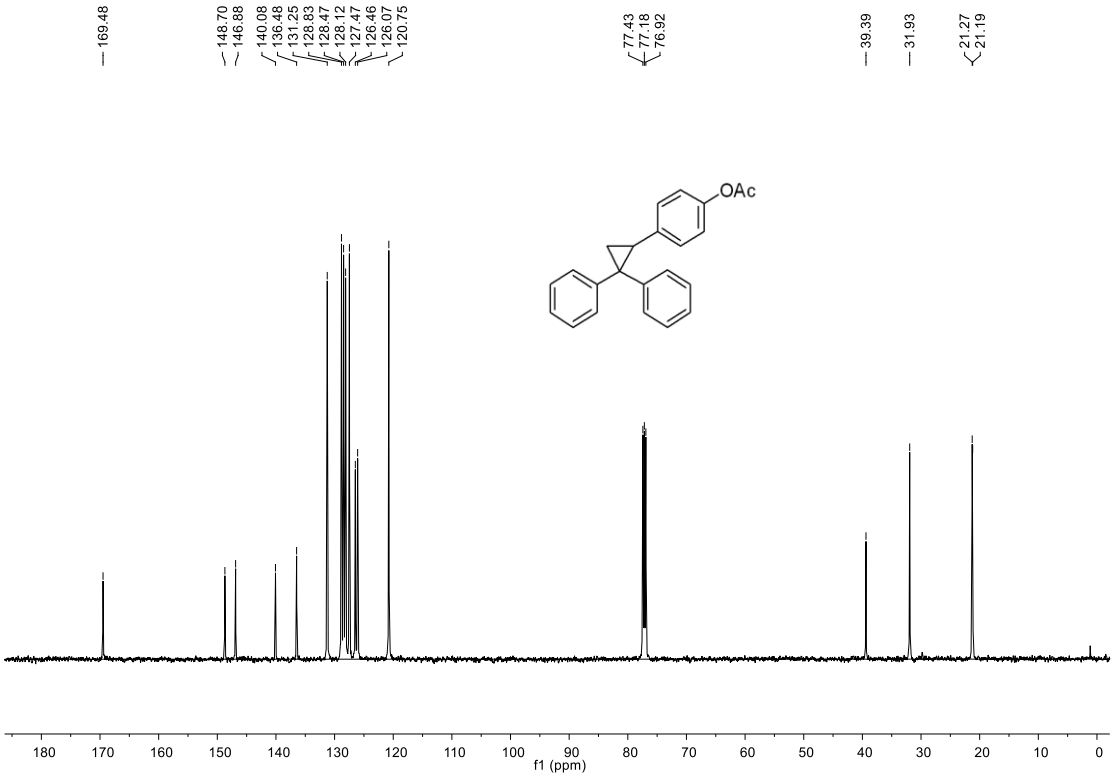


10. 4-(2,2-Diphenylcyclopropyl)phenyl acetate (3j)

^{1}H NMR (500 MHz, $CDCl_3$)

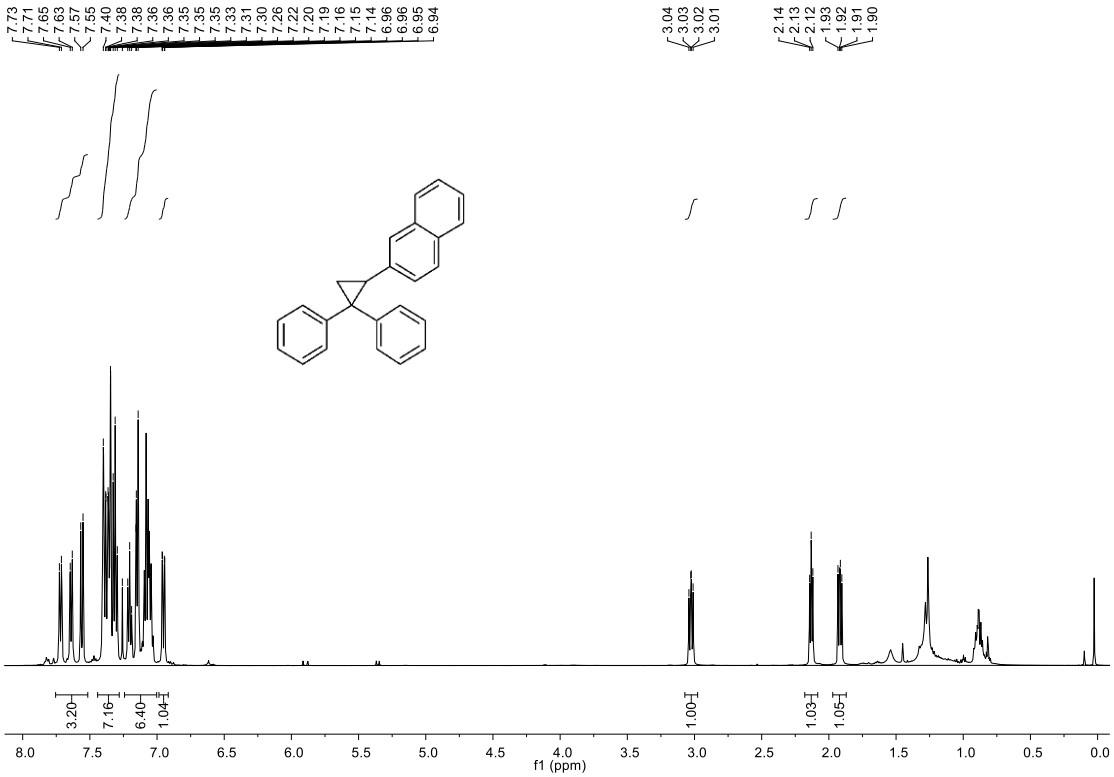


^{13}C NMR (125 MHz, $CDCl_3$)

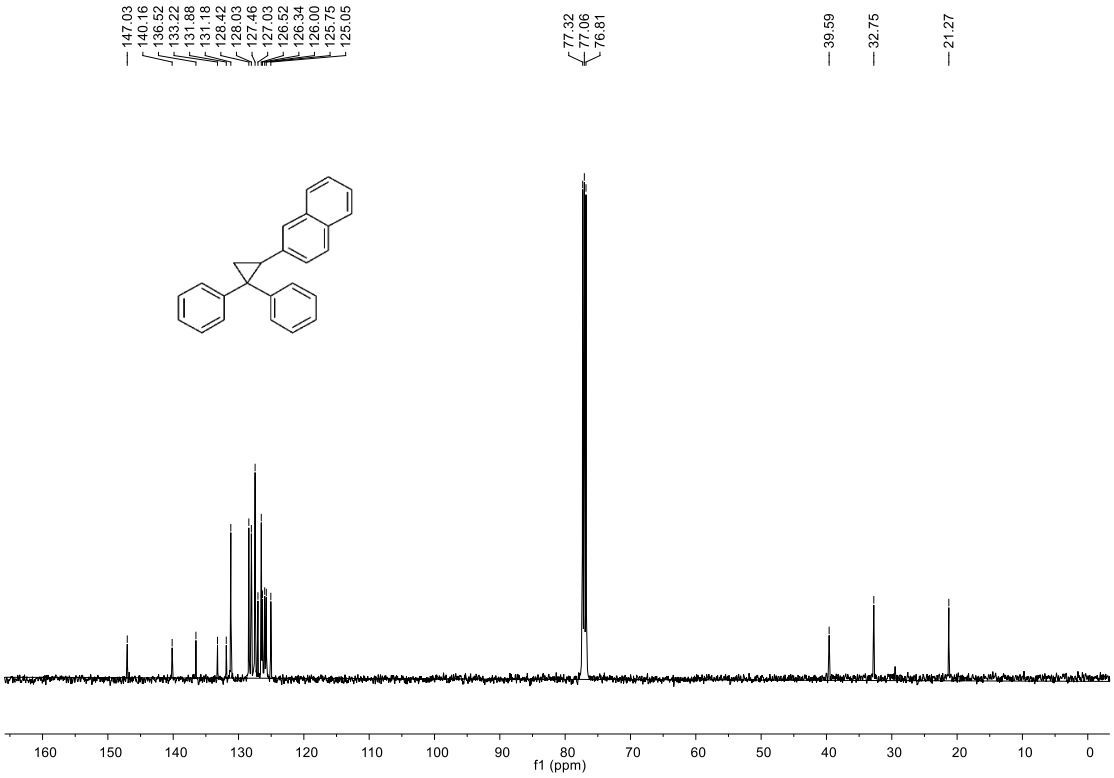


11. 2-(2,2-Diphenylcyclopropyl)naphthalene (3k)

^{1}H NMR (500 MHz, $CDCl_3$)

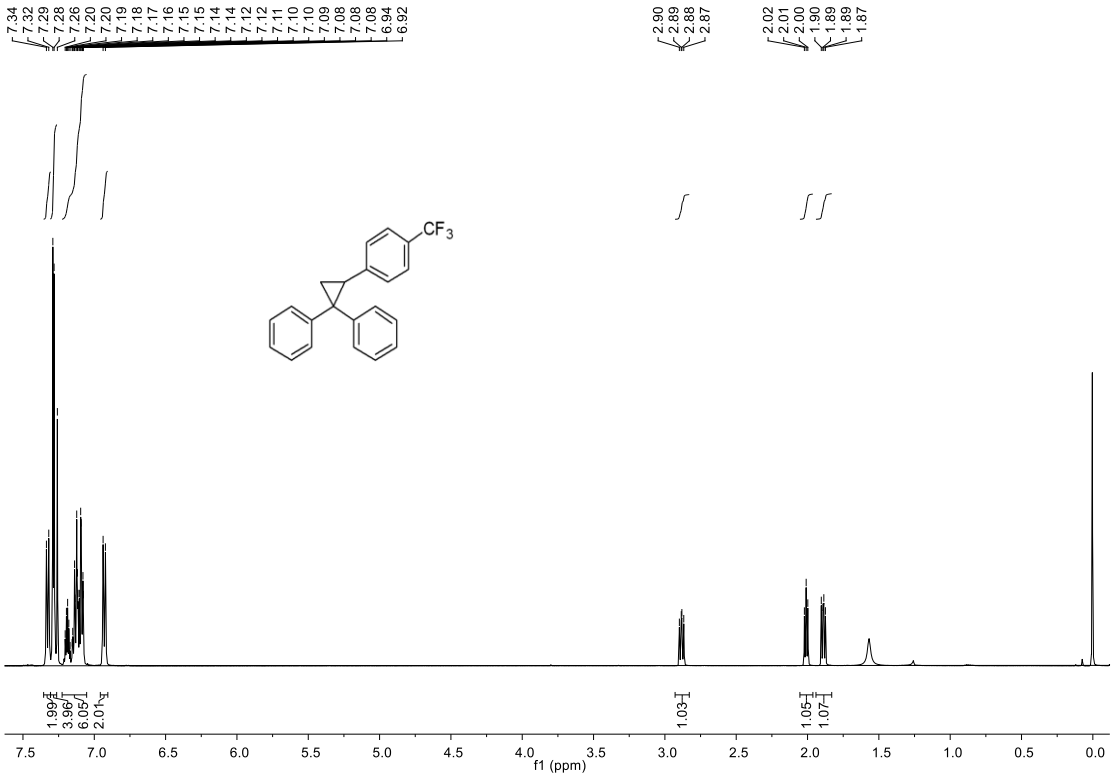


^{13}C NMR (125 MHz, $CDCl_3$)

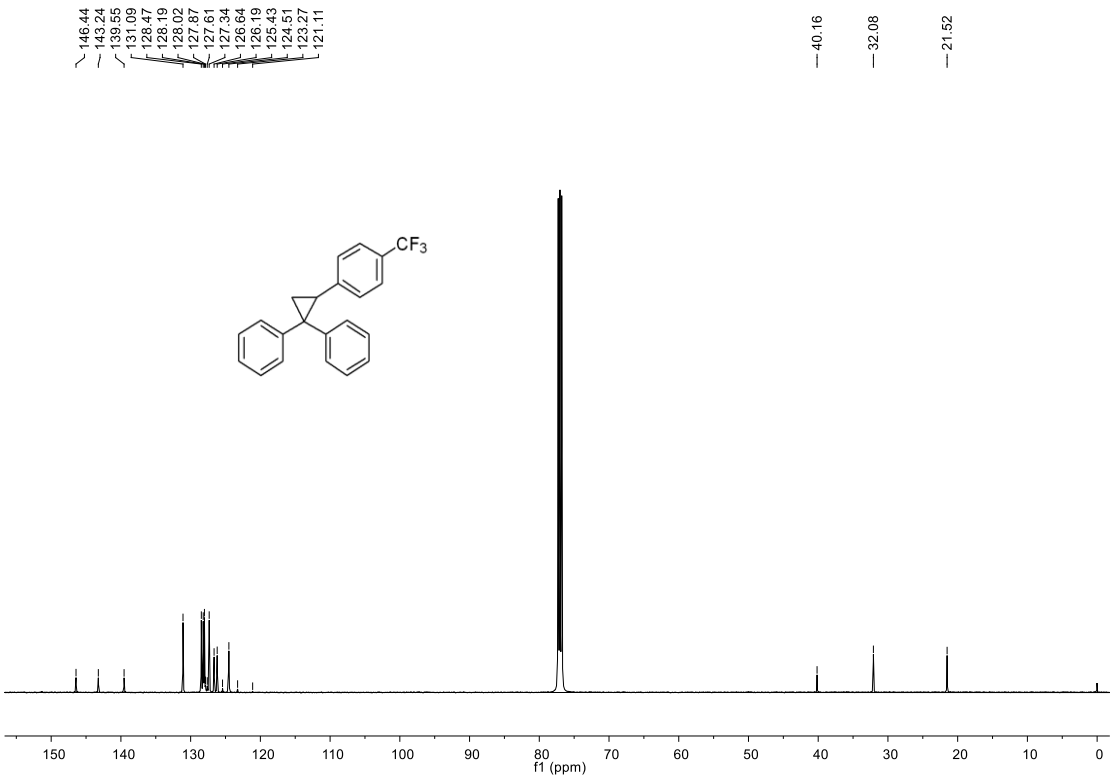


12. (2-(4-(Trifluoromethyl)phenyl)cyclopropane-1,1-diyl)dibenzene (3l)

^{1}H NMR (500 MHz, $CDCl_3$)

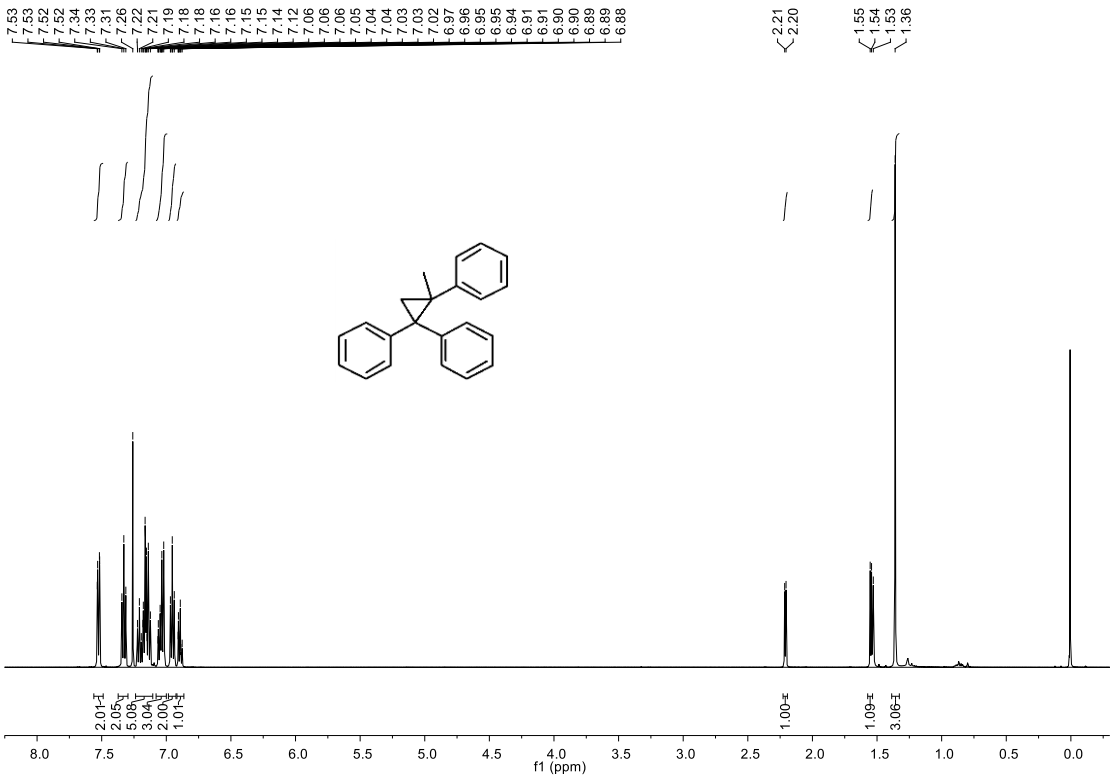


^{13}C NMR (125 MHz, $CDCl_3$)

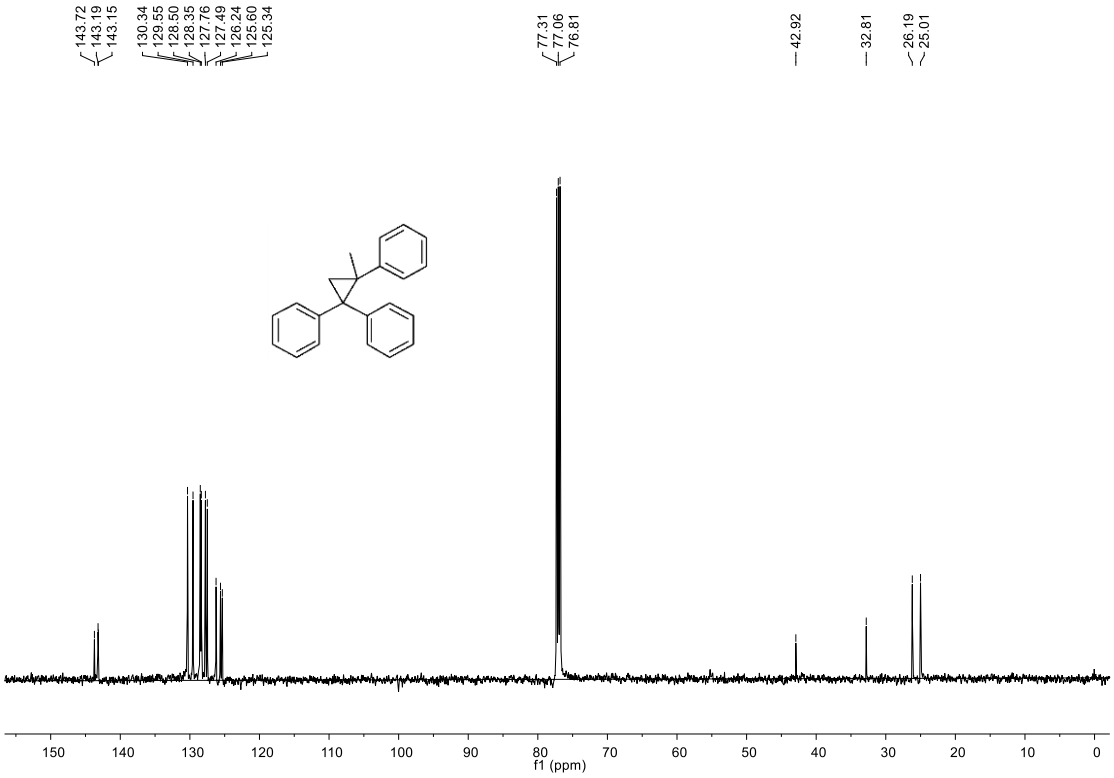


13. (2-Methylcyclopropane-1,1,2-triyl)tribenzene (3m)

^{1}H NMR (500 MHz, $CDCl_3$)

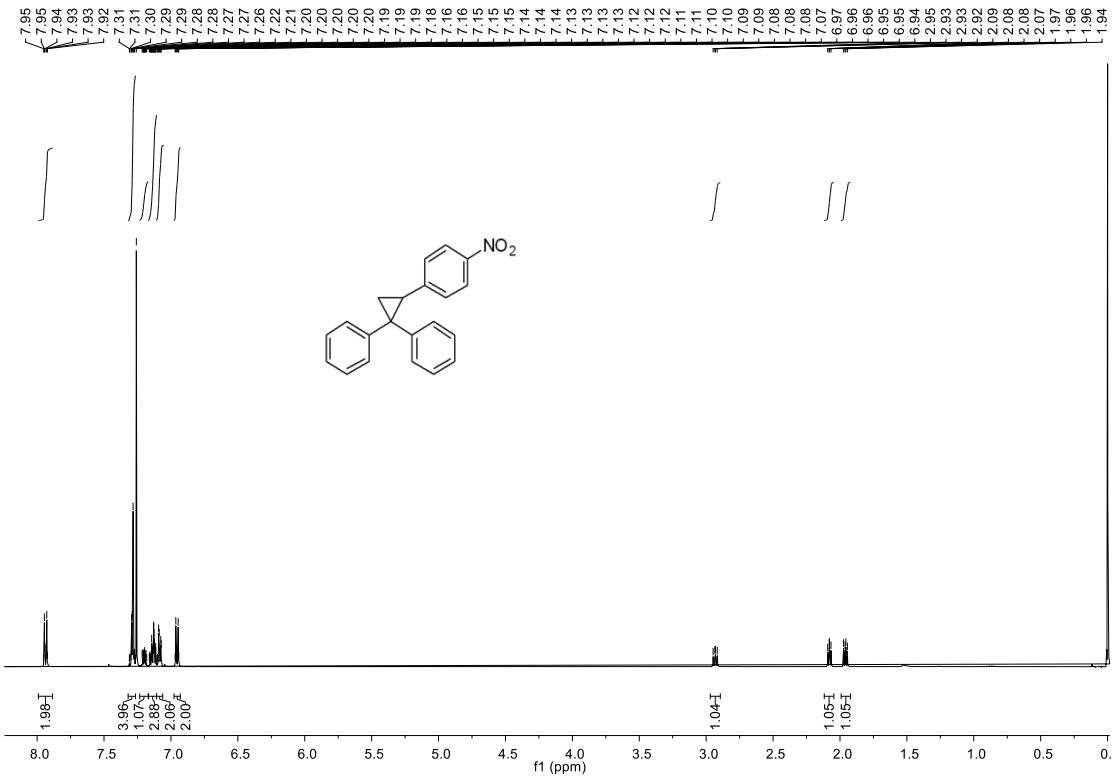


^{13}C NMR (125 MHz, $CDCl_3$)

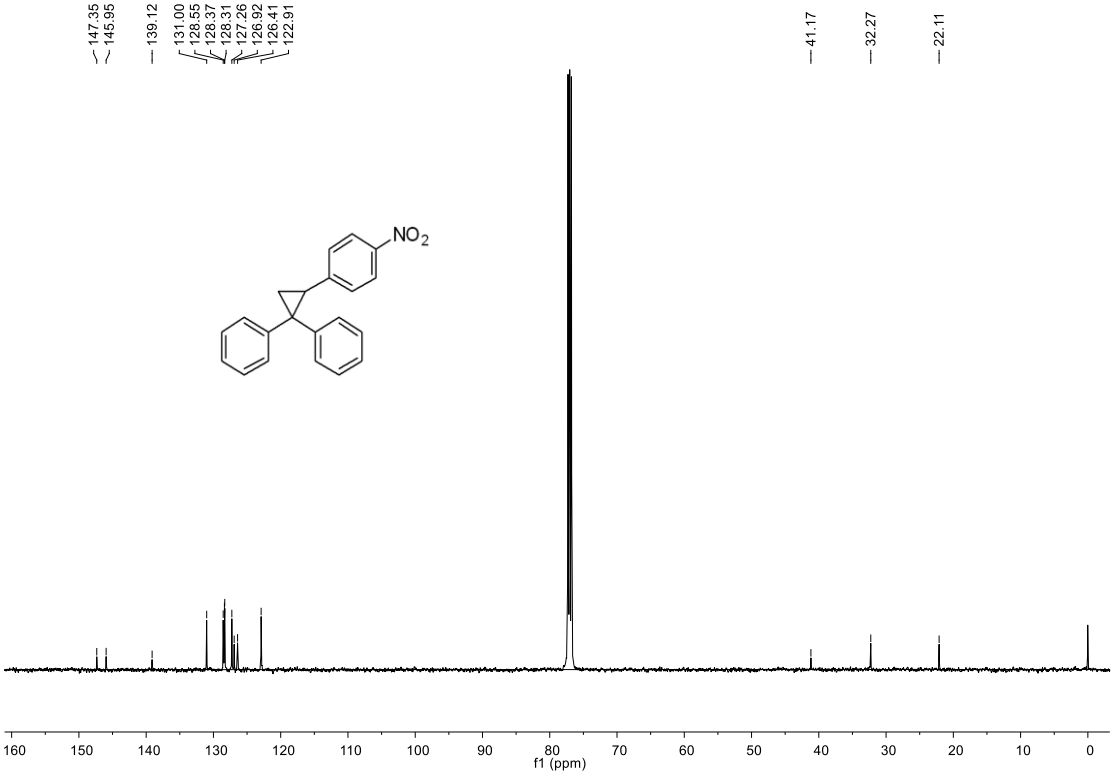


14. (2-(4-Nitrophenyl)cyclopropane-1,1-diyl)dibenzene (3n)

^{1}H NMR (500 MHz, $CDCl_3$)

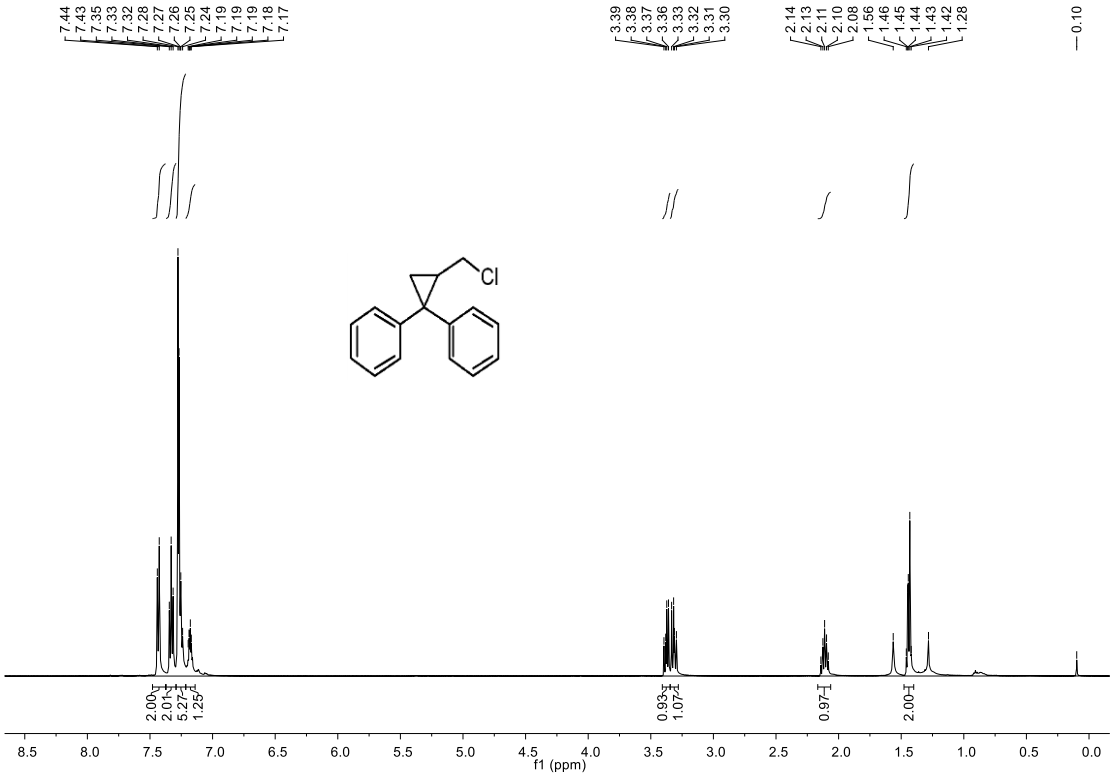


^{13}C NMR (125 MHz, $CDCl_3$)

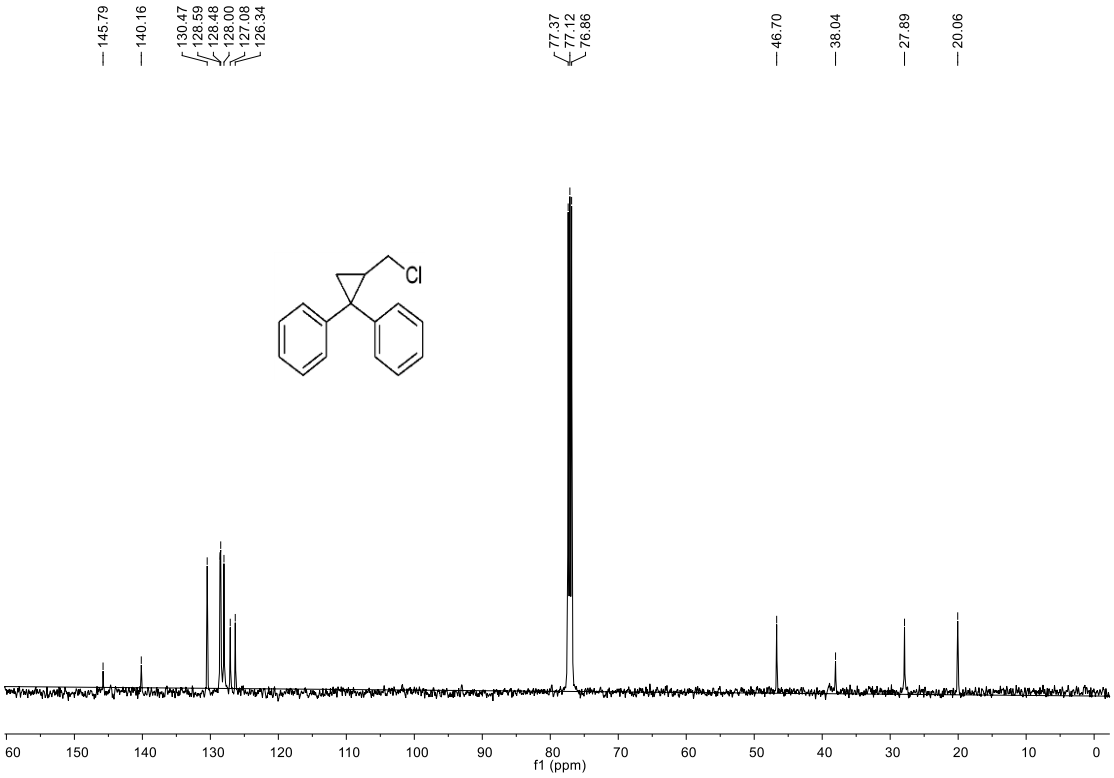


15. (2-(Chloromethyl)cyclopropane-1,1-diyl)dibenzene (3o)

^{1}H NMR (500 MHz, $CDCl_3$)

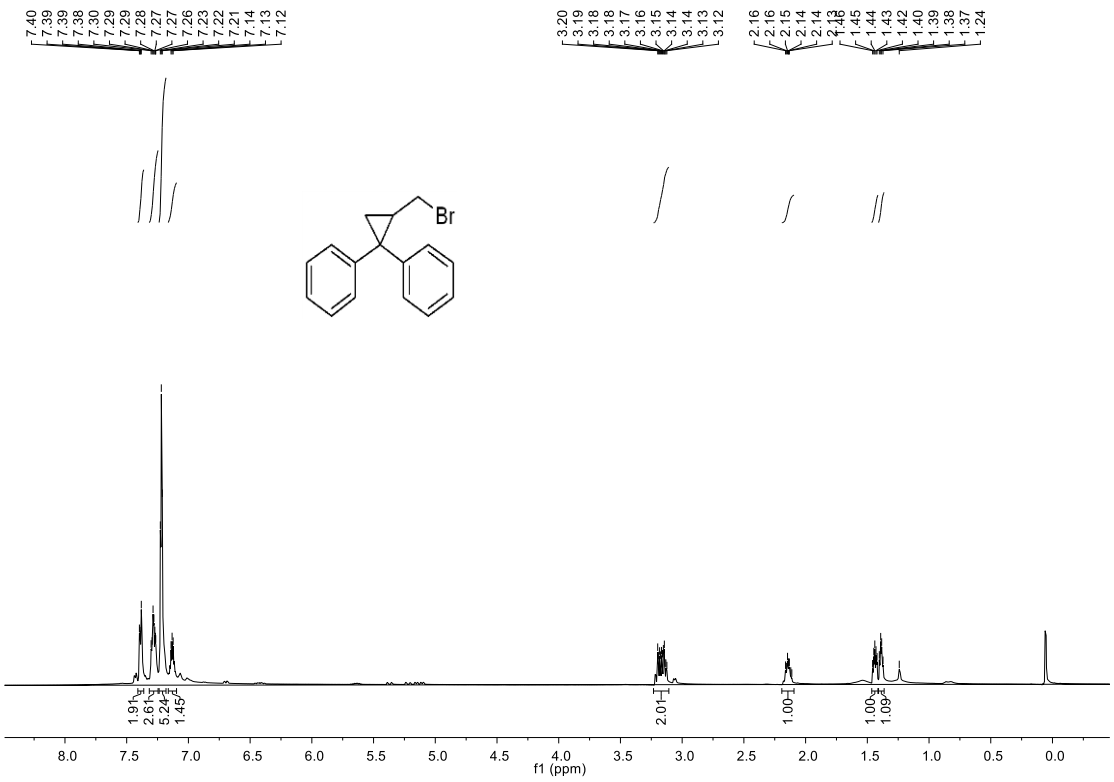


^{13}C NMR (125 MHz, $CDCl_3$)

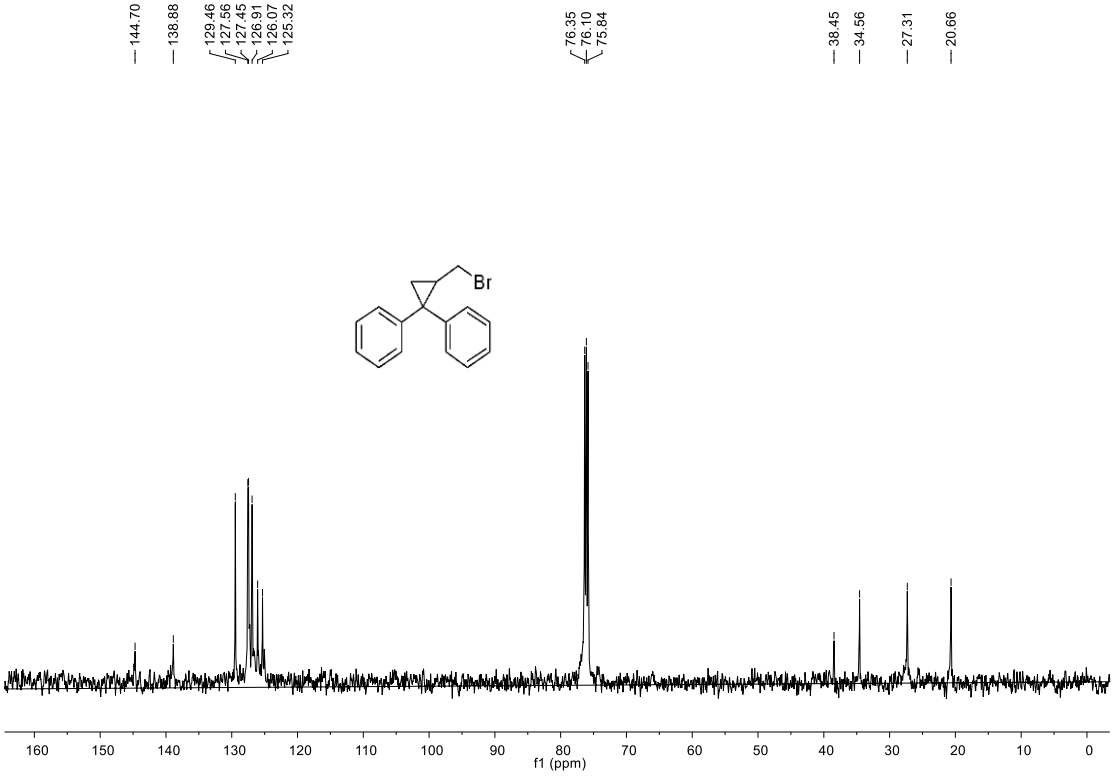


16. (2-(Bromomethyl)cyclopropane-1,1-diyl)dibenzene (3p)

^{1}H NMR (500 MHz, $CDCl_3$)

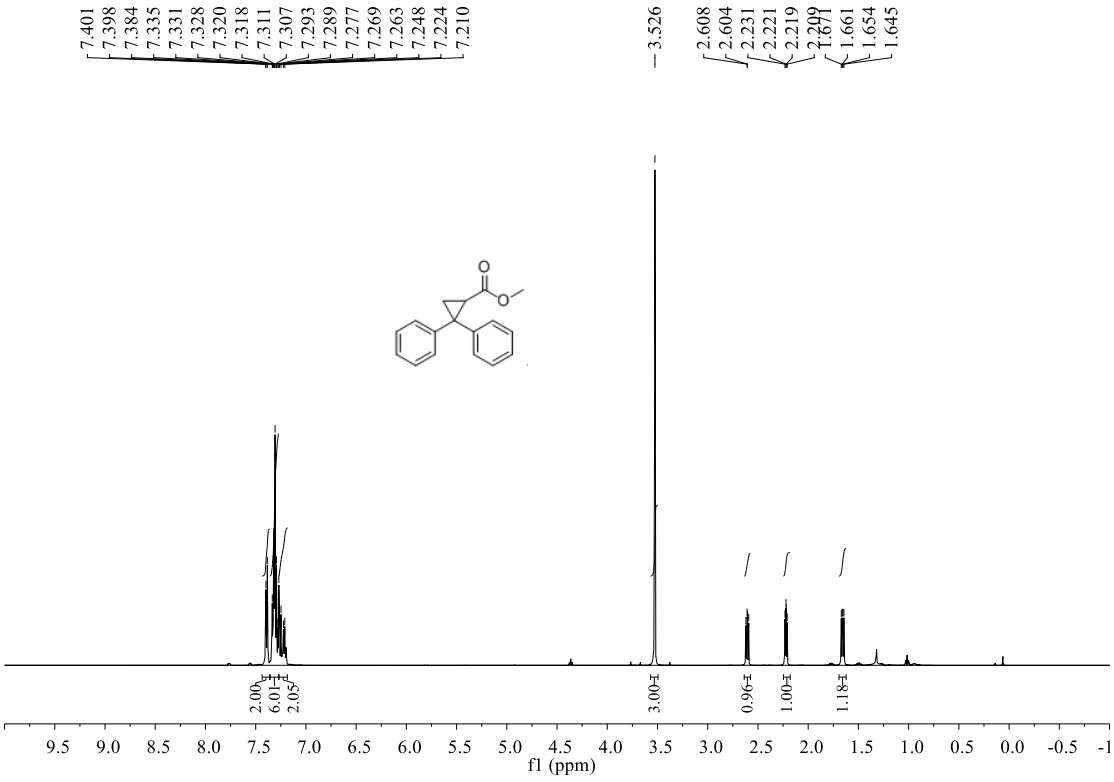


^{13}C NMR (125 MHz, $CDCl_3$)

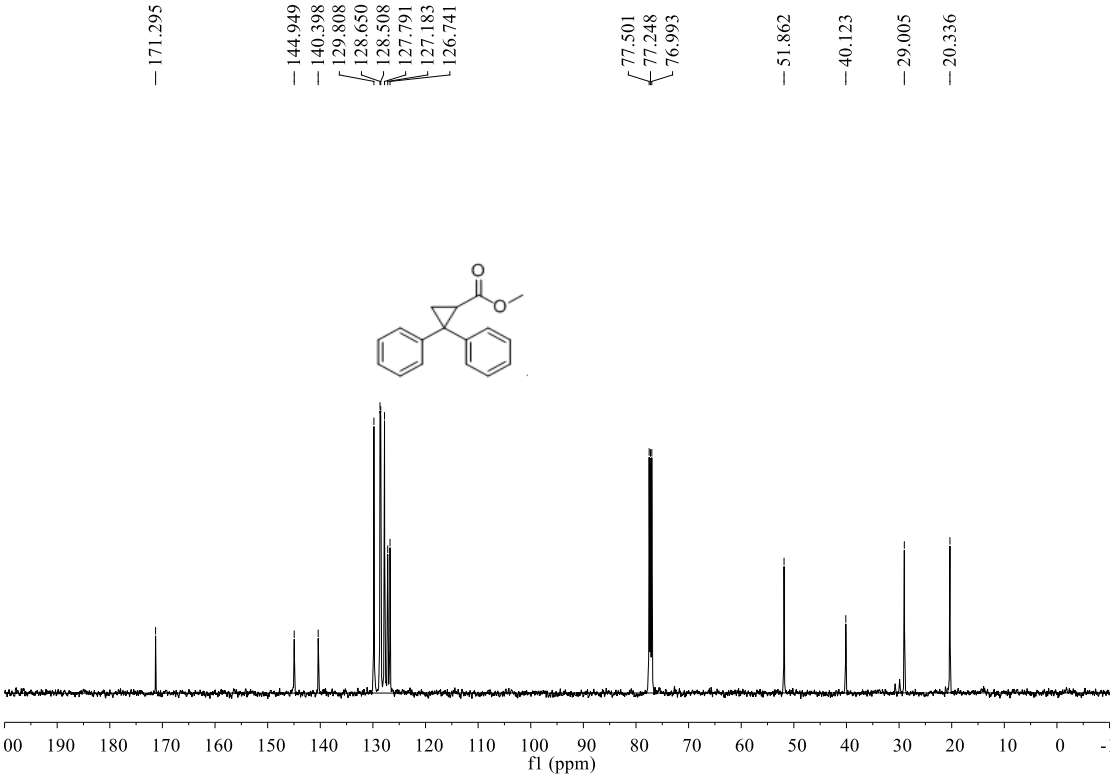


17. Methyl 2,2-diphenylcyclopropanecarboxylate (3q)

^{1}H NMR (500 MHz, $CDCl_3$)

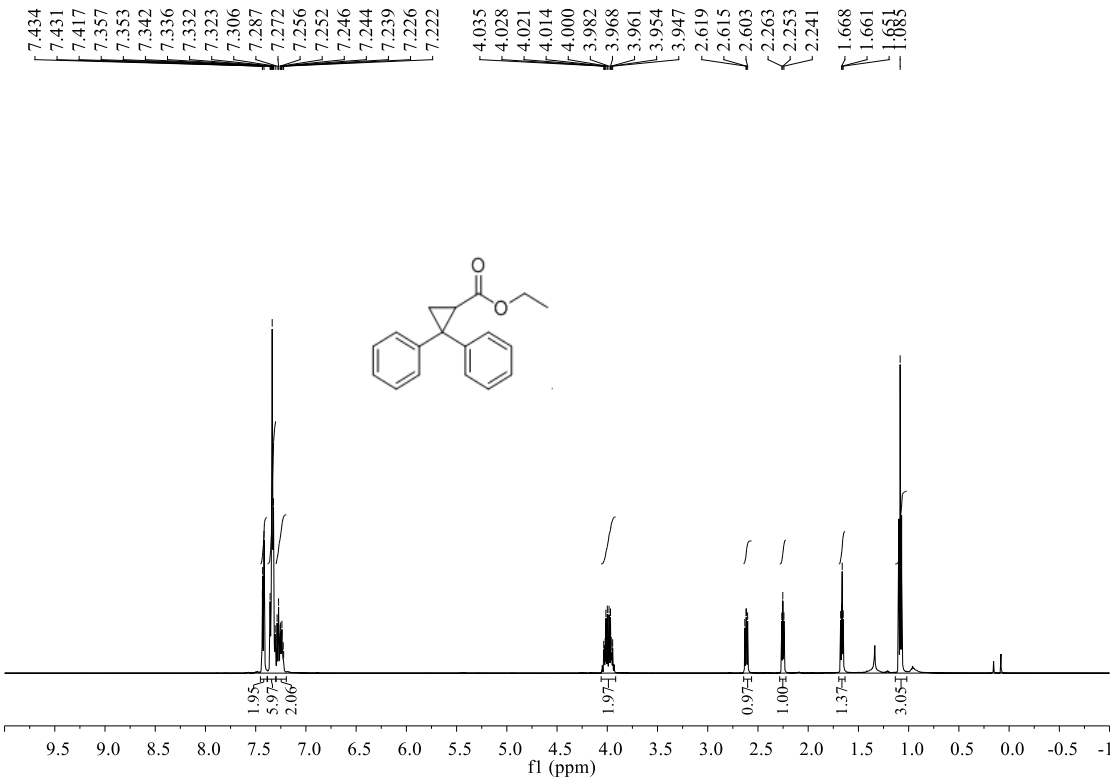


^{13}C NMR (125 MHz, $CDCl_3$)

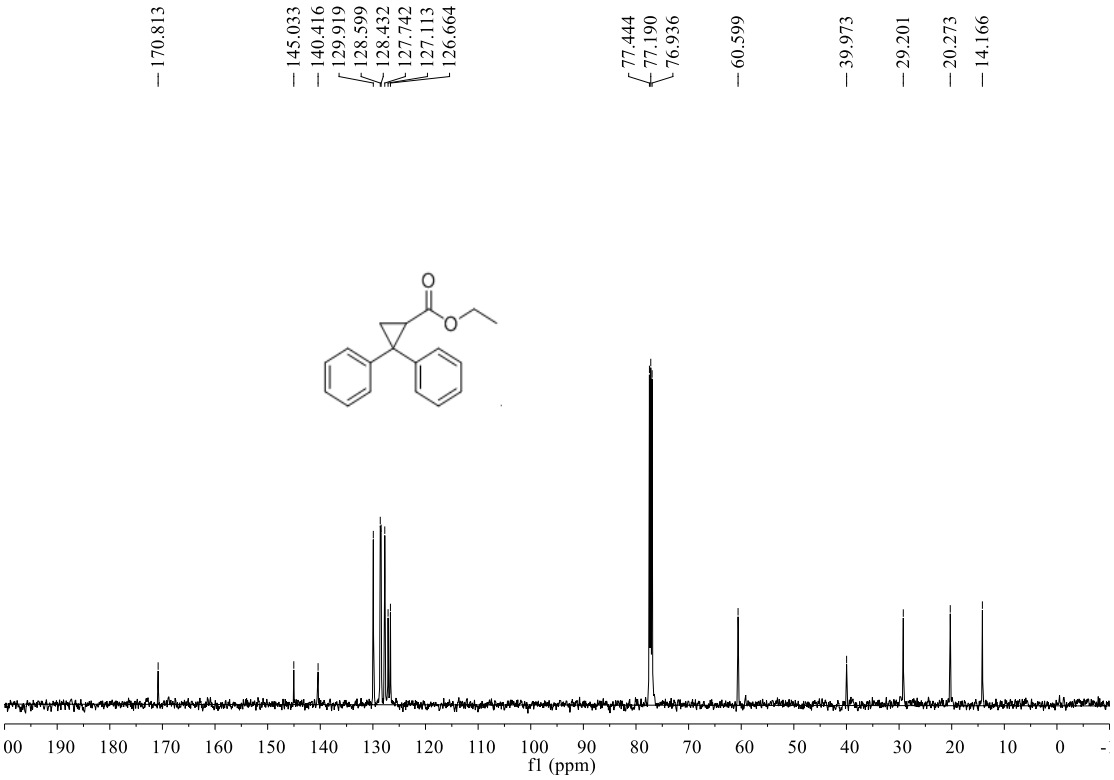


18. Ethyl 2,2-diphenylcyclopropanecarboxylate (3r)

^{1}H NMR (500 MHz, $CDCl_3$)

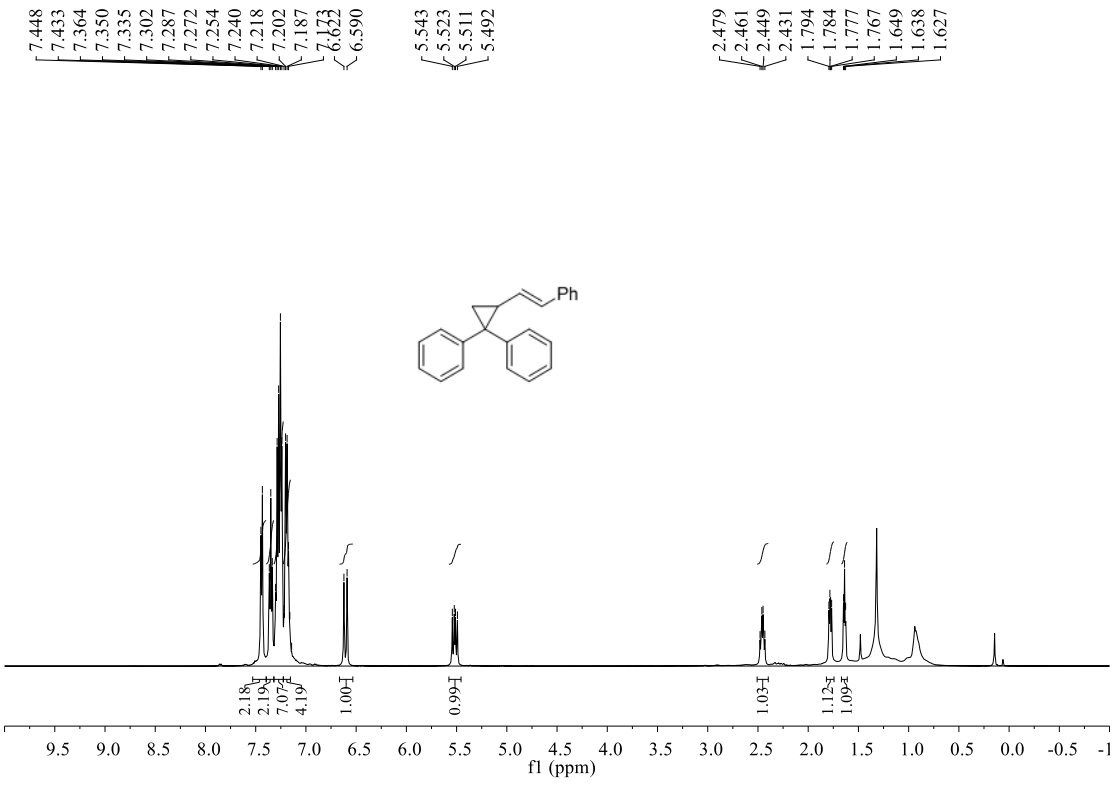


^{13}C NMR (125 MHz, $CDCl_3$)

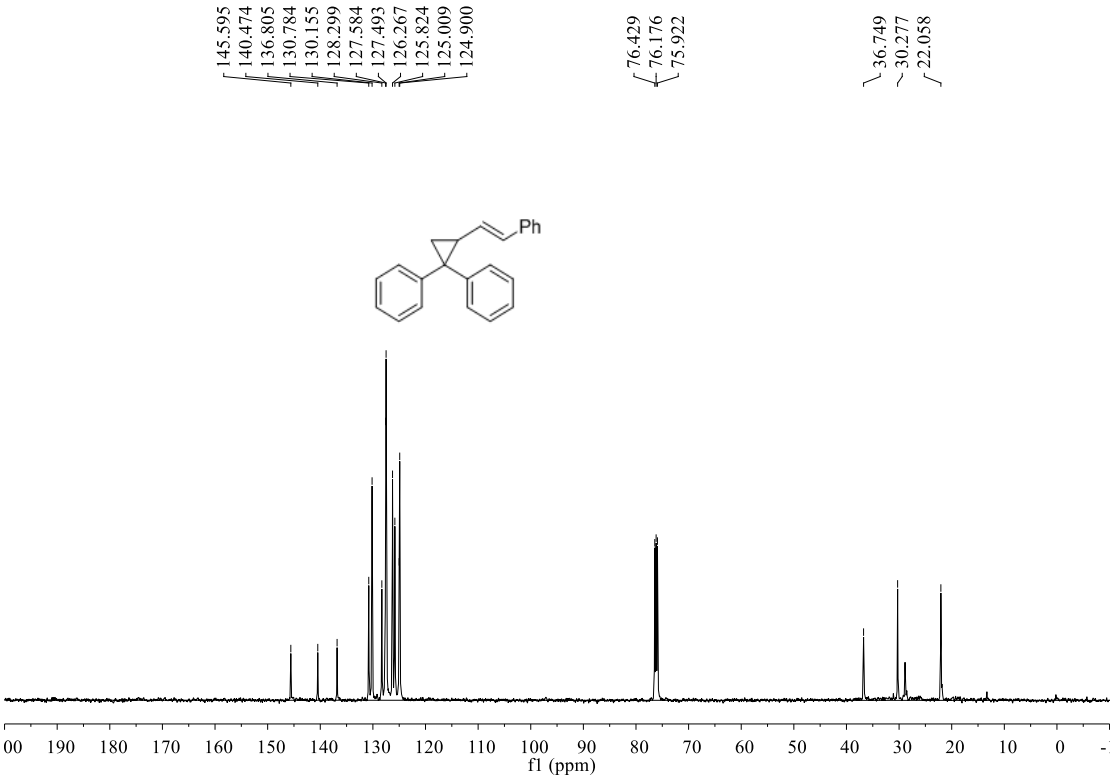


19. (*E*)-(2-styrylcyclopropane-1,1-diyl)dibenzene (3s)

^{1}H NMR (500 MHz, $CDCl_3$)

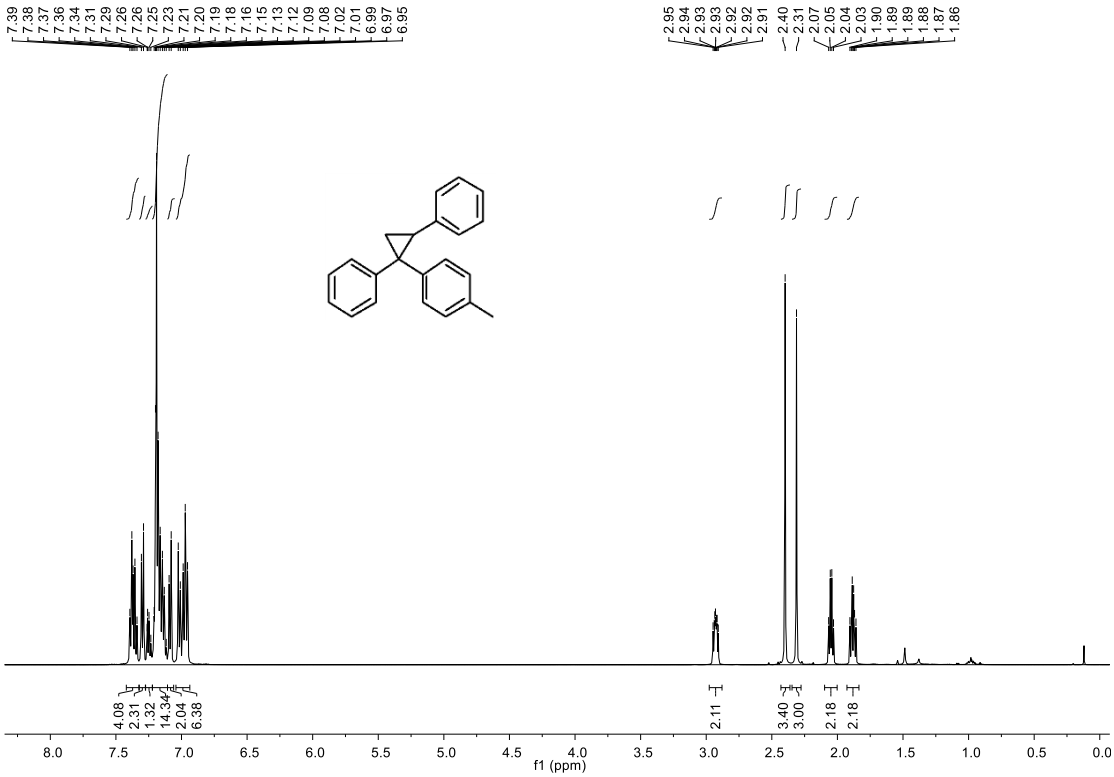


^{13}C NMR (125 MHz, $CDCl_3$)

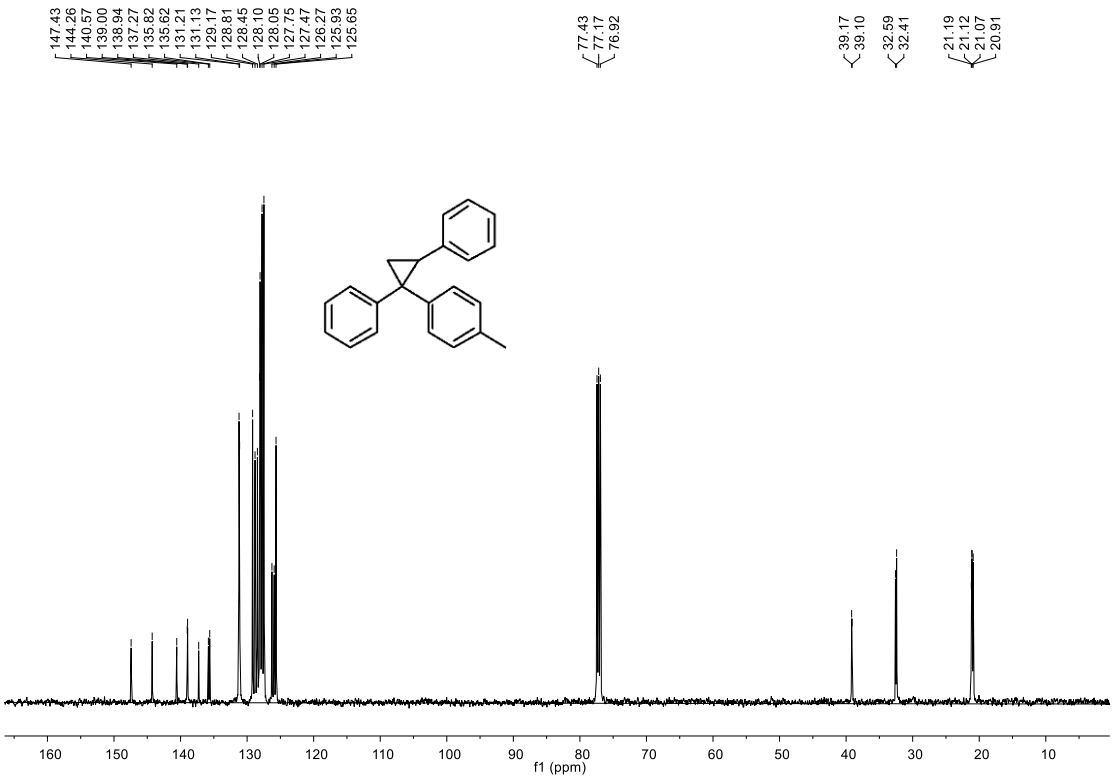


20. (1-(*p*-Tolyl)cyclopropane-1,2-diyl)dibenzene (mixture of diasteromers 1.1:1) (3t)

^{1}H NMR (500 MHz, $CDCl_3$)

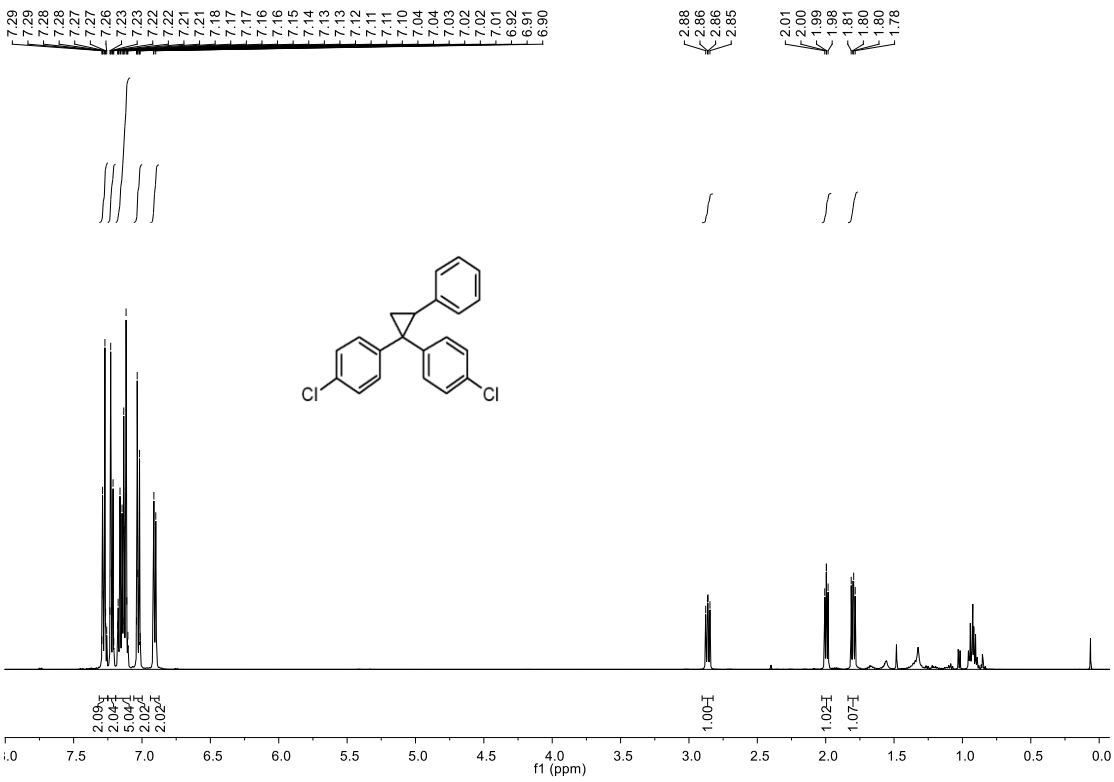


^{13}C NMR (125 MHz, $CDCl_3$)

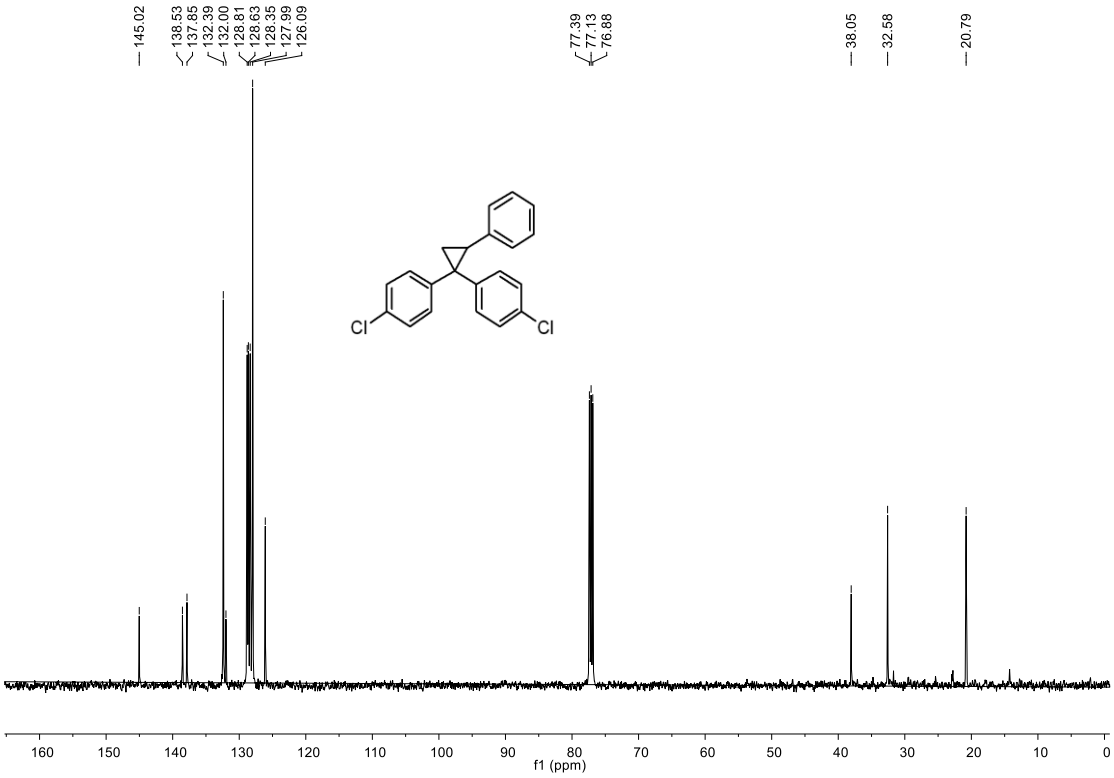


21. 4,4'-(2-Phenylcyclopropane-1,1-diyl)bis(chlorobenzene) (3u)

^{1}H NMR (500 MHz, $CDCl_3$)

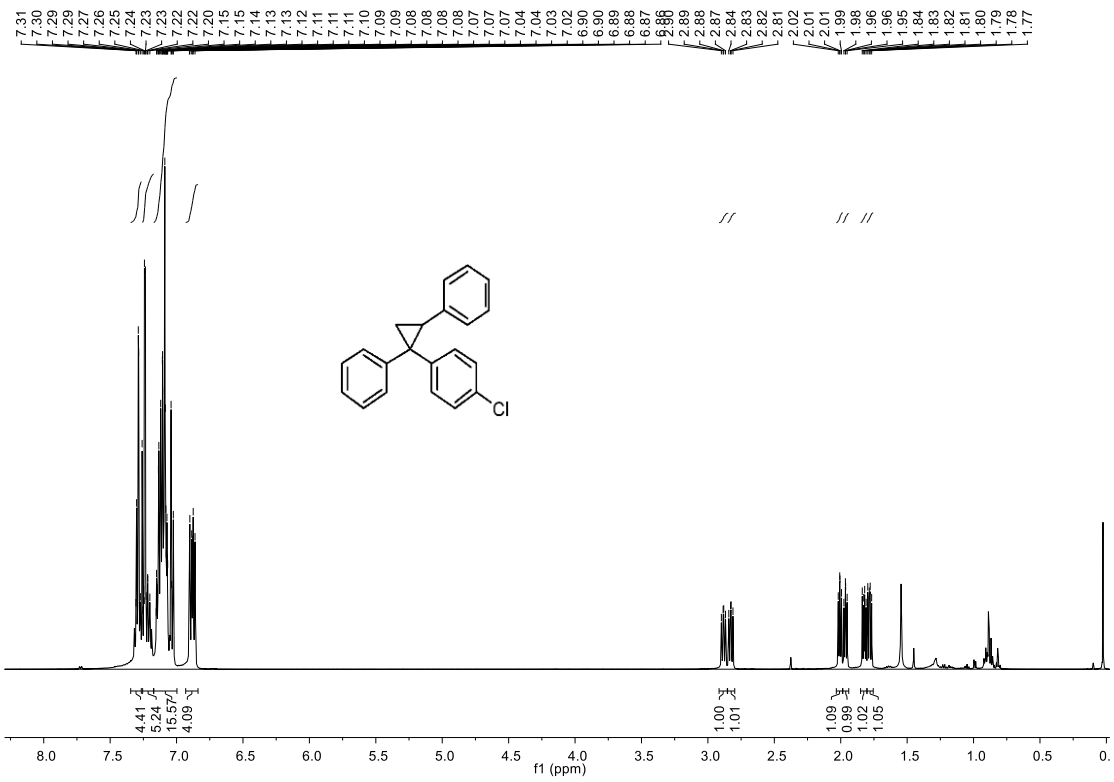


^{13}C NMR (125 MHz, $CDCl_3$)

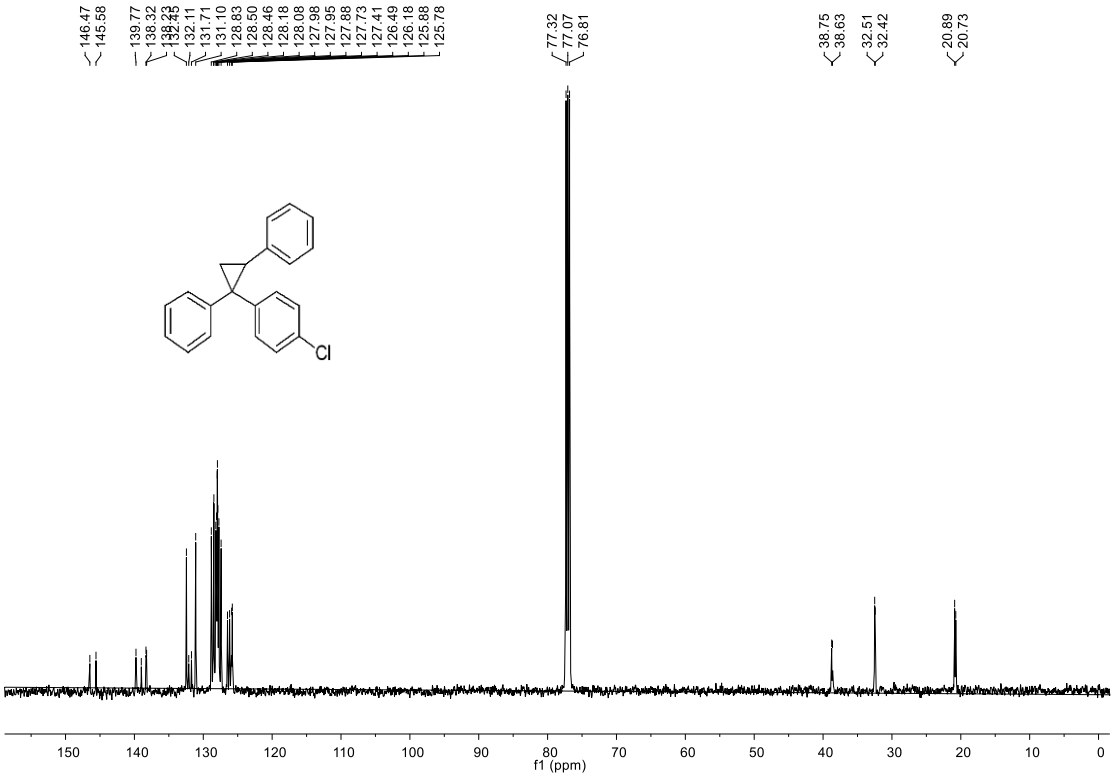


22. (1-(4-Chlorophenyl)cyclopropane-1,2-diyl)dibenzene (mixture of diasteromers 1:1) (3v)

^{1}H NMR (500 MHz, $CDCl_3$)

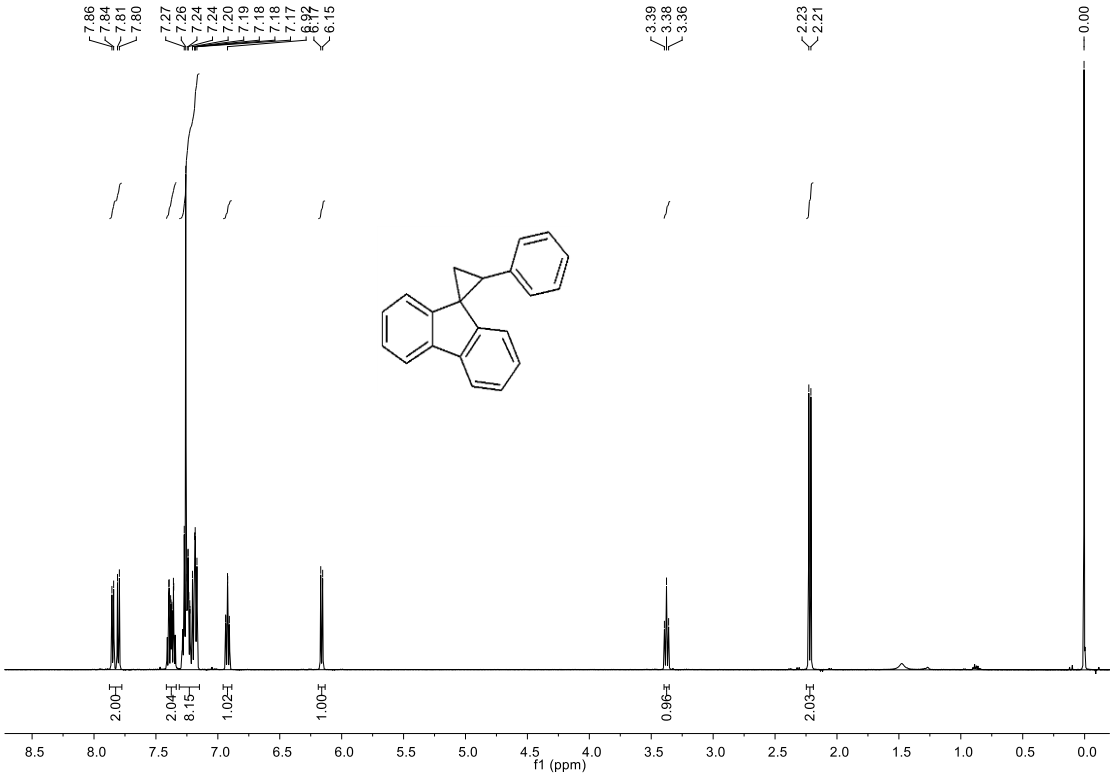


^{13}C NMR (125 MHz, $CDCl_3$)

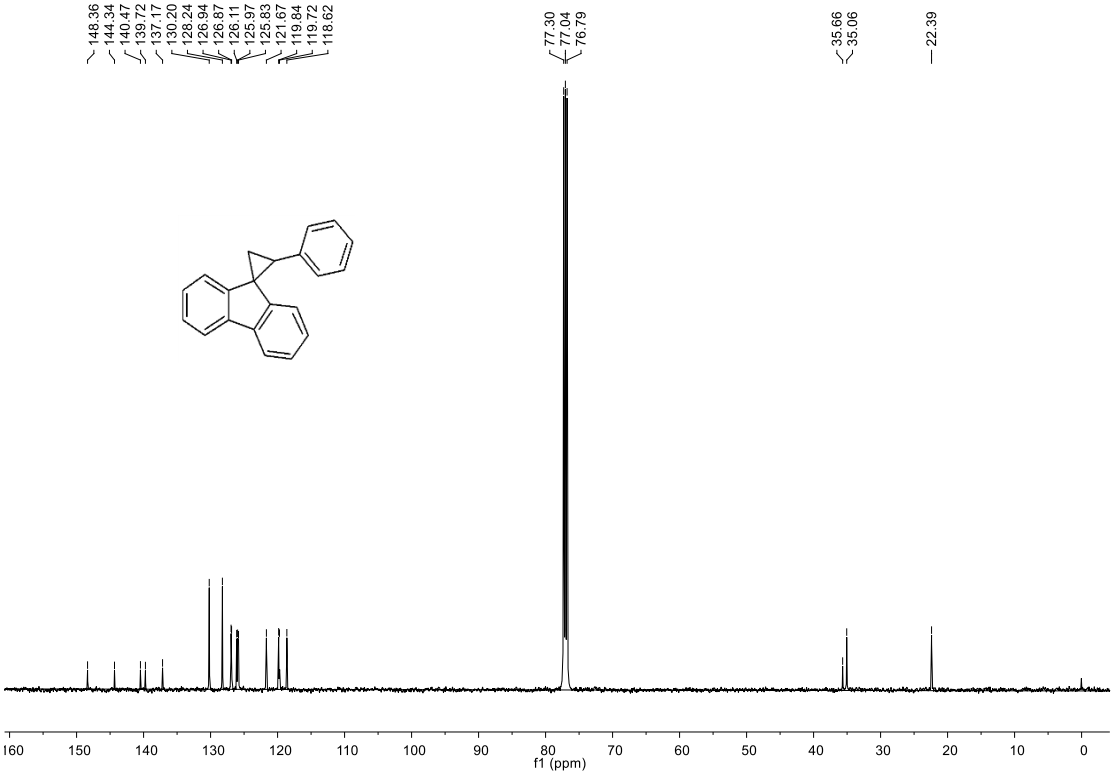


23. 2-Phenylspiro[cyclopropane-1,9'-fluorene] (3w)

^{1}H NMR (500 MHz, $CDCl_3$)

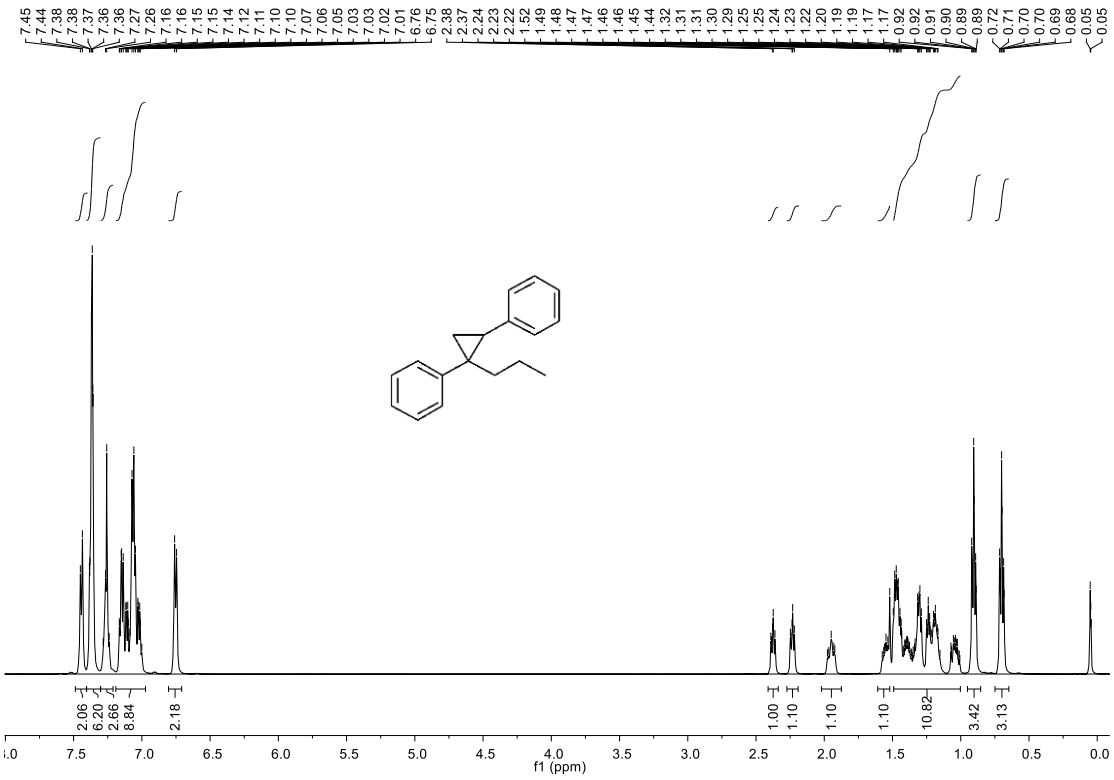


^{13}C NMR (125 MHz, $CDCl_3$)

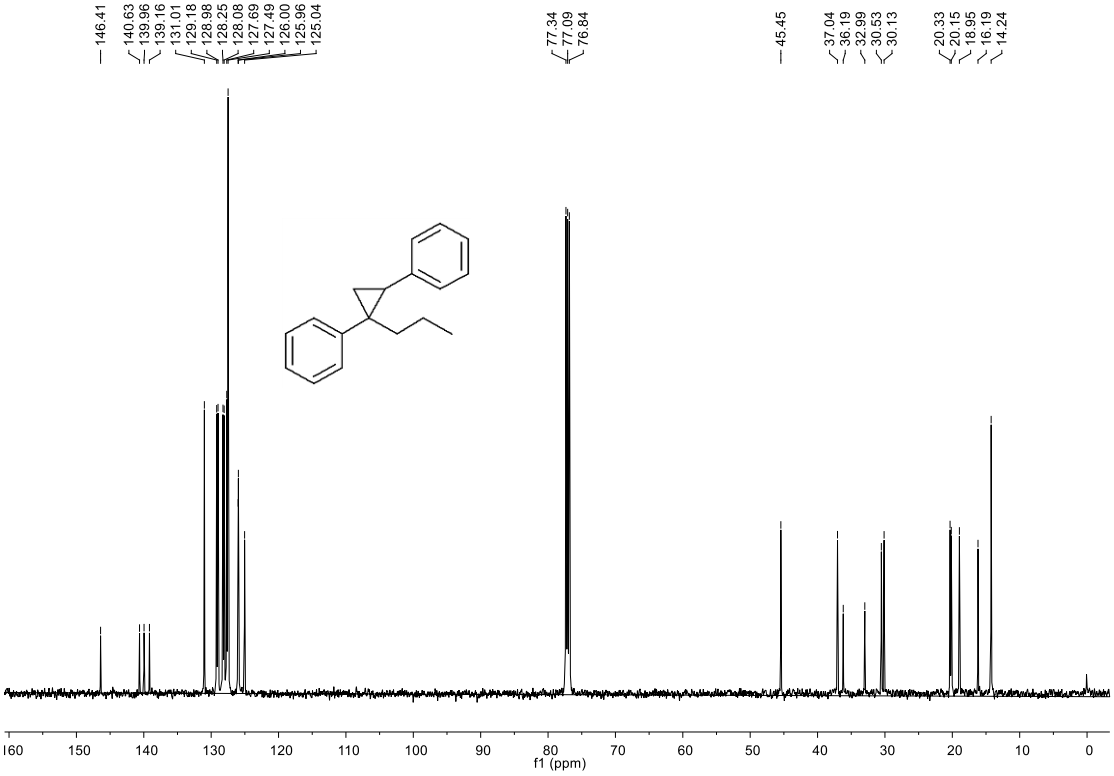


24. (1-Propylcyclopropane-1,2-diyl)dibenzene (mixture of diasteromers 1.1:1) (3x)

^{1}H NMR (500 MHz, $CDCl_3$)

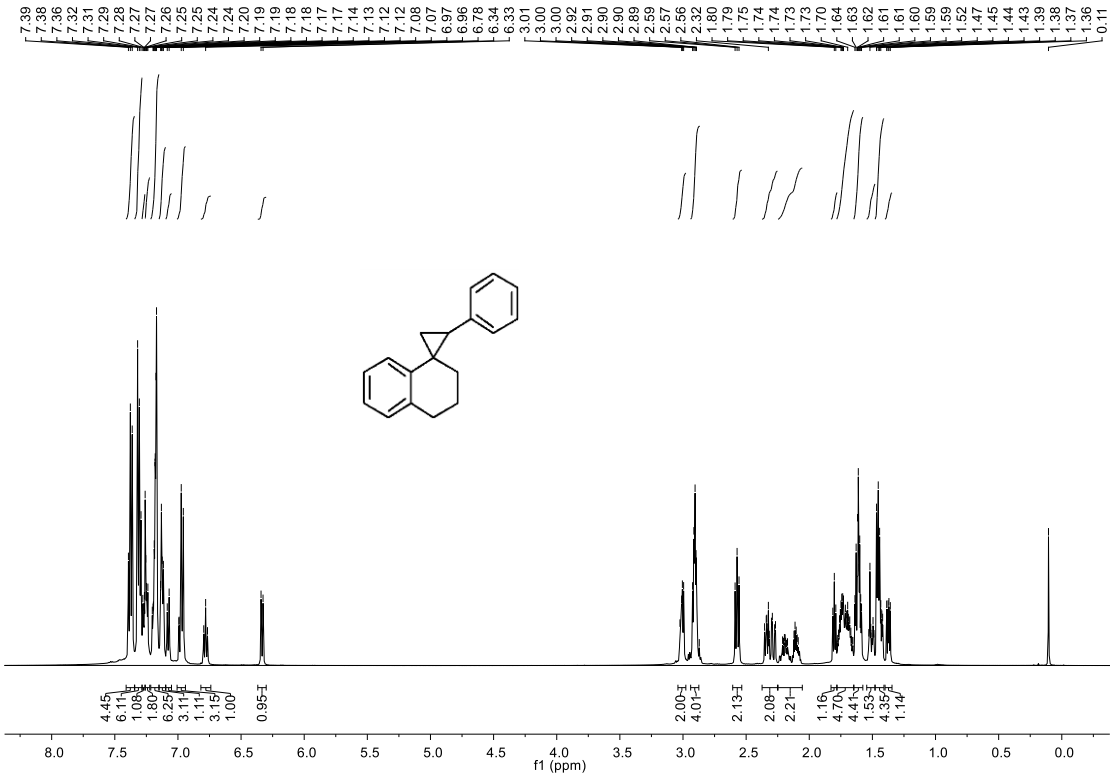


^{13}C NMR (125 MHz, $CDCl_3$)

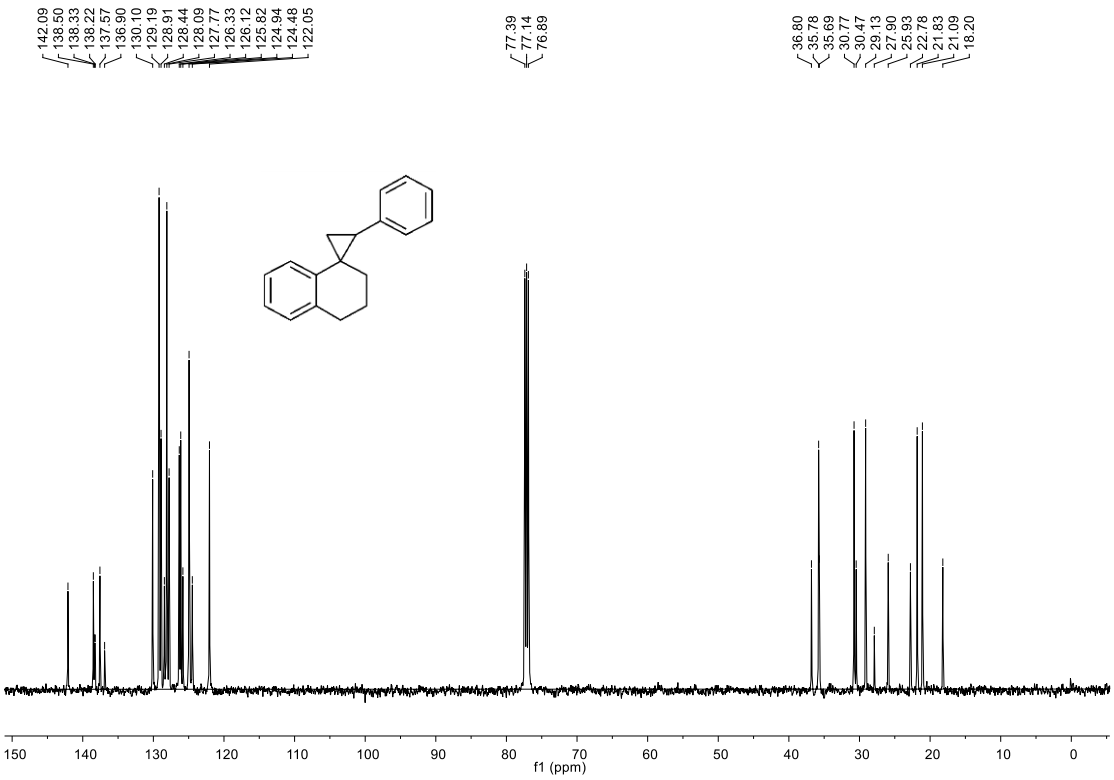


25. 2-Phenyl-3',4'-dihydro-2'H-spiro[cyclopropane-1,1'-naphthalene] (mixture of diasteromers 2:1) (3y)

^{1}H NMR (500 MHz, $CDCl_3$)

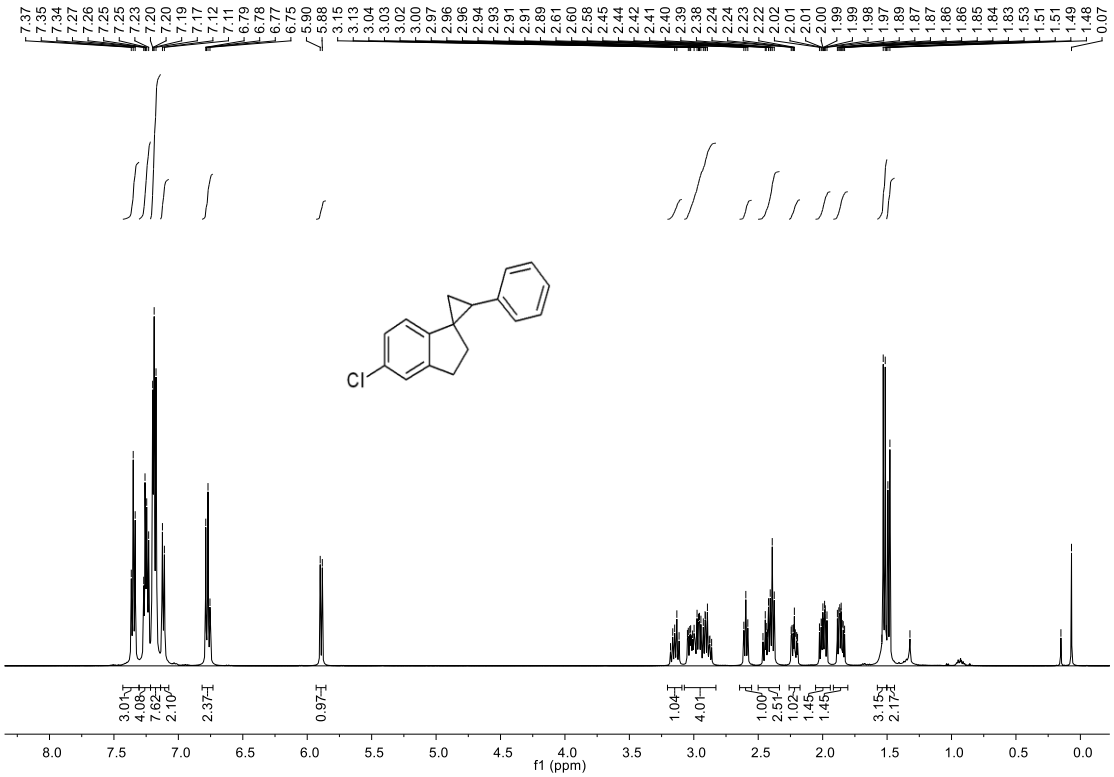


^{13}C NMR (125 MHz, $CDCl_3$)

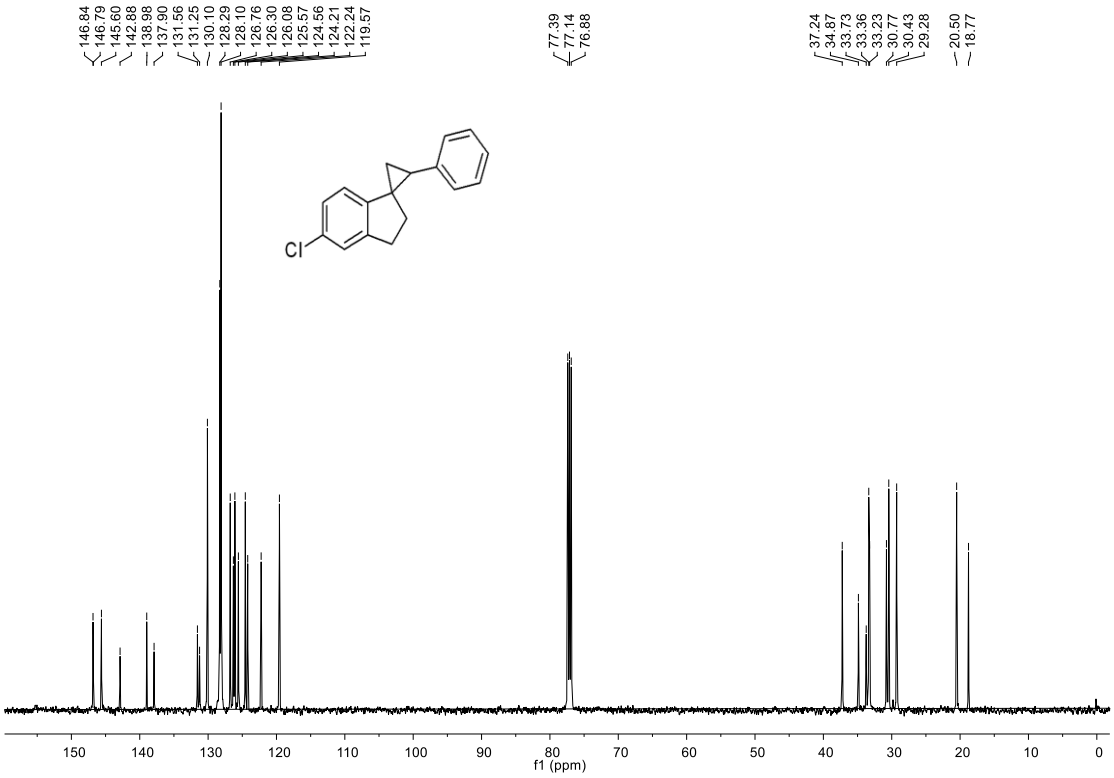


26. 5'-Chloro-2-phenyl-2',3'-dihydrospiro[cyclopropane-1,1'-indene] (mixture of diasteromers 1.5: 1) (3z)

^{1}H NMR (500 MHz, $CDCl_3$)

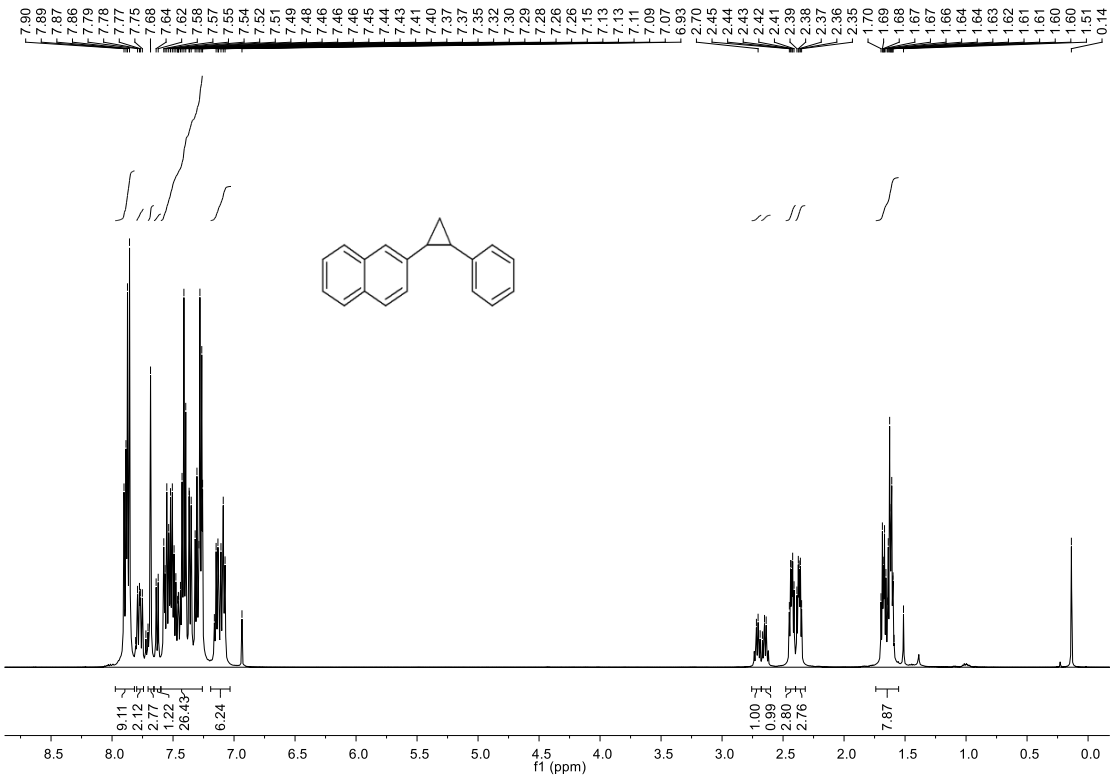


^{13}C NMR (125 MHz, $CDCl_3$)

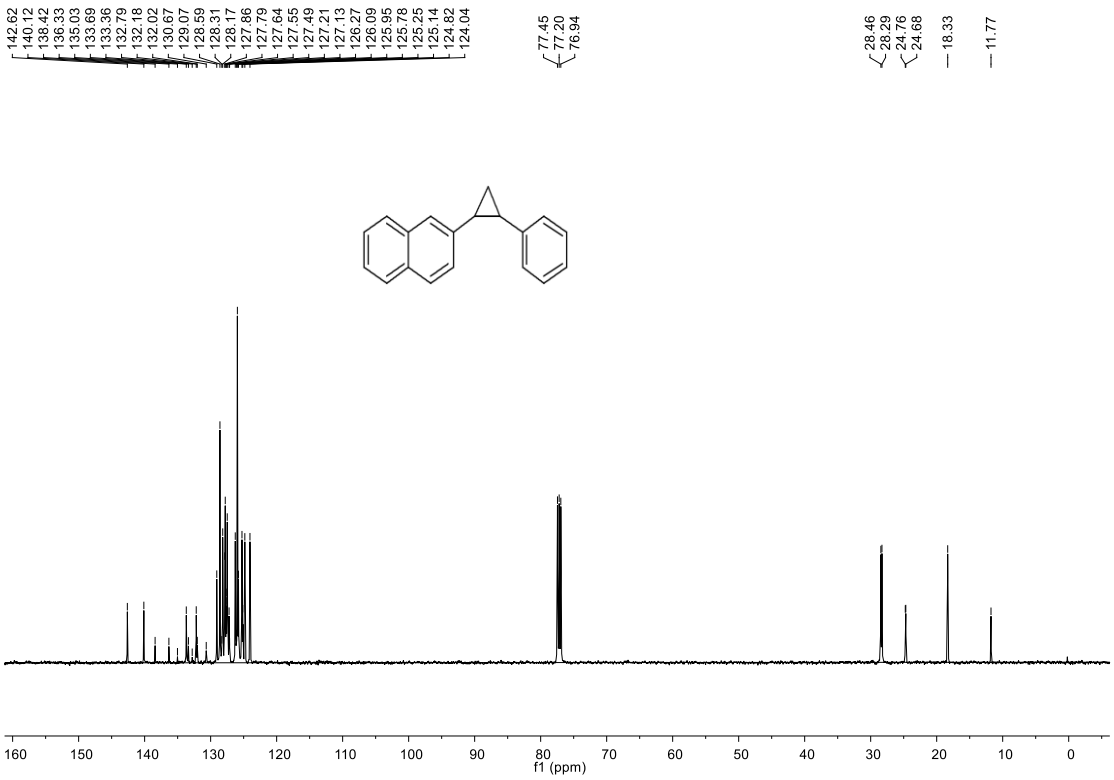


27. 2-(2-Phenylcyclopropyl)naphthalene (mixture of diasteromers 2.8:1) (3aa)

^{1}H NMR (500 MHz, $CDCl_3$)

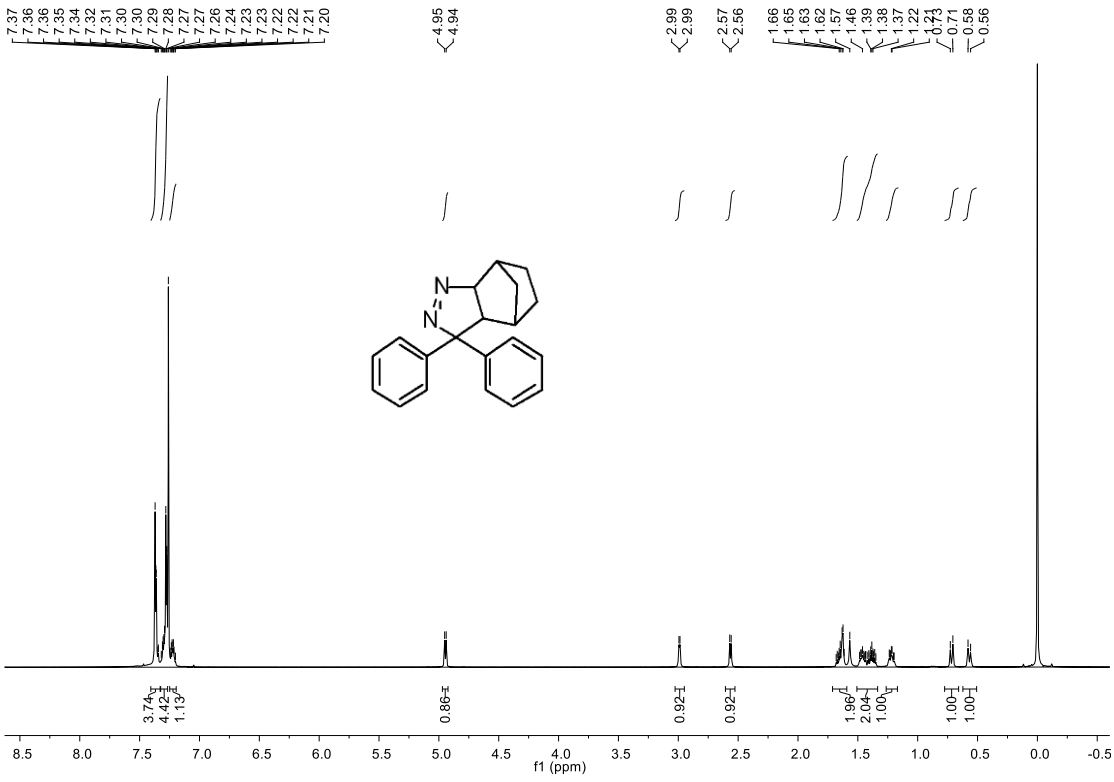


^{13}C NMR (125 MHz, $CDCl_3$)

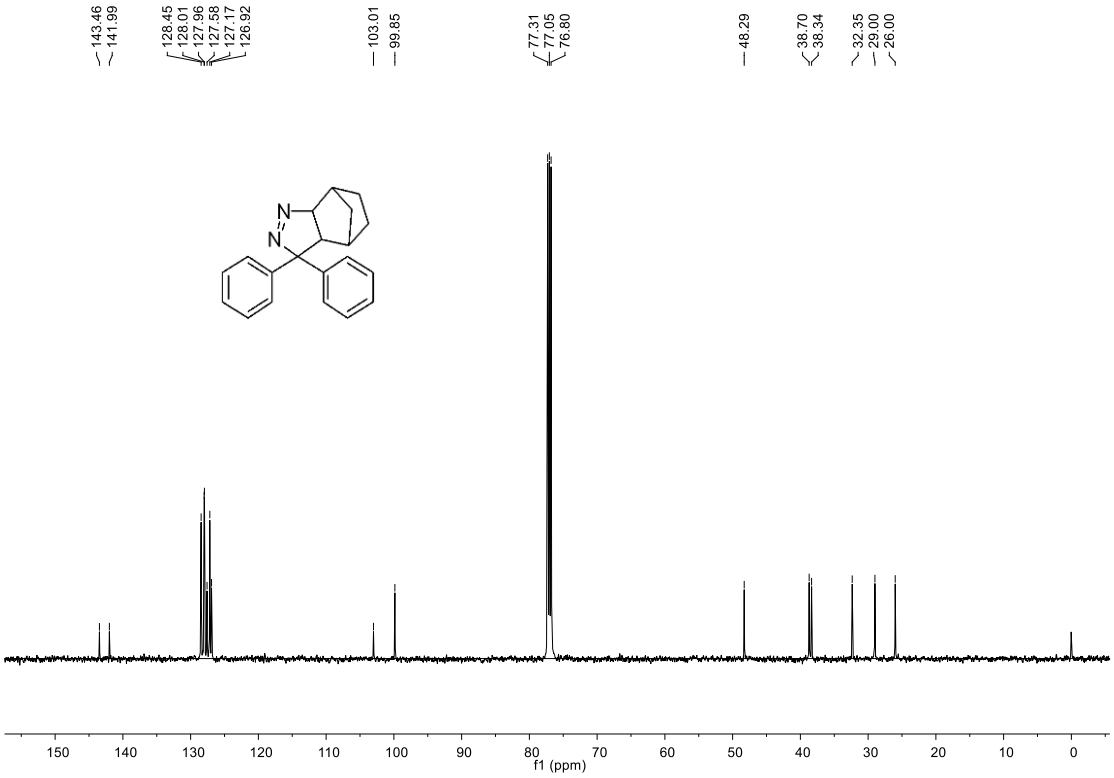


28. 3,3-Diphenyl-3a,4,5,6,7,7a-hexahydro-3H-4,7-methanoindazole (4)

^{1}H NMR (500 MHz, $CDCl_3$)

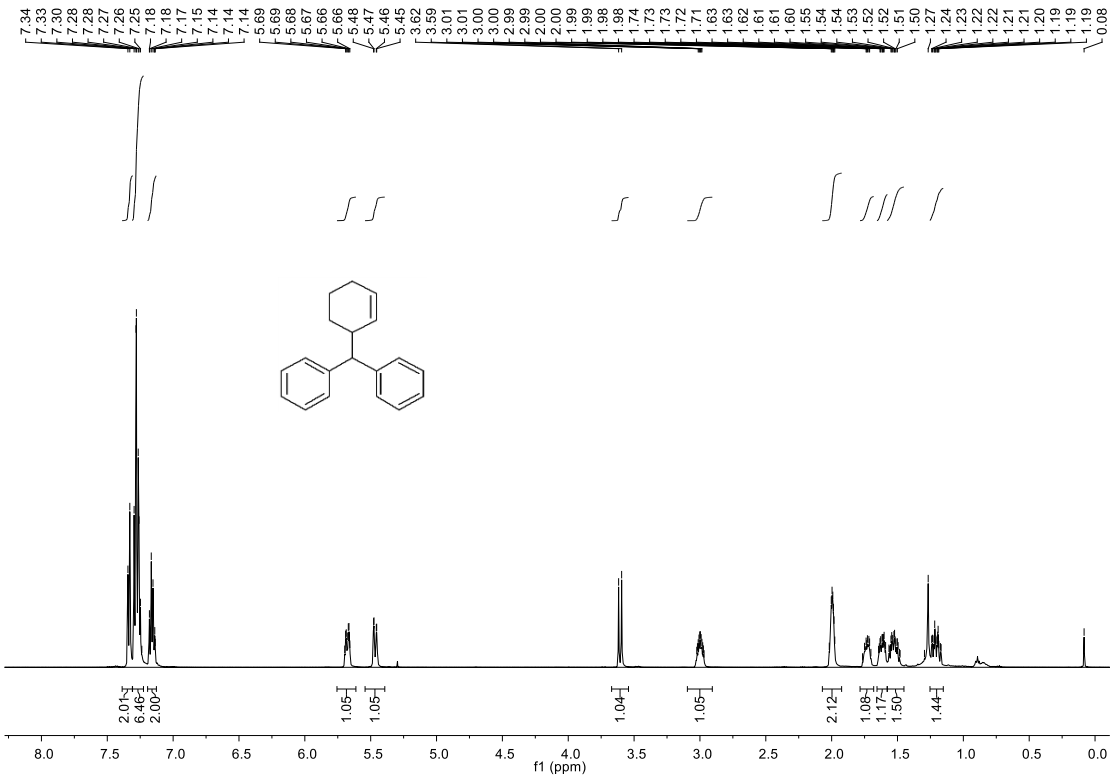


^{13}C NMR (125 MHz, $CDCl_3$)

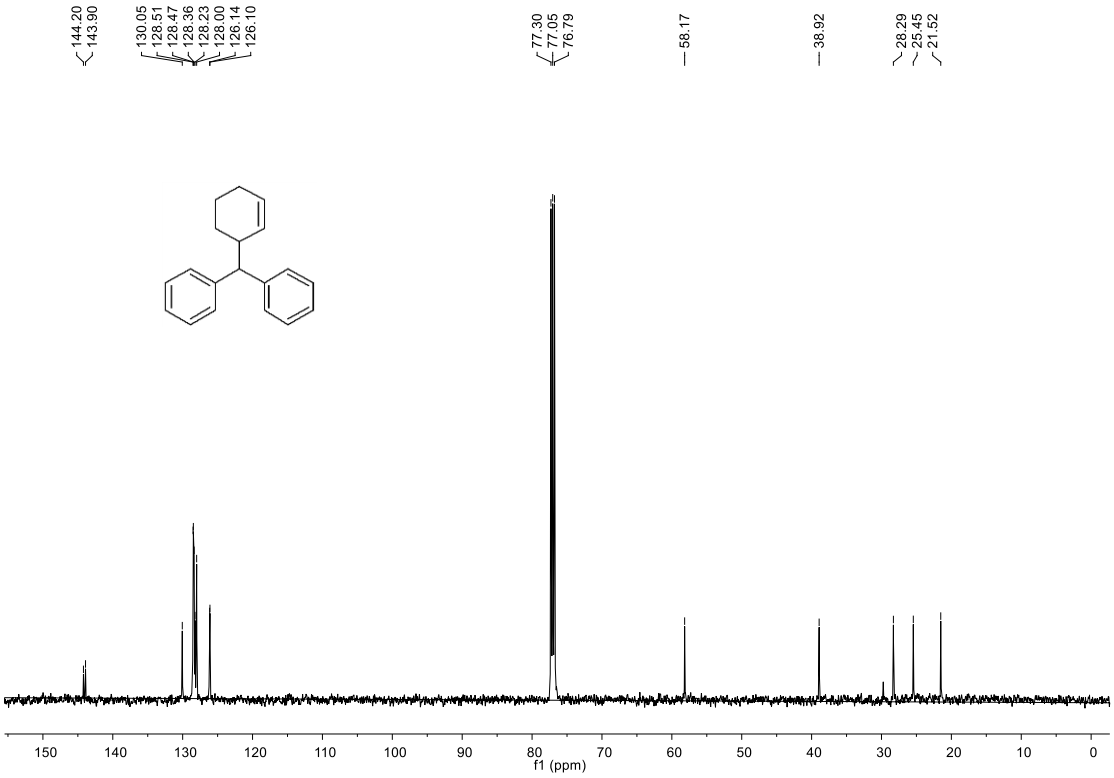


29. (Cyclohex-2-en-1-ylmethylene)dibenzene (5)

^{1}H NMR (500 MHz, $CDCl_3$)

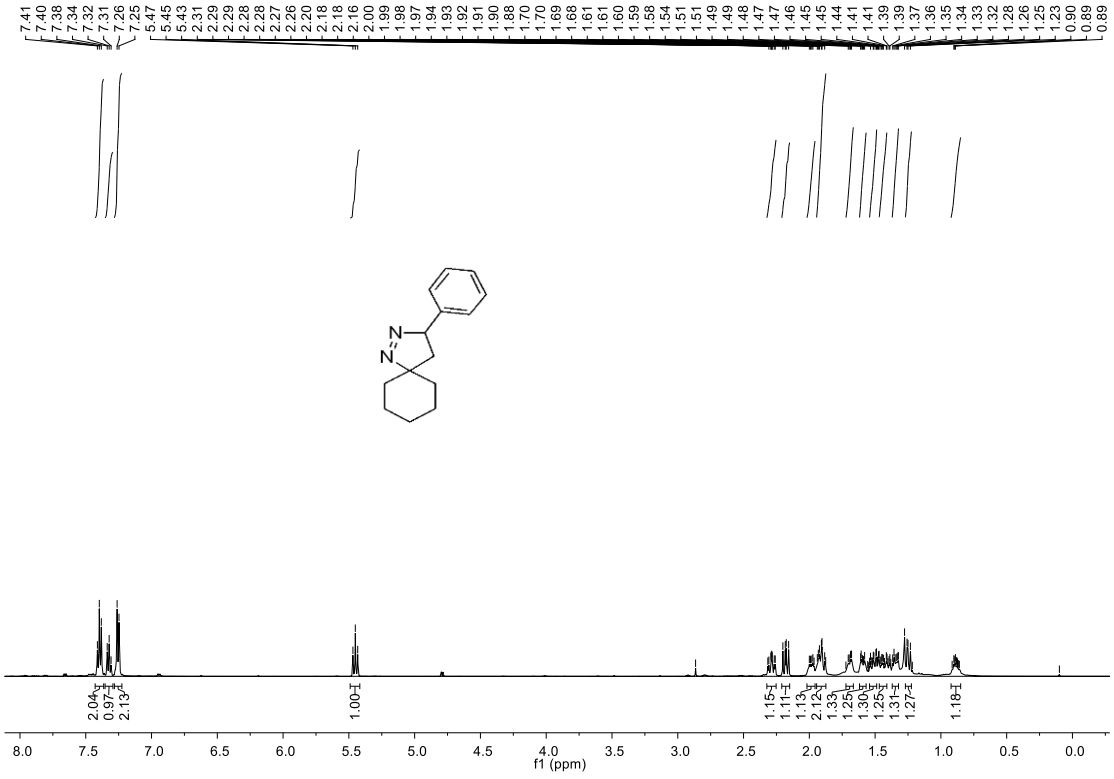


^{13}C NMR (125 MHz, $CDCl_3$)



30. 3-Phenyl-1,2-diazaspiro[4.5]dec-1-ene (6)

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)