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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 procedure

General

Alkenes 2a, 2b, 2g-2j, 2m and norbornene were used as received from commercially available sources, or synthesized according to literature. Iodosobenzene was freshly synthesized and dried according to literature. Petroleum ether refers to the fraction boiling in the 60-90 °C range. Column chromatography was performed with Silica Gel (200-300 mesh). H and C spectra were recorded at 500.0 MHz and 125.0 MHz on a Bruker DRX 500 spectrometer in CDCl3 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

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$_2$I$_2$ as internal standard.

Table S1. Yield of cyclopropane with different equivalents of styrene

<table>
<thead>
<tr>
<th>Entry</th>
<th>Styrene (equiv.)</th>
<th>Yield (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>55</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>68</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>74 (72$^b$)</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>71</td>
</tr>
</tbody>
</table>

$^a$ The yield was determined by 1H-NMR using CH$_2$I$_2$ 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); $R_f$ = 0.39 (petroleum ether); Yield: 72%.

   $^1$H NMR (500 MHz, CDCl$_3$): δ = 7.35-6.90 (comp, 15H), 2.82 (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; $R_f$ = 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; $R_f$ = 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; Rf = 0.39 (petroleum ether); Yield: 67%.

1H NMR (500 MHz, CDCl3): 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).

13C NMR (125 MHz, CDCl3): 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 C21H17Br: 348.0514, found 348.0511.

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

White solid; m.p. 91-92 °C; Rf = 0.40 (petroleum ether); Yield: 71%.

1H NMR (500 MHz, CDCl3): 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).

13C NMR (125 MHz, CDCl3): δ = 146.6, 141.4, 139.8, 131.3, 131.1, 129.2, 128.7, 128.5, 128.2, 127.5, 126.6, 126.2, 121.9, 39.8, 31.9, 21.1.

HRMS (EI, 70 eV): m/z (M+) calcd for C21H17Br: 348.0513, found 348.0511.

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

Colorless oil; Rf = 0.40 (petroleum ether); Yield: 74%.

1H NMR (500 MHz, CDCl3): 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).

13C NMR (125 MHz, CDCl3): 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)

Colorless oil; Rf = 0.39 (petroleum ether); Yield: 73%.

1H NMR (500 MHz, CDCl3): δ = 7.37-7.13 (comp, 10H), 6.97 (d, J = 8.0 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H), 2.90 (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).

13C NMR (125 MHz, CDCl3): 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)

Light yellow solid; m.p. 84-85 °C; Rf = 0.41 (petroleum ether); Yield: 70%.

1H NMR (500 MHz, CDCl3): 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$_3$): $\delta = 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$_{23}$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 ºC; $R_f = 0.55$ (petroleum ether/ethyl acetate = 10:1); Yield: 63%.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.28$-$7.07$ (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).

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 157.6, 147.2, 140.4, 131.3, 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 ºC; $R_f = 0.29$ (petroleum ether/ethyl acetate = 10:1); Yield: 68%.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.34$-$6.88$ (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$_3$): $\delta = 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$_3$): $\delta = 7.73$-$6.94$ (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$_3$): $\delta = 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$_{23}$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$_3$): $\delta = 7.33$ (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$_3$): $\delta = 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)$^4$

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S5
White solid; m.p. 70-71 °C; Rf = 0.34 (petroleum ether); Yield: 46%.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.53-6.88 \text{ (comp, 15H)}\), 2.21 (d, \(J = 5.5\) Hz, 2H), 1.55 (d, \(J = 5.5\) Hz, 2H), 1.36 (s, 3H).

\(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 143.7, 143.2, 143.1, 130.3, 129.6, 128.5, 128.4, 127.8, 127.5, 126.2, 125.6, 125.3, 42.9, 32.8, 26.2, 25.0\).

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

Light yellow solid; m.p. 103-104 °C; Rf = 0.41 (petroleum ether/ethyl acetate = 10:1); Yield: 81%.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.95-6.94 \text{ (comp, 14H)}\), 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).

\(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 147.4, 146.0, 139.1, 131.0, 128.6, 128.4, 128.3, 127.3, 126.9, 126.4, 122.9, 41.2, 32.3, 22.1\).

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)

White Oil; Rf = 0.46 (petroleum ether); Yield: 67%.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.44-7.17 \text{ (comp, 10H)}\), 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 (m, 2H).

\(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 145.8, 140.2, 130.5, 128.6, 128.5, 128.0, 127.1, 126.3, 43.7, 33.0, 27.9, 20.0\).

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

Colorless oil; Rf = 0.45 (petroleum ether); Yield: 51%.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.40-7.12 \text{ (comp, 10H)}\), 3.20-3.12 (m, 1H), 2.16-2.11 (m, 1H), 1.46-1.42 (m, 1H), 1.40-1.37 (m, 1H).

\(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 144.7, 138.9, 129.5, 127.5, 127.4, 126.9, 126.1, 125.3, 38.5, 34.6, 27.3, 20.1\).

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

Colorless oil; Rf = 0.36 (petroleum ether/ethyl acetate=20:1); Yield: 80%.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.40-7.38 \text{ (comp, 2H)}\), 7.34-7.27 (comp, 6H), 7.26-7.21 (comp, 2H), 3.53 (s, 3H), 2.60 (dd, \(J = 8.0\) Hz, \(J = 6.0\) Hz, 1H), 2.22 (dd, \(J = 6.0\) Hz, \(J = 5.0\) Hz, 1H), 1.66 (dd, \(J = 8.0\) Hz, \(J = 5.0\) Hz, 1H).

\(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 171.30, 144.95, 140.40, 129.81, 128.65, 128.51, 127.79, 127.18, 126.74, 51.86, 40.12, 29.01, 20.34\).

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

Colorless oil; Rf = 0.38 (petroleum ether/ethyl acetate=20:1); Yield: 79%.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.43-7.42 \text{ (comp, 2H)}\), 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, CDCl₃): 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)$^9$

![Structure](image)

White solid; m.p. 60-61 °C (Lit$^9$ m.p. 60-61 °C); Rf = 0.27 (petroleum ether); Yield: 91%.

$^1$H NMR (500 MHz, CDCl₃): 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, CDCl₃): 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) (3t)

![Structure](image)

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

$^1$H NMR (500 MHz, CDCl₃): 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, CDCl₃): 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 C₂₂H₂₃Cl: 284.1565, found 284.1560.

21. 4,4′-(2-Phenylcyclopropane-1,1-diyl)bis(chlorobenzene) (3u)$^{10}$

![Structure](image)

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

$^1$H NMR (500 MHz, CDCl₃): 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, CDCl₃): 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)

![Structure](image)

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

$^1$H NMR (500 MHz, CDCl₃): 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, CDCl₃): 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, 128.2, 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 C₂₁H₁₇Cl: 304.1019, found 304.1018.
23. 2-Phenylspiro[cyclopropane-1,9'-fluorene] (3w)\textsuperscript{11}

White Solid; \textbf{m.p.} 125-126 °C (Lit\textsuperscript{11} m.p. 127-128 °C); \textbf{R}_f = 0.30 (petroleum ether); Yield: 84%.

\textbf{^1H NMR (500 MHz, CDCl\textsubscript{3})}: \textbf{\delta} = 7.85 (d, \textit{J} = 7.0 Hz, 1H), 7.80 (d, \textit{J} = 7.5 Hz, 1H), 7.40-6.91 (comp, 11H), 6.16 (d, \textit{J} = 7.5 Hz, 1H), 3.38 (t, \textit{J} = 8.0 Hz, 1H), 2.22 (d, \textit{J} = 8.0 Hz, 1H).

\textbf{^13C NMR (125 MHz, CDCl\textsubscript{3})}: \textbf{\delta} = 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; \textbf{R}_f = 0.65 (petroleum ether); Yield: 86%.

\textbf{^1H NMR (500 MHz, CDCl\textsubscript{3})}: \textbf{\delta} = 7.44 (d, \textit{J} = 7.5 Hz, 1H), 7.38-7.00 (comp, 16.8H), 6.75 (d, \textit{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).

\textbf{^13C NMR (125 MHz, CDCl\textsubscript{3})}: \textbf{\delta} = 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.

\textbf{HRMS (EI, 70 eV)}: m/z (M\textsuperscript{+}) calcld for C\textsubscript{18}H\textsubscript{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; \textbf{m.p.} 68-69 °C; \textbf{R}_f = 0.52 (petroleum ether); Yield: 76%.

\textbf{^1H NMR (500 MHz, CDCl\textsubscript{3})}: \textbf{\delta} = 7.39-6.96 (comp, 25H), 6.78 (t, \textit{J} = 7.5 Hz, 1H), 6.33 (d, \textit{J} = 8.0 Hz, 2H), 3.02-2.87 (comp, 6H), 2.57 (t, \textit{J} = 8.0 Hz, 2H), 2.35-2.27 (comp, 4H), 1.80 (t, \textit{J} = 6.0 Hz, 1H), 1.77-1.36 (comp, 14H).

\textbf{^13C NMR (125 MHz, CDCl\textsubscript{3})}: \textbf{\delta} = 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.

\textbf{HRMS (EI, 70 eV)}: m/z (M\textsuperscript{+}) calcld for C\textsubscript{18}H\textsubscript{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; \textbf{R}_f = 0.60 (petroleum ether); Yield: 70%.

\textbf{^1H NMR (500 MHz, CDCl\textsubscript{3})}: \textbf{\delta} = 7.37-6.75 (comp, 19H), 5.89 (d, \textit{J} = 8.0 Hz, 1H), 3.18-3.11 (m, 1H), 3.05-2.86 (comp, 4H), 2.60 (t, \textit{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, \textit{J} = 7.0 Hz, 3H), 1.49 (d, \textit{J} = 8.0 Hz, 2H).

\textbf{^13C NMR (125 MHz, CDCl\textsubscript{3})}: \textbf{\delta} = 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.

\textbf{HRMS (EI, 70 eV)}: m/z (M\textsuperscript{+}) calcld for C\textsubscript{17}H\textsubscript{15}: 254.0862, found 254.0868.
27. 2-(2-Phenylcyclopropyl)naphthalene (mixture of diasteromers 2.8:1) (3aa)\(^\text{12}\)

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

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.90-7.07\) (comp, 45.6H), 2.72-2.64 (comp, 2H), 2.45-2.35 (comp, 5.6H), 1.70-1.59 (comp, 7.6H).

\(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 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, 127.5, 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)\(^\text{13}\)

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

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.37-7.20\) (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).

\(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 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)\(^\text{14}\)

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

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.34-7.14\) (comp, 10H), 5.70-5.66 (m, 1H), 5.48-5.45 (m, 1H), 3.61 (d, \(J = 15\) Hz, 1H), 2.81 (m, 1H, 1.77-1.70 (m, 1H), 1.64-1.59 (m, 1H), 1.56-1.48 (m, 1H), 1.24-1.17 (m, 1H).

\(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 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; \(R_f = 0.30\) (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\(_3\)): \(\delta = 7.41-7.25\) (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).

\(^1^3\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 139.9, 128.9, 127.7, 127.3, 94.4, 90.3, 37.9, 36.3, 33.2, 25.5, 23.7, 23.3.
References


Copies of $^1\text{H}, ^{13}\text{C}$ spectra

1. Cyclopropane-1,1,2-triyltribenzene (3a)
$^1\text{H}$ NMR (500 MHz, CDCl$_3$)

2. (2-(4-Chlorophenyl)cyclopropane-1,1-diyl)dibenzene (3b)
$^1\text{H}$ 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$_3$)
4. (2-(2-Bromophenyl)cyclopropane-1,1-diyl)dibenzene (3d)

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3})
\[ { } \]

\[ \text{\^{13}C NMR (125 MHz, CDCl}_3\text{)} \]

\[ \text{Br} \]
\[ \begin{array}{c}
\text{C NMR (125 MHz, CDCl}_3\text{)} \\
5. (2-(3-Bromophenyl)cyclopropane-1,1-diyldibenzene (3e) } \\
\text{H NMR (500 MHz, CDCl}_3\text{)} \]

\[ \text{Br} \]
\[ \begin{array}{c}
\text{H NMR (500 MHz, CDCl}_3\text{)} \\
5. (2-(3-Bromophenyl)cyclopropane-1,1-diyldibenzene (3e) }
\end{array} \]
$^{13}$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)

\( ^1H \) NMR (500 MHz, CDCl\(_3\))
\[ ^1\text{H} \text{ NMR (500 MHz, CDCl}_3 \]
$^{13}$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$_3$)
13C NMR (125 MHz, CDCl₃)

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

1H NMR (500 MHz, CDCl₃)
13C NMR (125 MHz, CDCl$_3$)

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

$^1$H NMR (500 MHz, CDCl$_3$)
13C NMR (125 MHz, CDCl₃)

1H NMR (500 MHz, CDCl₃)

14. (2-(4-Nitrophenyl)cyclopropane-1,1-diyl)dibenzene (3n)
13C NMR (125 MHz, CDCl₃)

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

1H NMR (500 MHz, CDCl₃)
$^{13}$C NMR (125 MHz, CDCl$_3$)

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

$^1$H NMR (500 MHz, CDCl$_3$)
13C NMR (125 MHz, CDCl₃)

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

1H NMR (500 MHz, CDCl₃)
13C NMR (125 MHz, CDCl₃)

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

¹H NMR (500 MHz, CDCl₃)
$^{13}$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) (3t)

$^1$H NMR (500 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 diastereomers 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$_3$)
13C NMR (125 MHz, CDCl₃)

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

1H NMR (500 MHz, CDCl₃)
25. 2-Phenyl-3',4'-dihydro-2'H-spiro[cyclopropane-1,1'-naphthale] (mixture of diasteromers 2:1) (3y)

$^{13}$C NMR (125 MHz, CDCl$_3$)

$^{1}$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)

$^1$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$_3$)

![Carbon NMR spectrum](image)

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

$^1$H NMR (500 MHz, CDCl$_3$)

![Hydrogen NMR spectrum](image)
$^{13}$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$_3$)