Supporting Information

Nickel-Catalyzed Alkyl-Alkyl Cross-Coupling Reactions of Non-activated Secondary Alkyl Bromides with Aldehydes as Alkyl Carbanion Equivalents

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Table of Contents

1. General Information ...............................................................S2
2. Preparation of substrates .......................................................S2
3. General procedure for the cross-coupling reaction .......................S3
4. General procedure for eq. 3 and 5 ..........................................S15
5. References..............................................................................S16
6. 1H, 13C, 19F NMR Spectra......................................................S17
1. General Information

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. Unless otherwise noted, all reactions were carried out under a argon atmosphere. $^1$H NMR spectra, $^{19}$F NMR spectra, $^{13}$C NMR spectra were recorded on a Bruker 300, 400 and 500 MHz spectrometer in CDCl$_3$. Data for $^1$H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for $^{13}$C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak (CDCl$_3$: 77.0 ppm). Tetrahydrofuran was distilled from sodium and benzophenone prior to use. Hydrazine hydrate was purchased from Alfa Aesar.

2. Preparation of substrates

\[
\text{alkyl} \begin{array}{c} \text{Br}_2, \text{PPh}_3, \text{imidazole} \end{array} \text{DCM, 0 °C to rt} \rightarrow \text{alkyl} \begin{array}{c} \text{Br} \end{array}
\]

Under a nitrogen atmosphere, PPh$_3$ (1.25 equiv.), imidazole (1.25 equiv.), DCM (30 mL) were added to a 50 mL round-bottomed flask. Br$_2$ (1.16 equiv.) was added slowly at 0 °C and the mixture was stirring for 30 min. Then secondary alcohol (1 equiv.) in DCM (5 mL) was added dropwise at 0 °C and warming the mixture to ambient temperature. The mixture was concentrated under reduced pressure on a rotary evaporator to an approximate volume, and diluted with petroleum ether. The resulting solid was filtered, and the filtrate was concentrated and purified by column chromatography (petroleum ether) to give a colorless liquid. Spectroscopic data match those reported in the literature ($2a^1$, $2c^2$, $2d^3$, $2e^4$). Other bromides were purchased.

\[
\text{R} \begin{array}{c} \text{OH} \end{array} \begin{array}{c} \text{N}_2\text{H}_4\text{H}_2\text{O} \end{array} \text{THF, RT} \rightarrow \text{R} \begin{array}{c} \text{NNH}_2 \end{array}
\]

To a solution of aldehyde (20 mmol, 1.0 equiv.) in THF (20 mL) was added hydrazine hydrate (98% purity, 24 mmol, 1.2 equiv.) and the mixture stirred at room temperature for 0.5 h. After the aldehyde consumed completely, the mixture was then evaporated under reduced pressure at room temperature to provide the desired hydrazone and used directly without further purification.\textsuperscript{5}
3. General procedure for the cross-coupling reaction of hydrazines and alkyl bromides.

\[
\text{Ni(COD)}_2 (8.3 \text{ mg, 0.03 mmol}), \text{dpf} (33 \text{ mg, 0.06 mmol}), \text{NaO}^\text{Bu} (58 \text{ mg, 0.6 mmol}) \text{ were added to a 10 mL sealing tube under a nitrogen atmosphere. Hydrazone (0.6 mmol, 2 equiv.), alkyl bromide (0.3 mmol) were added in THF (2 mL) and the mixture was stirring at 80 °C for 12 h. After alkyl bromide consumed completely, the resulting solid was filtered, and the filtrate was concentrated and purified by column chromatography (petroleum ether) to give a desired product.}
\]

(2-methylbutane-1,4-diyldibenzene (3a):

\[
\text{Ph} \quad \text{3a}
\]

Prepared according to general procedure from benzylidenehydrazine 1a (63 mg, 0.6 mmol) and (3-bromobutyl)benzene 2a (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3a as colorless oil (39 mg, 58%). \(^1\)H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.37-7.30 (m, 4H), 7.28-7.19 (m, 6H), 2.86-2.60 (m, 3H), 2.49 (dd, \(J = 12.0, 8.0\) Hz, 1H), 1.92-1.71 (m, 2H), 1.64-1.48 (m, 1H), 0.99 (d, \(J = 12.0\) Hz, 3H). \(^13\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 142.85, 141.34, 129.24, 128.41, 128.34, 128.17, 125.74, 125.67, 43.59, 38.52, 34.67, 33.54, 19.44. HRMS (EI) calcd. for \([\text{C}_{17}\text{H}_{20}]^+\): 224.1565, found: 224.1563.

1-methoxy-4-(2-methyl-4-phenylbutyl)benzene (3b):

\[
\text{Ph} \quad \text{3b}
\]

Prepared according to general procedure from (4-methoxybenzylidene)hydrizone 1b (90 mg, 0.6 mmol) and (3-bromobutyl)benzene 2a (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3b as colorless oil (46 mg, 61%). \(^1\)H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.33-7.28 (m, 2H), 7.22-7.18 (m, 3H), 7.11-7.06 (m, 2H), 6.89-6.80 (m, 2H), 3.82 (s, 3H), 2.79-2.57 (m, 3H), 2.40 (dd, \(J = 15.0, 9.0\) Hz, 1H), 1.84-1.64 (m, 2H), 1.56-1.45 (m, 1H), 0.95 (d, \(J = 6.0\) Hz, 3H). \(^13\)C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 157.73, 142.91, 133.39, 130.08, 128.40, 128.33, 125.64,
113.58, 55.26, 42.65, 38.44, 34.79, 33.55, 19.39. HRMS (EI) calcd. for $\text{[C}_{18}\text{C}_{22}\text{O}]^+$: 254.1671, found: 254.1672.

1-methyl-3-(2-methyl-4-phenylbutyl)benzene (3c):

![Chemical structure of 3c](image)

Prepared according to general procedure from (3-methylbenzylidene)hydrazine 1c (80 mg, 0.6 mmol) and (3-bromobutyl)benzene 2a (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3c as colorless oil (37, 53%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.34 (t, $J$ = 7.7 Hz, 2H), 7.29-7.20 (m, 4H), 7.07 (d, $J$ = 7.5 Hz, 1H), 7.01 (d, $J$ = 10.6 Hz, 2H), 2.84-2.62 (m, 3H), 2.45 (dd, $J$ = 15.0, 10.0 Hz, 1H), 2.40 (s, 3H), 1.89-1.74 (m, 2H), 1.59-1.52 (m, 1H), 1.00 (d, $J$ = 10.0 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 142.91, 141.29, 137.65, 130.05, 128.43, 128.34, 128.05, 126.48, 126.28, 125.66, 43.52, 38.57, 34.64, 33.55, 21.49, 19.49. HRMS (EI) calcd. for $\text{[C}_{18}\text{C}_{22}\text{O}]^+$: 238.1722, found: 238.1721.

1-methoxy-2-(2-methyl-4-phenylbutyl)benzene (3d):

![Chemical structure of 3d](image)

Prepared according to general procedure from (2-methoxybenzylidene)hydrazine 1d (90 mg, 0.6 mmol) and (3-bromobutyl)benzene 2d (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3d as colorless oil (41 mg, 54%). $^1$H NMR (300 MHz, CDCl$_3$) δ 7.34-7.29 (m, 2H), 7.26-7.18 (m, 4H), 7.14 (dd, $J$ = 6.0, 1.5 Hz, 1H), 6.91 (dd, $J$ = 12.0, 6.0 Hz, 2H), 3.83 (s, 3H), 2.85-2.59 (m, 3H), 2.47 (dd, $J$ = 15.0, 8.1 Hz, 1H), 1.99-1.67 (m, 2H), 1.63-1.49 (m, 1H), 0.97 (d, $J$ = 6.6 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 157.76, 143.19, 130.95, 129.91, 128.46, 128.27, 126.98, 125.56, 120.17, 110.32, 55.24, 38.85, 37.71, 33.53, 33.09, 19.70. HRMS (EI) calcd. for $\text{[C}_{18}\text{C}_{22}\text{O}]^+$: 254.1671, found: 254.1672.
1-chloro-4-(2-methyl-4-phenylbutyl)benzene (3e):

![Chemical structure](image)

Prepared according to general procedure from (4-chlorobenzylidene)hydrazine 1e (92 mg, 0.6 mmol) and (3-bromobutyl)benzene 2a (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3e as colorless oil (45 mg, 59%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.35-7.16 (m, 7H), 7.09 (d, \(J = 9.0\) Hz, 2H), 2.81-2.55 (m, 3H), 2.42 (dd, \(J = 15.0, 9.0\) Hz, 1H), 1.86-1.63 (m, 2H), 1.57-1.43 (m, 1H), 0.95 (d, \(J = 6.0\) Hz, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 142.64, 139.72, 131.44, 130.50, 129.87, 128.35, 128.25, 125.71, 42.85, 38.35, 34.54, 33.46, 19.29. HRMS (EI) calcd. for [C\(_{17}\)H\(_{19}\)Cl]\(^+\): 258.1175, found: 258.1176.

1-chloro-3-(2-methyl-4-phenylbutyl)benzene (3f):

![Chemical structure](image)

Prepared according to general procedure from (3-chlorobenzylidene)hydrazine 1f (92 mg, 0.6 mmol) and (3-bromobutyl)benzene 2a (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3f as colorless oil (52 mg, 68%). \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ 7.38-7.32 (m, 2H), 7.29-7.18 (m, 6H), 7.11-7.04 (m, 1H), 2.85-2.59 (m, 3H), 2.45 (dd, \(J = 15.0, 9.0\) Hz, 1H), 1.93-1.68 (m, 2H), 1.60-1.50 (m, 1H), 0.99 (d, \(J = 6.0\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 143.42, 142.63, 133.98, 129.42, 129.26, 128.40, 127.43, 125.99, 43.22, 38.42, 34.49, 33.48, 19.35. HRMS (EI) calcd. for [C\(_{17}\)H\(_{19}\)Cl]\(^+\): 258.1175, found: 258.1176.

1-chloro-2-(2-methyl-4-phenylbutyl)benzene (3g):

![Chemical structure](image)

Prepared according to general procedure from (2-chlorobenzylidene)hydrazine 1g (92 mg, 0.6 mmol) and (3-bromobutyl)benzene 2a (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3g as colorless oil (41 mg, 54%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.26-
7.24 (m, 1H), 7.22-7.16 (m, 2H), 7.12-7.01 (m, 6H), 2.76 (dd, J = 16.0, 8.0 Hz, 1H), 2.69-2.61 (m, 1H), 2.57-2.51 (m, 1H), 2.45 (dd, J = 16.0, 8.0 Hz, 1H), 1.87-1.79 (m, 1H), 1.66-1.61 (m, 1H), 1.52-1.41 (m, 1H), 0.86 (d, J = 8.0 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 142.80, 139.03, 134.32, 131.43, 129.51, 128.36, 127.23, 126.42, 125.64, 40.99, 38.70, 33.48, 33.27, 19.38. HRMS (EI) calcd. for [C17H19Cl]+: 258.1175, found: 258.1176.

1-fluoro-4-(2-methyl-4-phenylbutyl)benzene (3h):

prepared according to general procedure from (4-fluorobenzylidene)hydrazine 1h (83 mg, 0.6 mmol) and (3-bromobutyl)benzene 2a (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3h as colorless oil (45 mg, 62%). 1H NMR (400 MHz, CDCl3) δ 7.30-7.25 (m, 2H), 7.21-7.12 (m, 3H), 7.10-7.02 (m, 2H), 6.99-6.90 (m, 2H), 2.76-2.51 (m, 3H), 2.39 (dd, J = 12.0, 8.0 Hz, 1H), 1.80-1.61 (m, 2H), 1.51-1.40 (m, 1H), 0.91 (d, J = 4.0 Hz, 3H). 19F NMR (376 MHz, CDCl3) δ -118.04. 13C NMR (100 MHz, CDCl3) δ 162.45, 160.04, 142.69, 136.84 (d, J = 3.2 Hz), 130.41 (d, J = 7.7 Hz), 128.32 (d, J = 1.8 Hz), 125.67, 114.84 (d, J = 21.1 Hz), 42.67, 38.32, 34.65, 33.45, 19.27. HRMS (EI) calcd. for [C17H19F]+: 242.1471, found: 242.1470.

1-(2-methyl-4-phenylbutyl)-4-(trifluoromethoxy)benzene (3i):

Prepared according to general procedure from (4-(trifluoromethoxy)benzylidene)hydrazine 1i (122 mg, 0.6 mmol) and (3-bromobutyl)benzene 2a (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3i as colorless oil (56 mg, 61%). 1H NMR (400 MHz, CDCl3) δ 7.30-7.22 (m, 2H), 7.21-7.07 (m, 7H), 2.78-2.64 (m, 2H), 2.62-2.55 (m, 1H), 2.41 (dd, J = 12.0, 8.0 Hz, 1H), 1.81-1.61 (m, 2H), 1.52-1.42 (m, 1H), 0.91 (d, J = 8.0 Hz, 3H). 19F NMR (376 MHz, CDCl3) δ -57.89. 13C NMR (100 MHz, CDCl3) δ 147.39, 142.59, 140.02, 130.33, 128.35, 125.72, 121.84, 120.70, 119.29, 42.81, 38.33, 34.52, 33.43, 19.28. HRMS (EI) calcd. for [C18H19F3O]+: 308.1388, found: 308.1384.
methyl(4-(2-methyl-4-phenylbutyl)phenyl)sulfane (3j):

\[
\text{Ph} \quad \text{3j}
\]

Prepared according to general procedure from (4-(methylthio)benzylidene)hydrazine 1j (100 mg, 0.6 mmol) and (3-bromobutyl)benzene 2a (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3j as colorless oil (33 mg, 41%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.29-7.22 (m, 2H), 7.19-7.11 (m, 5H), 7.04 (d, \(J = 8.0\) Hz, 2H), 2.75-2.52 (m, 3H), 2.45 (s, 3H), 2.37 (dd, \(J = 12.0, 8.0\) Hz, 1H), 1.81-1.61 (m, 2H), 1.50-1.39 (m, 1H), 0.90 (d, \(J = 8.0\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.79, 138.46, 135.16, 129.78, 128.40, 128.36, 126.99, 125.70, 43.02, 38.44, 34.64, 33.53, 19.40, 16.37 (d, \(J = 3.8\) Hz). HRMS (EI) calcd. for [C\(_{18}\)H\(_{22}\)S]+: 270.1442, found: 270.1440.

4-(2-methyl-4-phenylbutyl)-1,1'-biphenyl (3k):

\[
\text{Ph} \quad \text{3k}
\]

Prepared according to general procedure from ([1,1'-biphenyl]-4-ylmethylene)hydrazine 1k (118 mg, 0.6 mmol) and (3-bromobutyl)benzene 2a (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3k as a white solid (55 mg, 62%), mp: 39-41 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.72-7.66 (m, 2H), 7.60 (d, \(J = 5.0\) Hz, 2H), 7.51 (t, \(J = 10.0\) Hz, 2H), 7.41 (t, \(J = 5.0\) Hz, 1H), 7.39-7.34 (m, 2H), 7.31-7.24 (m, 5H), 2.88-2.78 (m, 2H), 2.74-2.69 (m, 1H), 2.55 (dd, \(J = 10.0, 5.0\) Hz, 1H), 1.97-1.87 (m, 1H), 1.87-1.77 (m, 1H), 1.66-1.57 (m, 1H), 1.05 (d, \(J = 5.0\) Hz, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 142.86, 141.21, 140.51, 138.69, 129.69, 128.79, 128.45, 128.39, 127.06, 126.93, 125.73, 43.23, 38.56, 34.69, 33.58, 19.52. HRMS (EI) calcd. for [C\(_{23}\)H\(_{24}\)]+: 300.1878, found: 300.1880.
2-(2-methyl-4-phenylbutyl)furan (3l):

Prepared according to general procedure from (furan-2-ylmethylene)hydrazine 1l (66 mg, 0.6 mmol) and (3-bromobutyl)benzene 2a (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3l as colorless oil (27 mg, 42%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.34-7.31 (m, 1H), 7.31-7.27 (m, 2H), 7.22-7.17 (m, 3H), 6.30 (dd, $J = 3.1$, 1.9 Hz, 1H), 6.00 (d, $J = 3.2$ Hz, 1H), 2.74-2.59 (m, 3H), 2.53 (dd, $J = 15.0$, 9.0 Hz, 1H), 1.97-1.84 (m, 1H), 1.78-1.63 (m, 1H), 1.55-1.45 (m, 1H), 0.99 (d, $J = 6.0$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.20, 142.73, 140.80, 128.35, 128.29, 125.63, 110.04, 105.91, 38.37, 35.30, 33.42, 32.35, 19.58. HRMS (EI) calcd. for [C$_{15}$H$_{18}$O]$^+$: 214.1358, found: 214.1360.

1-(2-methyl-4-phenylbutyl)-Ferrocene (3m):

Prepared according to general procedure from 1m (137 mg, 0.6 mmol) and (3-bromobutyl)benzene 2a (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3m as yellow oil (52 mg, 53%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29-7.23 (m, 2H), 7.17-7.14 (m, 3H), 4.07 (s, 5H), 4.03 (s, 4H), 2.68-2.61 (m, 1H), 2.58-2.50 (m, 1H), 2.42 (dd, $J = 12.0$, 4.0 Hz, 1H), 2.23 (dd, $J = 16.0$, 8.0 Hz, 1H), 1.69-1.57 (m, 1H), 1.55-1.46 (m, 1H), 1.44-1.35 (m, 1H), 0.88 (d, $J = 4.0$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.96, 128.39, 128.29, 125.60, 87.25, 69.42, 69.15, 68.57, 67.17, 38.45, 37.67, 35.01, 33.55, 19.63. HRMS (EI) calcd. for [C$_{21}$H$_{24}$Fe]$^+$: 332.1227, found: 332.1224.

1-(2-methyl-4-phenylbutyl)naphthalene (3n):

Prepared according to general procedure from (naphthalen-1-ylmethylene)hydrazine 1n (102 mg,
0.6 mmol) and (3-bromobutyl)benzene 2a (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3n as colorless oil (50 mg, 61%). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.04-7.97 (m, 1H), 7.90-7.87 (m, 1H), 7.76 (d, $J$ = 6.0 Hz, 1H), 7.53-7.47 (m, 2H), 7.41 (dd, $J$ = 15.0, 9.0 Hz, 1H), 7.35-7.28 (m, 3H), 7.24-7.20 (m, 3H), 3.23 (dd, $J$ = 15.0, 6.0 Hz, 1H), 2.92-2.75 (m, 2H), 2.75-2.59 (m, 2H), 2.10-2.02 (m, 1H), 1.89-1.81 (m, 1H), 1.71-1.60 (m, 1H), 1.01 (d, $J$ = 6.0 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 142.76, 137.43, 133.98, 132.22, 128.75, 128.37, 128.32, 127.23, 126.61, 125.66, 125.58, 125.33, 124.12, 40.90, 39.08, 33.88, 33.53, 19.88. HRMS (EI) calcd. for [C$_{21}$H$_{22}$]$: 274.1722$, found: 274.1723.

(4-cyclopentyl-3-methylbutyl)benzene (3o):

![Ph]

Prepared according to general procedure from (cyclopentylmethylene)hydrazine 1o (67 mg, 0.6 mmol) and (3-bromobutyl)benzene 2a (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3o as colorless oil (13 mg, 20%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.32-7.28 (m, 2H), 7.22-7.18 (m, 3H), 2.71-2.65 (m, 1H), 2.2-2.56 (m, 1H), 1.95-1.83 (m, 1H), 1.81-1.71 (m, 2H), 1.71-1.58 (m, 3H), 1.57-1.41 (m, 4H), 1.39-1.31 (m, 1H), 1.26-1.18 (m, 1H), 1.14-1.01 (m, 2H), 0.96 (d, $J$ = 5.0 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 143.26, 128.36, 128.26, 125.52, 43.70, 39.33, 37.67, 33.46, 33.32, 32.66, 31.61, 25.15 (d, $J$ = 1.0 Hz), 19.89. HRMS (EI) calcd. for [C$_{16}$H$_{24}$]$: 216.1878$, found: 216.1876.

(3-methylheptyl)benzene (3p):$^6$

![Ph]

Prepared according to general procedure from butylidenehydrazine 1p (52 mg, 0.6 mmol) and (3-bromobutyl)benzene 2a (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3p as colorless oil (21mg, 38%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.34-7.28 (m, 2H), 7.23-7.19 (m, 3H), 2.72-2.67 (m, 1H), 2.63-2.57 (m, 1H), 1.72-1.62 (m, 1H), 1.53-1.44 (m, 2H), 1.41-1.28 (m, 5H), 1.24-1.15 (m, 1H), 0.97 (d, $J$ = 5.0 Hz, 3H), 0.93 (t, $J$ = 10.0 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 143.26, 128.37, 128.27, 125.53, 39.01, 36.64, 33.53, 32.53, 29.26, 23.06.
(3-methylhexane-1,6-diyl)dibenzene (3q):²

Prepared according to general procedure from (3-phenylpropyldene)hydrazine 1q (89 mg, 0.6 mmol) and (3-bromobutyl)benzene 2a (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 3q as colorless oil (36 mg, 48%). ¹H NMR (300 MHz, CDCl₃) δ 7.36-7.29 (m, 4H), 7.26-7.19 (m, 6H), 2.76-2.56 (m, 4H), 1.76-1.61 (m, 3H), 1.56-1.39 (m, 3H), 1.36-1.22 (m, 1H), 0.99 (d, J = 6.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 143.11, 142.87, 128.42, 128.38, 128.29, 128.28, 125.64, 125.58, 38.88, 36.57, 36.30, 33.49, 32.39, 28.95, 19.59.

4-(4-methyl-2-phenethylpentyl)-1,1'-biphenyl (4b):

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine 1k (118 mg, 0.6 mmol) and (3-bromo-5-methylhexyl)benzene 2b (76 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 4b as colorless oil (53 mg, 52%). ¹H NMR (300 MHz, CDCl₃) δ 7.71-7.68 (m, 2H), 7.61 (d, J = 9.0 Hz, 2H), 7.52 (t, J = 6.0 Hz, 2H), 7.47-7.20 (m, 8H), 2.84-2.62 (m, 4H), 1.98-1.76 (m, 2H), 1.77-1.62 (m, 2H), 1.40-1.26 (m, 2H), 0.99 (d, J = 6.0 Hz, 3H), 0.94 (d, J = 6.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 142.95, 141.19, 140.55, 138.60, 129.72, 128.80, 128.45, 128.36, 127.04, 126.93, 125.70, 43.37, 40.33, 36.91, 35.30, 32.84, 25.38, 23.08, 22.86. HRMS (EI) calcd. for [C₂₀H₃₀]⁺: 342.2348, found: 342.2350.

4-(2-phenethylhex-5-en-1-yl)-1,1'-biphenyl (4c):

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine 1k (118 mg, 0.6 mmol) and (3-bromohept-6-en-1-yl)benzene 2c (76 mg, 0.3 mmol), after flash column
chromatography (petroleum ether) afforded the product 4c as colorless oil (36 mg, 36%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59-7.57 (m, 2H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.41 (t, $J = 8.0$ Hz, 2H), 7.34-7.28 (m, 1H), 7.25 (t, $J = 8.0$ Hz, 2H), 7.21-7.13 (m, 5H), 5.83-5.73 (m, 1H), 5.04-4.89 (m, 2H), 2.71-2.54 (m, 4H), 2.24-1.98 (m, 2H), 1.84-1.70 (m, 1H), 1.65-1.59 (m, 2H), 1.45 (dd, $J = 16.0$, 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.80, 141.15, 140.39, 139.04, 138.70, 129.68, 128.80, 128.43, 128.39, 127.08, 127.04, 126.98, 125.74, 114.50, 39.95, 38.81, 35.00, 33.00, 32.47, 30.99. HRMS (EI) calcd. for [C$_{26}$H$_{28}$]+: 340.2191, found: 340.2194.

4-(4-phenyl-2-(trifluoromethyl)butyl)-1,1'-biphenyl (4d):

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine 1k (118 mg, 0.6 mmol) and (3-bromo-4,4,4-trifluorobutyl)benzene 2d (80 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 4d as colorless oil (45 mg, 43%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60-7.57 (m, 2H), 7.51 (d, $J = 8.0$ Hz, 2H), 7.43 (t, $J = 8.0$ Hz, 2H), 7.35-7.31 (m, 1H), 7.24-7.12 (m, 5H), 7.01 (d, $J = 8.0$ Hz, 2H), 3.08 (dd, $J = 16.0$, 8.0 Hz, 1H), 2.73-2.64 (m, 2H), 2.63-2.53 (m, 1H), 2.50-2.35 (m, 1H), 2.00-1.87 (m, 1H), 1.82-1.73 (m, 1H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -69.88. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.98, 140.81, 139.61, 137.23, 129.80, 129.54, 128.87, 128.51, 128.42, 127.33, 127.07, 126.14, 43.89, 43.63, 33.94, 33.02, 29.09. HRMS (EI) calcd. for [C$_{23}$H$_{21}$F$_3$]+: 354.1595, found: 354.1591.

4-(2-methyl-3-phenoxypropyl)-1,1'-biphenyl (4e):

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine 1k (118 mg, 0.6 mmol) and (2-bromopropoxy)benzene 2e (64 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 4e as colorless oil (48 mg, 54%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59-7.57 (m, 2H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.41 (t, $J = 8.0$ Hz, 2H), 7.34-7.22 (m, 5H), 6.97-6.86 (m, 3H), 3.87-3.74 (m, 2H), 2.91 (dd, $J = 12.0$, 8.0 Hz, 1H), 2.59 (dd, $J = 12.0$, 8.0 Hz, 2H), 2.11-2.04 (m, 2H), 1.81-1.73 (m, 1H), 1.45 (dd, $J = 16.0$, 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.98, 140.81, 139.61, 137.23, 129.80, 129.54, 128.87, 128.51, 128.42, 127.33, 127.07, 126.14, 43.89, 43.63, 33.94, 33.02, 29.09. HRMS (EI) calcd. for [C$_{23}$H$_{21}$F$_3$]+: 354.1595, found: 354.1591.
8.0 Hz, 1H), 2.34-2.22 (m, 1H), 1.05 (d, J = 8.0 Hz, 3H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 159.21, 141.09, 139.51, 138.91, 129.75, 129.49, 128.79, 127.10, 127.04, 120.61, 114.61, 71.92, 39.41, 35.27, 16.97. HRMS (EI) calcd. for [C\(_{22}\)H\(_{22}\)O]: 302.1671, found: 302.1668.

4-(2-methyl-3-phenylpropyl)-1,1'-biphenyl (4f):

\[\text{Ph} - \text{4f} - \text{Ph}\]

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine 1k (118 mg, 0.6 mmol) and (2-bromopropyl)benzene 2f (119 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 4f as colorless oil (36 mg, 42%). \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.61-7.55 (m, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 2H), 7.34-7.23 (m, 3H), 7.23-7.12 (m, 3H), 7.25-2.69 (m, 2H), 2.47-2.41 (m, 2H), 2.16-2.01 (m, 1H), 0.86 (d, J = 8.0 Hz, 3H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 141.28, 141.17, 140.46, 138.72, 129.65, 129.25, 128.78, 128.25, 128.14, 126.96, 125.84, 43.42, 43.00, 37.22, 19.30. HRMS (EI) calcd. for [C\(_{22}\)H\(_{22}\)]\(^+\): 286.1722, found: 286.1723.

4-(2-ethylbutyl)-1,1'-biphenyl (4g):

\[\text{Ph} - \text{4g} - \text{Ph}\]

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine 1k (118 mg, 0.6 mmol) and 3-bromopentane 2g (90 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 4g as colorless oil (37 mg, 53%). \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.61-7.55 (m, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 2H), 7.34-7.27 (m, 1H), 7.24-7.18 (m, 2H), 2.57 (d, J = 4.0 Hz, 2H), 1.58-1.50 (m, 1H), 1.38-1.27 (m, 4H), 0.89 (t, J = 8.0 Hz, 6H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 141.21, 141.09, 138.47, 129.65, 128.74, 127.01, 126.98, 126.85, 42.65, 39.38, 25.02, 10.90. HRMS (EI) calcd. for [C\(_{18}\)H\(_{22}\)]\(^+\): 238.1722, found: 238.1721.
4-(cyclopentylmethyl)-1,1'-biphenyl (4h):

![4h]

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine 1k (118 mg, 0.6 mmol) and bromocyclopentane 2h (45 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 4h as colorless oil (42 mg, 60%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.59-7.57 (m, 2H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.41 (t, $J = 8.0$ Hz, 2H), 7.34-7.27 (m, 1H), 7.23 (d, $J = 8.0$ Hz, 2H), 2.64 (d, $J = 8.0$ Hz, 2H), 2.19-2.04 (m, 1H), 1.77-1.69 (m, 2H), 1.68-1.59 (m, 2H), 1.59-1.49 (m, 2H), 1.30-1.14 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 141.60, 141.24, 138.53, 129.27, 128.75, 127.03, 126.99, 126.93, 42.04, 41.79, 32.58, 25.01. HRMS (EI) calcd. for [C$_{18}$H$_{20}$]$^+$: 236.1565, found: 236.1563.

4-(cyclohexylmethyl)-1,1'-biphenyl (4i):$^8$

![4i]

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine 1k (118 mg, 0.6 mmol) and bromocyclohexane 2i (49 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 4i as colorless oil (46 mg, 61%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.59-7.56 (m, 2H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.41 (t, $J = 8.0$ Hz, 2H), 7.34-7.28 (m, 1H), 7.20 (d, $J = 8.0$ Hz, 2H), 2.51 (d, $J = 4.0$ Hz, 2H), 1.76-1.61 (m, 5H), 1.59-1.52 (m, 1H), 1.29-1.12 (m, 3H), 1.01-0.91 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 141.22, 140.57, 138.53, 129.64, 128.73, 127.02, 126.97, 126.82, 43.81, 39.84, 33.24, 26.62, 26.38.

4-(cycloheptylmethyl)-1,1'-biphenyl (4j):

![4j]

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine 1k (118 mg, 0.6 mmol) and bromocycloheptane 2j (53 mg, 0.3 mmol), after flash column chromatography
(petroleum ether) afforded the product 4j as colorless oil (43 mg, 55%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.61-7.55 (m, 2H), 7.50 (d, $J = 12.0$ Hz, 2H), 7.41 (t, $J = 8.0$ Hz, 2H), 7.32-7.29 (m, 1H), 7.24-7.16 (m, 2H), 2.54 (d, $J = 8.0$ Hz, 2H), 1.85-1.54 (m, 7H), 1.52-1.34 (m, 4H), 1.25-1.16 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 141.22, 141.07, 138.53, 129.66, 128.75, 127.03, 127.00, 126.87, 44.21, 41.41, 34.52, 28.47, 26.42. HRMS (EI) calcd. for [C$_{20}$H$_{24}$]+: 264.1878, found: 264.1877.

4-octyl-1,1’-biphenyl (5):$^9$

Prepared according to general procedure from [(1,1’-biphenyl)-4-ylmethylene]hydrazine 1k (118 mg, 0.6 mmol) and 1-bromoheptane 2k (53 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 5 as colorless oil (23 mg, 43%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.59-7.57 (m, 2H), 7.51 (d, $J = 8.0$ Hz, 2H), 7.51 (t, $J = 8.0$ Hz, 2H), 7.31 (t, $J = 8.0$ Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 2H), 2.64 (t, $J = 8.0$ Hz, 2H), 1.68-1.64 (m, 2H), 1.41-1.20 (m, 10H), 0.88 (t, $J = 8.0$ Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 142.15, 141.22, 138.55, 128.85, 128.72, 127.02, 127.01, 126.97, 35.66, 31.94, 31.56, 29.54, 29.43, 29.32, 22.72, 14.16.

(3r,5r,7r)-1-[(1,1’-biphenyl)-4-ylmethyl]adamantane (6):

Prepared according to general procedure from [(1,1’-biphenyl)-4-ylmethylene]hydrazine 1k (118 mg, 0.6 mmol) and (3r,5r,7r)-1-(bromomethyl)adamantane 2l (53 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product 6 as a white solid (40 mg, 45%), mp: 84-86 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.63-7.57 (m, 2H), 7.52-7.47 (m, 2H), 7.42 (t, $J = 8.0$ Hz, 2H), 7.35-7.28 (m, 1H), 7.15 (d, $J = 8.0$ Hz, 2H), 2.41 (s, 2H), 1.94 (s, 3H), 1.67 (d, $J = 12.0$ Hz, 3H), 1.58 (d, $J = 8.0$ Hz, 3H), 1.51 (d, $J = 4.0$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 141.19, 138.52, 137.50, 131.03, 129.51, 128.72, 126.99, 126.23, 50.92, 42.44, 37.03, 33.64, 28.77. HRMS (EI) calcd. for [C$_{23}$H$_{36}$]+: 302.2035, found: 302.2032.
4. General procedure for eq. 3 and 5

NaO\textsubscript{t}Bu (38 mg, 0.4 mmol), alkyl bromide 2b (51 mg, 0.2 mmol) and THF (3 mL) were added to a 10 mL sealing tube under a nitrogen atmosphere and the mixture was stirring at 80 °C for 12 h. After alkyl bromide consumed completely, the resulting solid was filtered, and the filtrate was concentrated and purified by column chromatography (petroleum ether) to give a mixture product as colorless oil 7 (28 mg, 80%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.35-7.25 (m, 4H), 7.19-7.16 (m, 5H), 6.38 (d, J = 15.8 Hz, 0.27H), 6.25-6.18 (m, 1H), 5.63-5.43 (m, 2.33H), 5.40-5.39 (m, 0.92H), 3.40 (d, J = 6.9 Hz, 0.38H), 3.34 (d, J = 6.0 Hz, 1.92H), 2.70-2.62 (m, 1H), 2.31-2.20 (m, 2H), 2.04 (t, J = 6.9 Hz, 0.42H), 1.91 (t, J = 6.6 Hz, 1.96H), 1.69-1.57 (m, 1.44H), 1.36 (dd, J = 15.5, 6.8 Hz, 0.63H), 0.95 (d, J = 6.7 Hz, 3.41H), 0.92 (d, J = 6.7 Hz, 2H), 0.89 (d, J = 6.6 Hz, 6H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 141.15, 138.30, 130.79, 129.85, 129.68, 129.56, 128.50, 128.47, 128.31, 128.19, 128.72, 126.24, 125.89, 125.83, 125.65, 41.90, 39.12, 38.55, 36.39, 36.23, 34.41, 33.58, 30.98, 30.89, 28.72, 28.67, 28.45, 27.56, 22.61, 22.51, 22.41, 22.30.

Ni(COD\textsubscript{2}) (8.3 mg, 0.03 mmol), dppf (33 mg, 0.06 mmol), NaO\textsubscript{t}Bu (58 mg, 0.6 mmol) were added to a 10 mL sealing tube under a nitrogen atmosphere. Hydrazone 1k (0.6 mmol, 2 equiv.), alkyl bromide 2m (0.3 mmol) were added in THF (2 mL) and the mixture was stirring at 80 °C for 12 h. After alkyl bromide consumed completely, the resulting solid was filtered, and the filtrate was concentrated and purified by column chromatography (petroleum ether) to give a mixture product as colorless oil 9 (44 mg, 45%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.59-7.55 (m, 2H), 7.53-7.45 (m, 2H), 7.43-7.39 (m, 2H), 7.30 (t, J = 7.4 Hz, 1H), 7.26-7.06 (m, 7H), 5.57-5.16 (m, 2H), 2.77-1.98 (m, 7H), 1.80-1.63 (m, 1H), 1.02-0.80 (m, 2H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 142.78, 142.12, 141.78, 141.20, 140.11, 139.88, 138.66, 138.58, 136.19, 135.81, 134.78, 130.61, 130.00, 129.76, 129.73, 128.90, 128.72, 128.53, 128.44, 128.27, 128.23, 128.00, 127.88, 127.02, 127.00, 126.98, 126.80, 126.77, 126.73, 125.75,
5. References


6. $^1$H, $^{13}$C, $^{19}$F NMR Spectra