Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Pd-catalyzed reductive Heck reaction of olefins with aryl bromides for Csp2-Csp3 bond formation

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Table of Contents

1. General

All reactions were carried out under air atmosphere unless otherwise noted. All ^{1}H and ^{13}C NMR spectra were recorded on Bruker ADVANCE III 500 MHz spectrometer in deuterium solvents with tetramethylsilane (TMS) as internal standard. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad signal. Chemical shifts are given in ppm and are referenced to TMS (^{1}H, ^{13}C). All spectra were obtained at 25 ^{o}C in the solvent indicated. Coupling constants *J* are given in Hz. GC analyses were performed on Agilent 6890 instrument with FID detector using an HP-5 capillary column (30 m x 0.32 mm (i.d.), 0.25 μ). High-resolution mass spectra were recorded in the EI mode on Waters GCT Premier TOF MS. Column chromatography was performed on neutral silica gel (200-300 mesh) with ethyl acetate/petroleum ether as eluent. Pd_{CImPy*} were synthesized according to the reported methods.[1] All bases were commercial available and used directly. Flake KOH was utilized. All aryl bromides and most olefins were commercial available and used directly. **1n** was synthesized starting from BnCl and but-3-en-1-ol.[2]

2. General procedure for Pd-catalyzed intermolecular reductive Heck reaction

All the reactions followed the general procedure 1 or 2 unless noted.

General procedure 1

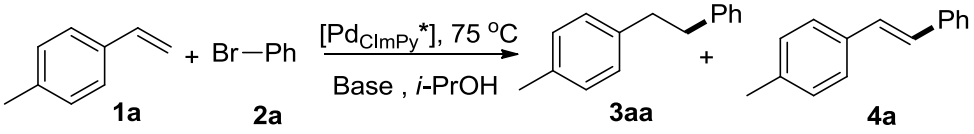
The Young tube was charged with Pd_{CImPy*} (14.9 mg, 2 mol%), KOH (140 mg, 2.5 mmol), alkene (1 mmol), aryl bromides (1.5 mmol) and *i*-PrOH (7.0 mL) was added. After stirring for 12 h at 75 ^{o}C, the reaction temperature was allowed to cool to the room temperature. Removed the solvent in vacuo and extracted the resulting mixture by ethyl acetate (50 mL) for three times. After drying and concentration, dissolved the crude product with dichloromethane (7.0 mL for aryl olefins, 2.0 mL for aliphatic olefins). At 0~10 ^{o}C, *m*-CPBA (0.1 mol/L) was added dropwise. Detecting the reaction by GC or TLC. When the Heck product was completely consumed, the solvent was removed in vacuo and the desired product was isolated

by column chromatography.

General procedure 2

The Young tube was charged with Pd_{CImPy*} (14.9 mg, 2 mol%), KOH (196 mg, 3.5 mmol), alkene (1 mmol), aryl bromides (3.0 mmol) and *i*-PrOH (7.0 mL) was added. After stirring for 12 h at 75 ^{o}C, the reaction temperature was allowed to cool to the room temperature. Removed the solvent in vacuo and extracted the resulting mixture by ethyl acetate (50 mL) for three times. After drying and concentration, dissolved the crude product with dichloromethane (7.0 mL). At 0~10 ^{o}C, *m*-CPBA (0.1 mol/L) was added dropwise. Detecting the reaction by GC or TLC. When the Heck product was completely consumed, the solvent was removed in vacuo and the desired product was isolated by column chromatography.

3. Optimization of the Pd-catalyzed reductive Heck reaction



1a **2a** **3aa** **4a**

Entry	[Pd]	Base	Conv.[%]	Yield[%]	
				3aa	**4a**
1	$PdCl_2$	*t*-BuOK	23	15	5
2	$Pd(OAc)_2$	*t*-BuOK	41	36	1
3	$PdCl_2(CH_3CN)_2$	*t*-BuOK	40	34	4
4	$PdCl_2(PPh_3)_2$	*t*-BuOK	13	9	1
5	$PdCl_2$(dppf)	*t*-BuOK	10	7	nd
6	Pd_{CImPy}*	*t*-BuOK	82	65	4
7	Pd_{CImPy}*	KOH	88	76	5
8	Pd_{CImPy}*	K_3PO_4	91	23	60
9	Pd_{CImPy}*	K_2CO_3	65	8	54
10	Pd_{CImPy}*	Cs_2CO_3	84	12	69
11	Pd_{CImPy}*	Na_2CO_3	3	trace	trace
12	Pd_{CImPy}*	Et_3N	2	trace	trace

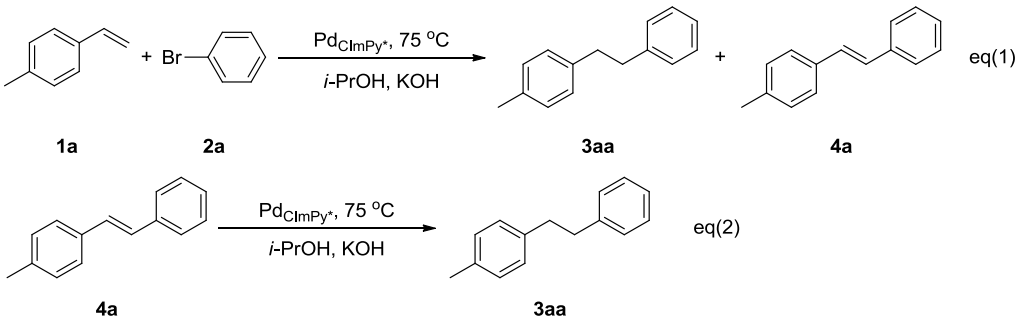
[a] Reaction conditions: [Pd_{CImPy}*] (2 mol%), 4-methylstyrene (1 mmol), PhBr (1.5 mmol), base (2.5 mmol), *i*-PrOH (7.0 mL), 75 ^{o}C, 12 h. Conversions and yields were determined by GC with area normalization.

To clarify the influence of the bidentate CImPy ligand, we examined the catalytic activity of

other Pd precatalysts with *t*-BuOK and *i*-PrOH as base and solvent, respectively. With those simple palladium compounds, such as $PdCl_2$, $Pd(OAc)_2$ and $PdCl_2(CH_3CN)_2$, the reactions proceeded with lower conversion (Table S1, entries 1-3). Even with the precatalyst $PdCl_2(PPh_3)_2$ or $PdCl_2$(dppf), the conversion was still limited (Table S1, entries 4 and 5). These results confirm the important role of bidentate iminopyridyl ligand in promoting this transformation. We further tested the effects from varied bases. Another strong base KOH could slightly improve the conversion to 88% without any loss of the selectivity (Table S1, entry 7), while the weaker bases gave the major product from normal Heck couplings (Table S1, entries 8-10). Both Na_2CO_3 and Et_3N led to less than 5% conversions (Table S1, entries 11 and 12). Thus, strong bases are crucial for the selectivity. It should be noted that we were not able to completely eliminate the Heck coupling products.

4. Mechanistic studies

4.1 Kinetic studies



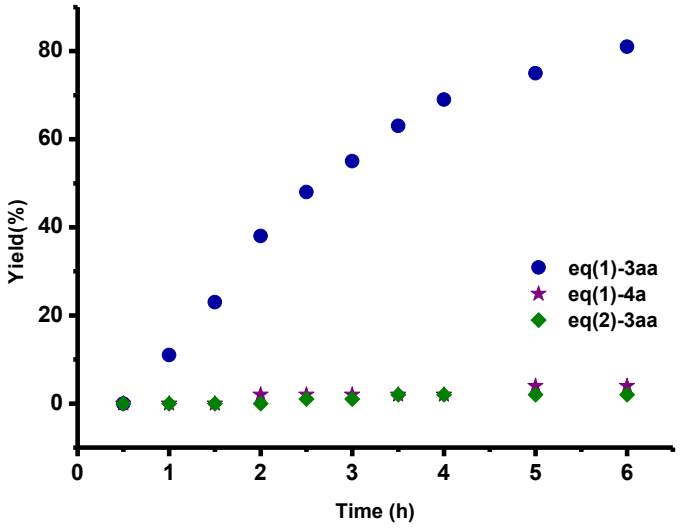
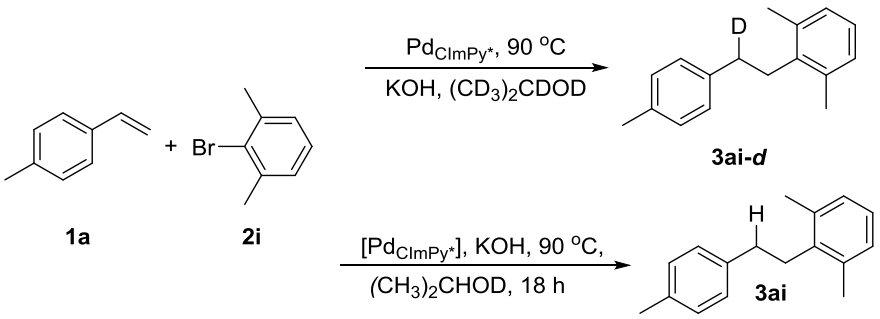


Figure S1. Kinetic profiles of the model reactions shown in eq(1) and eq(2)

The Young tube was charged with Pd_{ClmPy*} (14.9 mg, 2 mol%), KOH (140 mg, 2.5 mmol), 4-methylstyrene (132 μL, 1 mmol), bromobenzene (158 μL, 1.5 mmol) and *i*-PrOH (7.0 mL) was added. Another Young tube was charged with Pd_{ClmPy*} (14.9 mg, 2 mol%), KOH (140 mg, 2.5 mmol), 4-methyl-*trans*-stilbene (194 mg, 1 mmol) and *i*-PrOH (7.0 mL) was added. The two reactions were monitored every half hour by GC. The kinetic plots was shown in Figure S1.

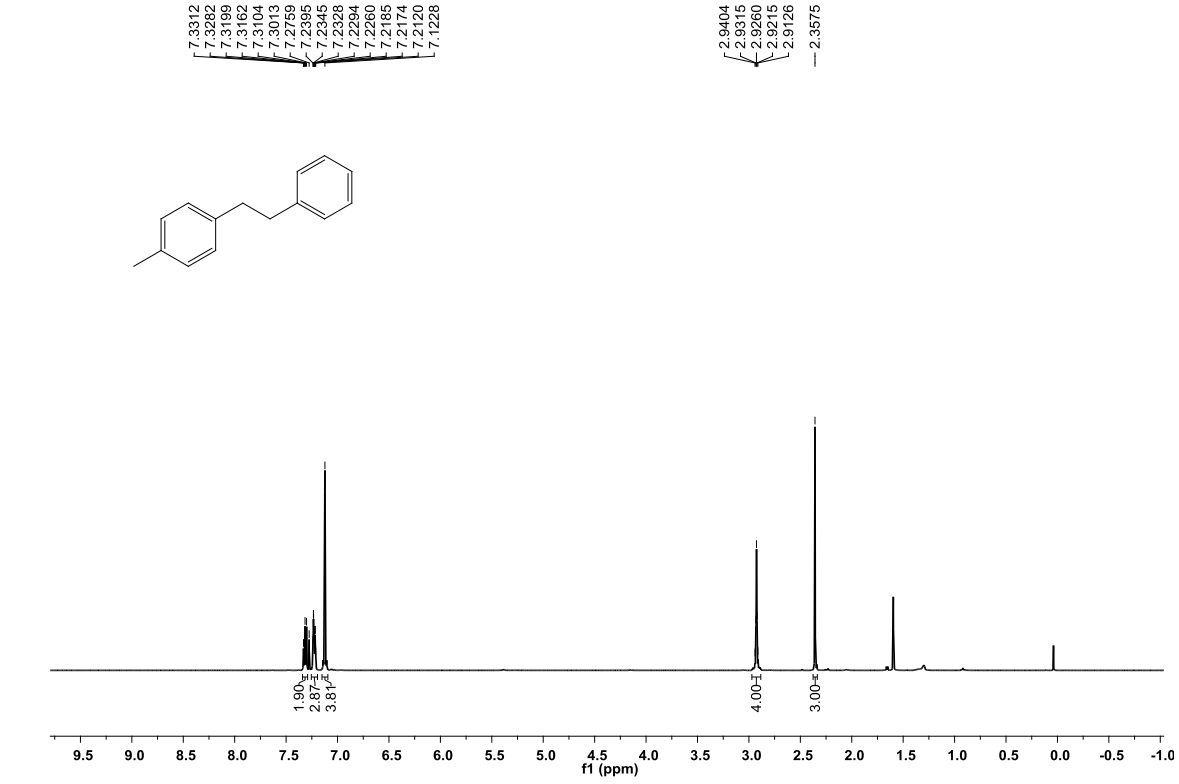
4.2 Deuterium labeling experiment



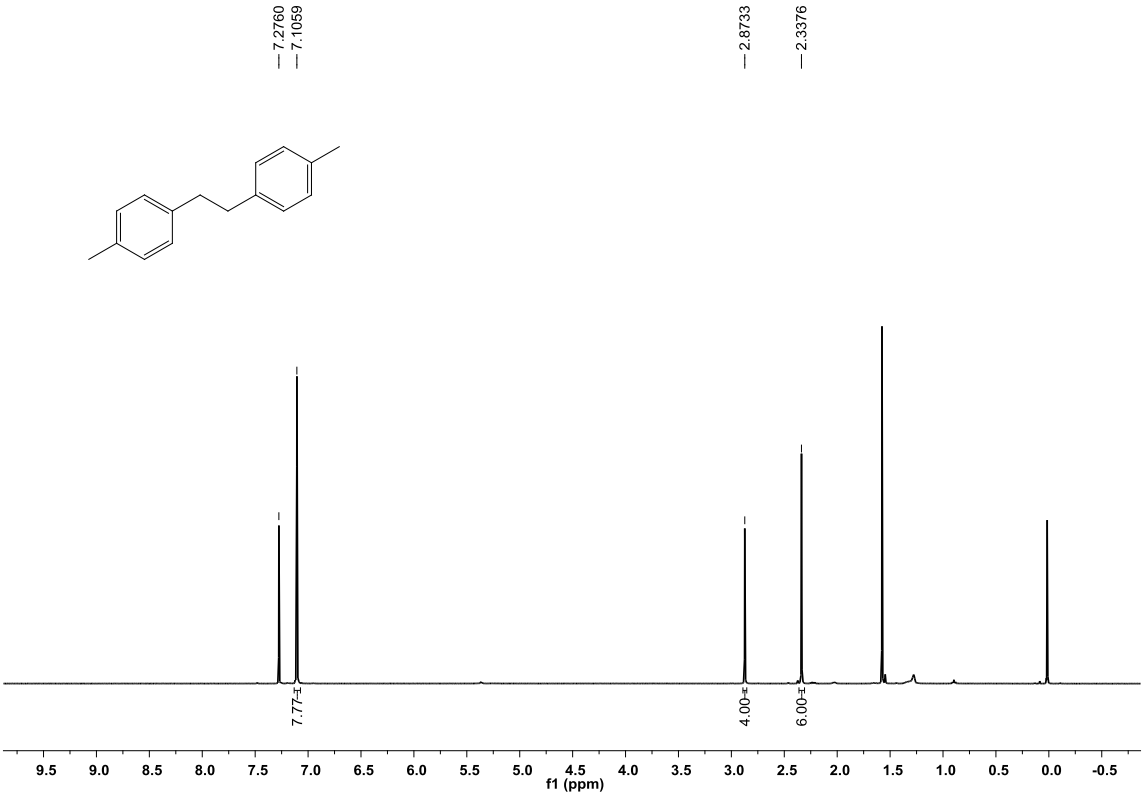
To a Young tube, Pd_{ClmPy*} (4.5 mg, 2 mol%), KOH (42 mg, 0.75 mmol), 4-methylstyrene (40 μL, 0.3 mmol), 2,6-dimethylbromobenzene (62 μL, 0.45 mmol) and the D-labeling solvent (0.5 mL) were added. After stirring for 18 h at 90 °C, the reaction temperature was allowed to cool to room temperature. The solvent was removed in vacuo and the resulting mixture was extracted by ethyl acetate. After drying and concentration, the product **3ai-*d*** was confirmed and the yield was determined by ^{1}H NMR.

5. NMR spectra of products

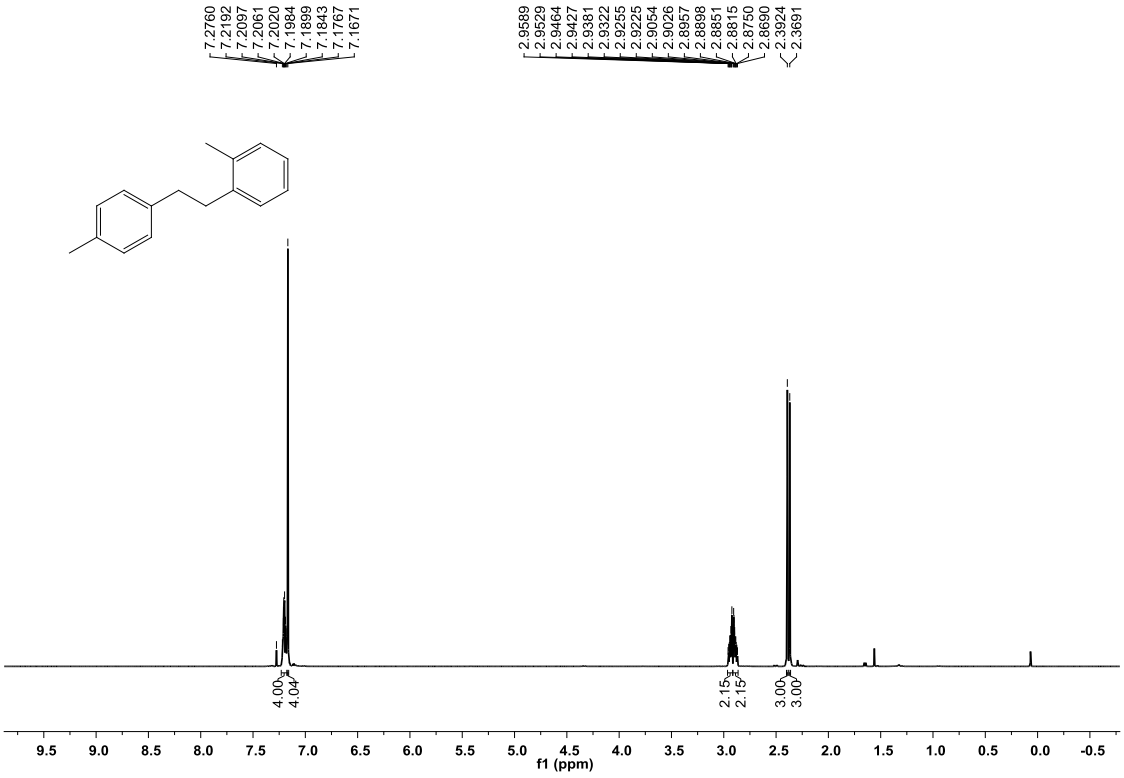
1-(4-Methylphenyl)-2-phenylethane (**3aa**)[3]: Following the general procedure **1**, 4-methylstyrene (118.2 mg, 1 mmol) and bromobenzene (235.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3aa** was obtained as colorless oil (130 mg, 69% yield) after purification by silica gel column chromatography (petroleum ether).
Following the general procedure **2**, styrene (104.1 mg, 1 mmol) and 4-bromotoluene (513.0 mg, 3.0 mmol) as substrates, KOH (196 mg, 3.5 mmol) as base. The title compound **3aa** was obtained as colorless oil (146 mg, 75% yield) after purification by silica gel column chromatography (petroleum ether).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33-7.30 (m, 2H), 7.24-7.21 (m, 3H), 7.12 (s, 4H), 2.94-2.91 (m, 4H), 2.36 (s, 3H).

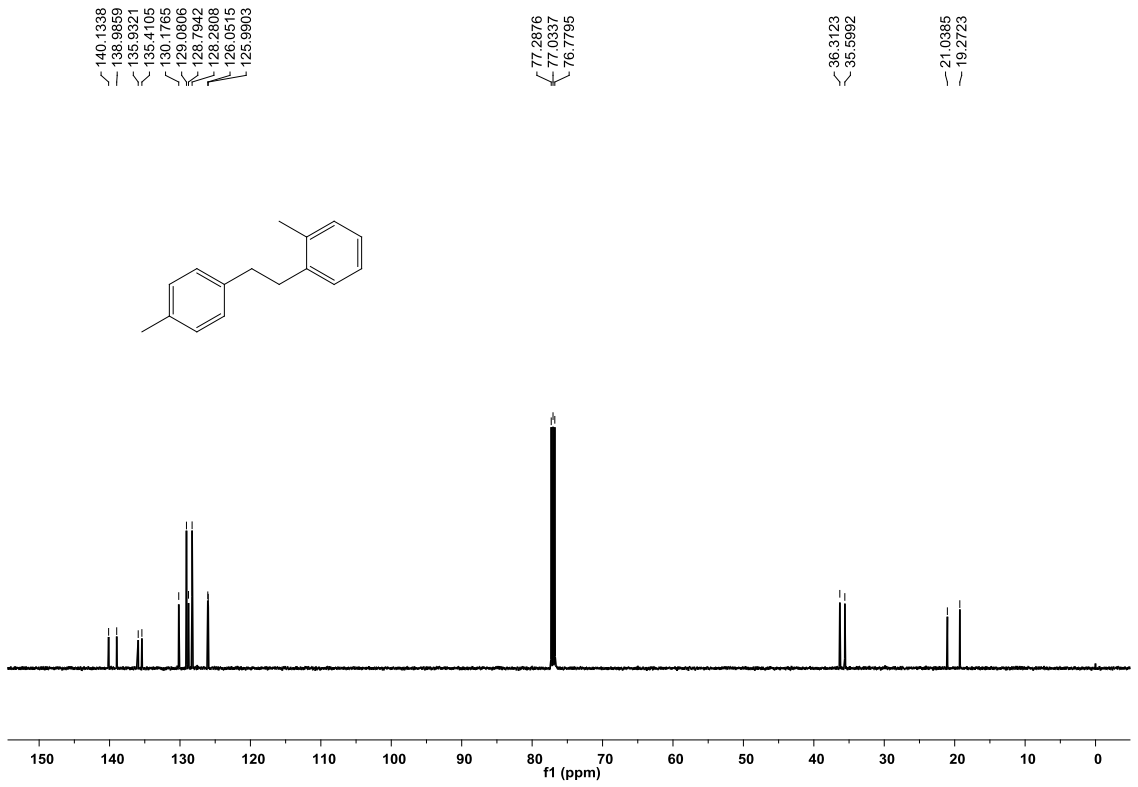


1,2-Bis(4-methylphenyl)ethane (**3ab**)[4]: Following the general procedure **1**, 4-methylstyrene (118.2 mg, 1 mmol) and 4-bromotoluene (256.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3ab** was obtained as white solid (163 mg, 78% yield) after purification by silica gel column chromatography (petroleum ether).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.10 (s, 8H), 2.87 (s, 4H), 2.33 (s, 6H).



1-(2-Methylphenyl)-2-(4-methylphenyl)ethane (**3ac**): Following the general procedure **1**, 4-methylstyrene (118.2 mg, 1 mmol) and 2-bromotoluene (256.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3ac** was obtained as colorless oil (175 mg, 87% yield) after purification by silica gel column chromatography (petroleum ether).
Following the general procedure **1**, 2-methylstyrene (118.2 mg, 1 mmol) and 4-bromotoluene (256.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3ac** was obtained as colorless oil (136 mg, 66% yield) after purification by silica gel column chromatography (petroleum ether).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.22-7.18 (m, 4H), 7.17 (s, 4H), 2.96-2.92 (m, 2H), 2.90-2.87 (m, 2H), 2.39 (s, 3H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 140.1, 139.0, 135.9, 135.4, 130.2, 129.1, 128.8, 128.3, 126.1, 126.0, 36.3, 35.6, 21.0, 19.3. HRMS (EI-TOF): m/z calculated for $C_{16}H_{18}$ 210.1409, found 210.1411.

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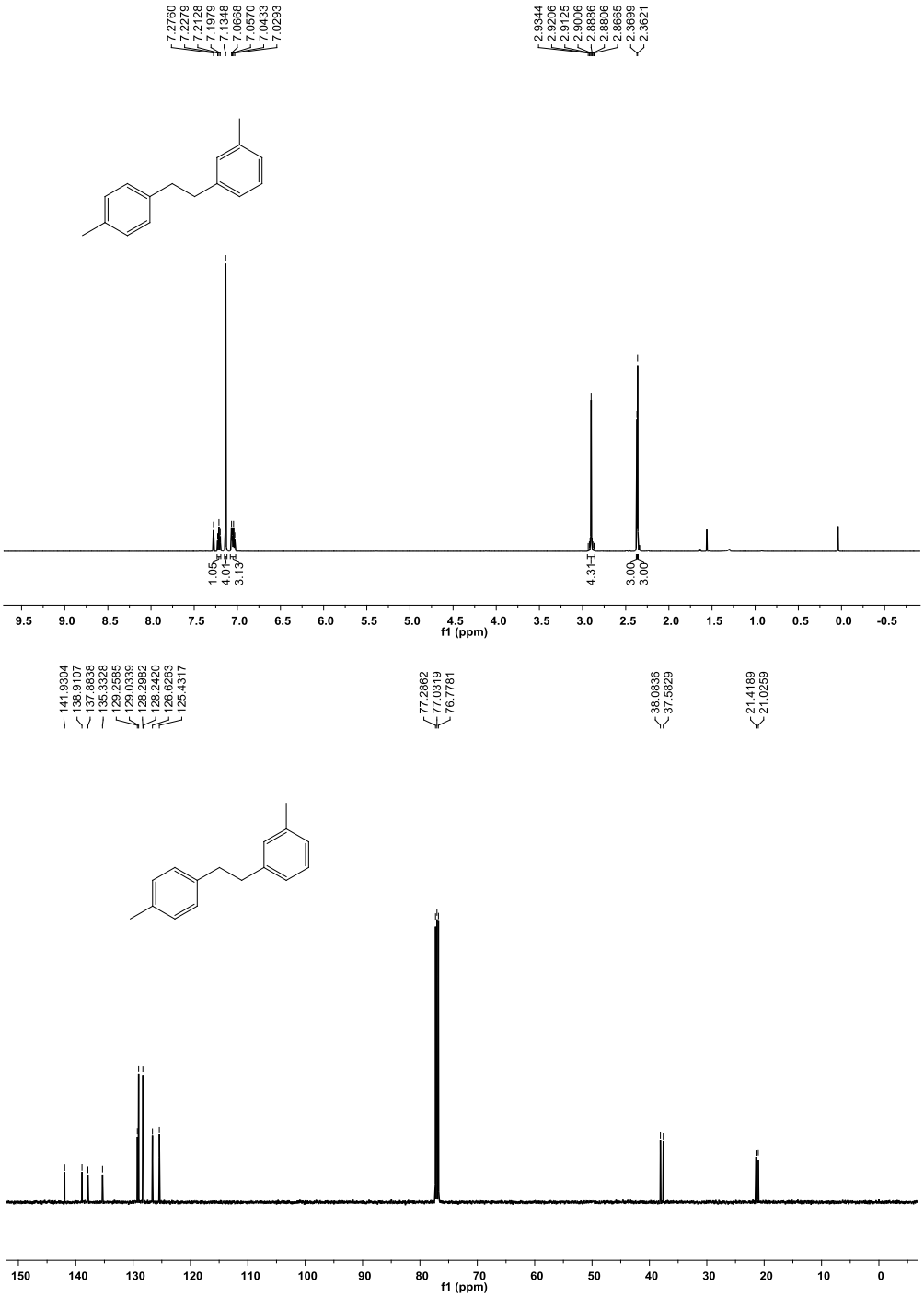
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

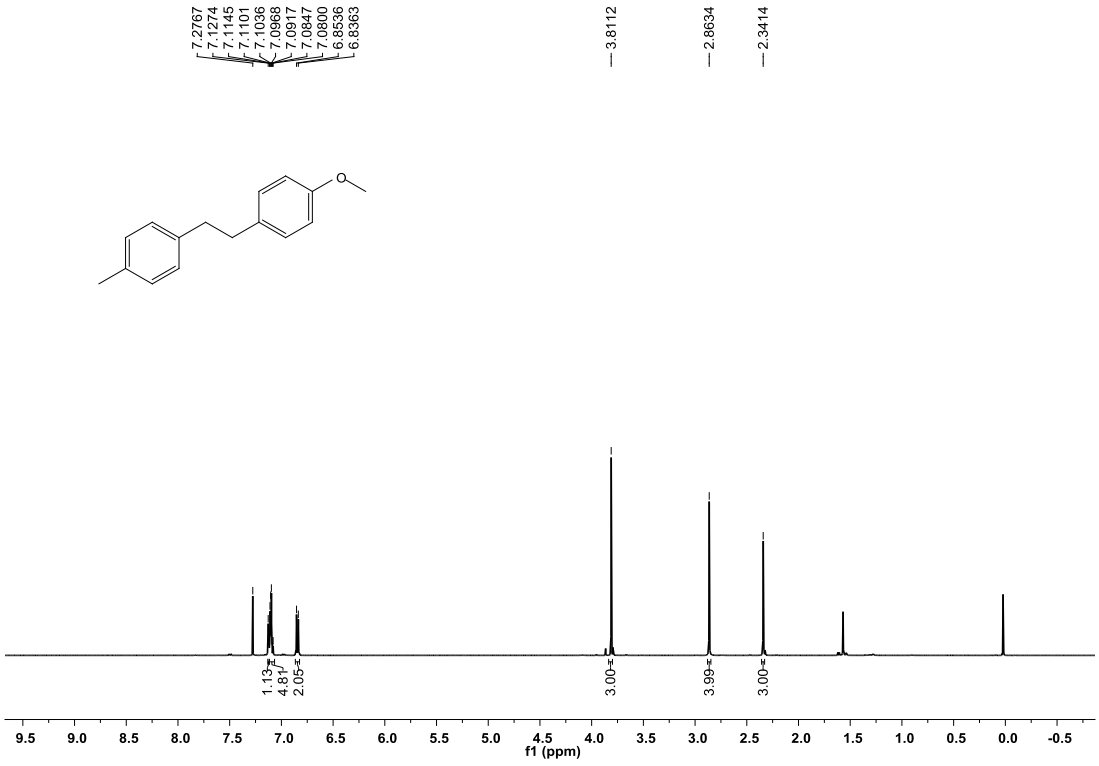
1-(3-Methylphenyl)-2-(4-methylphenyl)ethane (**3ad**): Following the general procedure **1**, 4-methylstyrene (118.2 mg, 1 mmol) and 3-bromotoluene (256.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3ad** was obtained as colorless oil (146 mg, 72% yield) after purification by silica gel column chromatography (petroleum ether).
^{1}H NMR ($CDCl_3$, 500 MHz): δ7.21 (t, *J* = 7.5 Hz, 1H), 7.13 (s, 4H), 7.07-7.03 (m, 3H), 2.93-2.86 (m, 4H), 2.37 (s, 3H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 141.9, 138.9, 137.9, 135.3, 129.2, 129.0, 128.3, 128.2, 126.6, 125.4, 38.1, 37.6, 21.4, 21.0. HRMS (EI-TOF): m/z calculated for $C_{16}H_{18}$ 210.1409, found 210.1396.



1-(4-Methylphenyl)-2-(4-methoxyphenyl)ethane (**3ae**)[3]: Following the general procedure **1**, 4-methylstyrene (118.2 mg, 1 mmol) and 1-bromo-4-methoxybenzene (280.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3ae** was obtained as yellow solid (155 mg, 71% yield) after purification by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1).

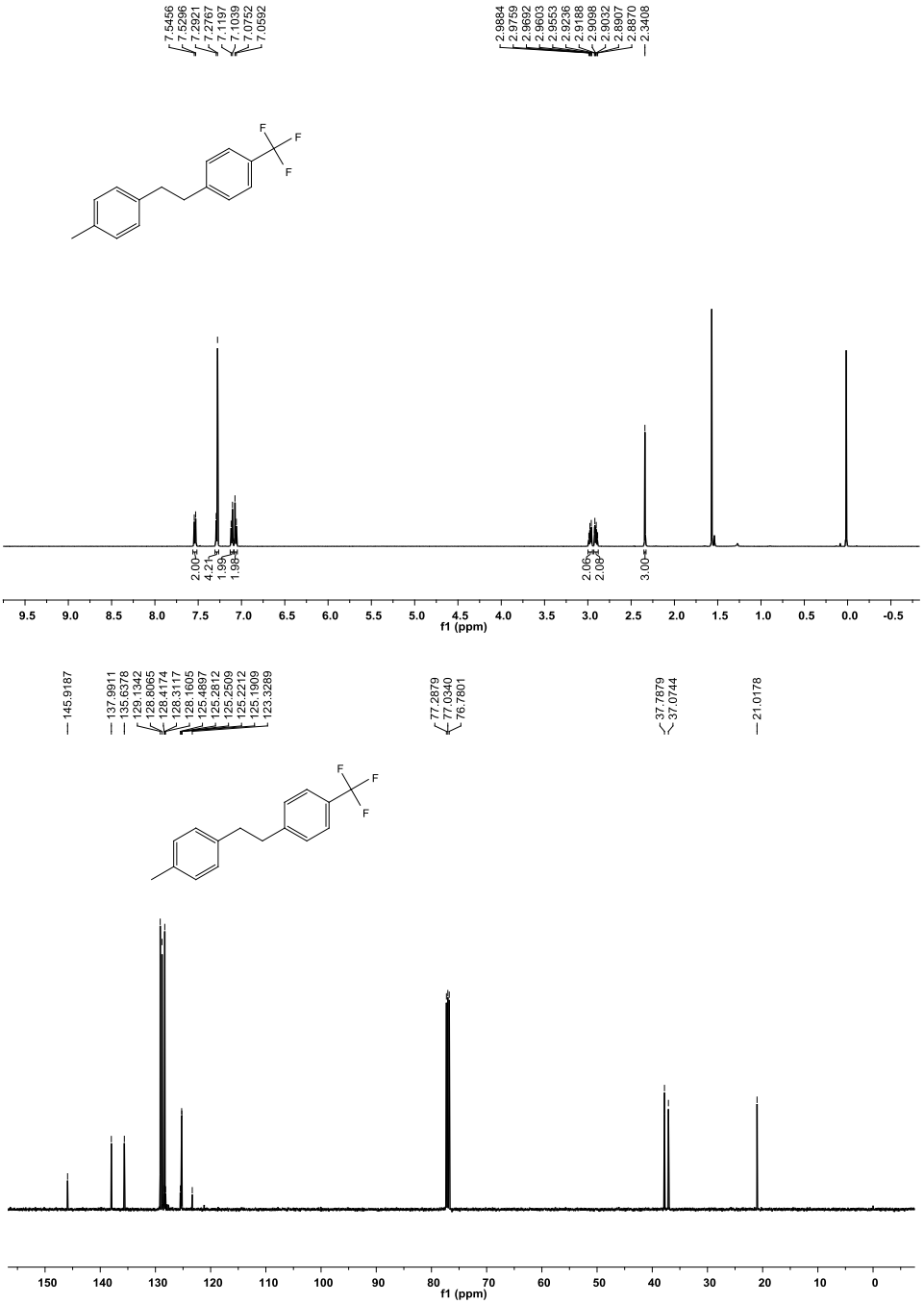
Following the general procedure **1**, 4-methoxystyrene (134.2 mg, 1 mmol) and 4-bromotoluene (256.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3ae** was obtained as yellow solid (170 mg, 79% yield) after purification by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.12 (s, 1H), 7.11-7.08 (m, 5H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 2.86 (s, 4H), 2.34 (s, 3H).



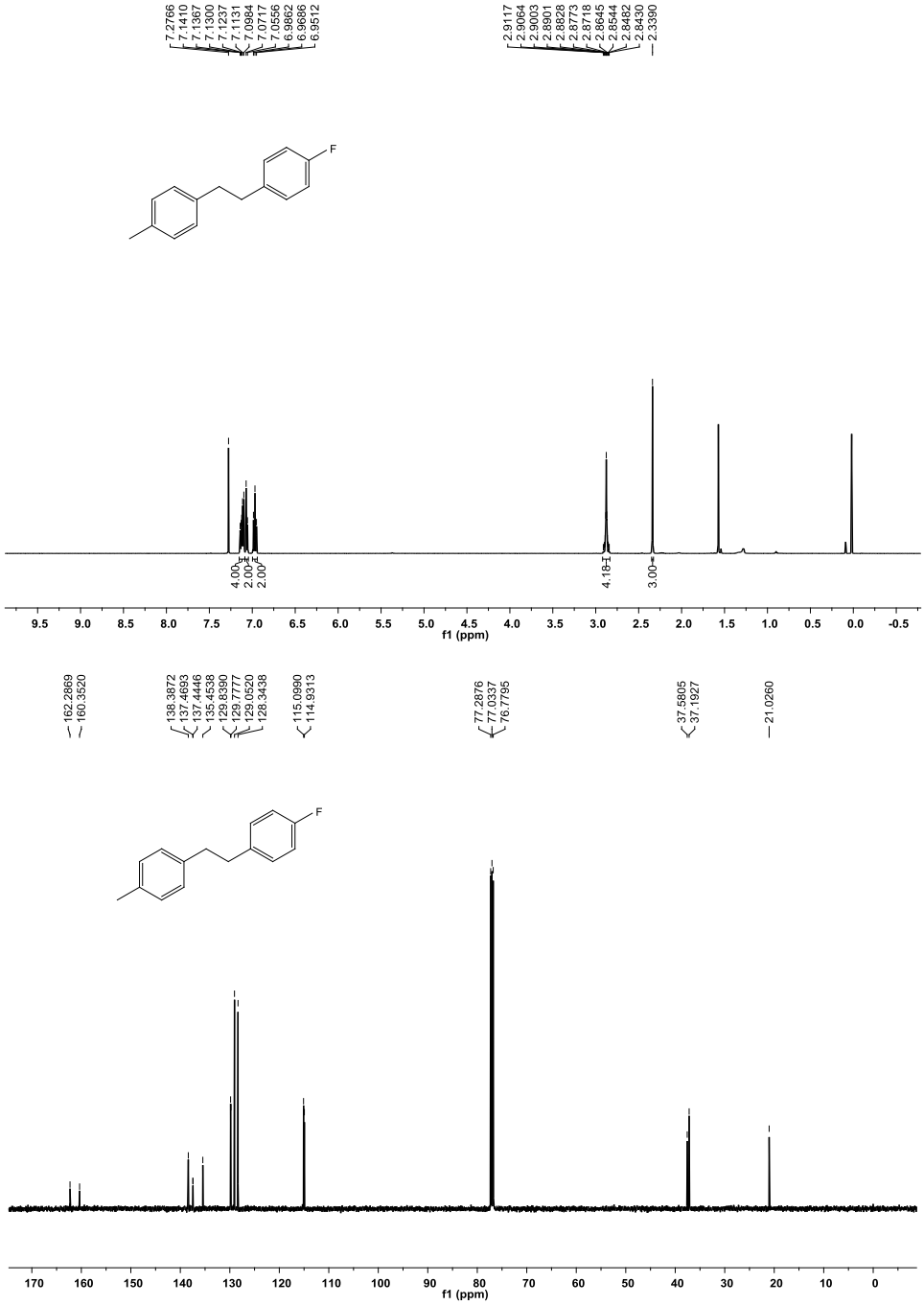
1-(4-Methylphenyl)-2-(4-trifluoromethylphenyl)ethane (**3af**): Following the general procedure **2**, 4-methylstyrene (118.2 mg, 1 mmol) and 1-bromo-4-(trifluoromethyl)benzene (675.0 mg, 3.0 mmol) as substrates, KOH (196 mg, 3.5 mmol) as base. The title compound **3af** was obtained as white solid (125 mg, 58% ^{1}H NMR yield) after purification by silica gel column chromatography (petroleum ether).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 2.99-2.95 (m, 2H), 2.92-2.89 (m, 2H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 145.9, 138.0, 135.6, 129.1, 128.8, 128.3, 125.2 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 272.1 Hz), 37.8, 37.1, 21.0. HRMS (EI-TOF): m/z calculated for $C_{16}H_{15}F_3$ 264.1126, found 264.1132.



1-(4-Methylphenyl)-2-(4-fluorophenyl)ethane (**3ag**): Following the general procedure **2**, 4-methylstyrene (118.2 mg, 1 mmol) and 1-bromo-4-fluorobenzene (525.0 mg, 3.0 mmol) as substrates, KOH (196 mg, 3.5 mmol) as base. The title compound **3ag** was obtained as white solid (158 mg, 77% yield) after purification by silica gel column chromatography (petroleum ether).

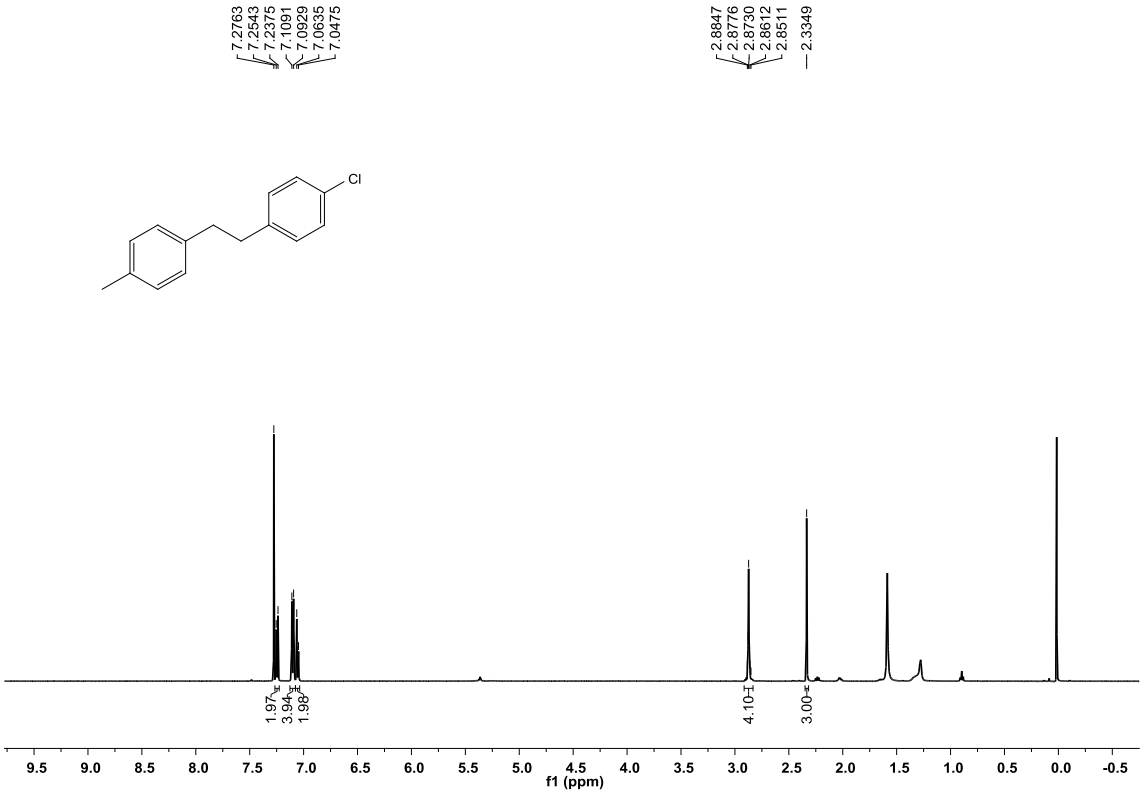
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.14-7.10 (m, 4H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.97 (t, *J* = 8.8 Hz, 2H), 2.91-2.84 (m, 4H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 161.3 (d, *J* = 243.4 Hz), 138.4, 137.4 (d, *J* = 3.1 Hz), 135.4, 129.8 (d, *J* = 7.7 Hz), 129.0, 128.3, 115.0 (d, *J* = 21.1 Hz), 37.6, 37.2, 21.0. HRMS (EI-TOF): m/z calculated for $C_{15}H_{15}F$, 214.1158, found 214.1155.

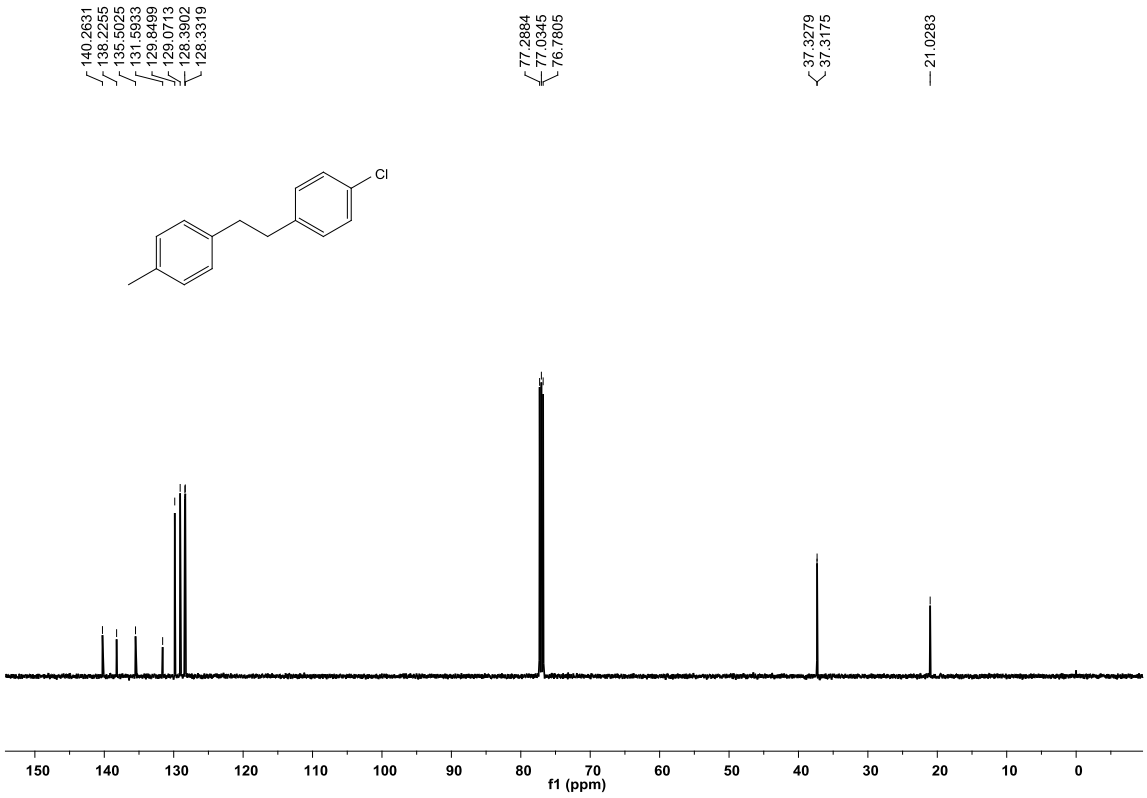


1-(4-Methylphenyl)-2-(4-chlorophenyl)ethane (**3ah**): Following the general procedure **2**, 4-methylstyrene (118.2 mg, 1 mmol) and 1-bromo-4-chlorobenzene (573.0 mg, 3.0 mmol) as substrates, KOH (196 mg, 3.5 mmol) as base. The title compound **3ah** was obtained as white solid (175 mg, 79% yield) after purification by silica gel column chromatography (petroleum ether).

Following the general procedure **2**, 4-chlorostyrene (138.6 mg, 1 mmol) and 4-bromotoluene (513.0 mg, 3.0 mmol) as substrates, KOH (196 mg, 3.5 mmol) as base. The title compound **3ah** was obtained as white solid (157 mg, 71% yield) after purification by silica gel column chromatography (petroleum ether).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 4H), 7.06 (d, *J* = 8.1 Hz, 2H), 2.88-2.85 (m, 4H), 2.33 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 140.2, 138.2, 135.5, 131.6, 129.8, 129.1, 128.4, 128.3 37.3, 37.3, 21.0. HRMS (EI-TOF): m/z calculated for $C_{15}H_{15}Cl$ 230.0862, found 230.0867.

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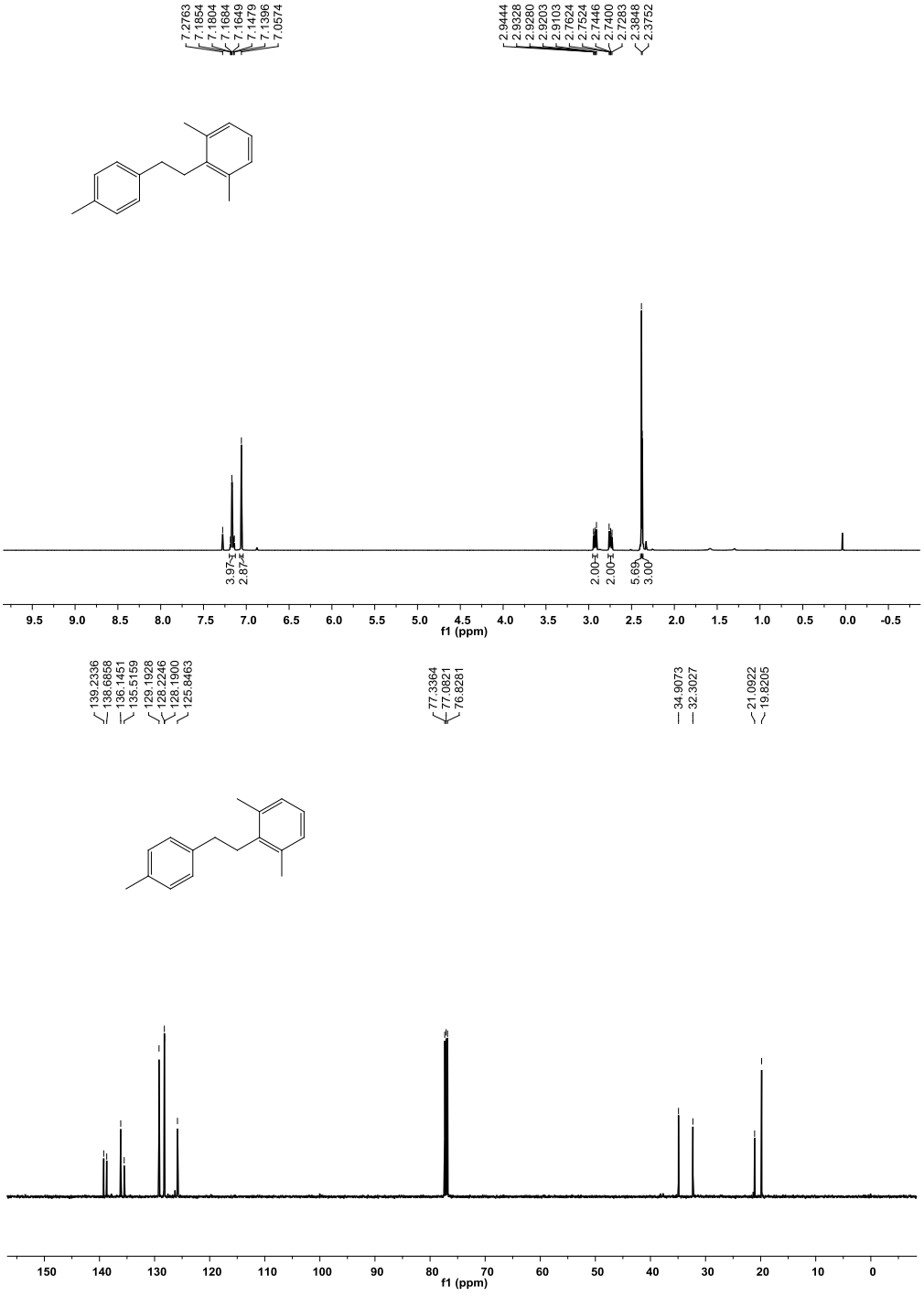
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

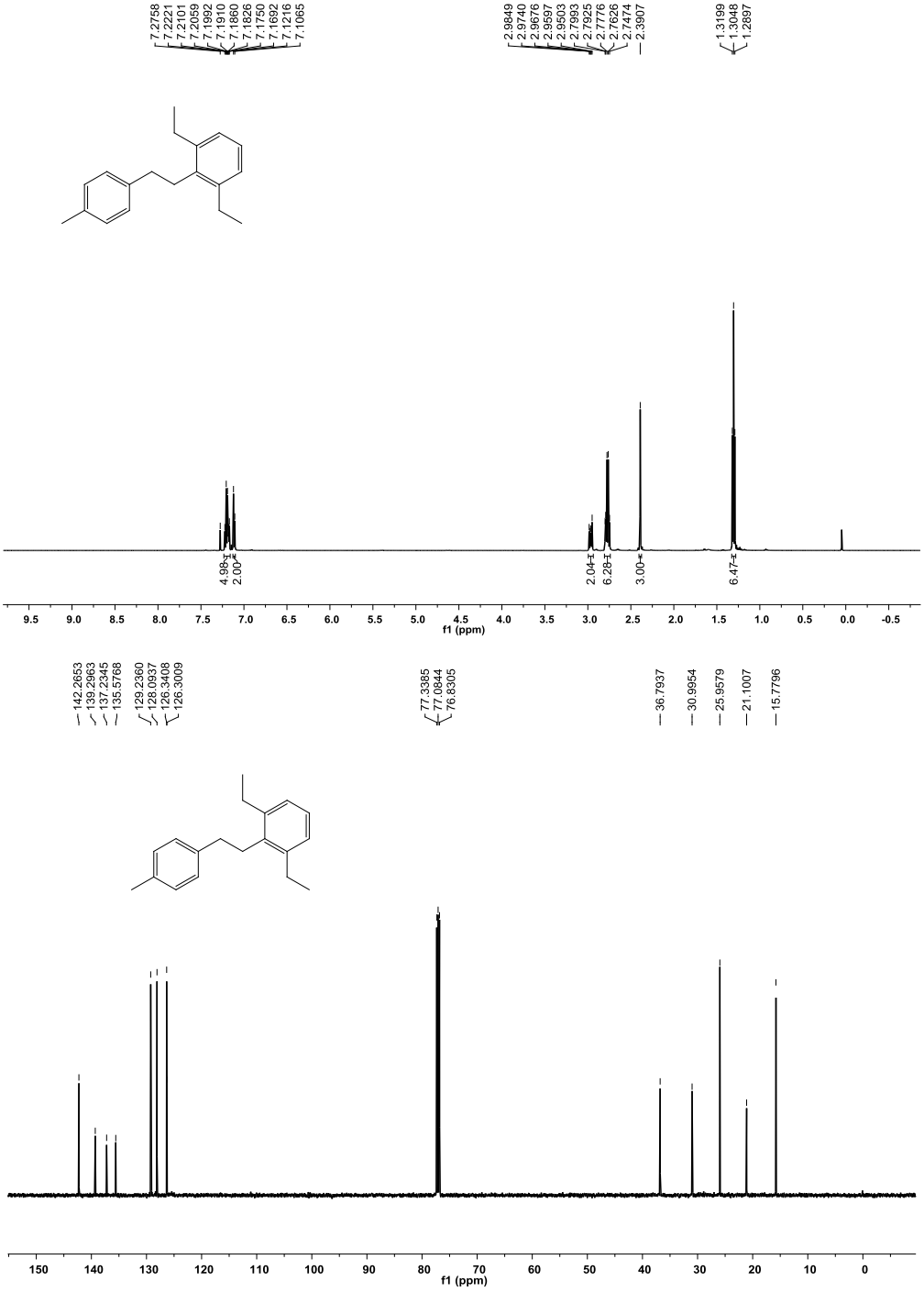
1-(2,6-Dimethylphenyl)-2-(4-methylphenyl)ethane (**3ai**): Following the general procedure, 4-methylstyrene (118.2 mg, 1 mmol) and 2,6-dimethylbromobenzene (555.0 mg, 3.0 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3ai** was obtained as colorless oil (174 mg, 81% yield) after purification by silica gel column chromatography (petroleum ether).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.18-7.14 (m, 4H), 7.06 (s, 3H), 2.94-2.91 (m, 2H), 2.76-2.73 (m, 2H), 2.38 (s, 6H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 139.2, 138.7, 136.1, 135.5, 129.2, 128.2, 128.2, 125.8, 34.9, 32.3, 21.1, 19.8. HRMS (EI-TOF): m/z calculated for $C_{17}H_{20}$ 224.1565, found 224.1565.



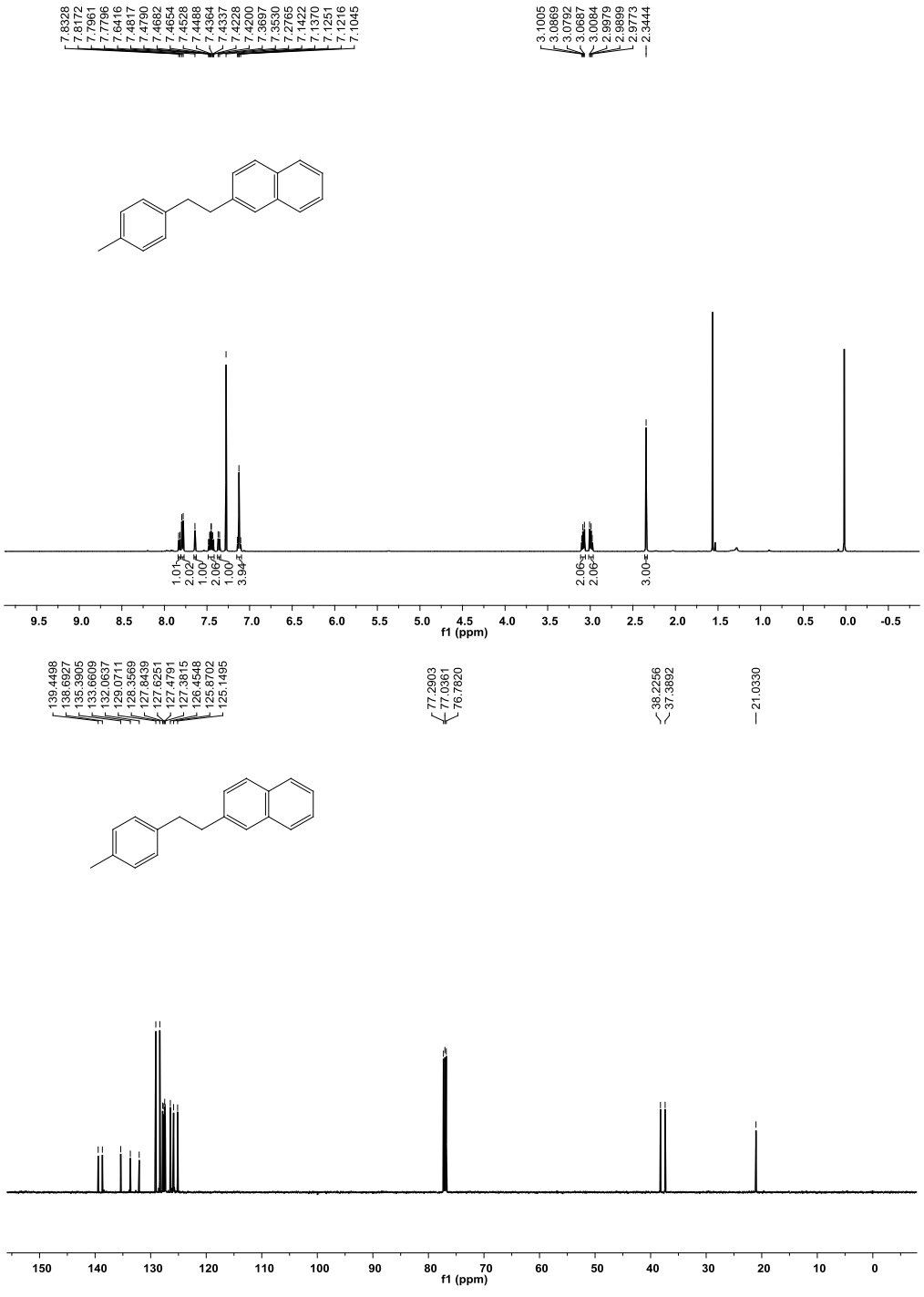
1-(2,6-Diethylphenyl)-2-(4-methylphenyl)ethane (**3aj**): Following the general procedure, 4-methylstyrene (118.2 mg, 1 mmol) and 2,6-diethylbromobenzene (639.0 mg, 3.0 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3aj** was obtained as colorless oil (188 mg, 78% yield) after purification by silica gel column chromatography (petroleum ether).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.22-7.17 (m, 5H), 7.11 (d, *J* = 7.5 Hz, 2H), 2.98-2.95 (m, 2H), 2.80-2.74 (m, 6H), 2.39 (s, 3H), 1.30 (t, *J* =7.5 Hz, 6H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 142.3, 139.3, 137.2, 135.6, 129.2, 128.1, 126.3, 126.3, 36.8, 31.0, 25.9, 21.1, 15.8. HRMS (EI-TOF): m/z calculated for $C_{19}H_{24}$ 252.1878, found 252.1872.



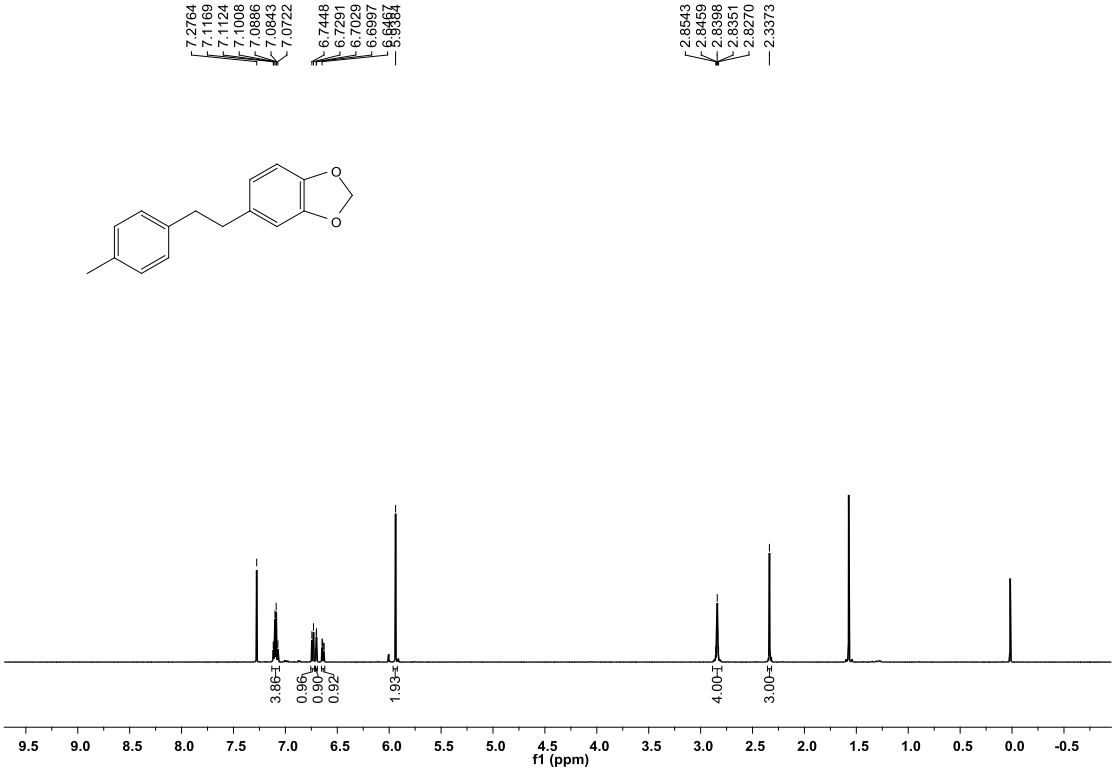
2-(4-Methylphenethyl)naphthalene (**3ak**): Following the general procedure **1**, 4-methylstyrene (118.2 mg, 1 mmol) and 2-bromonaphthalene (310.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3ak** was obtained as white solid (154 mg, 65% yield) after purification by silica gel column chromatography (petroleum ether).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.64 (s, 1H), 7.48-7.42 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.14-7.10 (m, 4H), 3.10-3.07 (m, 2H), 3.01-2.98 (m, 2H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 139.4, 138.7, 135.4, 133.6, 132.0, 129.1, 128.3, 127.8, 127.6, 127.5, 127.4, 126.4, 125.9, 125.1, 38.2, 37.4, 21.0. HRMS (EI-TOF): m/z calculated for $C_{19}H_{18}$ 246.1409, found 246.1397.



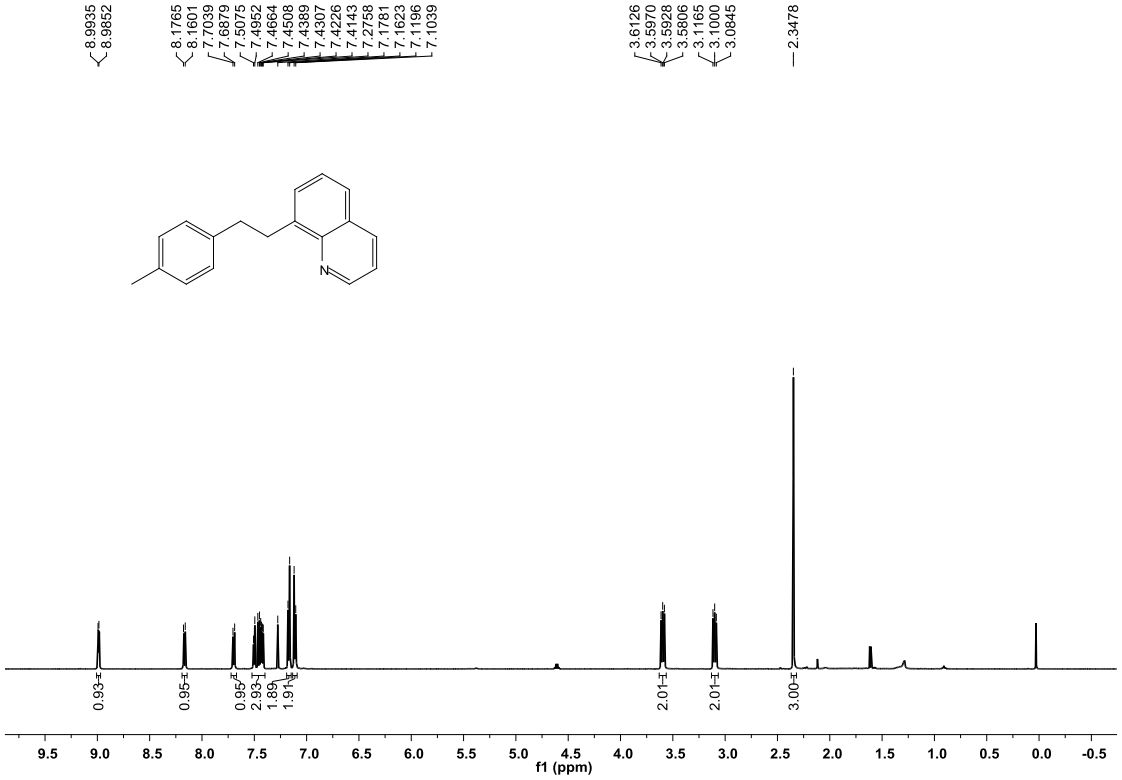
5-(4-Methylphenethyl)benzo[*d*][1,3]dioxole (**3al**)[5]: Following the general procedure **1**, 4-methylstyrene (118.2 mg, 1 mmol) and 5-bromo-1,3-benzodioxole (301.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3al** was obtained as yellow solid (142 mg, 62% yield) after purification by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.12-7.07 (m, 4H), 6.73 (d, J = 7.9 Hz, 1H), 6.70 (d, J = 1.7 Hz, 1H), 6.63 (dd, J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1H), 5.94 (s, 2H), 2.85-2.83 (m, 4H), 2.34 (s, 3H).



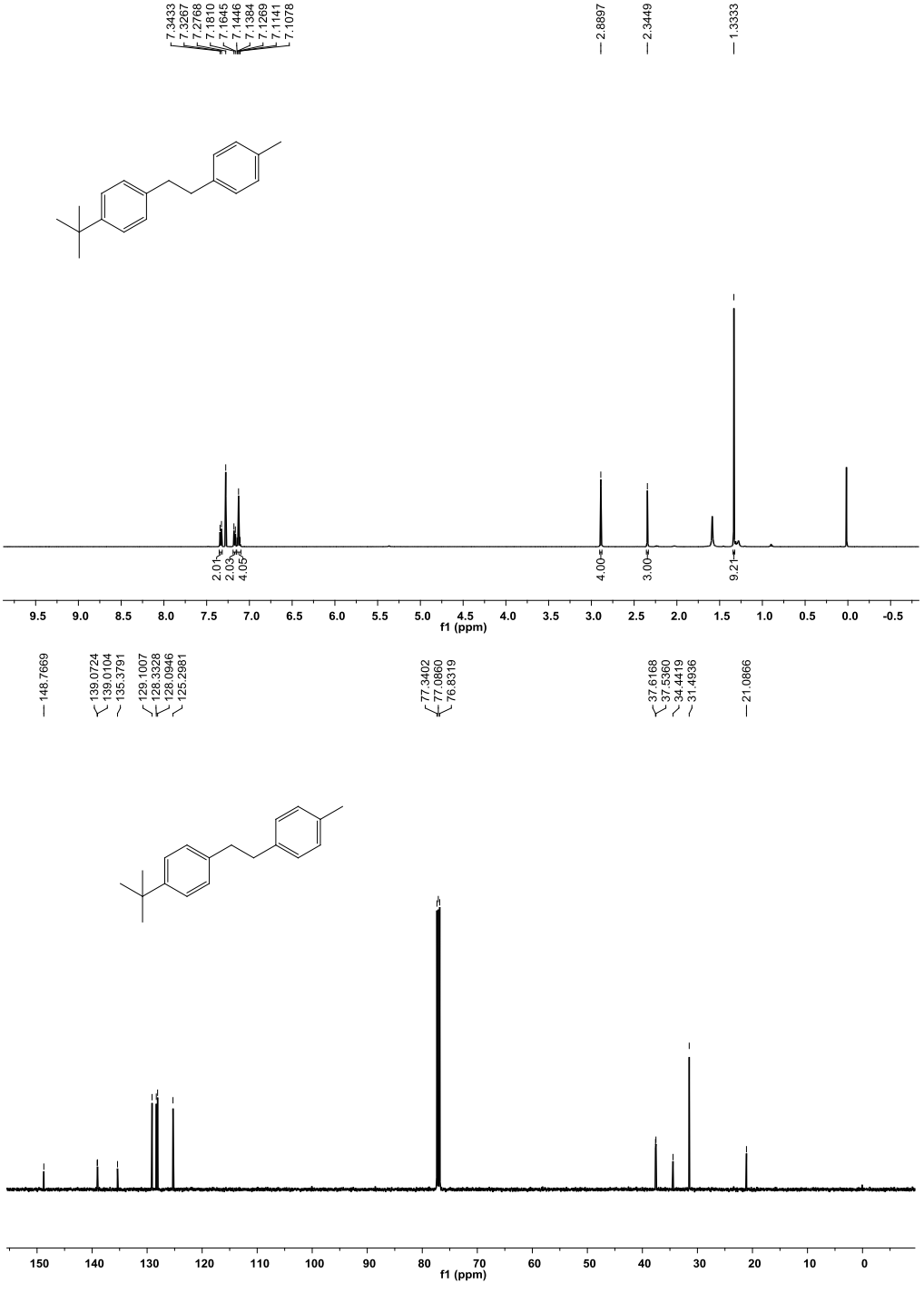
8-(4-Methylphenethyl)quinoline (**3am**)[6]: Following the general procedure **1**, 4-methylstyrene (118.2 mg, 1 mmol) and 8-bromoquinoline (312.0 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3am** was obtained as yellow oil (51 mg, 22% yield) after purification by silica gel column chromatography (petroleum ether).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.99 (d, *J* = 4.2 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.51-7.41 (m, 3H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 3.61-3.58 (m, 2H), 3.11-3.08 (m, 2H), 2.35 (s, 3H).



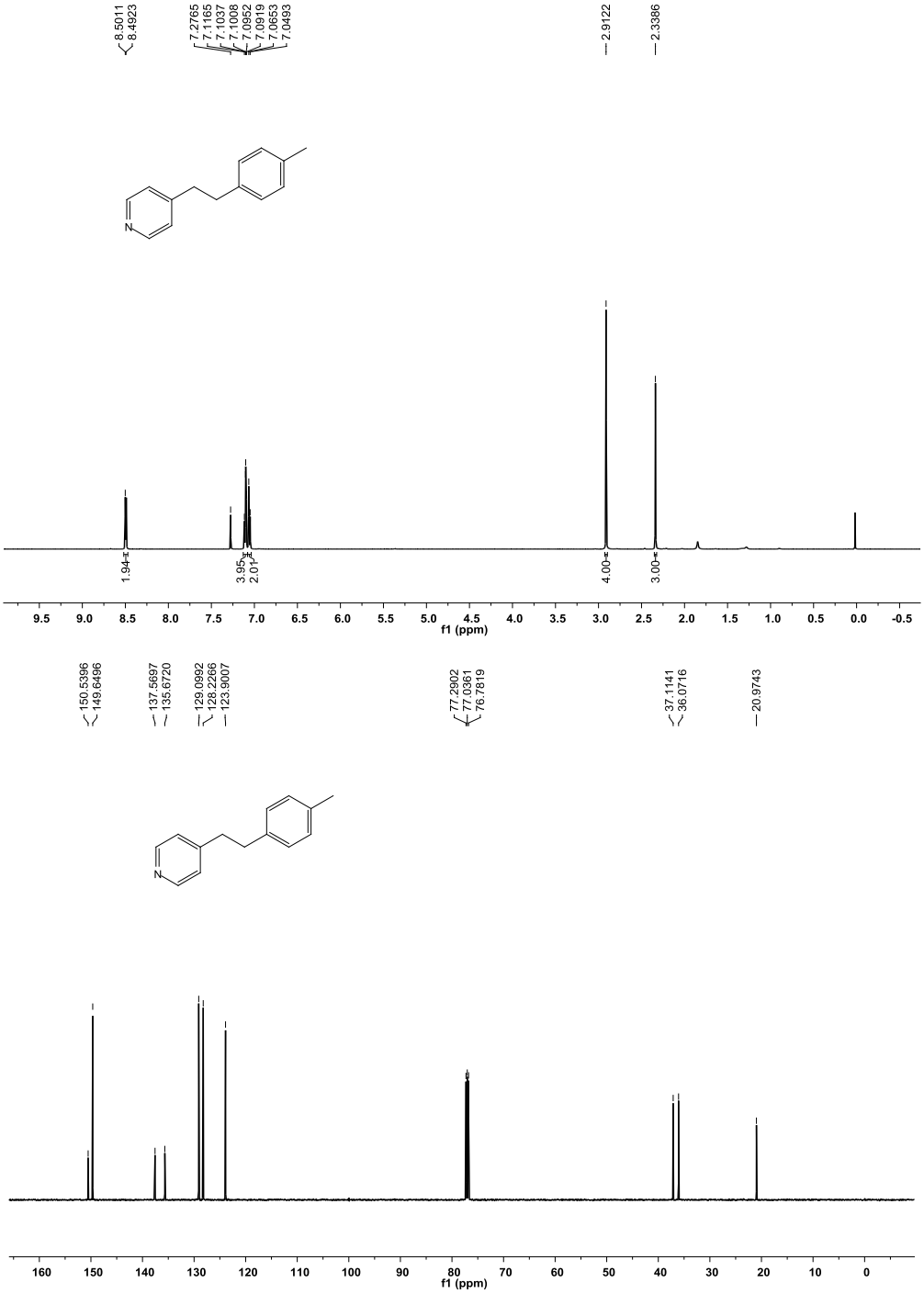
1-(4-Methylphenyl)-2-(4-*tert*-butylphenyl)ethane (**3eb**): Following the general procedure **1**, 4-*tert*-butylstyrene (160.2 mg, 1 mmol) and 4-bromotoluene (256.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3eb** was obtained as white solid (173 mg, 71% yield) after purification by silica gel column chromatography (petroleum ether).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.14-7.10 (m, 4H), 2.89 (s, 4H), 2.34 (s, 3H), 1.33 (s, 9H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 148.7, 139.1, 139.0, 135.4, 129.1, 128.3, 128.1, 125.3, 37.6, 37.5, 34.4, 31.5, 21.1. HRMS (EI-TOF): m/z calculated for $C_{19}H_{24}$ 252.1878, found 252.1860.

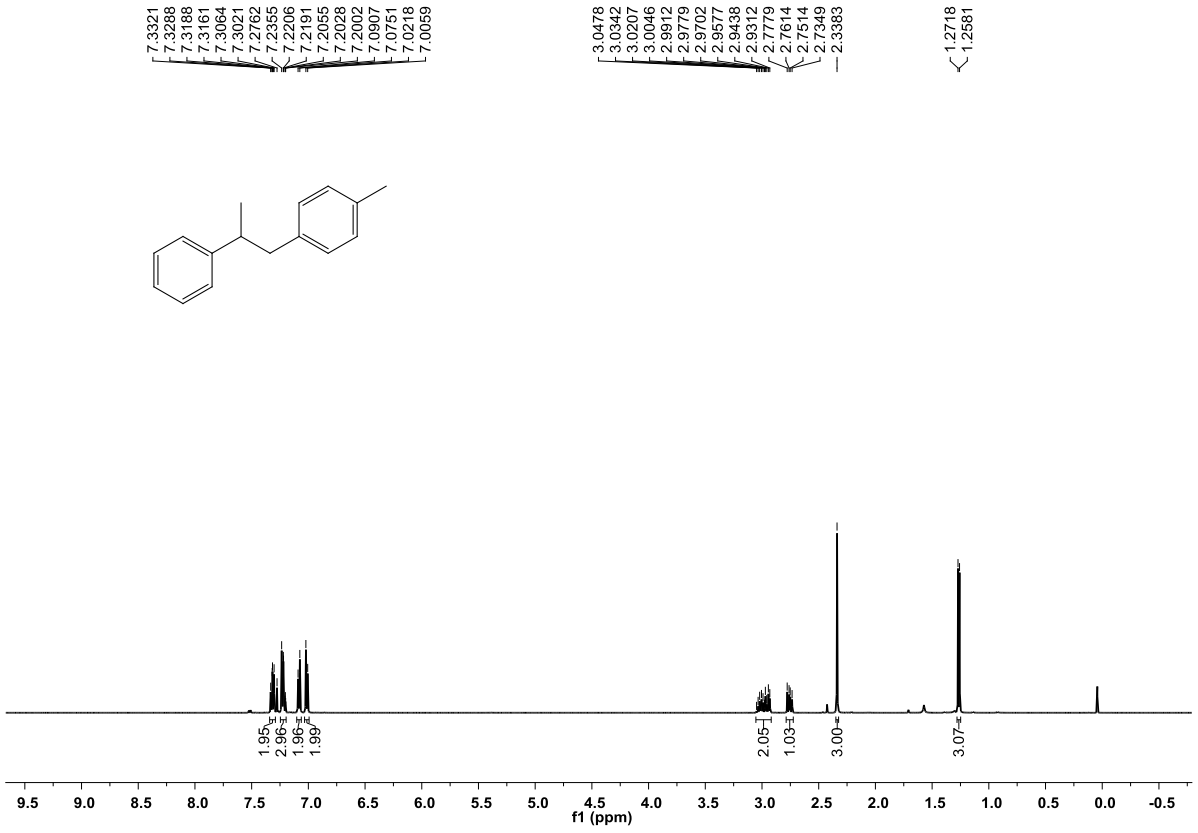


4-(4-Methylphenethyl)pyridine (**3gb**): Following the general procedure **2**, 4-vinylpyridine (105.1 mg, 1 mmol) and 4-bromotoluene (513.0 mg, 3.0 mmol) as substrates, KOH (196 mg, 3.5 mmol) as base. The title compound **3gb** was obtained as white solid (111 mg, 60% yield) after purification by silica gel column chromatography (petroleum ether/ethyl acetate/triethylamine = 20/4/1 → petroleum ether/ethyl acetate = 1/1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.50 (d, *J* = 4.4 Hz, 2H), 7.12-7.09 (m, 4H), 7.05 (d, *J* =8.0 Hz, 2H), 2.91 (s, 4H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 150.5, 149.6, 137.5, 135.7, 129.1, 128.2, 123.9, 37.1, 36.1, 21.0. HRMS (EI-TOF): m/z calculated for $C_{14}H_{15}N$ 197.1204, found 197.1200.

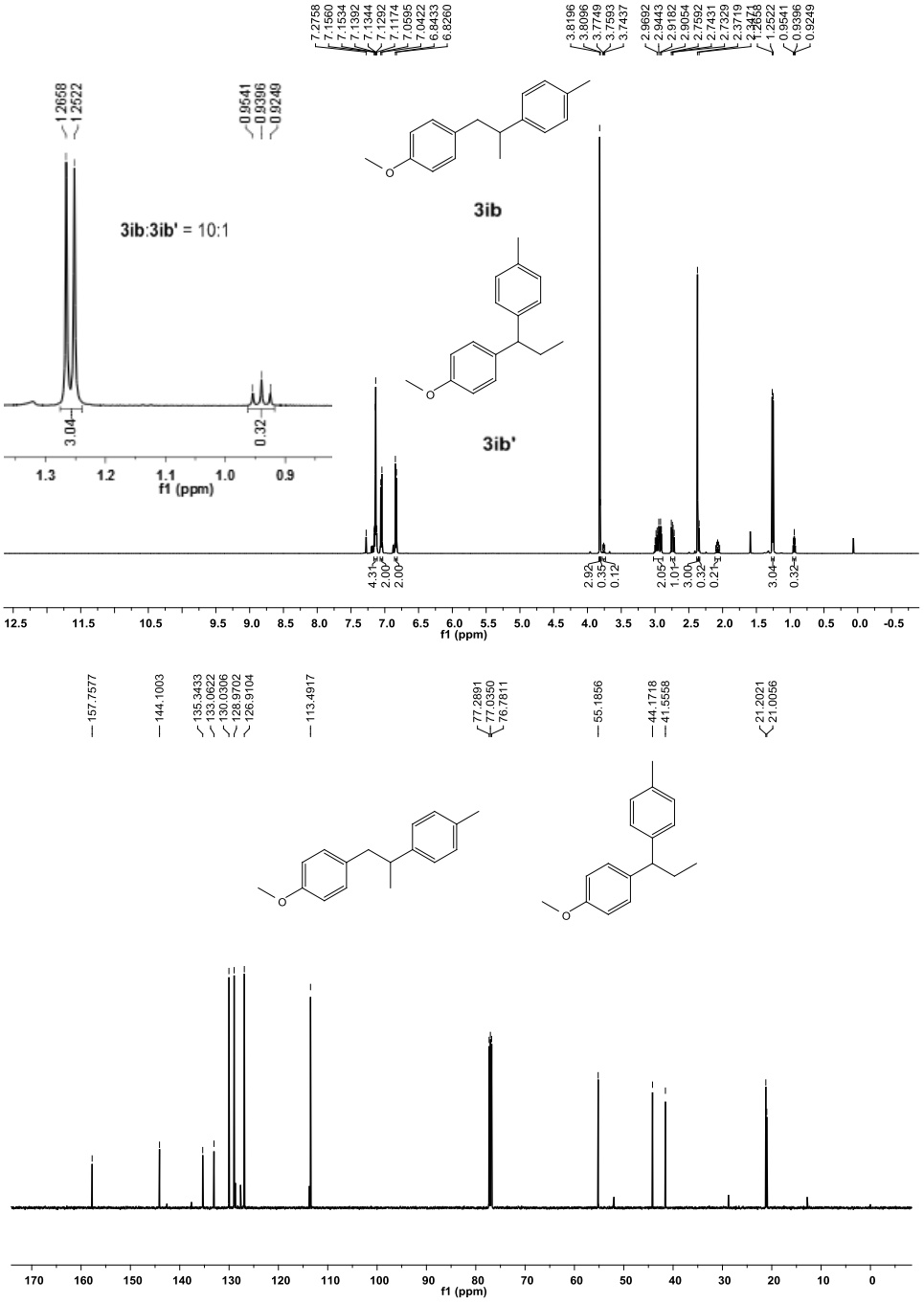


1-Methyl-4-(2-phenylpropyl)benzene (**3hb**)[3]: Following the general procedure **2**, α-methylstyrene (118.2 mg, 1 mmol) and 4-bromotoluene (513.0 mg, 3.0 mmol) as substrates, KOH (196 mg, 3.5 mmol) as base. The title compound **3hb** was obtained as colorless oil (121 mg, 58% yield) after purification by silica gel column chromatography (petroleum ether).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33-7.30 (m, 2H), 7.23-7.20 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 3.05-2.93 (m, 2H), 2.78-2.73 (m, 1H), 2.34 (s, 3H), 1.26 (d, *J* = 6.8 Hz, 3H).



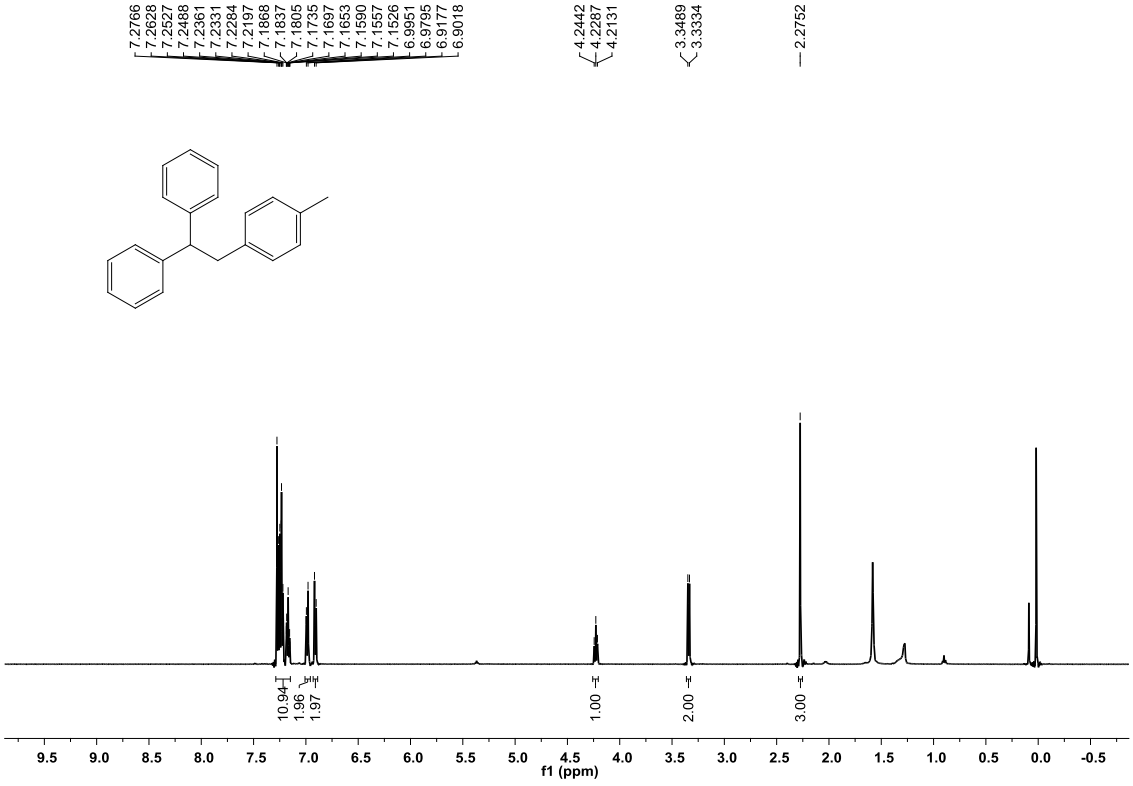
1-Methoxy-4-[2-(*p*-tolyl)propyl]benzene (**3ib**): Following the general procedure **2**, *trans*-Anethole (148.2 mg, 1 mmol) and 4-bromotoluene (513.0 mg, 3.0 mmol) as substrates, KOH (196 mg, 3.5 mmol) as base. The title compound **3ib** was obtained as colorless oil (143 mg, 61% yield) after purification by silica gel column chromatography (petroleum ether/toluene = 10/1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.16-7.12 (m, 4H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 3.00-2.90 (m, 2H), 2.76-2.71 (m, 1H), 2.37 (s, 3H), 1.26 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 157.7, 144.1, 135.3, 133.1, 130.0, 129.0, 126.9, 113.5, 55.2, 44.2, 41.5, 21.2, 21.0. HRMS (EI-TOF): m/z calculated for $C_{17}H_{20}O$ 240.1514, found 240.1506.

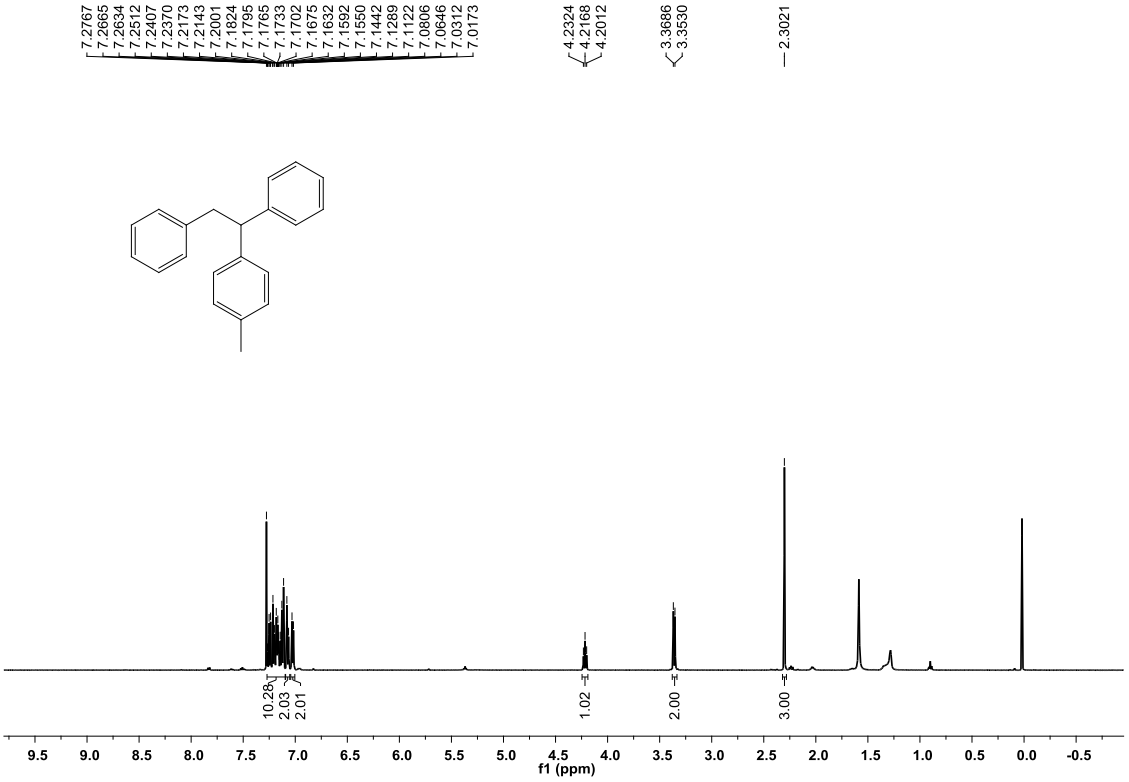


1-(2,2-Diphenylethyl)-4-methylbenzene (**3jb**)[7]: Following the general procedure **1**, 1,1-diphenylethylene (180.2 mg, 1 mmol) and 4-bromotoluene (256.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3jb** was obtained as yellow solid (51 mg, 19% yield) after purification by silica gel column chromatography (petroleum ether).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.28-7.15 (m, 10H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 4.23 (t, *J* = 7.8 Hz, 1H), 3.34 (d, *J* = 7.8 Hz, 2H), 2.27 (s, 3H).

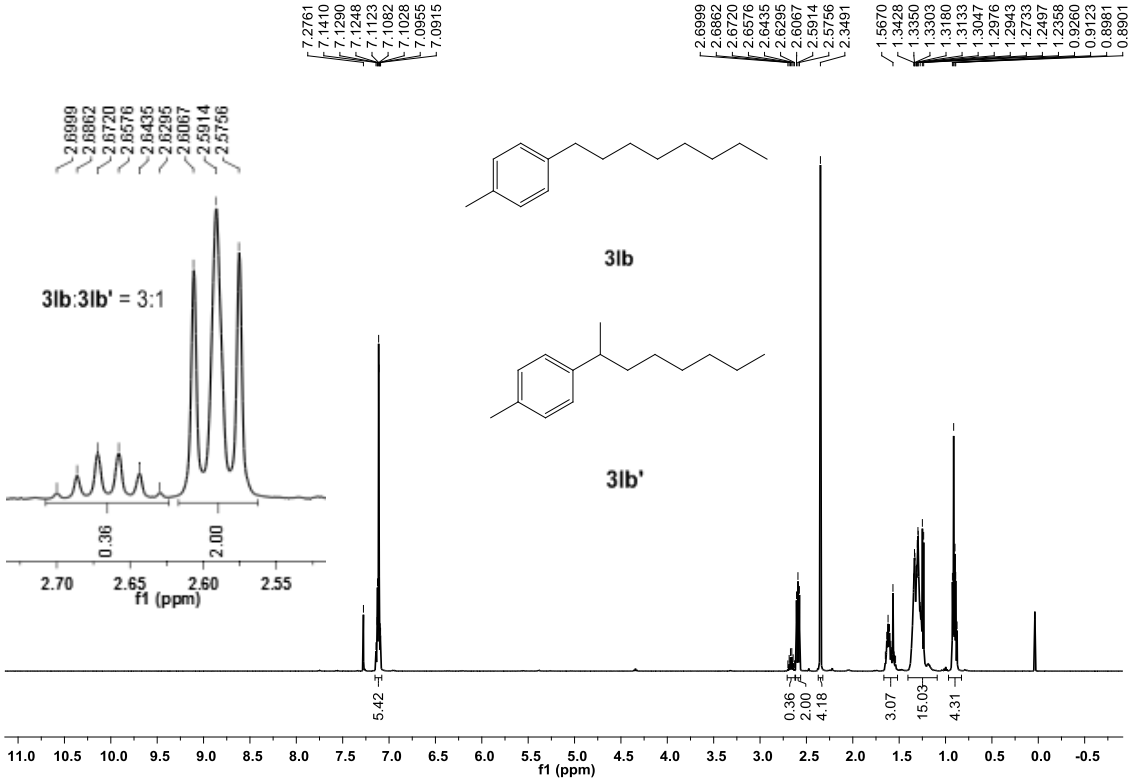


(1-*p*-Tolylethane-1,2-diyl)dibenzene (**3kb**)[8]: Following the general procedure **1**, *trans*-stilbene (180.2 mg, 1 mmol) and 4-bromotoluene (256.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3kb** was obtained as yellow oil (24 mg, 10% yield) after purification by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.27-7.11 (m, 10H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 4.22 (t, *J* = 7.8 Hz, 1H), 3.36 (d, *J* = 7.8 Hz, 2H), 2.30 (s, 3H).



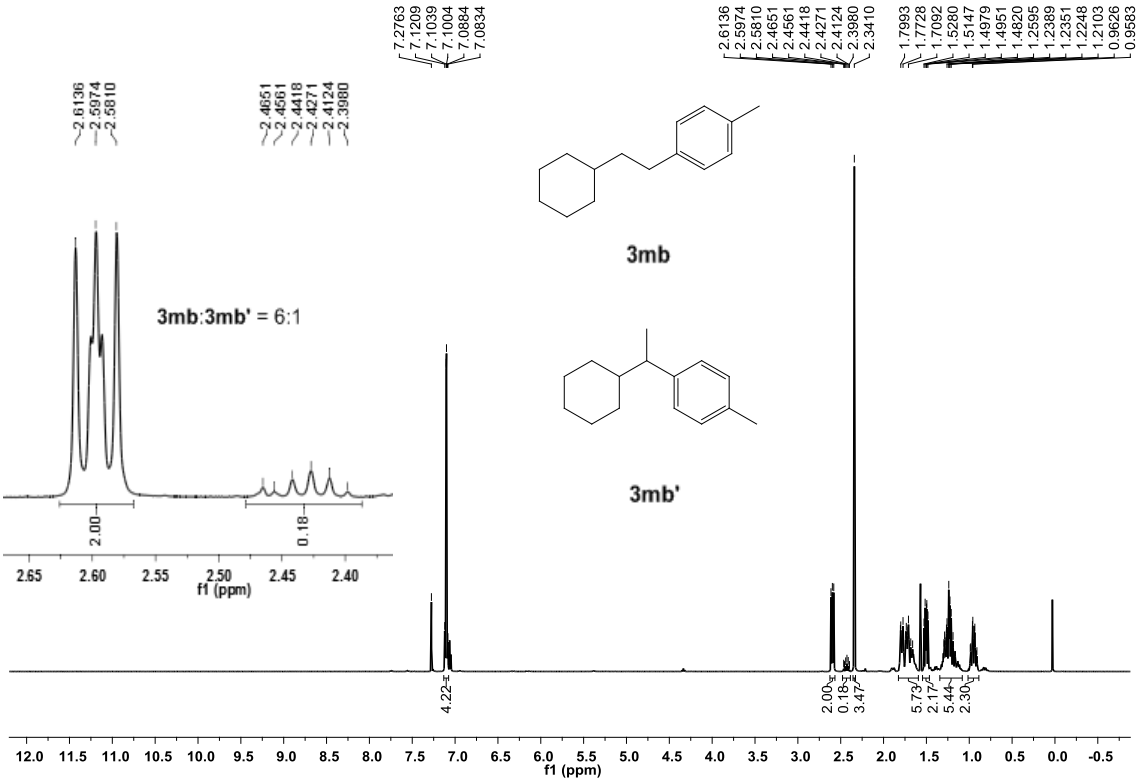
1-Methyl-4-octylbenzene (**3lb**)[9]: Following the general procedure **1**, 1-octene (112.2 mg, 1 mmol) and 4-bromotoluene (256.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3lb** was obtained as colorless oil (116 mg, 58% yield) after purification by silica gel column chromatography (petroleum ether).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.14-7.09 (m, 4H), 2.59 (t, *J* =7.8 Hz, 2H), 2.35 (s, 3H), 1.65-1.54 (m, 2H), 1.37-1.23 (m, 10H), 0.91 (t, *J* = 6.8 Hz, 3H).



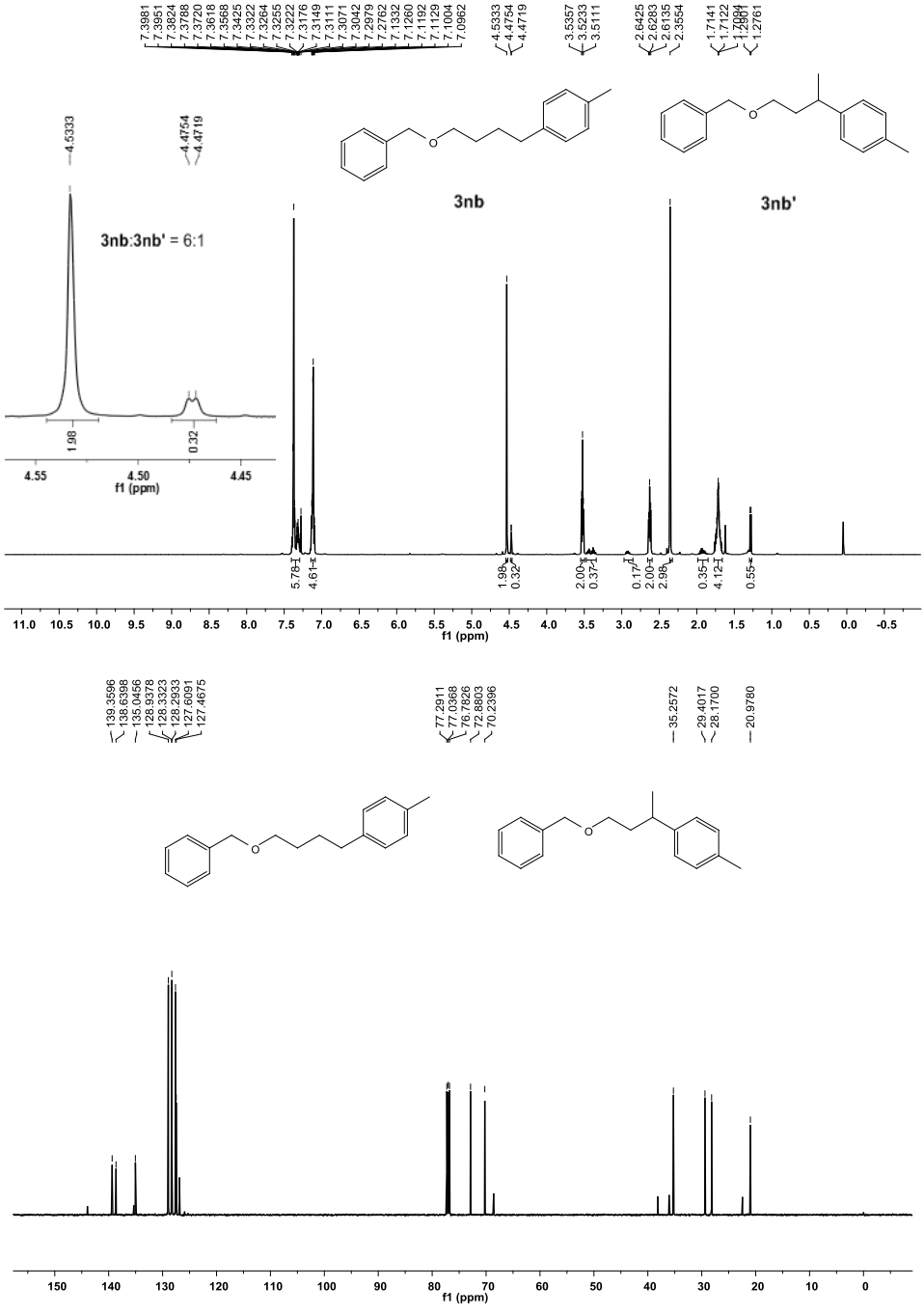
1-(2-Cyclohexylethyl)-4-methylbenzene (**3mb**)[10]: Following the general procedure **1**, vinylcyclohexane (110.2 mg, 1 mmol) and 4-bromotoluene (256.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3mb** was obtained as colorless oil (116 mg, 59% yield) after purification by silica gel column chromatography (petroleum ether).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.12-7.08 (m, 4H), 2.60 (t, *J* = 8.1 Hz, 2H), 2.34 (s, 3H), 1.80-1.66 (m, 4H), 1.53-1.48 (m, 2H), 1.29-1.19 (m, 5H), 0.99-0.91 (m, 2H).

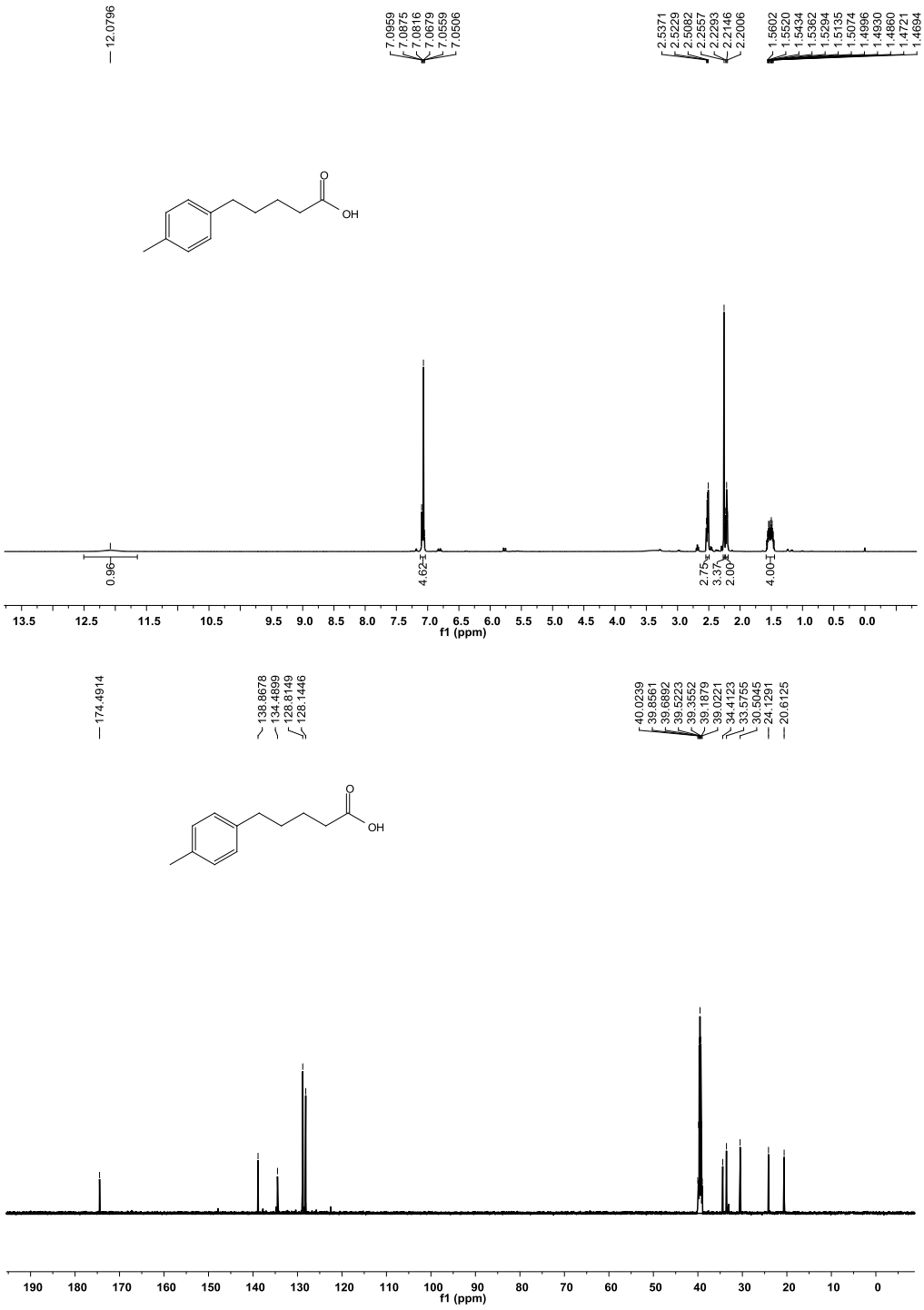


1-(4-Benzyloxybutyl)-4-methylbenzene (**3nb**): Following the general procedure **1**, 4-benzyloxy-1-butylene (162.2 mg, 1 mmol) and 4-bromotoluene (256.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3nb** was obtained as colorless oil (127 mg, 51% yield) after purification by silica gel column chromatography (petroleum ether/toluene = 2:1).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40-7.30 (m, 5H), 7.13-7.10 (m, 4H), 4.53 (s, 2H), 3.52 (t, *J* = 6.2 Hz, 2H), 2.63 (t, *J* = 7.3 Hz, 2H), 2.35 (s, 3H), 1.77-1.67 (m, 4H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 139.3, 138.6, 135.0, 128.9, 128.3, 128.2, 127.6, 127.4, 72.9, 70.2, 35.2, 29.4, 28.2, 21.0. HRMS (EI-TOF): m/z calculated for $C_{16}H_{18}$ 210.1409, found 210.1411. HRMS (EI-TOF): m/z calculated for $C_{18}H_{22}O$ 254.1671, found 254.1673.

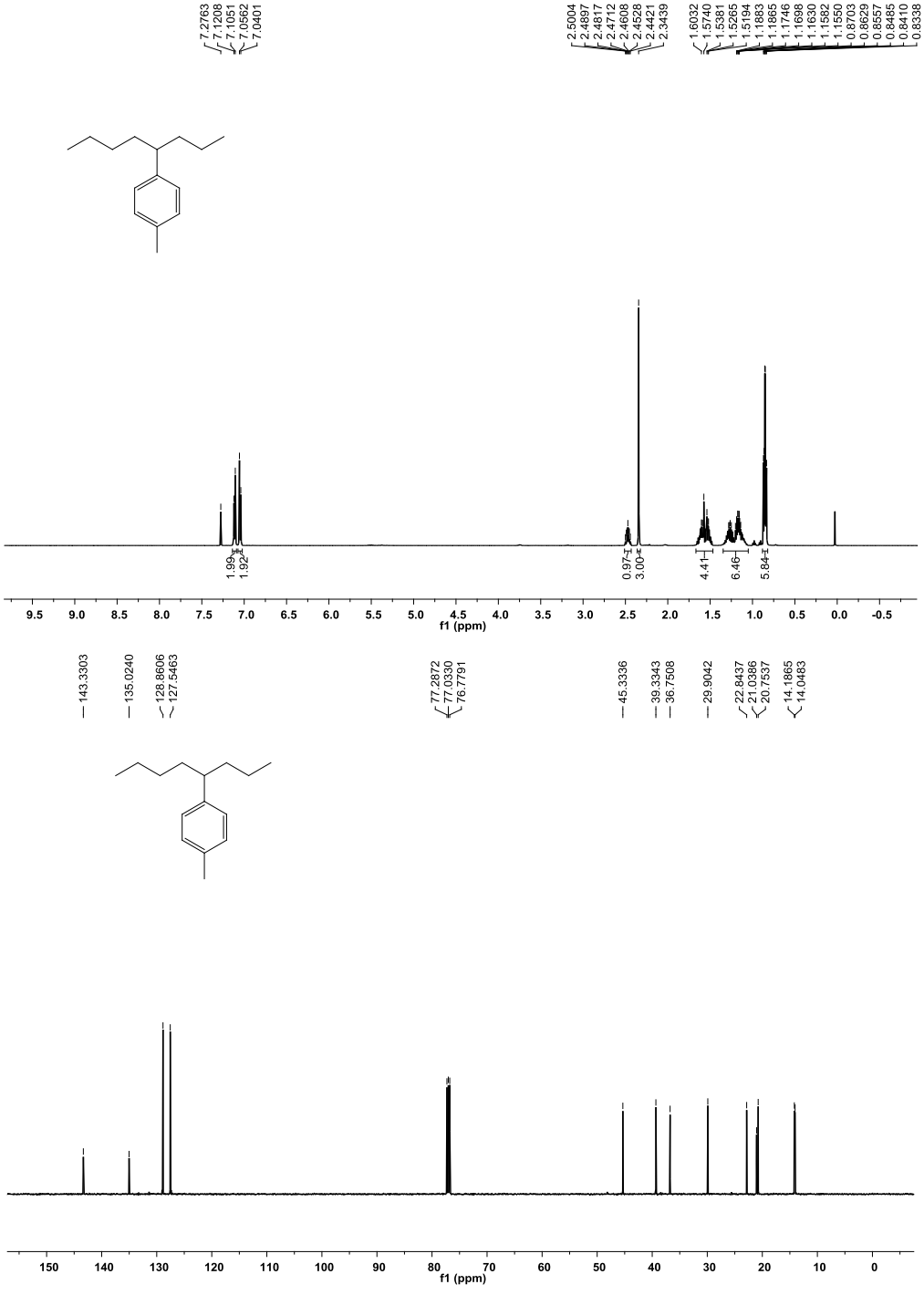


5-(*p*-Tolyl)pentanoic acid (**3ob**): Following the general procedure, 4-pentenoic acid (100.1 mg, 1 mmol) and 4-bromotoluene (256.5 mg, 1.5 mmol) as substrates, KOH (196 mg, 3.5 mmol) as base. The title compound **3ob** was obtained as white solid (60 mg, 32% yield) after purification by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1).
^{1}H NMR (DMSO-d^6, 500 MHz): δ 12.08 (sbr, 1H), 7.09-7.05 (m, 4H), 2.52 (t, J = 7.1 Hz, 2H), 2.25 (s, 3H), 2.21 (t, J = 7.4 Hz, 2H), 1.57-1.45 (m, 4H). ^{13}C NMR (DMSO-d^6, 126 MHz): δ 174.5, 138.9, 134.5, 128.8, 128.1, 34.4, 33.6, 30.5, 24.1, 20.6. HRMS (EI-TOF): m/z calculated for $C_{12}H_{16}O_2$ 192.1150, found 192.1156.

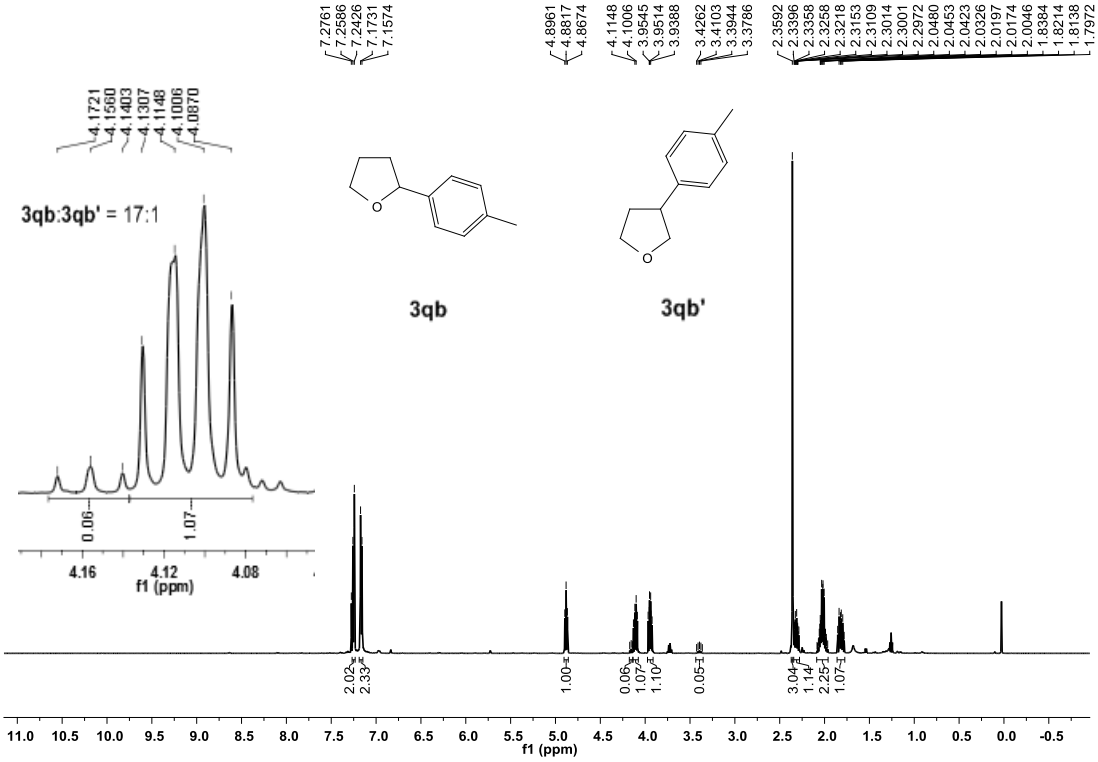


1-Methyl-4-(4-octyl)benzene (**3pb**): Following the general procedure, *trans*-4-octene (112.2 mg, 1 mmol) and 4-bromotoluene (513.0 mg, 3.0 mmol) as substrates, KOH (196 mg, 3.5 mmol) as base. The title compound **3pb** was obtained as colorless oil (72% ^{1}H NMR yield using 1,2-dibromoethane as an internal standard) after purification by silica gel column chromatography (petroleum ether).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.11 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 2.50-2.44 (m, 1H), 2.34 (s,3H), 1.65-1.48 (m, 4H), 1.33-1.07 (m, 6H), 0.87-0.83 (m, 6H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ 143.3, 135.0, 128.9, 127.5, 45.3, 39.3, 36.7, 29.9, 22.8, 21.0, 20.7, 14.2, 14.0. HRMS (EI-TOF): m/z calculated for $C_{15}H_{24}$ 204.1878, found 204.1895.

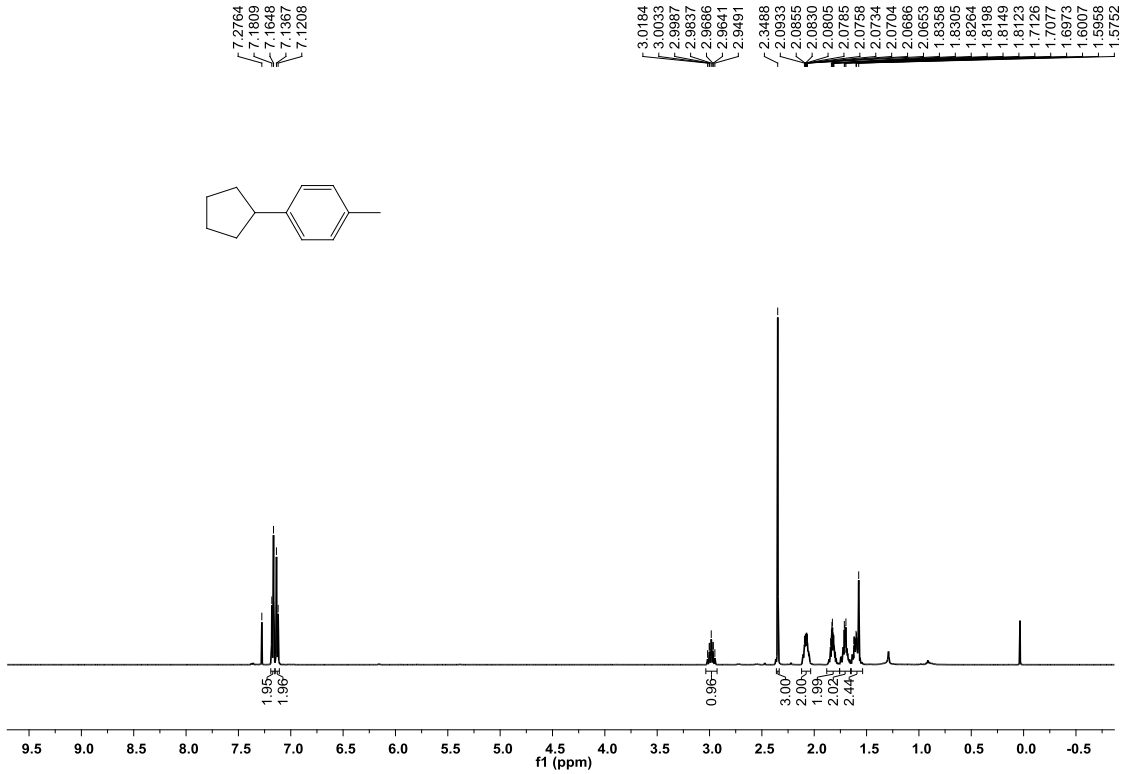


2-(*p*-Tolyl)tetrahydrofuran (**3qb**)[11]: Following the general procedure **1**, 2,3-dihydrofuran (70.1 mg, 1 mmol) and 4-bromotoluene (256.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3qb** was obtained as yellow oil (107 mg, 67% yield) after purification by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1).
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.25 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.88 (t, *J* = 7.2 Hz, 1H), 4.13-4.08 (m, 1H), 3.96-3.92 (m, 1H), 2.36 (s, 3H), 2.34-2.28 (m, 1H), 2.08-1.96 (m, 2H), 1.85-1.78 (m, 1H).



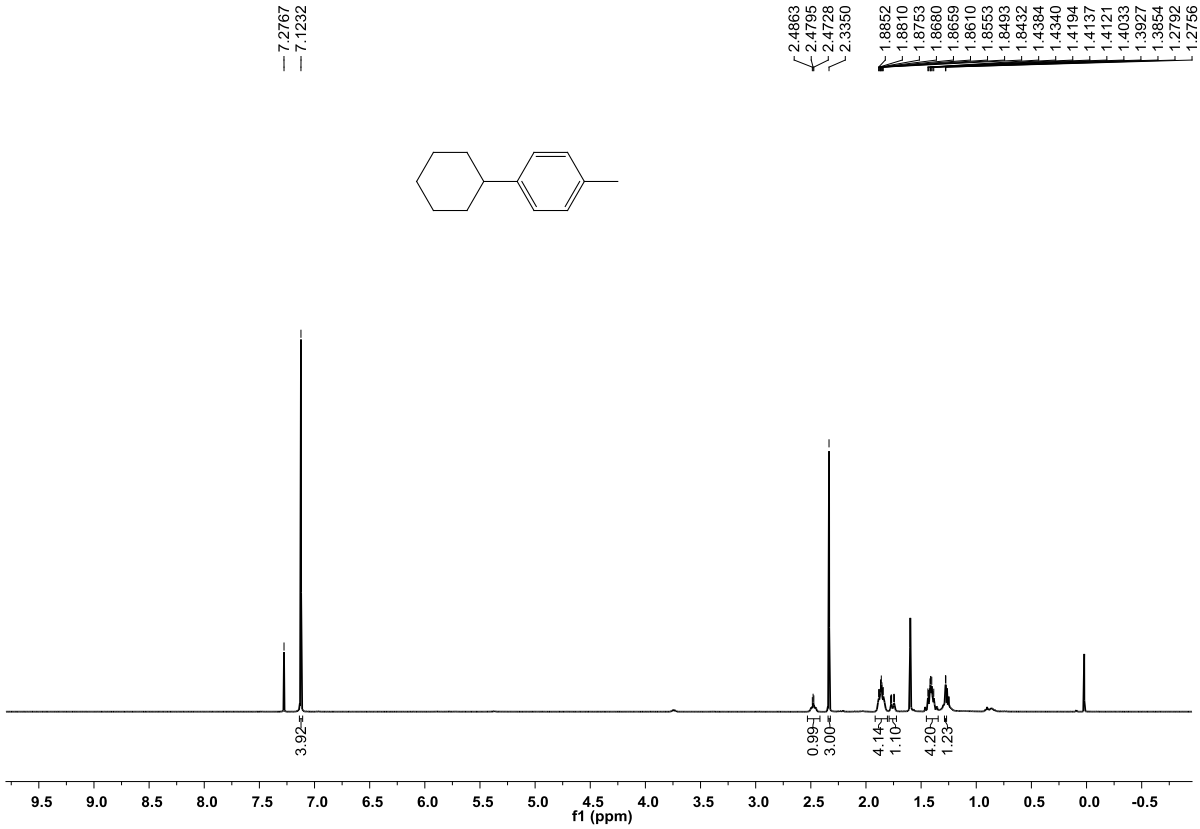
1-Cyclopentyl-4-methylbenzene (**3rb**)[12]: Following the general procedure **1**, cyclopentene (68.1 mg, 1 mmol) and 4-bromotoluene (256.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3rb** was obtained as colorless oil (73 mg, 48% yield) after purification by silica gel column chromatography (petroleum ether).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.17 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 3.02-2.95 (m, 1H), 2.35 (s, 3H), 2.12-2.03 (m, 2H), 1.84-1.78 (m, 2H), 1.72-1.68 (m, 2H), 1.62-1.57 (m, 2H).



1-Cyclohexyl-4-methylbenzene (**3sb**)[13]: Following the general procedure **1**, cyclohexene (82.1 mg, 1 mmol) and 4-bromotoluene (256.5 mg, 1.5 mmol) as substrates, KOH (140 mg, 2.5 mmol) as base. The title compound **3sb** was obtained as colorless oil (27 mg, 16% yield) after purification by silica gel column chromatography (petroleum ether).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.12 (s, 4H), 2.50-2.45 (m, 1H), 2.33 (s, 3H), 1.91-1.81 (m, 4H), 1.78-1.73 (m, 1H), 1.46-1.34 (m, 4H), 1.29-1.27 (m, 1H).



6. References

1. Y. Lai, Z. J. Zong, Y. J. Tang, W. M. Mo, N. Sun, B. X. Hu, Z. L. Shen, L. Q. Jin, W. H. Sun and X. Q. Hu, *Beilstein J. Org. Chem.* 2017, **13**, 213-221.
2. T. Connolly, Z. Y. Wang, M. A. Walker, I. M. McDonald and K. M. Peese, *Org. Lett.* 2014, **16**, 4444-4447.
3. P. Basnet, S. Thapa, D. A. Dickie and R. Giri, *Chem. Commun.*, 2016, **52**, 11072-11075.
4. Y. J. Liu, S. H. Xiao, Y. Qi, and F. Du, *Chem. - Eur. J.*, 2017, **12**, 673-678.
5. C. H. Basch, J. Liao, J. Y. Xu, J. J. Piane and M. P. Watson. *J. Am. Chem. Soc.*, 2017, **139**, 5313-5316.
6. R. Sharma, I. Kumar, R. Kumar and U. Sharma, *Adv. Synth. Catal*, 2017, **359**, 3022-3028.
7. S. Donck, A. Baroudi, L. Fensterbank, J. P. Goddard and C. Ollivier, *Adv. Synth. Catal.* 2013, **355**, 1477-1482.
8. K. B. Urkalan and M. S. Sigman, *Angew. Chem. Int. Ed.* 2009**, 48**, 3146-3149.
9. Z. Li, H. M. Sun and Q. Shen, *Org. Biomol. Chem.* 2016, **14**, 3314-3321.
10. R. B. Bedford, M. Betham, D. W. Bruce, A. A. Danopoulos, R. M. Frost and M. Hird, *J. Org. Chem.*, 2006, **71**, 1104-1110.
11. B. J. Shields and A. G. Doyle, *J. Am. Chem. Soc.*, 2016, **138**, 12719-12722.
12. Z. L. Duan, W. Li and A. W. Lei, *Org. Lett.*, 2016, **18**, 4012-4015.
13. D. Liu, Y. X. Li, X. T. Qi, C. Liu, Y. Lan and A. W. Lei, *Org. Lett.*, 2015, **17**, 998-1001.