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Supporting Information

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N-Tosylhydrazones as Reagents for Cross-Coupling Reactions: A Novel Route for the Synthesis of Polysubstituted Olefins

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- **Experimental procedures and spectroscopic data**
- **^{13}C NMR spectra for compounds 3**

Experimental procedures and spectroscopic data

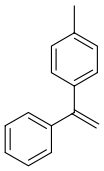
General considerations: All reactions were carried out under nitrogen atmosphere in a RR98030 12 place Carousel Reaction Station™ from Radleys Discovery Technologies, equipped with gas-tight threaded caps with a valve, cooling reflux head system, and digital temperature controller. Dioxane, dichloromethane, pentane and hexanes were dried using the procedures described in D. Perrin *Purification of Laboratory Chemicals,* Pergamon Press Ltd. 1980, 2nd Ed. $Pd_2(dba)_3$ is purchased from Strem Chemical co. and used without further purification. All ligands are commercially available from Strem Chemical co. or Aldrich Chemical co. and used without further purification. LiO^{t}Bu was purchased from Fluka, stored in a flask purged with nitrogen and weighted in the air. All aryl halides are commercially available from Aldrich Chemical co. and Acros Organics Chemical co. and used without further purification. *N*-Tosylhydrazones derived from ketones and aldehydes **1** were prepared following the procedure described in P.-L. Wu, S.-Y. Peng, and J. Magrath, *Synthesis* **1996**, 249. NMR spectra were recorded at 400 or 300 MHz for ^{1}H and 100 or 75 MHz for ^{13}C, with tetramethylsilane as internal standard for ^{1}H and the residual solvent signals as standard for ^{13}C. Chemical shifts are given in ppm. The data is being reported as s = singlet, d = doublet, t = triplet, c = quatriplet and m = multiplet or unresolved, chemical shifts in ppm and coupling constant(s) in Hz. Stereochemistry of olefins **3g**, **3h**, **3j**, and **3k** was determined by the

value of the coupling constants or by NOESY experiments. Mass spectra were obtained by EI (70 eV).

General procedure for the cross-coupling of *N*-Tosylhydrazones derived from ketones and aldehyde (1) with aryl halides (2)

A carousel reaction tube under nitrogen atmosphere was charged with 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (Xphos) (0.02 mmol, 2 mol %), tris(dibenzylideneacetone)dipalladium(0) (0.005 mmol, 1 mol %), lithium *t*-butoxide (2.2 mmol), the tosylhydrazone **1** (1 mmol) and dioxane (6 mL). After 1 minute, the aryl halide **2** (1 mmol) was added. The system was heated at 70º, 90º or 110ºC with stirring and reflux. The reaction was monitored by TLC analysis. When the reaction was completed, the crude reaction mixture was allowed to cool to room temperature, taken up in dry pentane, hexanes or dichloromethane (15 mL), and filtered through celite. The solvents were evaporated under reduced pressure; if necessary, the residue was purified by flash chromatography on silica gel.

1-Phenyl-1-*p*-tolyl-ethylene (3a):



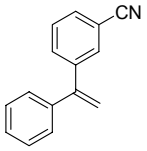
Colourless oil. Yield 98% from 4-bromotoluene and 96% from 4-clorotoluene.

HRMS: calcd. for $C_{15}H_{14}$: 194.1090, found: 194.1089.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.41 (s, 3H), 5.45 (s, 1H), 5.47 (s, 1H), 7.18 (d, ^{3}J = 8.0 Hz, 2H), 7.28 (d, ^{3}J = 8.0 Hz, 2H), 7.36-7.38 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.1 (CH_3), 113.6 (CH_2), 127.6 (CH), 128.0 (CH), 128.1 (CH), 128.2 (CH), 128.8 (CH), 137.4 (C), 138.5 (C), 141.6 (C), 149.8 (C).

Spectroscopic data in agreement with those reported in D. Xing, B. Guan, G. Cai, Z. Fang, L. Yang, and Z. Shi, *Org. Lett*. **2006;** *8*, 693.

3-(1-phenylvinyl)benzonitrile (3b):



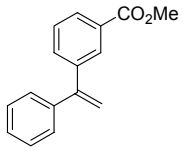
Brown oil. Yield 98%.

HRMS: calcd. for $C_{15}H_{11}N$: 205.0886, found: 205.0885.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.52 (s,1H), 5.58 (s, 1H), 7.30-7.32 (m, 2H), 7.37-7.39 (m, 3H), 7.44-7.48 (t, ^3J = 7.7 Hz,, 1H), 7.59-7.65 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 112.3 (C), 115.9 (CH_2), 118.5 (C), 127.9 (CH), 128.1 (CH), 128.3 (CH), 128.9 (CH), 131.0 (CH), 131.5 (CH), 132.3(CH), 139.9 (C), 142.5 (C), 148.0 (C).

Spectroscopic data in agreement with those reported in D. R. Arnold, X. Du, and J. Chen, *Can. J. Chem*. **1995**, *73*, 307.

Methyl 3-(1-phenylvinyl)benzoate (3c):

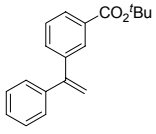


Colourless liquid. Yield 40%, **3c** was purified by flash chromatography using a gradient of a mixture pentane/dichloromethane 3:1 to 1:1 as eluent. R_f (pentane/CH_2Cl_2 1:1) = 0.42.

HRMS: calcd. for $C_{16}H_{14}O_2$: 238.0994, found: 238.0992.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.93 (s, 3H), 5.52 (s, 1H), 5.55 (s, 1H), 7.33-7.37 (m, 5H), 7.41-7.44 (m, 1H), 7.52-7.54 (m,1H), 8.00-8.04 (m, 1H), 8.07-8.08 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 52.2(CH_3), 115.2 (CH_2), 128.0 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 128.9 (CH), 129.3 (CH), 130.3 (C), 132.8 (CH), 140.9 (C), 141.9 (C), 149.2 (C), 167.0 (C).

***t*-Butyl 3-(1-phenylvinyl)benzoate (3c'):**

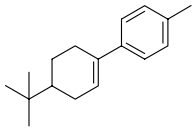


Colourless liquid. Yield 42%. R_f(pentane/CH_2Cl_2 1:1) = 0.64.

HRMS: calcd. for $C_{19}H_{20}O_2$: 280.1463, found: 280.1465.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.61 (s, 9H), 5.52 (s, 1H), 5.54 (s, 1H), 7.32-7.41 (m, 6H), 7.46-7.48 (m, 1H), 7.95-7.97 (m, 1H), 8.03-8.04 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.2 (CH_3), 81.1 (C), 115.0 (CH_2), 127.9 (CH), 128.0 (CH), 128.1 (CH), 128.3 (CH), 128.7 (CH), 129.1 (CH), 132.2 (C), 132.3 (CH), 141.0 (C), 141.7 (C), 149.4 (C), 165.7 (C).

1-(4-*t*-Butylcyclohex-1-enyl)-4-methylbenzene (3d):



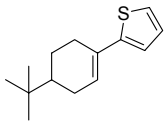
White solid. Yield 74%. **3d** was purified by flash chromatography using hexanes as eluent. R_f(hexanes) = 0.54.

HRMS: calcd. for $C_{17}H_{24}$: 228.1872, found: 228.1874.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.95 (s, 9H), 1.26-1.44 (m, 2H), 1.94-2.03 (m, 2H), 2.23-2.32 (m, 1H), 2.38 (s, 3H), 2.42-2.58 (m, 2H), 6.12-6.13 (m, 1H), 7.15 (d, ^3J = 8.1 Hz, 2H), 7.32 (d, ^3J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.0 (CH_3), 24.3 (CH_2), 27.1 (CH_3), 27.3 (CH_2), 28.8 (CH_2), 32.1 (C), 43.7 (CH), 124.0 (CH), 124.7 (CH), 128.8 (CH), 135.9 (C), 136.0 (C), 139.3 (C).

Spectroscopic data in agreement with those reported in M. E. Limmert, A. H. Roy, and J. F. Hartwig, *J. Org. Chem.* **2005**, *70*, 9364.

2-(4-*t*-butylcyclohex-1-enyl)thiophene (3e):

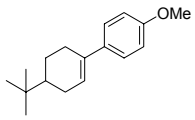


Brown oil. Yield 90%.

HRMS: calcd. for $C_{14}H_{20}S$: 220.1280, found: 220.1279.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.94 (s, 9H), 1.30-1.42 (m, 2H), 1.95-2.02 (m, 2H), 2.22-2.30 (m, 1H), 2.37-2.47 (m, 1H), 2.57-2.64 (m, 1H), 6.20-6.23 (m, 1H), 6.95-6.99 (m, 2H), 7.10-7.12 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 24.0 (CH_2), 27.1 (CH_3), 27.1 (CH_2), 28.9 (CH_2), 32.1 (C), 43.7 (CH), 121.0 (CH), 122.5 (CH), 124.1 (CH), 127.0 (CH), 130.9 (C), 146.6 (C).

1-(4-*t*-butylcyclohex-1-enyl)-4-methoxybenzene (3f):

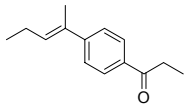


Brown oil. Yield 95%.

HRMS: calcd. for $C_{17}H_{24}O$: 244.1822, found: 244.1820.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.93 (s, 9H), 1.28-1.42 (m, 2H), 1.93-2.02 (m, 2H), 2.22-2.28 (m, 1H), 2.34-2.56 (m, 2H), 3.81 (s, 3H), 6.05-6.06 (m, 1H), 6.86 (d, ^3J = 8.8 Hz, 2H), 7.34 (d, ^3J = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 24.3 (CH_2), 27.2 (CH_3), 27.3 (CH_2), 28.8 (CH_2), 32.1 (C), 43.7 (CH), 55.1 (CH_3), 113.4 (CH), 123.2 (CH), 125.8 (CH), 134.8 (C), 135.5 (C), 158.3 (C).

1-[4-((*E*)-Pent-2-en-2-yl)phenyl]propan-1-one (3g):

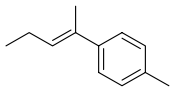


Yellow liquid. Yield 78%. **3g** was purified by flash chromatography using a mixture of hexanes/ethyl acetate 10:1 as eluent. R_f(hexanes/ethyl acetate 5:1) = 0.53.

HRMS: calcd. for $C_{14}H_{18}O$: 202.1352, found: 202.1354.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.00 (t, ^3J = 7.6 Hz, 3H), 1.24 (t, ^3J = 7.2 Hz, 3H), 1.84 (d, ^3J = 7.2 Hz, 3H), 2.55 (c, ^3J = 7.6 Hz, 2H), 3.00 (c, ^3J = 7.2 Hz, 2H), 5.87 (c, ^3J = 7.2 Hz, 1H), 7.42-7.44 (m, 2H), 7.91-7.93 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 8.4 (CH_3), 13.2 (CH_3), 14.1 (CH_3), 22.3 (CH_2), 31.7 (CH_2), 124.4 (CH), 126.1 (CH), 128.1 (CH), 134.9 (C), 141.6 (C), 147.7 (C), 200.5 (C).

1-methyl-4-[(*E*)-pent-2-en-3-yl]benzene (3h):



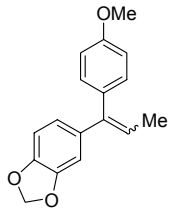
Colourless oil. Yield 80%. **3h** was purified by flash chromatography using hexanes as eluent. R_f(hexanes) = 0.54.

HRMS: calcd. for $C_{12}H_{16}$: 160.1246, found: 160.1245.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.02 (t, ^3J = 7.5 Hz, 3H), 1.82 (d, ^3J = 6.9 Hz, 3H), 2.37 (s, 3H), 2.47 (c, ^3J = 7.5 Hz, 2H), 5.74 (c, ^3J = 6.9 Hz, 1H), 7.14 (d, ^3J = 8.0 Hz, 2H), 7.27 (d, ^3J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.2 (CH_3), 13.8

(CH_3), 20.9 (CH_3), 22.5 (CH_2), 121.2 (CH), 125.9 (CH), 128.8 (CH), 135.9 (C), 140.1 (C), 142.0 (C).

5-[1-(4-methoxyphenyl)prop-1-enyl]benzo[*d*][1,3]dioxole (3i):

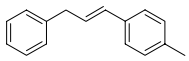


Yellow liquid. Yield 80% of *E*:*Z* mixture of isomers 1:1. **3i** was purified by flash chromatography using mixture of hexanes/ethyl acetate 8:1 as eluent. R_f(hexanes/ethyl acetate 5:1) = 0.37.

HRMS: calcd. for $C_{17}H_{16}O_3$: 268.1094, found: 268.1095.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.76-1.79 (2 d overlapped, 6H), 3.81 (s, 3H), 3.86 (s, 3H), 6.00 (s, 2H), 6.02 (s, 2H), 6.03-6.08 (m, 2H), 6.67-6.74 (m, 4H), 6.77-6.78 (m, 1H), 6.82-6.86 (m, 3H), 6.92-6.95 (m, 2H), 7.12-7.14 (m, 2H), 7.17-7.19 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 15.7 (2xCH_3 overlapped), 55.2 (CH_3), 55.3 (CH_3), 100.9 (2xCH_2 overlapped), 107.7 (CH), 107.8 (CH), 108.0 (CH), 110.5 (CH), 113.4 (CH), 113.5 (CH), 121.0 (CH), 122.4 (CH), 122.7 (CH), 123.4 (CH), 128.3 (CH), 131.2 (CH), 132.4 (C), 134.1 (C), 135.8 (C), 138.0 (C), 141.4 (C), 141.6 (C), 146.3 (C), 146.5 (C), 147.4 (C), 147.5 (C), 158.5 (C), 158.6 (C).

1-methyl-4-[(*E*)-3-phenylprop-1-enyl]benzene (3j):

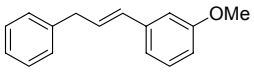


Colourless liquid. Yield 75%. **3j** was purified by flash chromatography using hexanes as eluent. R_f(hexanes): 0.19.

HRMS: calcd. for $C_{16}H_{16}$: 208.1252, found: 208.1249.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.37 (s, 3H), 3.59 (d, ^3J = 8.0 Hz, 2H), 6.36 (dt, ^3J = 8.0 Hz, $^3J_{trans}$= 16.0 Hz, 1H), 6.48 (d, $^3J_{trans}$ = 16.0 Hz, 1H), 7.15 (d, ^3J = 8.0 Hz, 2H), 7.25-7.38 (m, 7H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.1 (CH_3), 39.3 (CH_2), 125.9 (CH), 126.0 (CH), 128.1 (CH), 128.4 (CH), 128.6 (CH), 129.1 (CH), 130.8 (CH), 134.6 (C), 136.8 (C), 140.3 (C).

1-(4-methoxycinnamyl)benzene (3k):



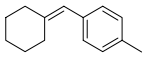
Yellow liquid. Yield 68%. **3k** was purified by flash chromatography using a mixture of hexanes/ethyl acetate 8:1 as eluent. R_f(hexanes/ethyl acetate 5:1) = 0.42.

HRMS: calcd. for $C_{16}H_{16}O$: 224.1196, found: 224.1193.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.61 (d, ^3J = 6.4 Hz, 2H), 3.85 (s, 3H), 6.38-6.45 (m, 1H), 6.48 (d, $^3J_{trans}$ = 16.0 Hz, 1H), 6.82-6.84 (m, 1H), 6.97 (m, 1H), 7.01-7.03 (m, 1H), 7.25-7.39 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 39.4 (CH_2), 55.2 (CH_3), 111.4 (CH), 112.9 (CH), 118.9 (CH), 126.3 (CH), 128.6 (CH), 128.8 (CH), 129.5 (CH), 129.6 (CH), 131.0 (CH), 139.0 (C), 140.2 (C), 159.8 (C).

Spectroscopic data in agreement with those reported in K. Manabe, K. Nakada, N. Aoyama, and S. Kobayashi, *Adv. Synth. Catal.* **2005**, *347*, 1499.

1-(cyclohexylidenemethyl)-4-methylbenzene (3l):



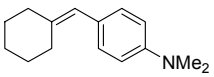
Brown liquid. Yield 99%.

HRMS: calcd. for $C_{14}H_{18}$: 186.1403, found: 186.1400.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.64-1.69 (m, 6H), 2.32-2.46 (m, 7H), 6.27 (s, 1H), 7.17 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 21.0 (CH_3), 26.6 (CH_2), 27.8 (CH_2), 28.5 (CH_2), 29.4 (CH_2), 37.5 (CH_2), 121.7 (CH), 128.6 (CH), 128.7 (CH), 135.2 (C), 135.4 (C), 142.7 (C).

Spectroscopic data in agreement with those reported in A. R. Katritzky, D. Cheng, S. A. Henderson, and J. Li, *J. Org. Chem.* **1998**, *63*, 6704.

4-(cyclohexylidenemethyl)-*N*,*N*-dimethylbenzenamine (3m):



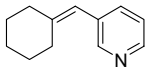
Yellow liquid. Yield 62%. **3m** was purified by flash chromatography using a mixture of hexanes/ethyl acetate 10:1 as eluent. R_f(hexanes/ethyl acetate 10:1) = 0.43.

HRMS: calcd. for $C_{15}H_{21}N$: 215.1668, found: 215.1667.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.60-1.70 (m, 6H), 2.29-2.32 (m, 2H), 2.45-2.48 (m, 2H), 2.99 (s, 6H), 6.22 (s, 1H), 6.76 (d, ^3J = 8.8 Hz, 2H), 7.18 (d, ^3J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.9 (CH_2), 27.9 (CH_2), 28.7 (CH_2), 29.5 (CH_2), 37.7

(CH_2), 40.8 (CH_3), 112.3 (CH), 121.8 (CH), 127.0 (C), 129.8 (CH), 141.0 (C), 148.8 (C).

3-(cyclohexylidenemethyl)pyridine (3n):

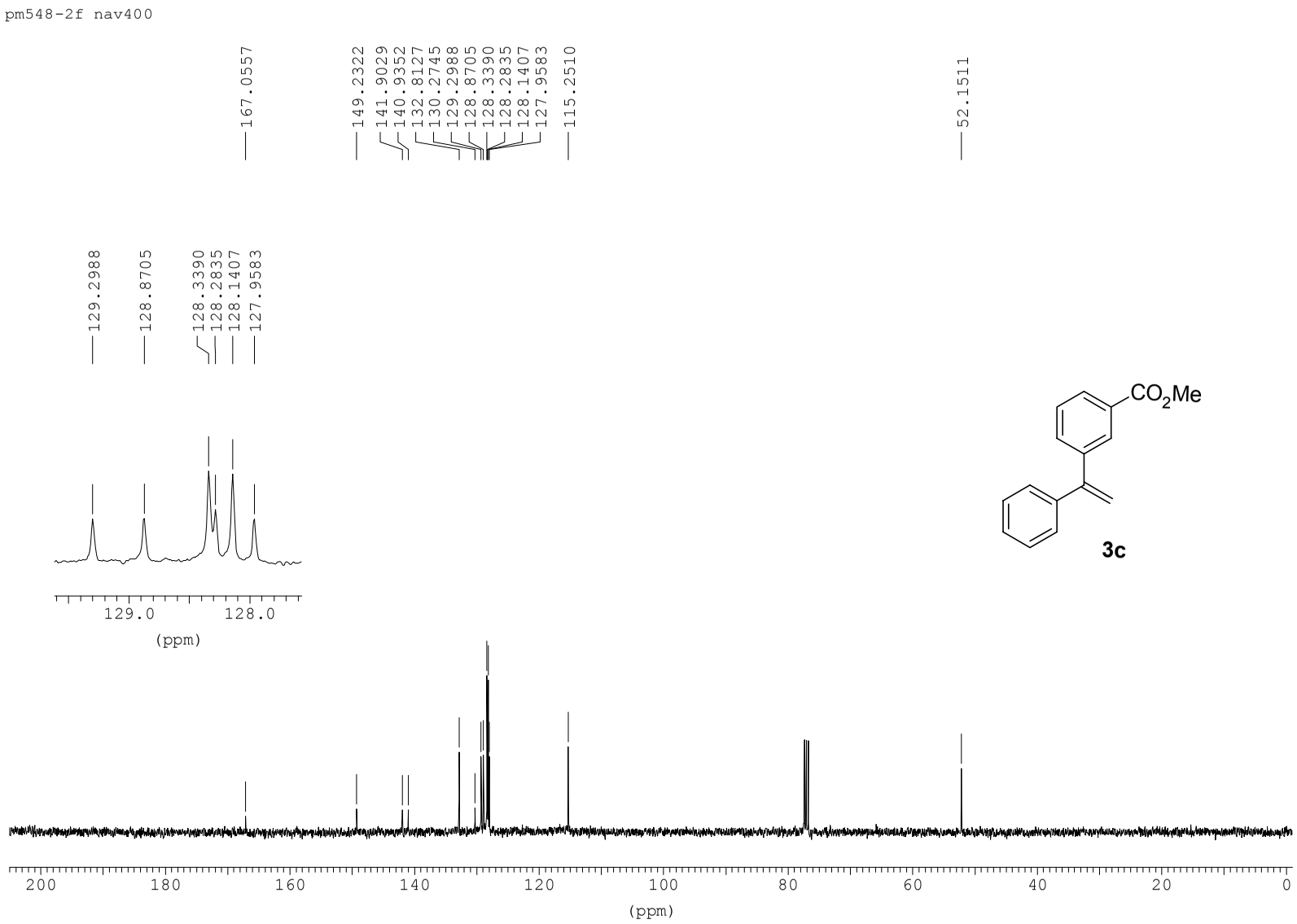


Yellow oil. Yield 52%. **3n** was purified by flash chromatography using a mixture of hexanes/ethyl acetate 3:1 as eluent. R_f(hexanes/ethyl acetate 1:1) = 0.40.
HRMS: calcd. for $C_{12}H_{15}N$: 173.1199; found: 173.1203.
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.54-1.68 (m, 6H), 2.27-2.35 (m, 4H), 6.16 (s, 1H), 7.23-7.28 (m, 1H), 7.50-7.52 (m, 1H), 8.42-8.46 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.4 (CH_2), 27.7 (CH_2), 28.4 (CH_2), 29.4 (CH_2), 37.5 (CH_2), 118.0 (CH), 123.0 (CH), 134.0 (C), 136.2 (CH), 146.2 (C), 146.4 (CH), 149.6 (CH).

^{13}C NMR spectra for compounds 3:

21.1087
113.5833
127.5668
128.0453
128.0762
128.2228
128.7861
137.4371
138.5252
141.6043
149.8154
3a
128.7861
128.2228
128.0762
128.0453
127.5668
128.0
(ppm)
0
20
40
60
80
100
120
140
160
180
200
(ppm)

CN
3b
147.9770
142.5277
139.9577
132.3349
131.5417
131.0023
128.9083
128.3054
128.0913
127.8850
118.5569
115.9393
112.2588
127.8850
128.0913
128.3054
128.9083
129
(ppm)
(ppm)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167.0557
149.2322
141.9029
140.9352
132.8127
130.2745
129.2988
128.8705
128.3390
128.2835
128.1407
127.9583
115.2510
52.1511
129.2988
128.8705
128.3390
128.2835
128.1407
127.9583
129.0
128.0
(ppm)
CO2Me
3c
200
180
160
140
120
100
80
60
40
20
0
(ppm)

28.1957
81.1052
115.0375
127.8903
128.0212
128.1376
128.2831
128.6758
129.1341
132.1454
132.3055
141.0049
141.7032
149.3698
165.7431
O
O^{t}Bu
3c'
(ppm)

139.2896
136.0098
135.9558
128.7789
124.6888
123.9634
43.6895
32.1292
28.7568
27.3446
27.1439
24.3117
20.9625
3d
(ppm)

146.5819
130.8852
127.0266
124.1250
122.5121
121.0227
43.7431
32.1056
28.9184
27.1280
23.9949
DEPT 135
3e
S
(ppm)

158.2734
135.5464
134.7901
125.8073
123.1603
113.4290
55.1490
43.7276
32.1210
28.8258
27.3287
27.1512
24.3421
OMe
3f
(ppm)

200.4578
147.6616
141.6174
134.9385
128.1011
126.1339
124.3730
31.7021
22.3343
14.1166
13.2044
8.3579
3g
O
(ppm)
0
20
40
60
80
100
120
140
160
180
200

142.0327
140.1124
135.8718
128.7798
125.9358
121.1933
22.4879
20.9386
13.8321
13.1775
3h
(ppm)

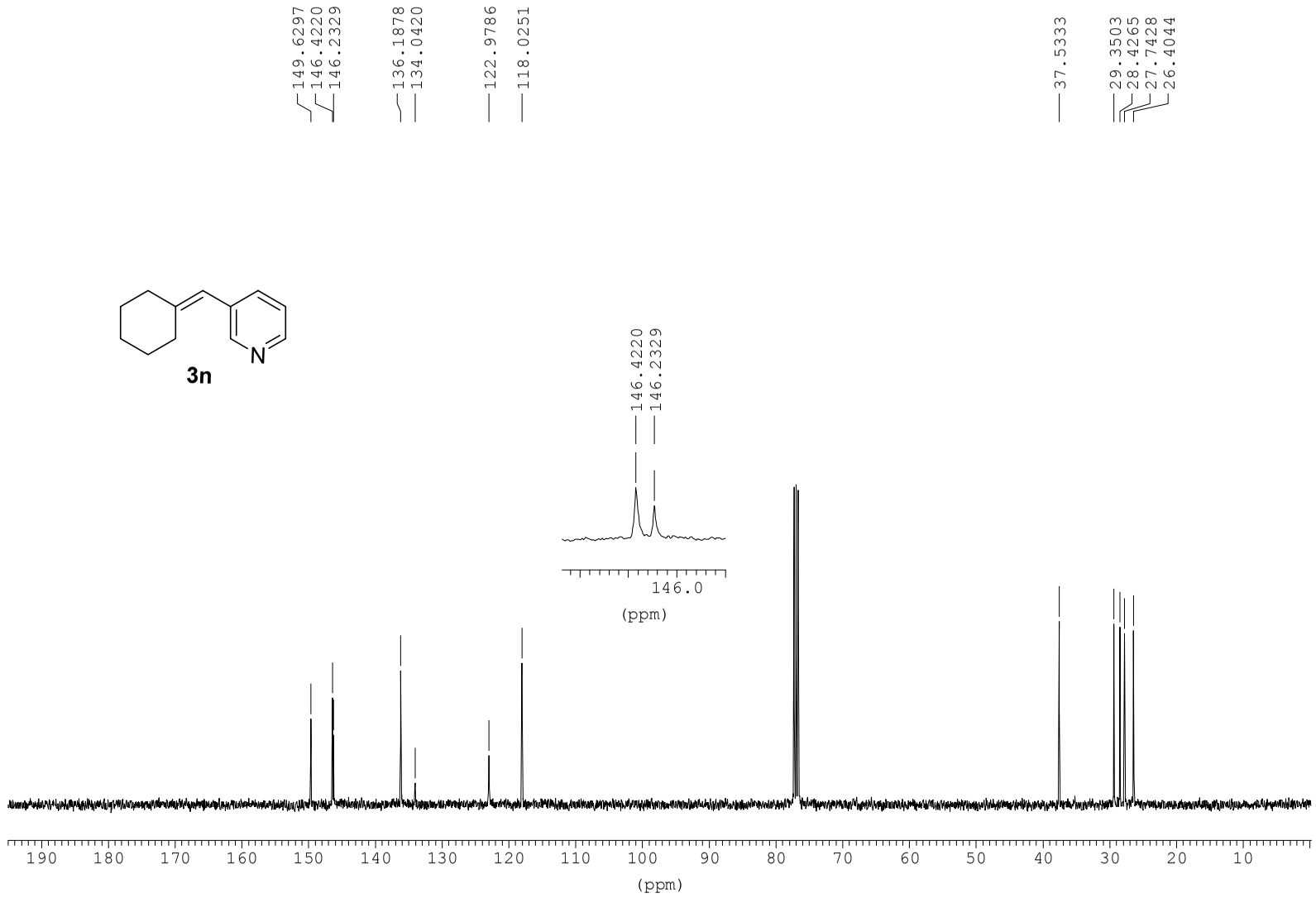
158.6318
158.4731
147.4792
147.4316
146.4639
146.3291
141.5777
141.4508
137.9924
135.8031
134.0660
132.3765
131.1708
128.2835
123.4132
122.6993
122.4217
121.0018
113.5298
113.4505
110.4997
108.0566
107.7949
107.7631
100.9336
55.2684
55.2288
15.7348
MeO
Me
3i
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
(ppm)

140.2683
136.7478
134.6312
130.8561
129.1176
128.5866
128.3830
128.0920
126.0481
125.9463
129.1176
128.5866
128.3830
128.0920
129
128
(ppm)
3j
39.2718
21.0727
180
160
140
120
100
80
60
40
20
(ppm)

OMe
3k
159.8454
140.1499
138.9919
131.0280
129.6320
129.5368
128.7515
128.5611
126.2687
118.8839
112.9111
111.4119
129.6320
129.5368
128.7515
128.5611
129
(ppm)
55.2288
39.3804
(ppm)

142.6924
135.3534
135.1991
128.7012
128.6009
121.6863
37.5462
29.3506
28.5248
27.7608
26.6187
21.0238
3l
(ppm)
(ppm)

148.8118
140.9511
129.7668
126.9747
121.8188
112.3479
40.7526
37.7464
29.5287
28.7276
27.9423
26.8635
NMe2
3m
(ppm)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136.1878
134.0420
122.9786
118.0251
37.5333
29.3503
28.4265
27.7428
26.4044
3n
N
146.4220
146.2329
146.0
(ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)