

General information

All reactions that required anhydrous conditions were carried by standard procedures under nitrogen atmosphere. Commercially available reagents from Alfa Aesar and Aldrich were used as received. The solvents were dried by distillation over the appropriate drying reagents.

Melting points were measured on a Meltemp melting point apparatus and were not corrected. ¹H NMR spectra were recorded on commercial instruments (300 MHz or 600 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl₃, δ = 7.26). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ¹³C NMR spectra were collected on commercial instruments (300 MHz or 600 Hz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard (CDCl₃, δ = 77.0).

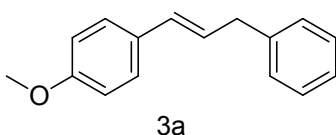
Dhps were prepared according the previous literature¹.

Nitro-olefines were prepared according to the previous literature².

General procedural for synthesis of trans-olefins via alkyl transfer reactions.

A reaction tube was charged with the DHP (0.4 mmol, 2 eq.), nitro-olefin (0.2 mmol, 1.0 eq.), *n*-butyl ether (2 mL), AIBN (1 eq.). The system was heated at 80 °C with stirring under a nitrogen atmosphere. The reaction was monitored by TLC. When the reaction was completed, the crude reaction mixture was allowed to reach room temperature, the solvent was eliminated, and the residue was directly purified by chromatography on silica gel.

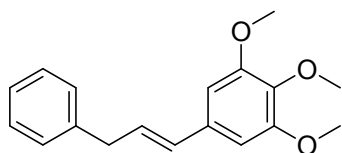
Characterization of the trans-olefin products



¹ G. Li, R. Chen, L. Wu, Q. Fu, X. Zhang, Z. Tang, *Angew. Chem. Int. Ed.* 2013, 52, 8432.

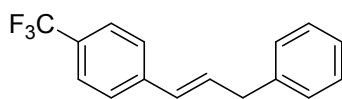
² L. Wu, G. -X Li, Q. -Q. Fu, L. -T. Yu, Z. Tang, *Org. Biomol. Chem.* 2013, 443-447.

Colorless oil³; ¹H NMR (600 MHz, CDCl₃) δ 7.30 (dd, *J* = 7.8, 5.7 Hz, 4H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.44 – 6.38 (m, 1H), 6.22 (dt, *J* = 15.6, 6.9 Hz, 1H), 3.80 (s, 3H), 3.53 (d, *J* = 6.8 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 158.88, 140.47, 130.46, 130.36, 128.65, 128.45, 127.23, 127.08, 126.10, 113.95, 55.29, 39.33.



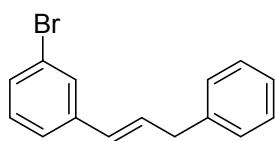
3b

Colorless oil⁴, ¹H NMR (300 MHz, CDCl₃) δ 7.37–7.19 (m, 5H), 6.56 (t, *J* = 8.4 Hz, 2H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.33–6.20 (m, 1H), 3.85 (s, 6H), 3.83 (s, 3H) 3.54 (d, *J* = 6.3 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 153.4, 140.2, 137.6, 133.4, 131.0, 129.0, 128.8, 128.6, 126.4, 103.3, 61.0, 56.2, 39.4.



3c

Colorless oil⁵, ¹H NMR (600 MHz, CDCl₃) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.0 Hz, 3H), 6.47 (s, 2H), 3.58 (s, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 140.95, 139.53, 132.13, 129.81, 128.68, 128.60, 126.38, 126.24, 125.46, 125.44, 125.41, 39.34.



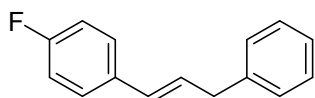
3d

Light yellow oil⁴. ¹H NMR (600 MHz, CDCl₃) δ 7.14–7.52 (m, 9H), 6.38–6.39 (m, 2H), 3.56 (d, 2H, *J* = 4.2 Hz); ¹³C NMR (151 MHz, CDCl₃) δ 139.67, 130.96, 129.97, 129.61, 128.97, 128.64, 128.54, 126.30, 124.76, 122.70, 39.25.

³ Man-Bo Li, Yong Wang, and Shi-Kai Tian, *Angew. Chem. Int. Ed.* 2012, 51, 2968.

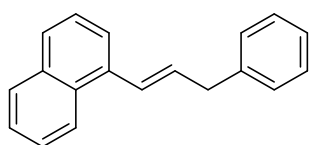
⁴ Yang, H.-L., Sun, P., Zhu, Y., Yan, H., etc., *Chem. Commun.* 2012, 48, 7847.

⁵ Takashi Mino, Taketo Kogure, Taichi Abe, Tomoko Koizumi, Tsutomu Fujita, Masami Sakamoto, *Eur. J. Org. Chem.*, 2013: 1501.



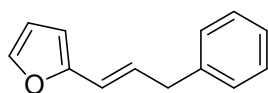
3e

Colorless oil⁶. ¹H NMR (600 MHz, CDCl₃) δ 7.34–7.18 (m, 7H), 7.00–6.93 (m, 2H), 6.40 (d, *J* = 15.5 Hz, 1H), 6.26 (dt, *J* = 15.5, 6.9 Hz, 1H), 3.53 (d, *J* = 6.9 Hz, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 162.0, 140.0, 133.6, 129.8, 129.0, 128.6, 128.5, 127.5, 126.2, 115.3, 39.3.



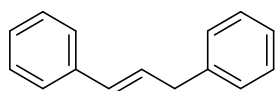
3g

Colorless oil⁷. ¹H NMR (600 MHz, CDCl₃) δ 8.13 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 7.1 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.43 (dd, *J* = 14.8, 7.3 Hz, 2H), 7.38 – 7.32 (m, 4H), 7.21 (d, *J* = 15.5 Hz, 1H), 6.41 (dt, *J* = 15.4, 6.9 Hz, 1H), 3.70 (d, *J* = 6.9 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 140.18, 135.31, 133.65, 132.47, 131.19, 128.72, 128.57, 128.50, 128.39, 127.53, 126.24, 125.90, 125.68, 125.65, 123.89, 123.73, 39.74.



3h

colorless oil⁸. ¹H NMR (600 MHz, CDCl₃) δ 7.31 (t, *J* = 7.5 Hz, 3H), 7.25 – 7.20 (m, 3H), 6.35 (dd, *J* = 5.7, 3.5 Hz, 1H), 6.32 (dd, *J* = 11.1, 4.4 Hz, 1H), 6.24 (d, *J* = 15.7 Hz, 1H), 6.16 (d, *J* = 3.2 Hz, 1H), 3.53 (d, *J* = 6.7 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 153.02, 141.45, 139.88, 128.70, 128.50, 128.28, 126.21, 119.68, 111.11, 106.62, 39.04.



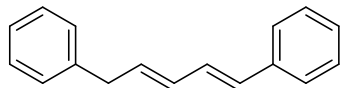
3i

⁶ Masaki Sekine, Laurean Ilies, and Eiichi Nakamura, *Org. Lett.* 2013, 15, 714.

⁷ H.-L. Yang, H. Yan, P. Sun, Y. Zhu, L. -H. Lu, D. -F. Liu, G. -W. Rong, J. -C. Mao, *Green Chem.*, 2013, 15, 976.

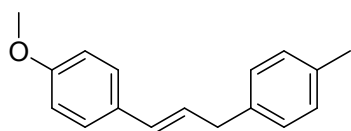
⁸ X.-L. Tang, Z. Wu, M.-B. Li, Y. -H. Gu, S.-K. Tian, *Eur. J. Org. Chem.*, 2012: 4107.

Colorless oil⁸. ¹H NMR (600 MHz, CDCl₃) δ 7.38-7.17 (m, 10H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.36 (dt, *J* = 15.6, 6.8 Hz, 1H), 3.55 (d, *J* = 6.8 Hz, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 140.2, 137.5, 131.1, 129.3, 128.7, 128.5, 127.1, 126.2, 126.1, 39.4.



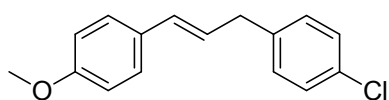
3j

Colorless oil⁹. ¹H NMR (600 MHz, CDCl₃) δ 7.42 (dd, *J* = 12.5, 6.1 Hz, 1H), 7.37 (s, 1H), 7.31 (dt, *J* = 7.7, 4.8 Hz, 4H), 7.21 (dd, *J* = 8.4, 6.8 Hz, 4H), 6.79 (dd, *J* = 15.7, 10.3 Hz, 1H), 6.49 (d, *J* = 15.7 Hz, 1H), 6.37 – 6.19 (m, 1H), 6.06 – 5.89 (m, 1H), 3.50 (d, *J* = 6.9 Hz, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 140.13, 137.50, 133.70, 131.71, 131.00, 128.98, 128.64, 128.57, 128.49, 127.26, 126.21, 126.16, 39.20.



3l

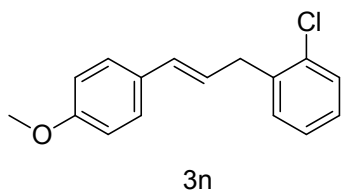
Colorless oil⁴. ¹H NMR (600 MHz, CDCl₃) δ 7.26 (t, *J* = 11.6 Hz, 2H), 7.12 (m, 4H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.38 (d, *J* = 15.7 Hz, 1H), 6.31–6.10 (m, 1H), 3.78 (s, 3H), 3.48 (d, *J* = 6.7 Hz, 2H), 2.32 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 158.8, 137.4, 135.6, 130.4, 130.2, 129.2, 128.5, 127.4, 127.2, 113.9, 55.3, 38.9, 21.0.



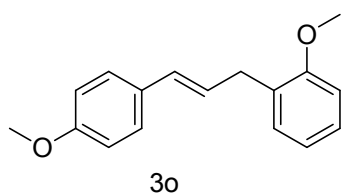
3m

Colorless oil⁴. ¹H NMR (600 MHz, CDCl₃) δ 7.27 (t, *J* = 7.8 Hz, 4H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.24–6.08 (m, 1H), 3.79 (s, 3H), 3.48 (d, *J* = 6.7 Hz, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 158.9, 138.9, 131.8, 130.8, 130.0, 128.7, 128.5, 127.2, 126.4, 114.0, 55.3, 38.6.

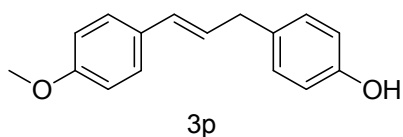
⁹ G. G. K. S. N. Kumar, K. K. Laali, Org. Biomol. Chem., 2012, 10, 7347.



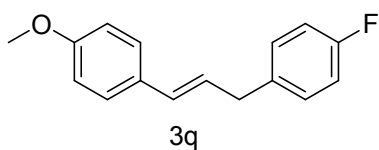
Colorless oil⁴. ¹H NMR (600 MHz, CDCl₃) δ 7.36 (d, *J* = 7.4 Hz, 1H), 7.33–7.25 (m, 3H), 7.23–7.11 (m, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.26–6.11 (m, 1H), 3.79 (s, 3H), 3.63 (d, *J* = 6.6 Hz, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 158.9, 138.1, 134.0, 131.1, 130.4, 130.2, 129.4, 127.6, 127.3, 126.9, 125.0, 113.9, 55.3, 36.8.



Colorless oil¹⁰. ¹H NMR (300 MHz, CDCl₃) δ 7.37 – 7.27 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 2H), 6.89 (dd, *J* = 13.4, 7.6 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.38 (d, *J* = 16.8 Hz, 1H), 6.30 – 6.17 (m, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.51 (d, *J* = 6.7 Hz, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 158.71, 157.30, 130.68, 130.06, 129.81, 128.99, 127.56, 127.31, 127.15, 126.74, 120.52, 113.87, 110.38, 55.40, 55.28, 33.31.



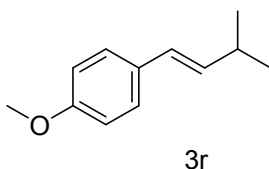
Off-white solid, M.P 75°C¹¹ ¹H NMR (300 MHz, CDCl₃) δ 7.30 (s, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.80 (dd, *J* = 17.3, 8.6 Hz, 4H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.24 – 6.12 (m, 1H), 4.69 (s, 1H), 3.80 (s, 3H), 3.45 (d, *J* = 6.7 Hz, 2H); ¹³C NMR (151 MHz, DMSO) δ 158.82, 154.03, 132.51, 130.42, 130.14, 129.75, 127.51, 127.20, 115.30, 113.95, 77.23, 77.02, 76.81, 55.30, 38.42.



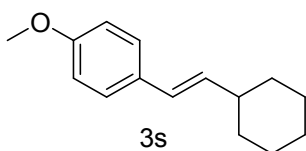
¹⁰ J. O. Oluwadiya, W. Basil Whalley, J. Chem. Soc., Perkin Trans. 1, 1978, 88.

¹¹ E. Schmidl, Gy. Frhter, H.-J. Hansen, H. Schmid, Helvetica Chimica Acta, 1972, 55, 1625.

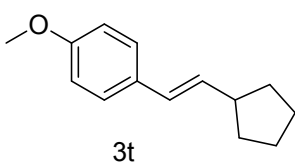
^1H NMR (300 MHz, DMSO) δ 7.30 (dd, $J = 16.6, 7.9$ Hz, 3H), 7.19 (dd, $J = 8.5, 5.6$ Hz, 2H), 6.99 (t, $J = 8.7$ Hz, 2H), 6.85 (t, $J = 7.4$ Hz, 2H), 6.38 (d, $J = 15.9$ Hz, 1H), 6.18 (dt, $J = 15.7, 6.8$ Hz, 1H), 3.80 (s, 3H), 3.49 (d, $J = 6.7$ Hz, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 158.96, 130.61, 130.19, 130.01, 129.96, 127.24, 126.83, 115.24, 115.09, 113.97, 55.29, 38.46.



Colorless oil¹² ^1H NMR (300 MHz, CDCl_3) δ 7.31-7.26 (m, 2H), 6.87-6.83 (m, 2H), 6.29 (d, $J = 16.0$ Hz, 1H), 6.05 (dd, $J = 16.0, 6.4$ Hz, 1H), 3.78 (s, 3H), 2.45 (m, 1H), 1.08 (d, $J = 6.8$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 136.2, 127.7, 127.2, 126.4, 114.2, 114.1, 55.5, 31.7, 22.8.



Colorless oil¹³. ^1H NMR (600 MHz, CDCl_3) δ 7.28 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 6.29 (d, $J = 15.9$ Hz, 1H), 6.04 (dd, $J = 16.0, 7.0$ Hz, 1H), 3.80 (s, 3H), 2.15 – 2.05 (m, 1H), 1.81 – 1.74 (m, 3H), 1.68 (d, $J = 12.7$ Hz, 1H), 1.30 (ddd, $J = 17.7, 16.5, 11.3$ Hz, 3H), 1.24 – 1.12 (m, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 158.61, 134.80, 130.93, 126.99, 126.55, 113.91, 55.29, 41.11, 33.10, 26.21, 26.09.

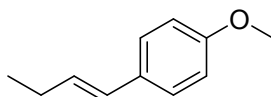


Colorless oil¹⁴. ^1H NMR (600 MHz, CDCl_3) δ 7.27 (d, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.7$ Hz, 2H), 6.31 (d, $J = 15.8$ Hz, 1H), 6.06 (dd, $J = 15.8, 7.8$ Hz, 1H), 3.80 (s, 3H), 2.57 (dd, $J = 16.2, 8.1$ Hz, 1H), 1.85 (d, $J = 6.9$ Hz, 2H), 1.70 (d, $J = 8.3$ Hz, 2H), 1.60 (dd, $J = 7.2, 4.6$ Hz, 2H), 1.38 (dd, $J = 12.2, 8.2$ Hz, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 158.59, 133.60, 130.82, 127.19, 126.97, 113.91, 55.29, 43.79, 33.30, 25.22.

¹² Andrew M. Lauer, Farzeen Mahmud, and Jimmy Wu, *J. Am. Chem. Soc.* 2011 133, 9119.

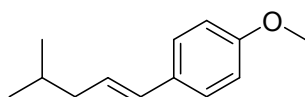
¹³ Anders T. Lindhardt, Thomas M. Gøgsig, and Troels Skrydstrup, *J. Org. Chem.*, 2009 74, 135.

¹⁴ Jang, Yeong-Jiunn; Shih, Yuh-Kuo; Liu, Jing-Yuan; Kuo, Wen-Yu; Yao, Ching-Fa, *Chem.-Eur. J.*, 2003, 9, 2123.



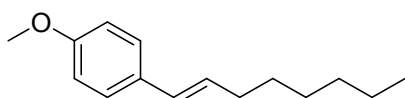
3v

Colorless oil¹⁵. ¹H NMR (600 MHz, CDCl₃) δ 7.29 – 7.26 (m, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.12 (dt, *J* = 15.8, 6.6 Hz, 1H), 3.80 (s, 3H), 2.24 – 2.17 (m, 2H), 1.08 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 158.62, 130.83, 130.53, 128.13, 126.96, 113.91, 55.28, 29.70, 26.01, 13.78.



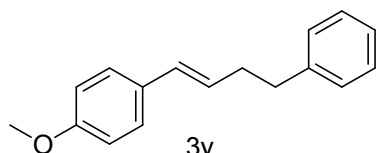
3w

Colorless oil¹⁶. ¹H NMR (600 MHz, CDCl₃) δ 7.28 (t, *J* = 5.8 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.31 (d, *J* = 15.7 Hz, 1H), 6.13 – 6.03 (m, 1H), 3.80 (s, 3H), 2.07 (t, *J* = 7.0 Hz, 2H), 1.77 – 1.66 (m, 1H), 0.94 (d, *J* = 6.6 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 158.64, 130.85, 130.12, 127.73, 126.99, 113.91, 55.29, 42.40, 28.68, 22.36.



3x

Colorless oil¹⁷. ¹H NMR (600 MHz, CDCl₃) δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.33 (d, *J* = 15.7 Hz, 1H), 6.09 (dt, *J* = 15.7, 7.0 Hz, 1H), 3.81 (s, 3H), 2.19 (q, *J* = 7.5 Hz, 2H), 1.50–1.42 (m, 2H), 1.40–1.26 (m, 6H), 0.93–0.88 (m, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 158.6, 130.8, 129.1, 129.0, 126.9, 113.9, 55.2, 33.0, 31.8, 29.5, 28.9, 22.6, 14.1.



3y

Colorless oil¹⁸. ¹H NMR (600 MHz, CDCl₃) δ 7.32 – 7.25 (m, 5H), 7.21 (dd, *J* = 18.2, 7.4 Hz, 3H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.37 (d, *J* = 15.8 Hz, 1H), 6.18 – 6.07 (m, 1H), 3.81 (s, 3H), 2.79 (t, *J* = 7.8 Hz, 2H), 2.52 (dd, *J* =

¹⁵ Wang, Tongqiang; Hu, Yuanyuan; Zhang, Songlin, *Org. Biomol. Chem.*, 2010, 8, 2312.

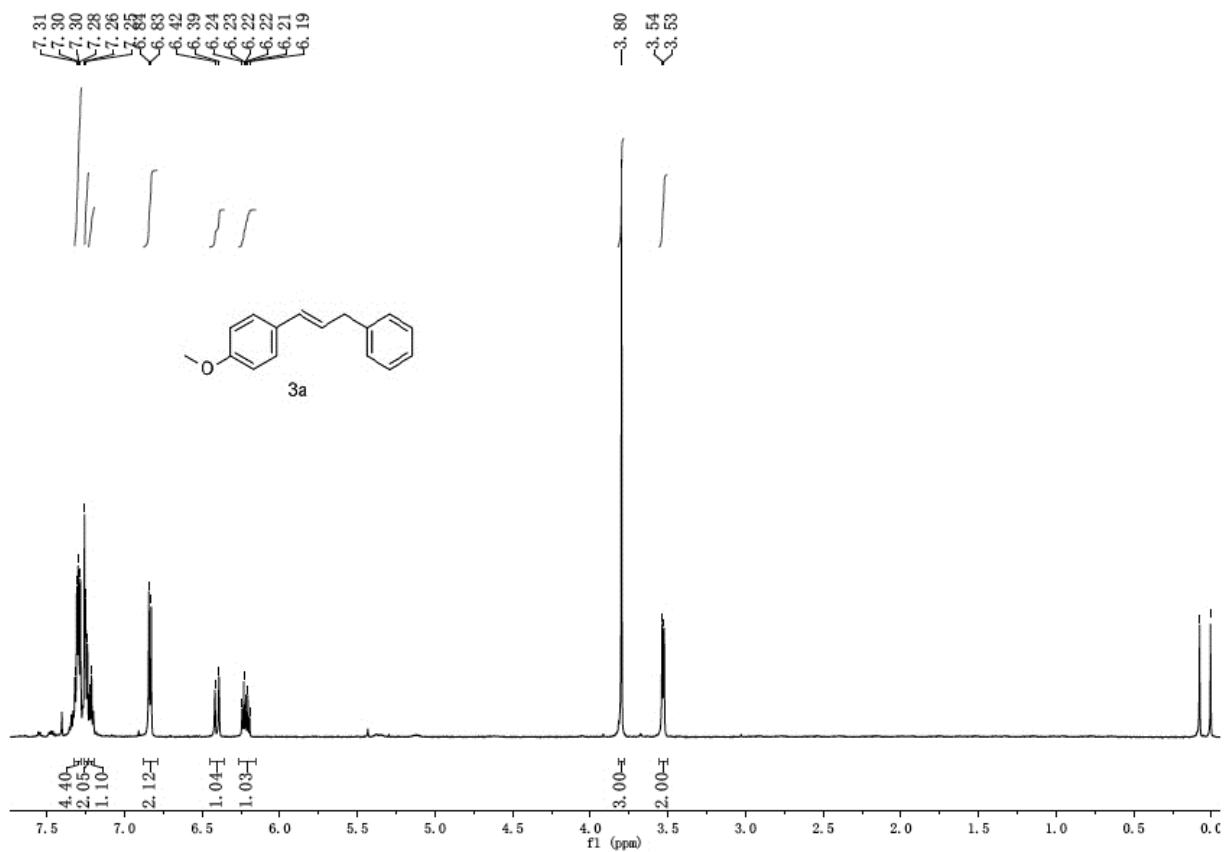
¹⁶ Buu-Hoi; Hoan, *J. Org. Chem.*, 1949, 14, 1023.

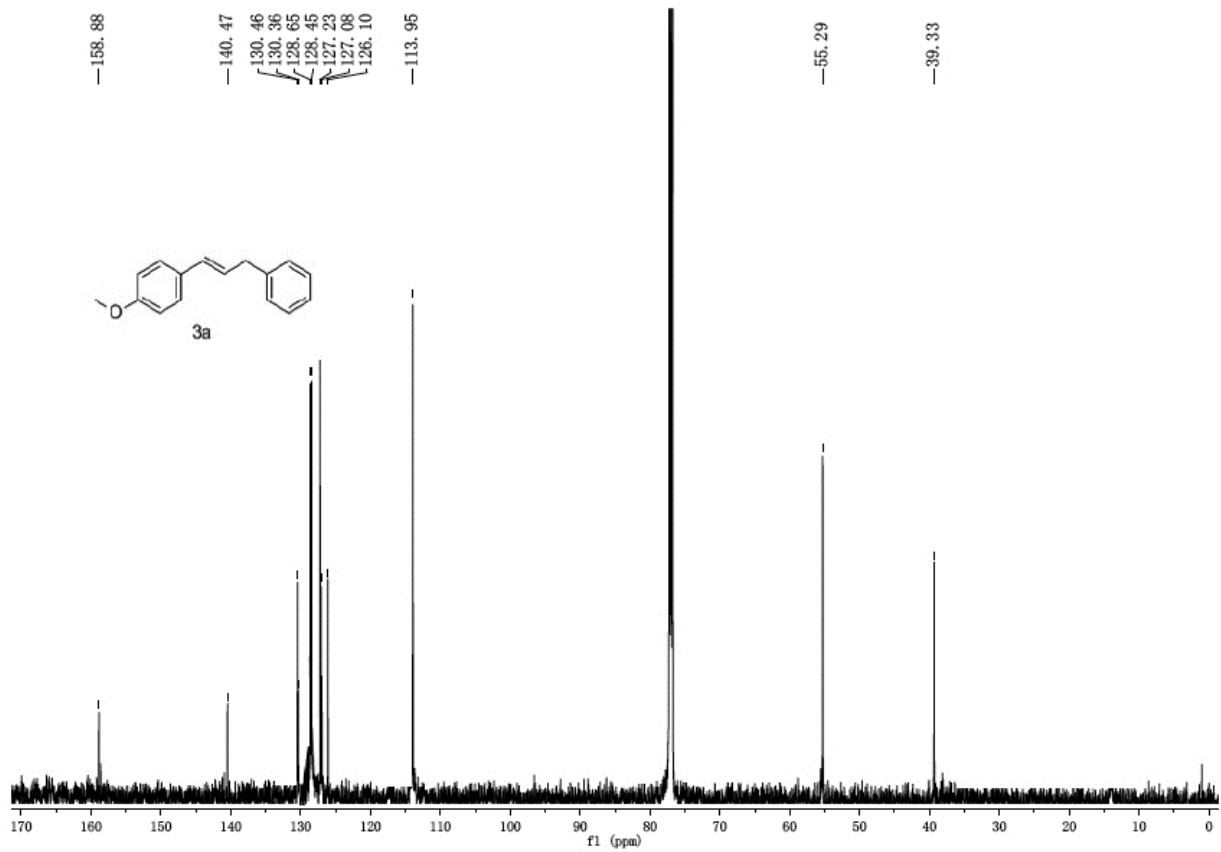
¹⁷ Yoshiaki Nakao, Hidekazu Imanaka, Akhila K. Sahoo, Akira Yada, Tamejiro Hiyama, *J. Am. Chem. Soc.* 2005 127, 6952.

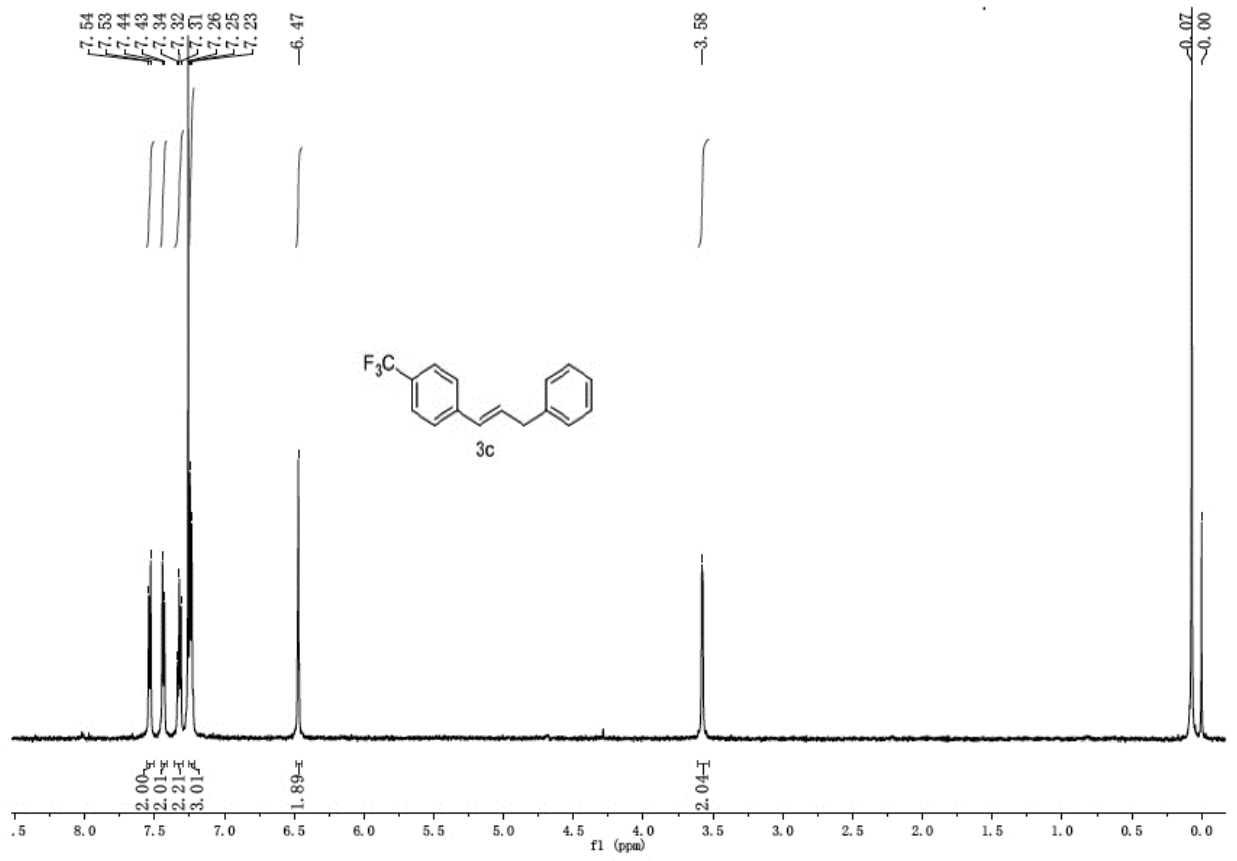
¹⁸ Saumen Hajra, Biswajit Maji, Dipakranjan Mal, *Adv. Synth. Catal.* 2009, 351, 859–864.

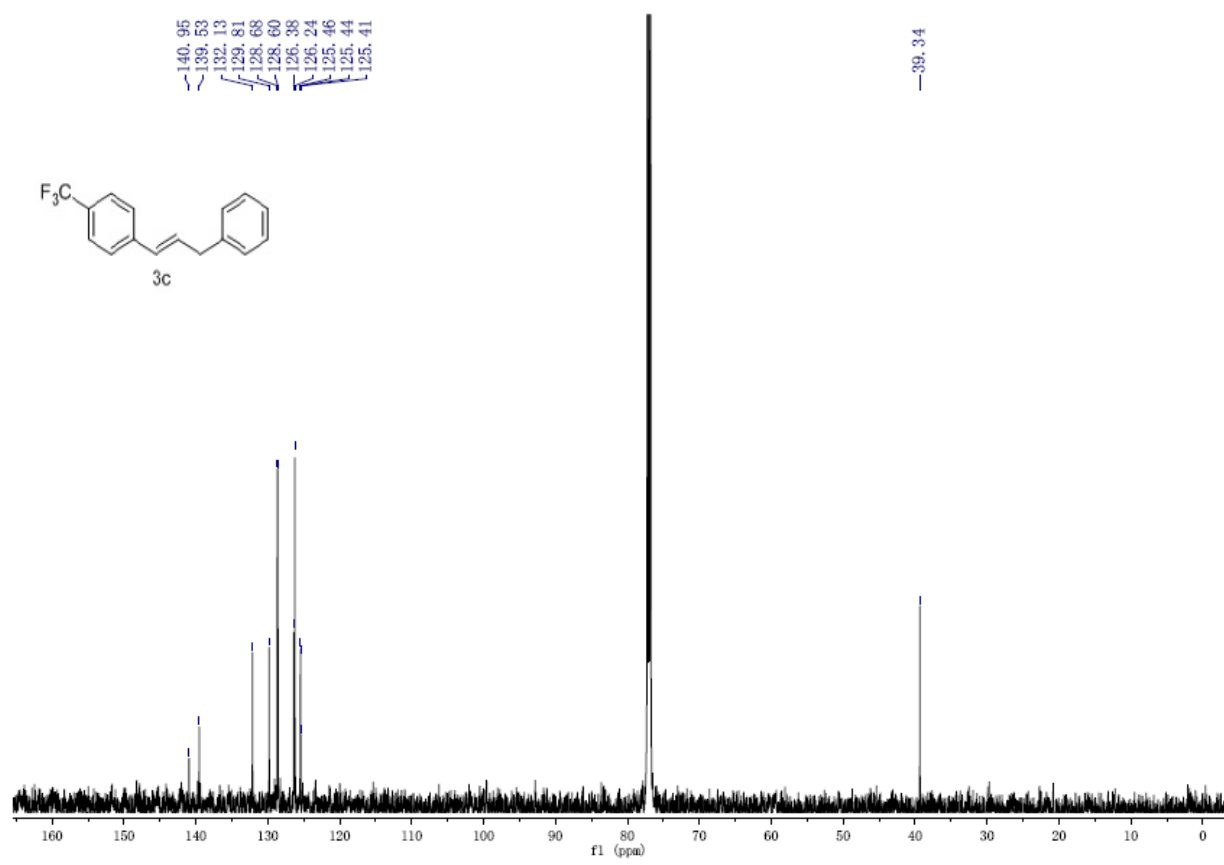
15.1, 7.3 Hz, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 158.76, 141.88, 132.00, 129.71, 128.47, 128.33, 127.83, 127.07, 125.83, 113.94, 55.29, 36.04, 34.85.

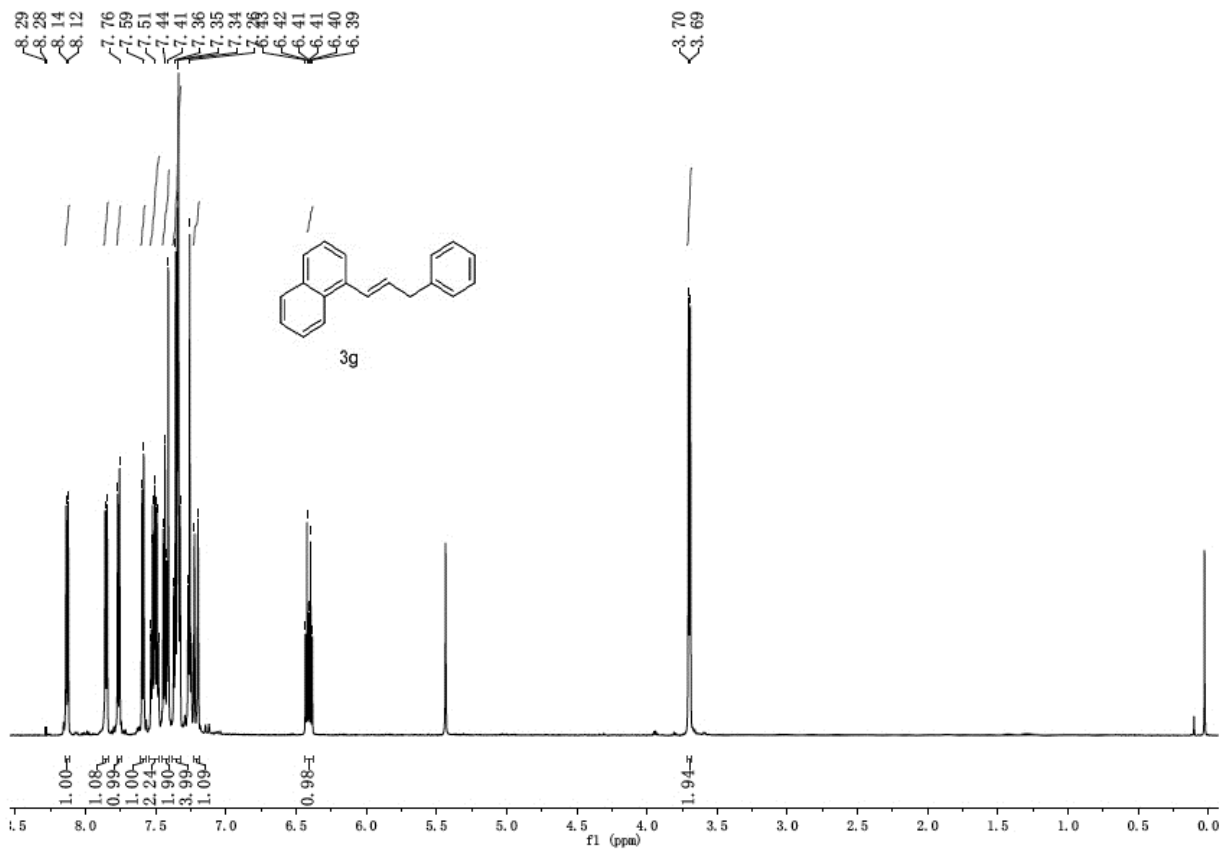
Selected NMR spectrums





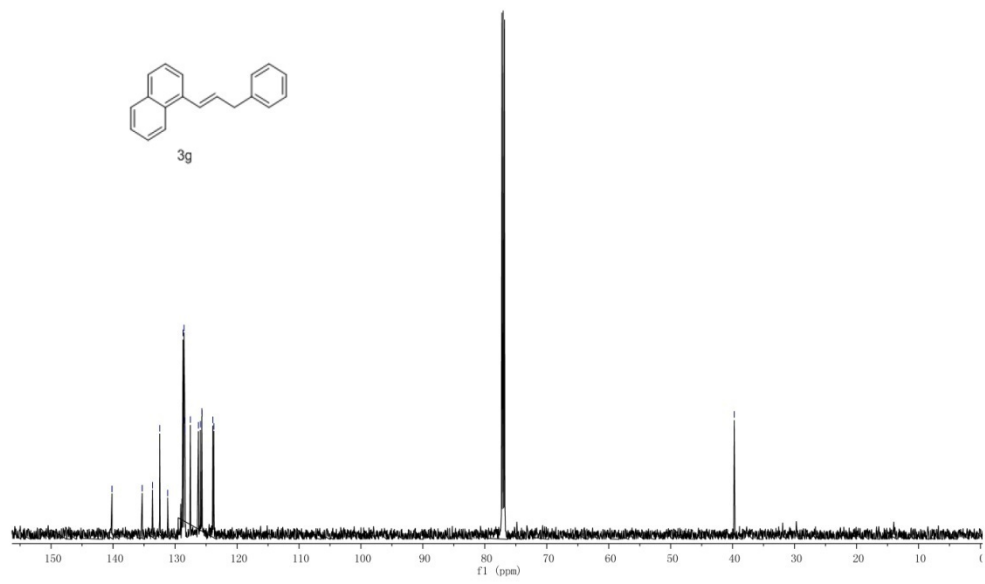
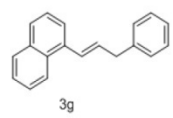


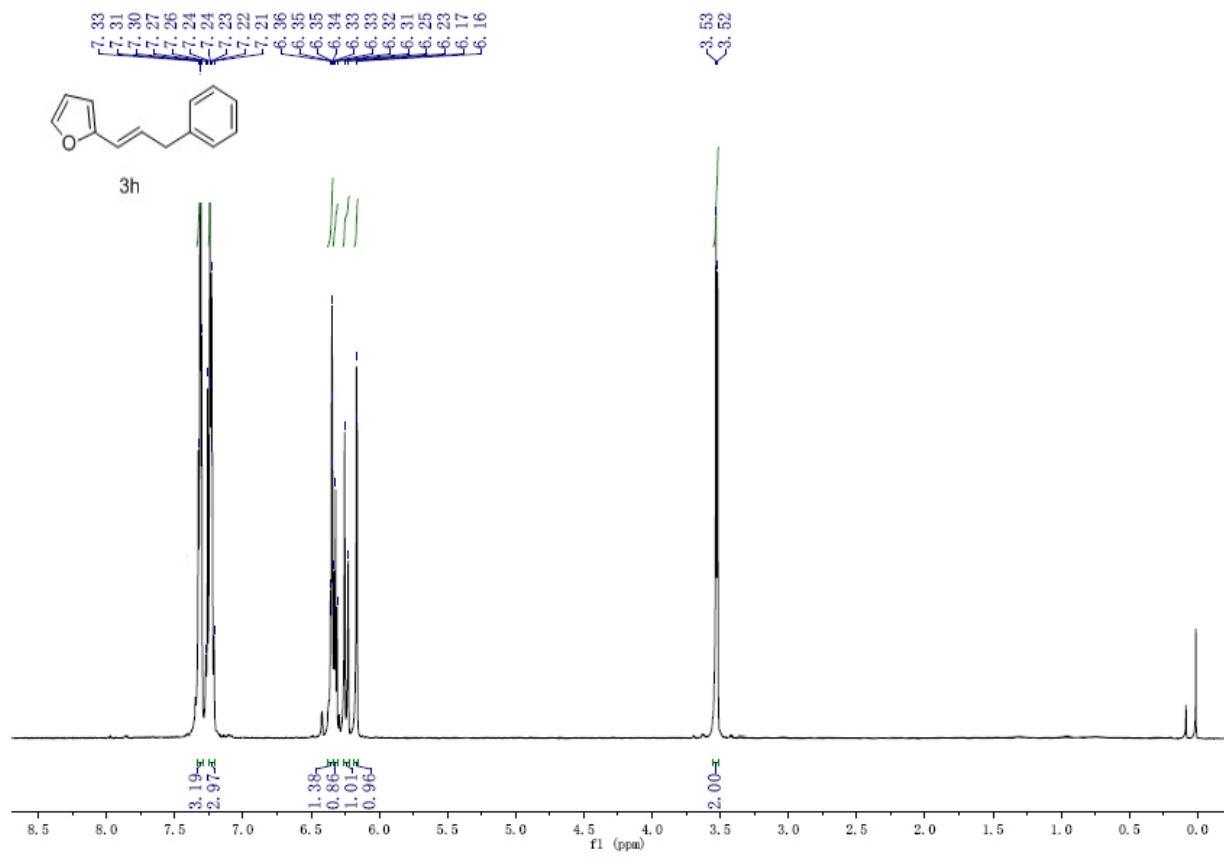


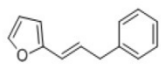


140.18
135.31
133.65
132.47
131.19
128.72
128.50
128.39
127.53
126.24
125.90
125.68
125.65
123.89
123.73

39.74







3h

