

Supplementary Information

Deep Eutectic Solvents-Catalyzed Meyer-Schuster Rearrangement of Propargylic Alcohols under Mild and Bench Reaction Conditions

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1. General Methods

All reagents were obtained from commercial suppliers and used without further purification. Deep eutectic solvents [$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{glycerol}$ (*Gly*) (3:1 mol mol⁻¹); ZnCl_2/Gly (2:1 mol mol⁻¹); MnCl_2/Gly (2:1 mol mol⁻¹); $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{Gly}$ (2:1 mol mol⁻¹); *ChCl* (choline chloride)/ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1:2 mol mol⁻¹); *ChCl*/ ZnCl_2 (1:2 mol mol⁻¹); *ChCl*/ $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (1:2 mol mol⁻¹); *ChCl*/ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1:2 mol mol⁻¹); *ChCl*/ H_2O (1:2 mol mol⁻¹), *ChCl*/*Gly* (1:2 mol mol⁻¹), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{mono-ethylene glycol}$ (*MEG*) (2:1 mol mol⁻¹)] were prepared by heating under stirring up to 75 °C for 10–30 min the corresponding individual components until a clear solution was obtained. All these *DESs* are stable at room temperature and reaction conditions. ESI⁺ experiments were carried out to record mass spectra on a Hewlett-Packard 1100 HPLC/MS (electrospray) instrument. ¹H-NMR spectra (CDCl_3 and MeOD) were obtained using a Bruker DPX-300 (¹H, 300.13 MHz; ¹³C{¹H}, 75.4 MHz) spectrometer and employing the δ scale (ppm) for chemical shifts. Calibration was made on the signal of the solvent (¹H: CDCl_3 , 7.26 ppm; ¹³C: CDCl_3 , 77.0 ppm). HPLC analyses to determine the degree of conversion were carried out on an Agilent RR1200 HPLC system, using a reversed phase column (Zorbax Eclipse XDB-C18, RR, 18 μm , 4.6 x 50 mm, Agilent). Analytical thin layer chromatography (TLC) was carried out on pre-coated 0.25 mm thick plates of Kieselgel 60 F254; visualization was accomplished by UV light (254 nm) or by spraying with a solution of 5 % (w/v) ammonium molybdate and 0.2 % (w/v) cerium(III) sulfate in 100 mL 17.6 % (w/v) aq. sulfuric acid and heating to 473 K until blue spots appear. Chromatography was conducted by using silica gel 60 with a particle size distribution 40–63 μm and 230–400 ASTM.

2. Protocols

2.1 General procedure for the catalytic propargylic isomerization of 1,1-diphenyl-2-propyn-1-ol (**1a**) in *LADES*s

In a typical experiment, **1a** (0.2 mmol) and 0.8 mL of *LADES* were loaded into a glass open vial and stirred at room temperature for the required time (Table 1). The course of the reaction was monitored by regular sampling and analysis by TLC and HPLC. After completion of the reaction, the obtained crude was extracted with cyrene (2 x 400 μ L). The organic layers were separated by centrifugation (90 s, 13000 rpm), combined, and finally dried over Na₂SO₄. The crude was filtered through silica gel (hexane-ethyl acetate 10:1).

3,3-diPhenylpropenal (1b): Light yellow oil. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 6.63 (d, *J* 7.5 Hz, 1H), 7.25-7.55 (m, 10 H), 9.56 (d, *J* 7.5 Hz, 1H); ¹³C-NMR (75.5 MHz, CDCl₃) δ (ppm): 127.3 (CH), 128.4 (CH), 128.6 (CH), 128.7 (CH), 129.5 (CH), 130.5 (CH), 130.7 (CH), 136.7 (C), 139.7 (C), 162.3 (C), 193.5 (C=O). NMR data are in good agreement with those reported in: A. Antiñolo, F. Carrillo-Hermosilla, V. Cadierno, J. García-Álvarez, A. Otero, *ChemCatChem* 2012, **4**, 123.

2.2 General procedure for the catalytic isomerization of propargylic alcohols (**1a-14a**) in FeCl₃·6H₂O/*Gly* (2:1)

In a typical experiment, the specific propargylic alcohol **1a-14a** (0.2 mmol) and 0.8 mL of FeCl₃·6H₂O/*Gly* (3:1) were loaded into a glass open vial and stirred at the specified temperature (RT or 40 °C) for the required time (Table 2). The course of the reaction was monitored by regular sampling and analysis by TLC and HPLC. After completion of the reaction, the obtained crude was extracted with cyrene (2 x 400 μ L). The organic layers were separated by centrifugation (90 s, 13000 rpm), combined, and finally dried over Na₂SO₄. The crude of the reaction was filtered through silica gel (hexane-ethyl acetate mixtures). **3-Phenylbut-2-enal (2b), mixture *E/Z* of isomers**:¹ Light yellow oil. ¹H NMR (300 MHz, CDCl₃) δ (ppm): For *E* isomer: 10.21 (d, *J* = 6.0 Hz, 1H), 7.10-7.60 (m, 5 H), 6.42 (d, *J* = 6.0 Hz, 1H), 2.60 (s, 3H); For *Z*-isomer: 9.50 (d, *J* = 6.0 Hz, 1H), 7.10-7.60 (m, 5 H), 6.15 (d, *J* = 6.0 Hz, 1H), 2.35 (s, 3H). NMR data are in good

¹ The reported *E/Z* ratio was 86:14 (see Table 2, entry 2).

agreement with those reported in: A. Antiñolo, F. Carrillo-Hermosilla, V. Cadierno, J. García-Álvarez, A. Otero, *ChemCatChem* 2012, **4**, 123.

(E)-Cinnamaldehyde (3b): Light yellow oil. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 9.72 (d, $J = 7.5$ Hz, 1H), 7.35-7.55 (m, 6 H), 6.71 (dd, $J = 16.0$ and 7.5 Hz, 1H); ^{13}C -NMR (75.5 MHz, CDCl_3) δ (ppm): 128.5 (CH), 128.6 (CH), 129.1 (CH), 131.3 (CH), 134.0 (CH), 152.9 (C), 194.2 (C=O). NMR data are in good agreement with those reported in: A. Antiñolo, F. Carrillo-Hermosilla, V. Cadierno, J. García-Álvarez, A. Otero, *ChemCatChem* 2012, **4**, 123.

3,3-Bis(4-methylphenyl)acrylaldehyde (4b): Light yellow oil. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 6.57 (d, $J = 8.0$ Hz, 1H), 7.25-7.35 (m, 4 H), 9.55 (d, $J = 8.0$ Hz, 1H); ^{13}C -NMR (75.5 MHz, CDCl_3) δ (ppm): 21.4 (CH_3), 126.5 (CH), 128.8 (CH), 129.0 (CH), 129.3 (CH), 130.8 (CH), 133.9 (C), 137.1 (C), 140.0 (C), 141.0 (C), 162.5 (C), 193.7 (C=O). NMR data are in good agreement with those reported in: A. Antiñolo, F. Carrillo-Hermosilla, V. Cadierno, J. García-Álvarez, A. Otero, *ChemCatChem* 2012, **4**, 123.

3,3-bis(4-chlorophenyl)acrylaldehyde (5b): Light yellow oil. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 6.58 (d, $J = 7.8$ Hz, 1H), 7.20-7.35 (m, 4 H), 7.46 (d, $J = 2.0$ Hz, 2H), 7.48 (d, $J = 2.0$ Hz, 2H), 9.54 (d, $J = 7.8$ Hz, 1H); ^{13}C -NMR (75.5 MHz, CDCl_3) δ (ppm): 127.7 (CH), 128.9 (CH), 129.1 (CH), 129.8 (CH), 131.9 (CH), 134.6 (C), 136.0 (C), 137.0 (C), 137.8 (C), 159.4 (C), 192.6 (C=O). NMR data are in good agreement with those reported in: A. Antiñolo, F. Carrillo-Hermosilla, V. Cadierno, J. García-Álvarez, A. Otero, *ChemCatChem* 2012, **4**, 123.

3,3-Bis(4-methoxyphenyl)acrylaldehyde (6b): Light yellow oil. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 3.87 (s, 3H), 3.90 (s, 3H), 6.51 (d, $J = 8.0$ Hz, 1H), 6.92 (d, $J = 9.0$ Hz), 2H), 6.98 (d, $J = 9.0$ Hz), 7.26 (d, $J = 9.0$ Hz, 2H), 7.34 (d, $J = 9.0$ Hz, 2H), 9.51 (d, $J = 8.0$ Hz, 1H). NMR data are in good agreement with those reported in: A. Antiñolo, F. Carrillo-Hermosilla, V. Cadierno, J. García-Álvarez, A. Otero, *ChemCatChem* 2012, **4**, 123.

3,3-Bis([1,1'-biphenyl]-4-yl)acrylaldehyde (7b): Light yellow oil. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 6.71 (d, $J = 9.0$ Hz, 1H), 7.30-7.60 (m, 10 H), 7.65-7.80 (m, 8H), 9.66 (d, $J = 9.0$ Hz, 1H); ^{13}C -NMR (75.5 MHz, CDCl_3) δ (ppm): 127.1 (CH), 127.1 (CH), 127.2 (CH), 127.3 (CH), 127.9 (CH), 128.0 (CH), 129.0 (CH), 129.3 (CH), 131.4 (CH), 135.5 (C), 138.6 (C), 140.0 (C), 140.1 (C), 142.4 (C), 143.4 (C), 161.5 (C), 193.4 (C=O). MS (ESI $^+$) m/z (rel. intensity): 361.2 [(M+H) $^+$, 100], 383.2 [(M+Na) $^+$, 10].

3-Isopropyl-4-methylpent-3-en-2-one (8b): Light yellow oil. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.07 (d, *J* = 9.0 Hz, 6H), 1.65 (s, 3H), 1.71 (s, 3H), 2.27 (s, 3H), 2.81 (heptet, *J* = 9.0 Hz, 1H); ¹³C-NMR (75.5 MHz, CDCl₃) δ (ppm): 19.2 (CH₃), 21.3 (CH₃), 22.0 (CH₃), 28.7 (CH₃), 33.3 (CH₃), 127.1 (C), 143.4 (C), 209.7 (C=O). NMR data are in good agreement with those reported in: V. Cadierno, S. E. Garrido, J. Gimeno, *Adv. Synth. Catal.* 2006, **348**, 101.

1-Acetylcyclohexene (9b): Light yellow oil. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.55-1.65 (m, 4H), 2.15-2.25 (m, 4H), 2.28 (s, 3H), 6.91 (s, 3H); ¹³C-NMR (75.5 MHz, CDCl₃) δ (ppm): 21.5 (CH₂), 21.9 (CH₂), 23.0 (CH₂), 24.0 (CH₂), 25.2 (CH₃), 139.7 (CH), 140.9 (C), 199.4 (C=O). NMR data are in good agreement with those reported in: V. Cadierno, S. E. Garrido, J. Gimeno, *Adv. Synth. Catal.* 2006, **348**, 101.

1-Acetylcycloheptene (10b): Light yellow oil. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.40-1.60 (m, 4H), 1.70-1.85 (m, 2H), 2.32 (s, 3H), 2.35-2.40 (m, 2H), 2.50-2.55 (m, 2H), 7.10 (t, *J* = 6.0 Hz, 1H); ¹³C-NMR (75.5 MHz, CDCl₃) δ (ppm): 25.3 (CH₃), 25.4 (CH₂), 25.8 (CH₂), 26.1 (CH₂), 29.1 (CH₂), 32.3 (CH₂), 145.6 (CH), 146.6 (C), 192.0 (C=O). NMR data are in good agreement with those reported in: V. Cadierno, S. E. Garrido, J. Gimeno, *Adv. Synth. Catal.* 2006, **348**, 101.

1,3,3-Triphenylprop-2-en-1-one (11b): Yellow pale solid. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.17 (s, 1H), 7.20-7.25 (m, 2H), 7.25-7.30 (m, 3H), 7.30-7.45 (m, 7H), 7.45-7.50 (m, 1H), 7.97 (d, *J* = 6.0 Hz, 2H); ¹³C-NMR (75.5 MHz, CDCl₃) δ (ppm): 124.1 (CH), 128.1 (CH), 128.4 (CH), 128.5 (CH), 128.6 (CH), 128.8 (C), 129.4 (CH), 129.8 (CH), 132.7 (CH), 138.3 (C), 139.1 (C), 141.4 (C), 154.7 (C), 192.7 (C=O). NMR data are in good agreement with those reported in: A. Antiñolo, F. Carrillo-Hermosilla, V. Cadierno, J. García-Álvarez, A. Otero, *ChemCatChem* 2012, **4**, 123.

1-Phenyl-3,3-di-*p*-tolylprop-2-en-1-one (12b): Yellow pale solid. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 2.36 (s, 3H), 2.43 (s, 3H), 7.05–7.10 (m, 5H), 7.15–7.20 (m, 2H), 7.26–7.30 (m, 2H), 7.35–7.40 (m, 2H), 7.45–7.50 (m, 1H), 7.96 (d, *J* = 6.0 Hz, 2H 2H); ¹³C-NMR (75.5 MHz, CDCl₃) δ (ppm): 21.3 (CH₃), 21.4 (CH₃), 122.7 (CH), 128.4 (CH), 128.6 (CH), 128.7 (CH), 128.8 (CH), 129.1 (CH), 129.8 (CH), 132.5 (CH), 136.3 (C), 138.2 (C), 138.6 (C), 138.9 (C), 139.6 (C), 155.3 (C), 192.5 (C=O). NMR data are in good agreement with those reported in: S. Tanaka, T. Kunisawa, Y. Yoshii, T. Hattori, *Org. Lett.* 2019, **21**, 8509.

(3,3)-Bis(4-fluorophenyl)-1-phenylprop-2-en-1-one (13b): Yellow pale solid. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 6.95-7.20 (m, 7H), 7.35-7.45 (m, 4H), 7.50-7.55 (m,

1H), 7.92 (d, $J = 8.0$ Hz, 2H); ^{13}C -NMR (75.5 MHz, CDCl_3) δ (ppm): 115.3 (2CH, $J_{\text{CF}} = 22$ Hz), 115.6 (2CH, $J_{\text{CF}} = 22$ Hz), 124.0 (CH), 128.5 (2CH), 128.7 (2CH), 130.4 (2CH, $J_{\text{CF}} = 8$ Hz), 131.6 (2CH, $J_{\text{CF}} = 8$ Hz), 132.9 (CH), 134.7 (C, $J_{\text{CF}} = 3$ Hz), 137.4 (C, $J_{\text{CF}} = 3$ Hz), 138.1 (C), 152.6 (C), 162.8 (C, $J_{\text{CF}} = 248$ Hz), 163.6 (C, $J_{\text{CF}} = 250$ Hz), 192.3 (C=O). NMR data are in good agreement with those reported in: N. Naveen, G. Ramesh, R. Balamurugan, *Chemistry Select* 2019, **4**, 13610.

1,1-Bis(4-fluorophenyl)hept-1-en-3-one (14b): Light yellow oil. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 0.86 (t, $J = 7.5$ Hz, 2H), 1.20-1.30 (m, 2H), 1.45-1.60 (m, 2H), 2.33 (t, $J = 6.0$ Hz, 2H), 6.56 (s, 1H), 7.00-7.15 (m, 4H), 7.16-7.22 (m, 2H), 7.25-7.32 (m, 2H); ^{13}C -NMR (75.5 MHz, CDCl_3) δ (ppm): 13.8 (CH_3), 22.3 (CH_2), 26.4 (CH_2), 43.3 (CH_2), 115.3 (2CH, $J_{\text{CF}} = 22$ Hz), 115.5 (2CH, $J_{\text{CF}} = 22$ Hz), 126.2 (CH), 130.2 (2CH, $J_{\text{CF}} = 8$ Hz), 131.30 (2CH, $J_{\text{CF}} = 8$ Hz), 134.6 (C), 137.1 (C), 151.2 (C), 164.6 (C), 165.2 (C), 201.6 (C=O). MS (ESI $^+$) m/z (rel. intensity): 301.2 [(M+H) $^+$, 100].

2.3 General procedure for the catalytic hydration of phenylacetylene (**15**) in $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{Gly}$ (2:1)

Phenylacetylene (**15**, 0.3 mmol) and 1.0 mL of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{Gly}$ (3:1) were loaded into a glass open vial and stirred at 45 °C over 18 h. The course of the reaction was monitored by regular sampling and analysis by HPLC. After completion of the reaction, the resulting crude was extracted with cyrene (2 x 400 μL). The organic layers were separated by centrifugation (90 s, 13000 rpm), combined, and finally dried over Na_2SO_4 . The crude product was finally filtered through silica gel yielding pure acetophenone (**16**, >95% yield).

Acetophenone (16): Colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 2.60 (s, 3H), 7.35-7.45 (m, 2H), 7.45-7.55 (m, 1H), 7.85-7.95 (m, 2H); ^{13}C -NMR (75.5 MHz, CDCl_3) δ (ppm): 26.6 (CH_3), 128.3 (CH), 128.6 (CH), 133.1 (CH), 137.1 (C), 198.1 (C=O). NMR data are in good agreement with those reported in: J. R. Cabrero-Antonino, A. Leyva-Pérez, A. Corma, *Chem. Eur. J.*, 2012, **18**, 11107.

The LADES-based catalytic system was recycled for 4 runs following the procedure described in the Section 3.3.1 (Figure S1).

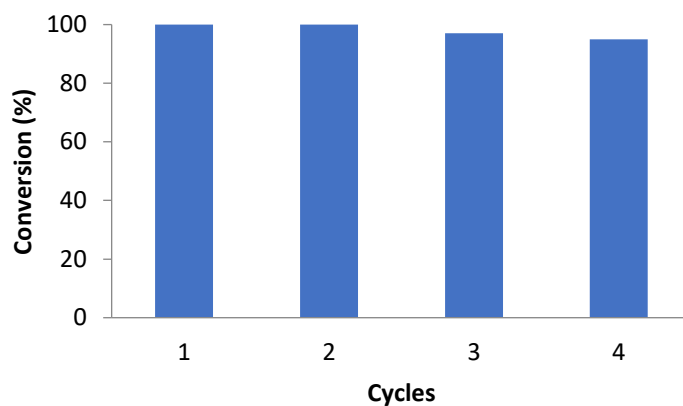


Figure S1. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{Gly}$ -catalyzed hydration of **15**.

2.4 General procedure for the catalytic cyclization of *N*-prop-2-ynylbenzamide (17**) into 5-methyl-2-phenyloxazole (**18**) in $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{Gly}$ (2:1)**

N-prop-2-ynylbenzamide (**17**, 0.2 mmol) and 1.0 mL of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{Gly}$ (3:1) were loaded into a glass open vial and stirred at 40 °C over 4 h. The course of the reaction was monitored by regular sampling and analysis by TLC and HPLC. After completion of the reaction (c >99%), the obtained crude was extracted with cyrene (2 x 400 μL). The organic layers were separated by centrifugation (90 s, 13000 rpm), combined, and finally dried over Na_2SO_4 . The resulting product was filtered through silica gel yielding pure 5-methyl-2-phenyloxazole (**18**, 60% yield). It should be noted that the high volatility of **18** decreased the isolated yield.

5-methyl-2-phenyloxazole (18**):** Colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ (ppm): 2.42 (s, 3H), 6.86 (s, 1H), 7.25-7.45 (m, 3H), 8.00-8.05 (m, 2H). NMR data are in good agreement with those reported in: G. C. Senadi, W.-P. Hu, J.-S. Hsiao, J. K. Vandavasi, C.-Y. Chen, J. J. Wang, *Org. Lett.*, 2012, **14**, 4478.

The *LADES*-based catalytic system was recycled for 5 runs following the procedure described in the Section 3.3.1 (Figure S2).

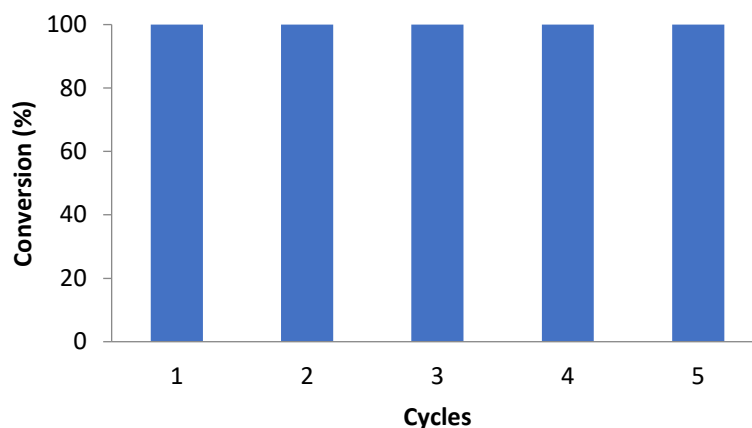


Figure S2. FeCl₃·6H₂O/*Gly*-catalyzed cyclization of **17**.

2.5 General procedure for the catalytic hydrolysis of substituted methyl benzoates (**19–22**) in FeCl₃·6H₂O/*Gly* (2:1)

Methyl benzoate (**19**, 0.4 mmol) and 1.0 mL of FeCl₃·6H₂O/*Gly* (3:1) were loaded into a glass open vial and stirred at 70 °C over 14 h. The course of the reaction was monitored by regular sampling and analysis by HPLC. After completion of the reaction, the obtained crude was extracted with cyrene (2 x 400 μL). The organic layers were separated by centrifugation (90 s, 13000 rpm), combined, and finally dried over Na₂SO₄. The resulting product was filtered through silica gel yielding pure benzoic acid (**23**, *c* >99%, 95% yield).

Benzoic acid (23): White solid. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.47 (t, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 2H); ¹³C-NMR (75.5 MHz, CDCl₃) δ (ppm): 128.5 (CH), 129.3 (C), 130.2 (CH), 133.8 (CH), 172.1 (C=O). NMR data are in good agreement with those reported in: X. Lian, S. Fu, T. Ma, S. Li, W. Zeng, *Appl. Organometal. Chem.* 2011, **25**, 443.

The *LADES* catalytic system was recycled for 5 runs following the procedure described in the Section 3.3.1 (Figure S3).

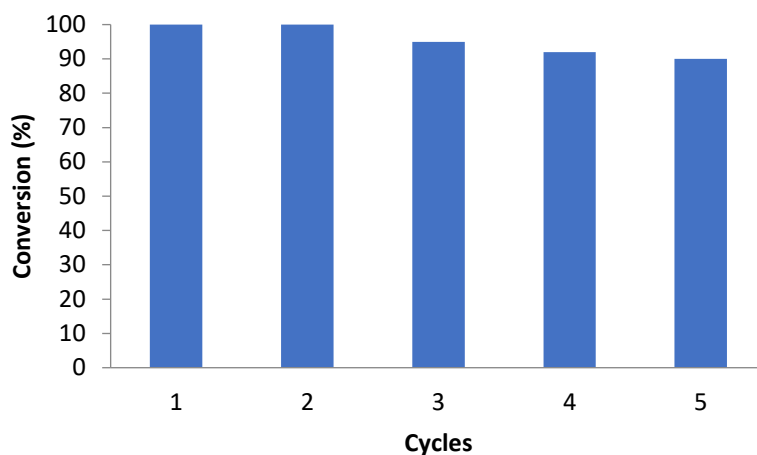


Figure S3. FeCl₃·6H₂O/*Gly*-catalyzed hydrolysis of **19**.

The hydrolysis of methyl esters of *m*-methylbenzoate (**20**), *p*-nitrobenzoate (**21**) and *p*-cyanobenzoate (**22**) was accomplished under identical reactions conditions with yields higher than 85%.

3-Methylbenzoic acid (24): 93% yield. White solid. ¹H NMR (300 MHz, MeOD) δ (ppm): 2.39 (s, 3H), 7.30-7.45 (m, 2H), 7.75-7.90 (m, 2H); ¹³C-NMR (75.5 MHz, MeOD) δ (ppm): 126.5 (CH), 128.0 (CH), 129.8 (CH), 130.4 (C), 133.3 (CH), 138.0 (C), 172.1 (C=O). NMR data are in good agreement with those reported in: K. Kobayashi, Y. Kondo, *Org. Lett.* 2009, **11**, 2035.

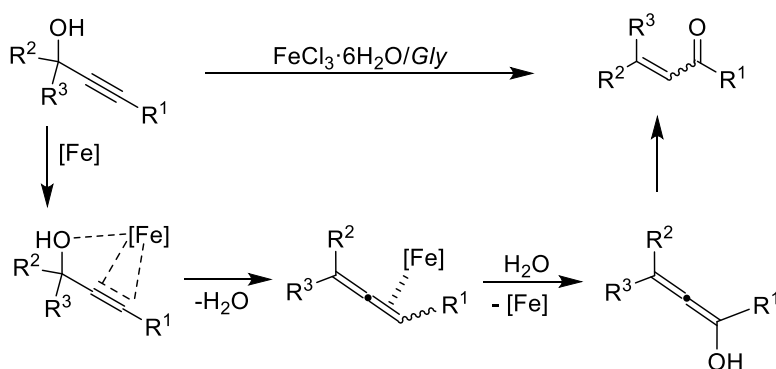
4-Nitrobenzoic acid (25): 90% yield. White solid. ¹H NMR (300 MHz, MeOD) δ (ppm): 8.25 (d, *J* = 9.0 Hz, 2H), 8.34 (d, *J* = 9.0 Hz, 2H); ¹³C-NMR (75.5 MHz, MeOD) δ (ppm): 123.1 (CH), 130.5 (CH), 129.8 (CH), 136.2 (C), 150.5 (C), 166.2 (C=O). NMR data are in good agreement with those reported in: M. Yoshida, Y. Katagiri, W.-B. Zhu, K. Shishido, *Org. Biomol. Chem.* 2009, **7**, 4062.

4-Cyanobenzoic acid (26): 85% yield. White solid. ¹H NMR (300 MHz, MeOD) δ (ppm): 7.87 (d, *J* = 9.0 Hz, 2H), 8.18 (d, *J* = 9.0 Hz, 2H); ¹³C-NMR (75.5 MHz, MeOD) δ (ppm): 115.8 (C), 1117.6 (C), 129.9 (CH), 132.0 (CH), 134.8 (C), 166.5 (C=O). NMR data are in good agreement with those reported in: A. Littke, M. Soumeillant, R. F. Kaltenbach, R. J. Cherney, C. M. Tarby, S. Kian, *Org. Lett.* 2007, **9**, 1711.

3. Mechanism of the Meyer-Schuster rearrangement

Gimeno and coworkers reviewed the catalytic isomerization of allylic alcohols which occurs through three different reaction pathways, namely Meyer-Schuster and Rupe rearrangements and the redox-type isomerization (*Dalton Trans.*, **2010**, 39, 4015-4031). As FeCl_3 and InCl_3 exhibit a similar reactivity as Lewis acids (*Chem. Eur. J.* 2000, **6**, 3491), we envision that a similar pathway may be also followed for the described FeCl_3 -catalyzed MS and Rupe rearrangements.

Meyer-Schuster rearrangement



4. Optimization of downstream processing

4.1 Study of miscibility of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{Gly}$ (2:1) and organic solvents

To several vials containing 1 mL of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{Gly}$ (3:1), 1 mL of different organic solvents was added and the mixture was shaken vigorously and subjected to centrifugation (Figure S4). The following results were obtained:

1- Solvents leading to miscible solutions:

THF, 2-Me-THF, 1,4-dioxane, MTBE, CPME, MEK, MIBK, DMI

2-Solvents leading to immiscible solutions:

n-Hexane, *n*-heptane, cyclohexane, EtOAc, *i*PrOAc, toluene, CHCl_3 , CH_2Cl_2 , cyrene

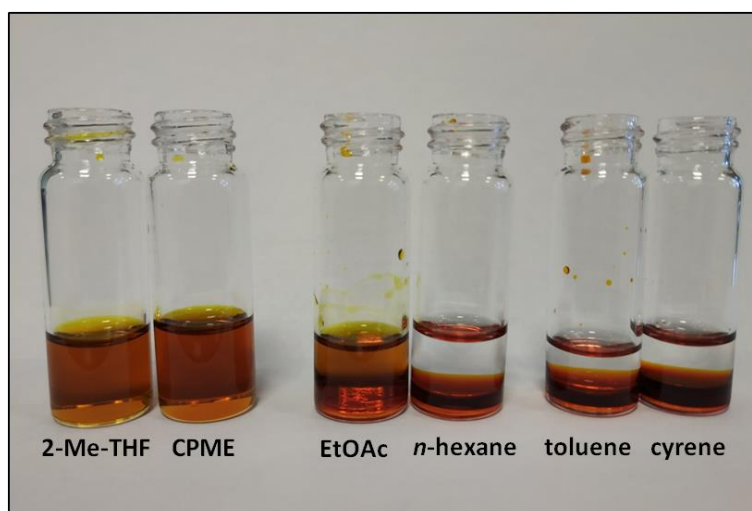


Figure S4

4.2 Study on the extraction of products from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{Gly}$ (2:1)

A set of 9 vials containing **1a** (0.2 mmol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{Gly}$ (3:1) (0.8 mL) were enabled to react according to the conditions reported in Table 1 (entry 6). After 15 min, the reaction mixtures were extracted (2 x 0.5 mL) with the nine solvents leading to immiscible solutions reported in Section 3.1. EtOAc and *i*PrOAc were discarded due to partial leaching of FeCl_3 . The resulting **1b** was poorly extracted in *n*-hexane, *n*-heptane and cyclohexane (determined by TLC and HPLC). Conversely, toluene, cyrene, CH_2Cl_2 and CHCl_3 led to quantitative extraction of **1b**.

4.3. Recycling of the catalytic system in the *CDES*-mediated Meyer Schuster isomerization

4.3.1. Recycling procedure based on extractive workup

1a (0.2 mmol) and 0.8 mL of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{Gly}$ (3:1) were loaded into a glass open vial and stirred at RT over 10 min. Then, the reaction was extracted with cyrene (2 x 400 μL). The upper organic phases were successively separated by centrifugation (90 s, 13000 rpm), combined, and finally dried over Na_2SO_4 . The conversion was assessed by HPLC analysis. The remaining lower phase ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{Gly}$) was supplemented with **1a** (0.2 mmol) to start the second cycle, and so on. Results are collected in Figure S5.

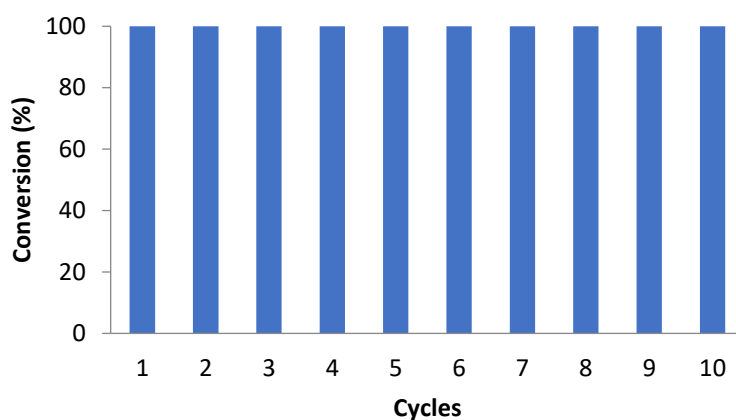


Figure S5. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{Gly}$ -catalyzed Meyer-Schuster isomerization of **1a**.

4.3.2. Recycling procedure based on filtration/precipitation workup

11a (0.2 mmol) and 0.8 mL of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{Gly}$ (3:1) were loaded into a glass open vial and stirred at RT. Almost immediately, the formation of a precipitate was observed and the stirring was maintained over 30 min. After this time, the reaction mixture was diluted with 1 mL of water and stirred vigorously for a few seconds. Then, the solid was filtered off and washed twice with water (2 x 1.0 mL), providing pure **11b**. The *LADES* was reconstituted from the filtrate by evaporation of water under reduced pressure so as to be ready for a new reaction cycle. Results are collected in Table S6.

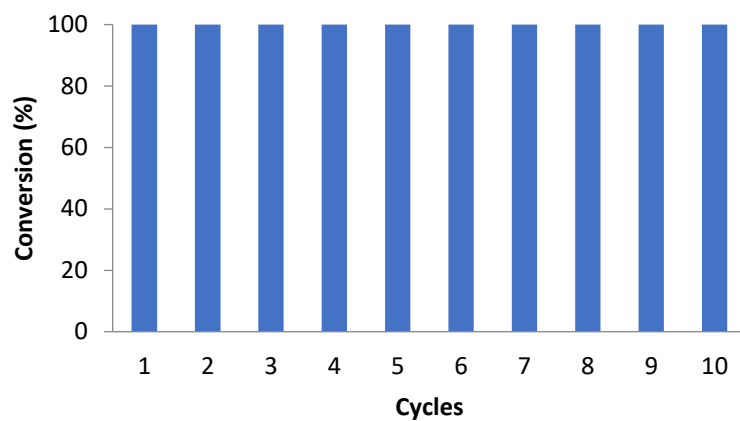


Figure S6. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{Gly}$ -catalyzed Meyer-Schuster isomerization of **11a**.

5.- NMR spectra data

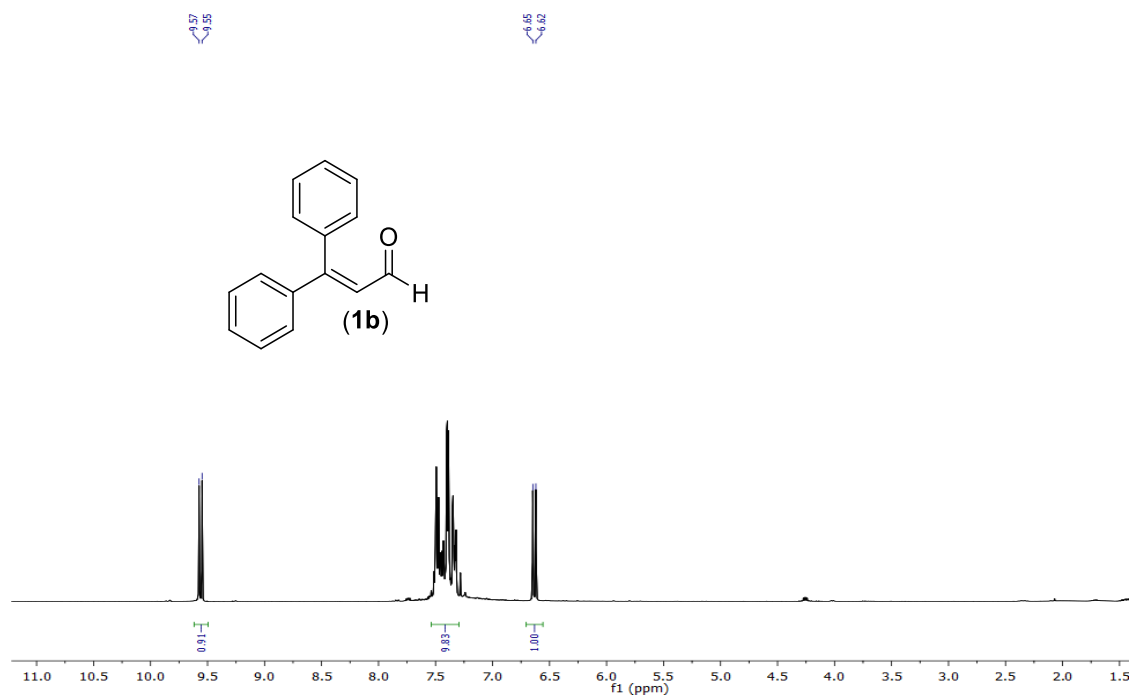


Figure S1. $^1\text{H-NMR}$ full chart for **1b** in CDCl₃.

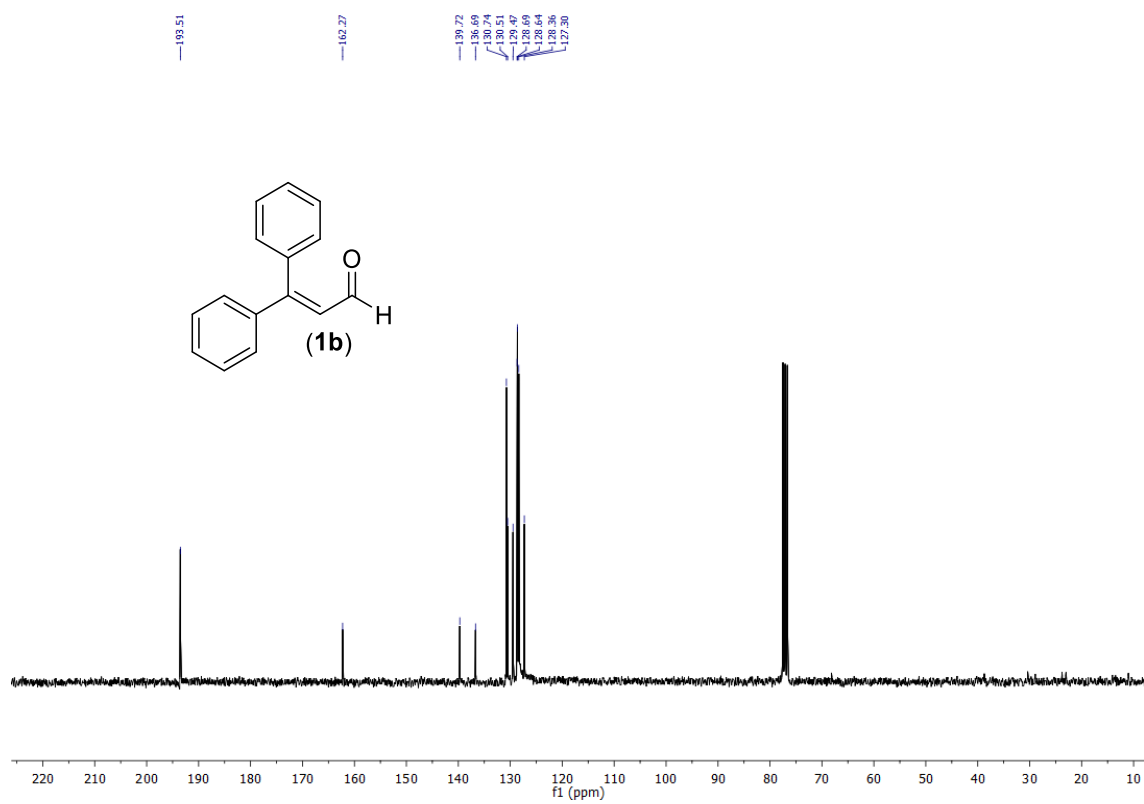


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ -NMR full chart for **1b** in CDCl₃.

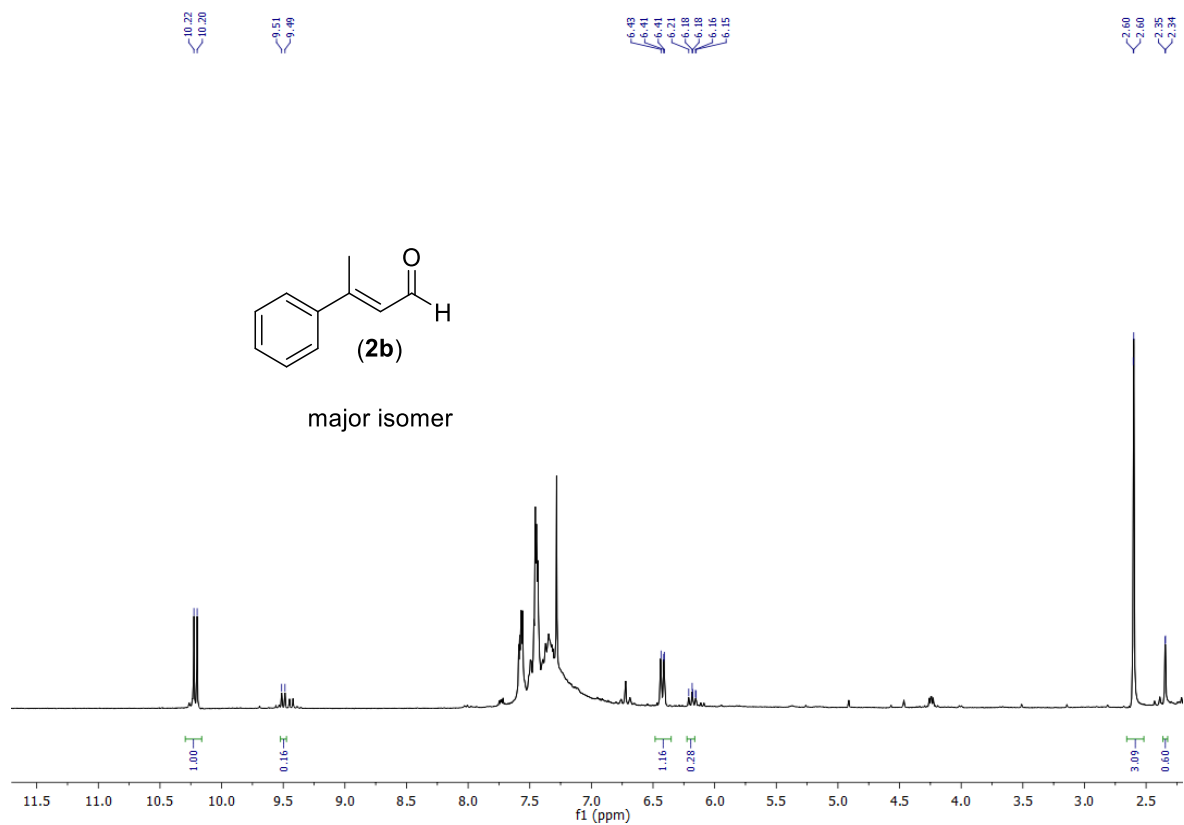


Figure S3. $^1\text{H-NMR}$ full chart for **2b** in CDCl_3 .

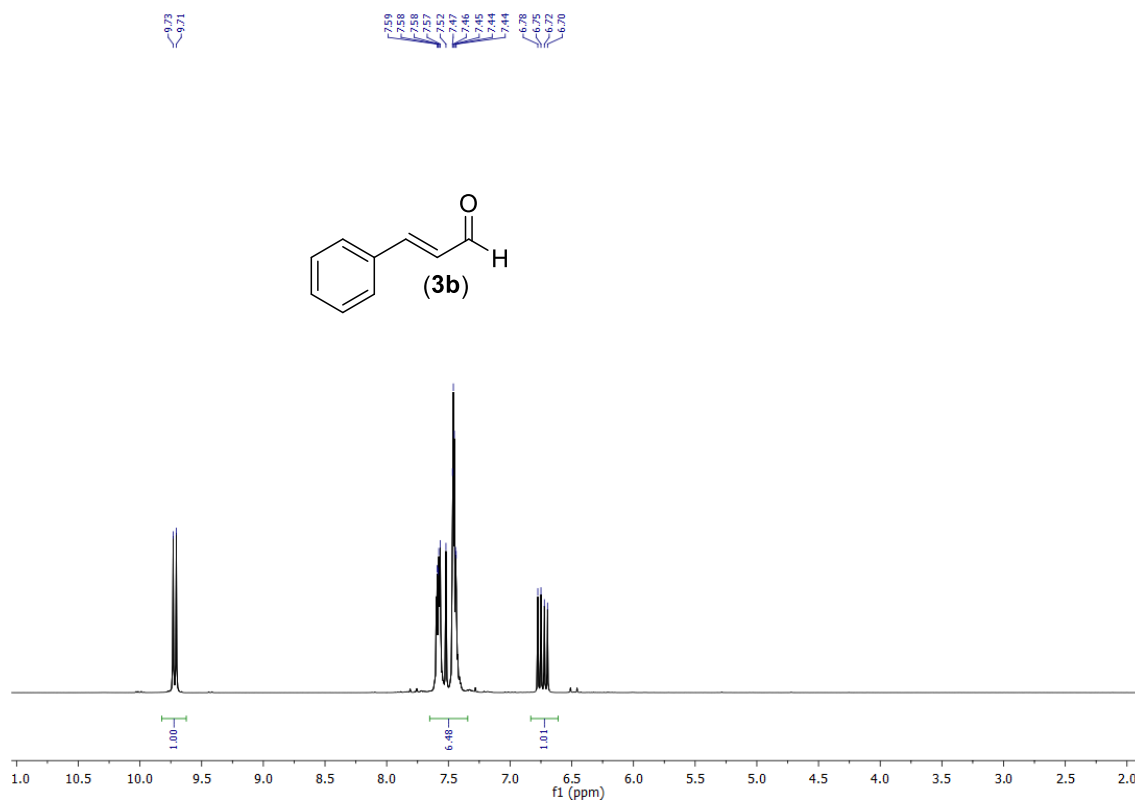


Figure S4. $^1\text{H-NMR}$ full chart for **3b** in CDCl_3 .

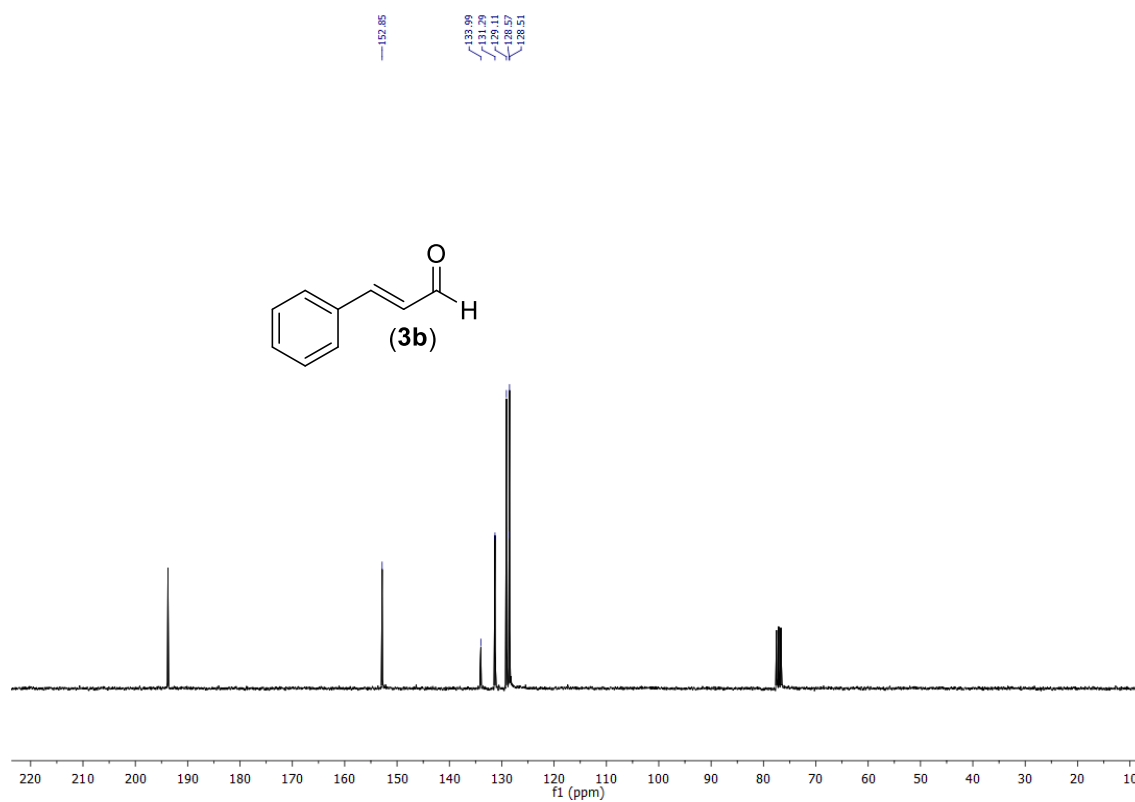


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ -NMR full chart for **3b** in CDCl_3 .

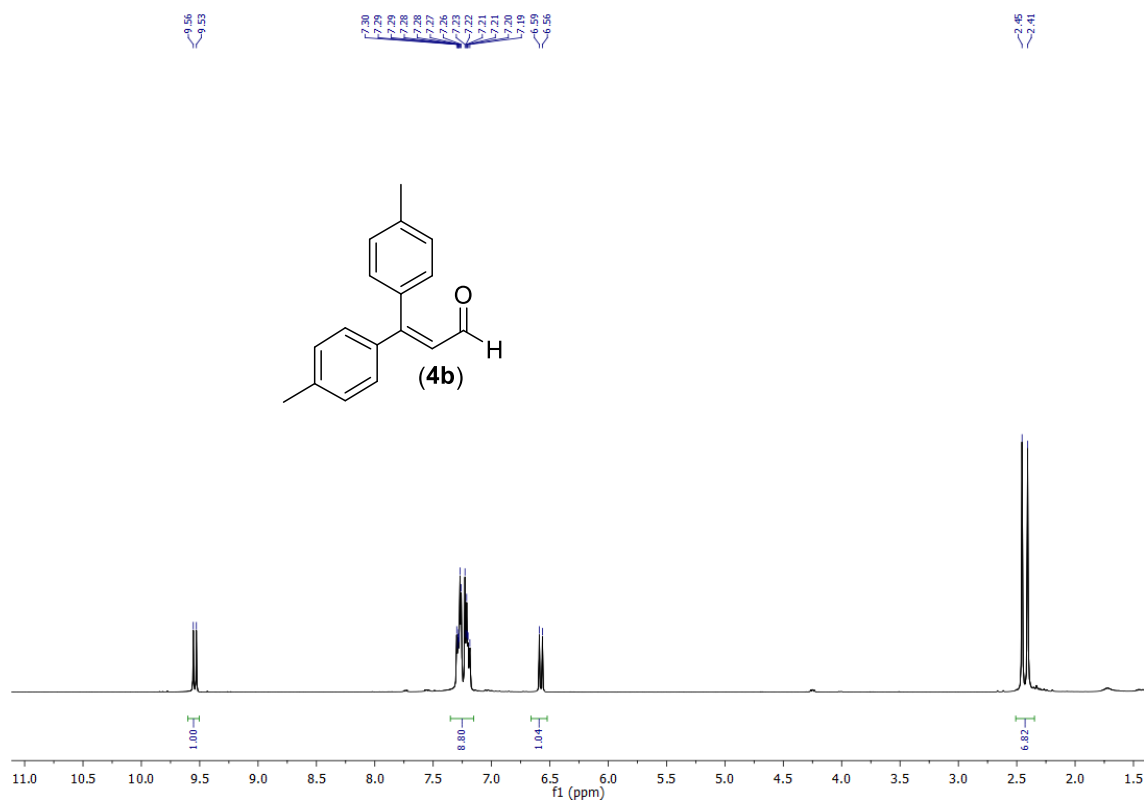


Figure S6. $^1\text{H-NMR}$ full chart for **4b** in CDCl_3 .

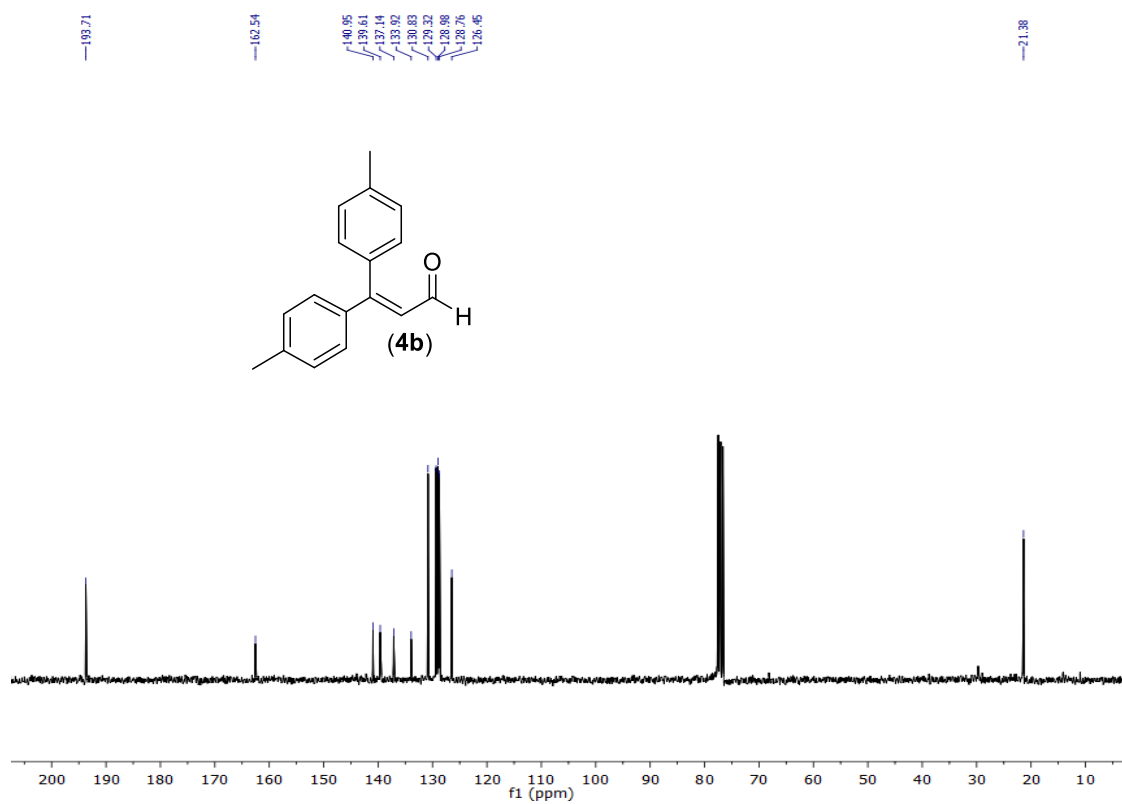


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ -NMR full chart for **4b** in CDCl_3 .

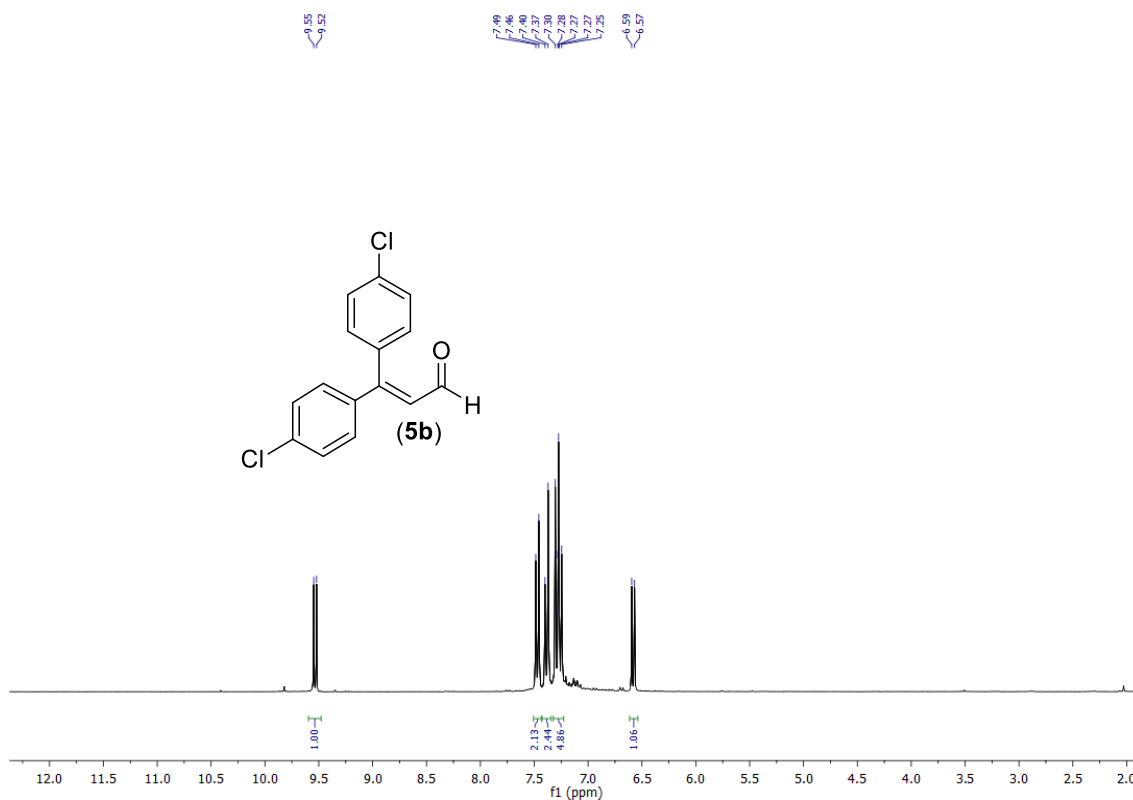


Figure S8. $^1\text{H-NMR}$ full chart for **5b** in CDCl_3 .

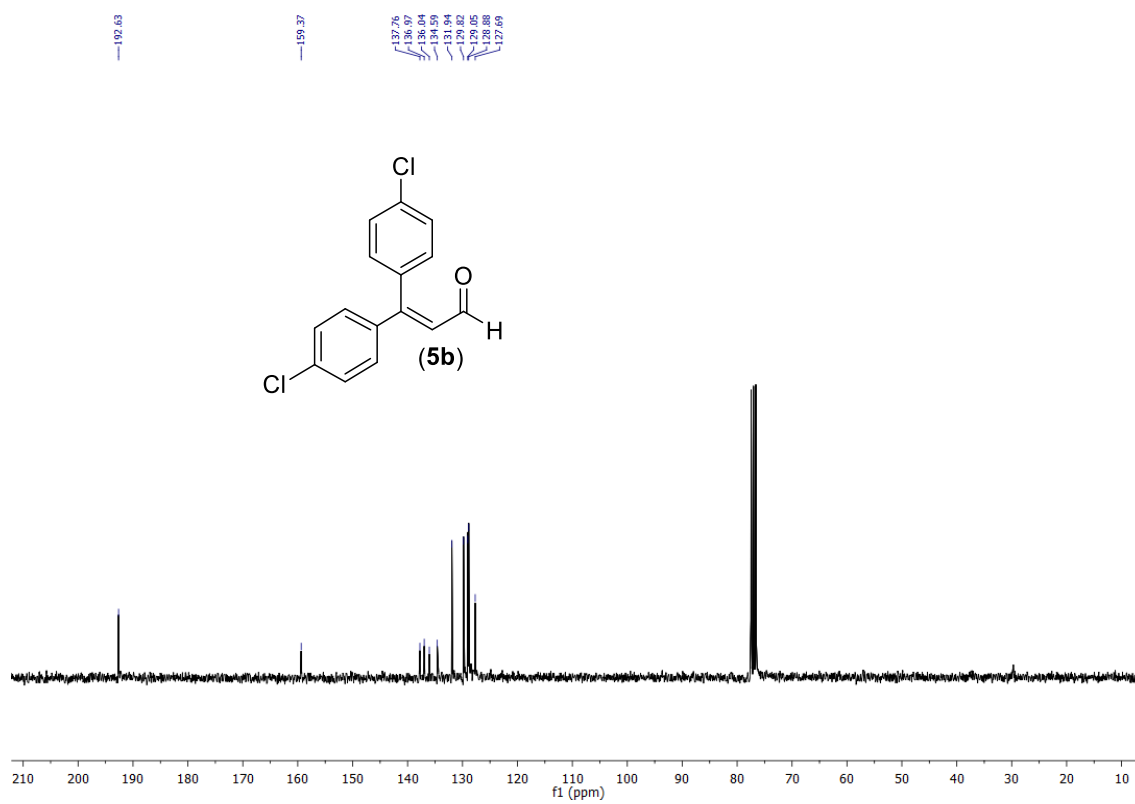


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ -NMR full chart for **5b** in CDCl_3 .

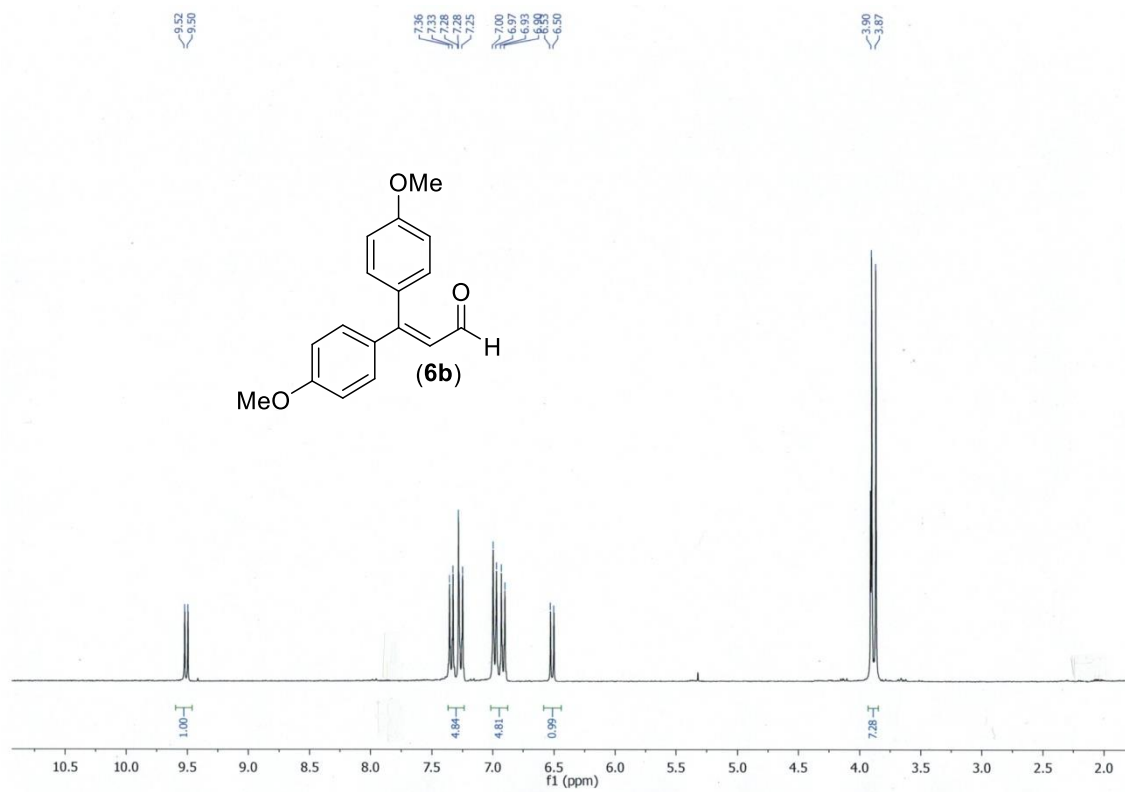


Figure S10. $^1\text{H-NMR}$ full chart for **6b** in CDCl₃.

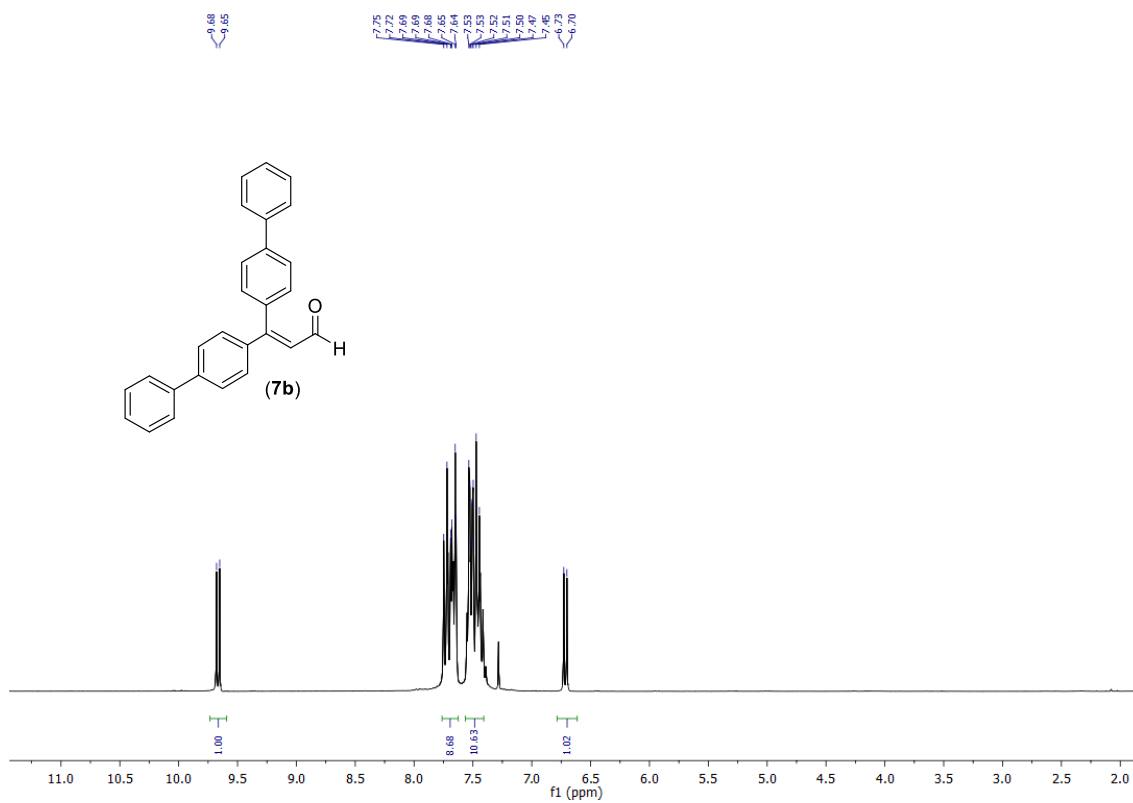


Figure S11. ¹H-NMR full chart for **7b** in CDCl₃.

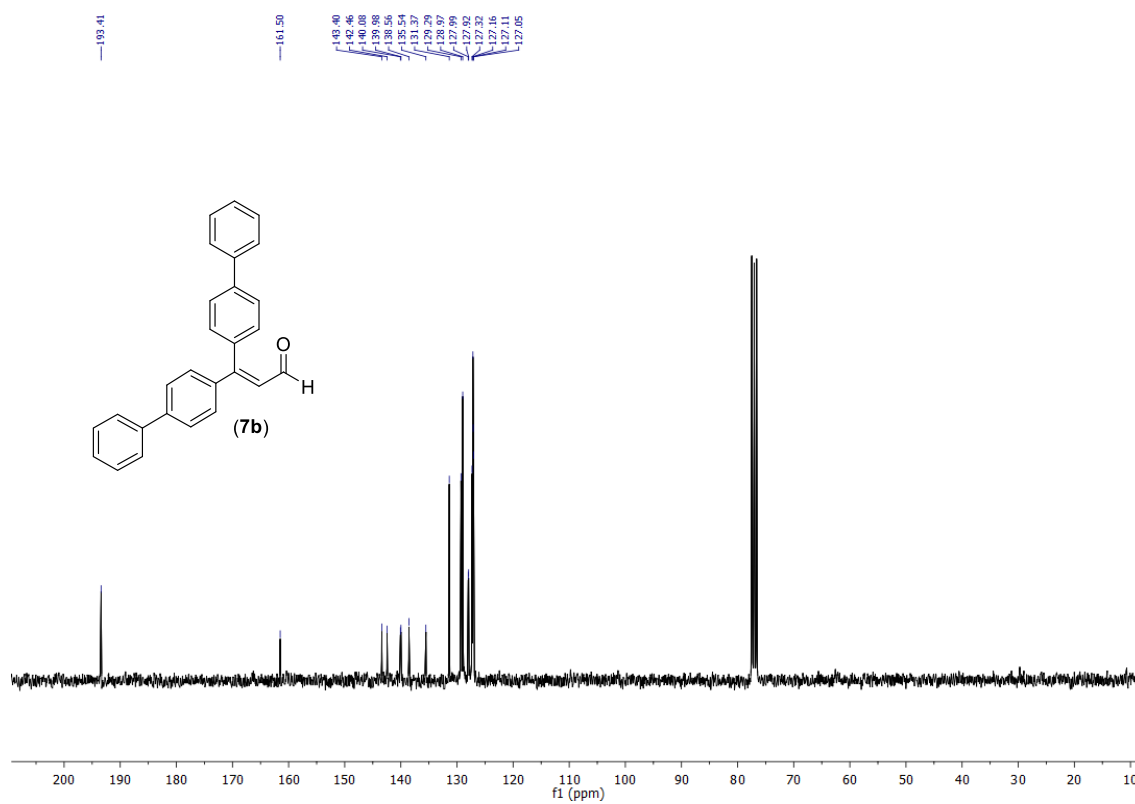


Figure S12. ¹³C{¹H}-NMR full chart for **7b** in CDCl₃.

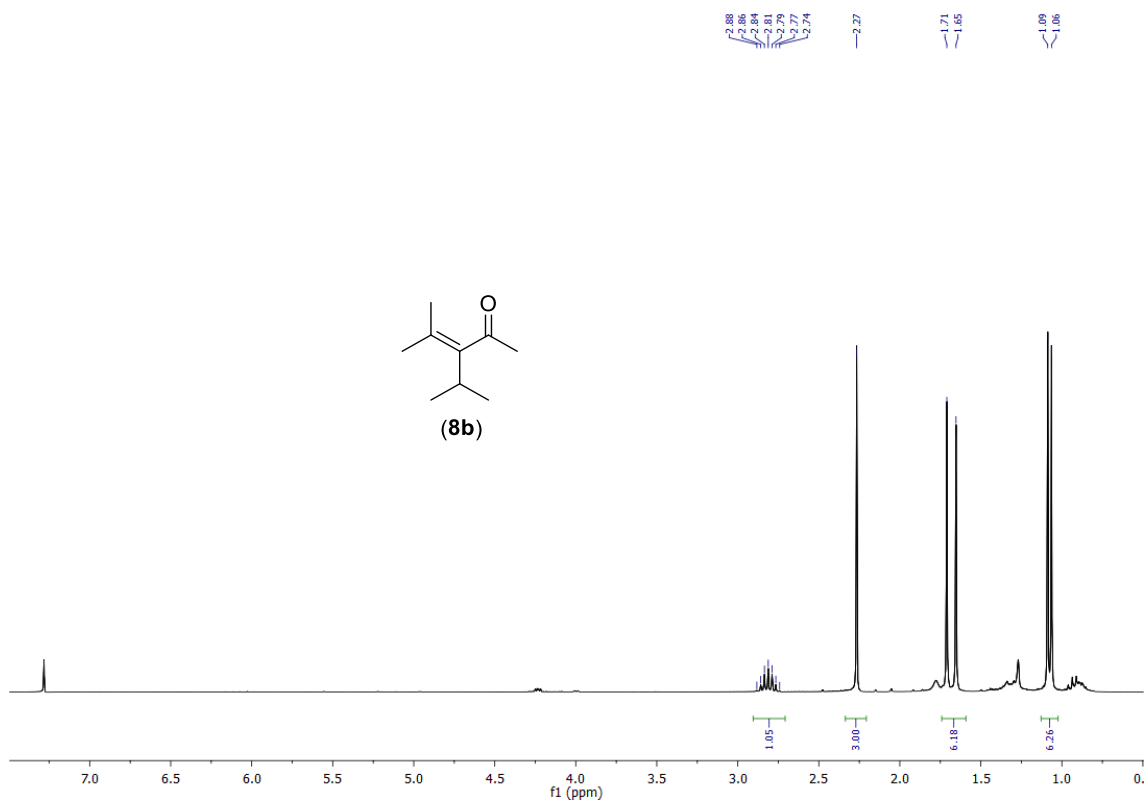


Figure S13. $^1\text{H-NMR}$ full chart for **8b** in CDCl₃.

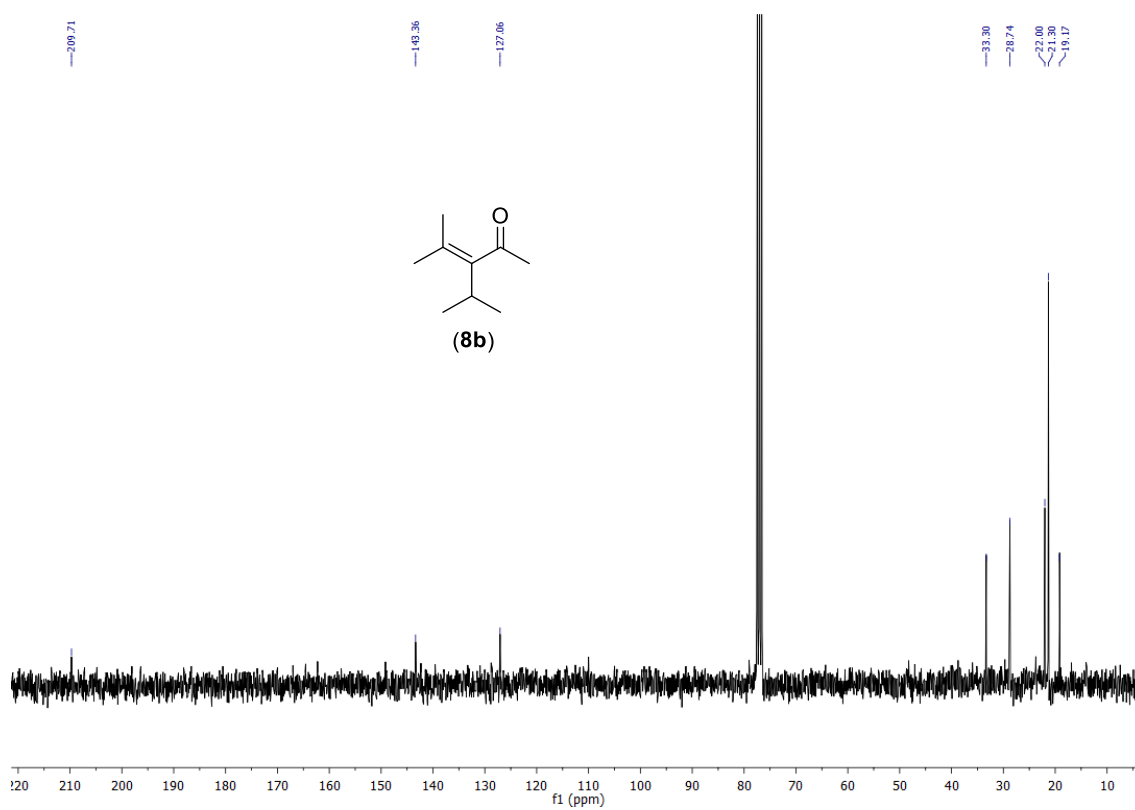


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ -NMR full chart for **8b** in CDCl₃.

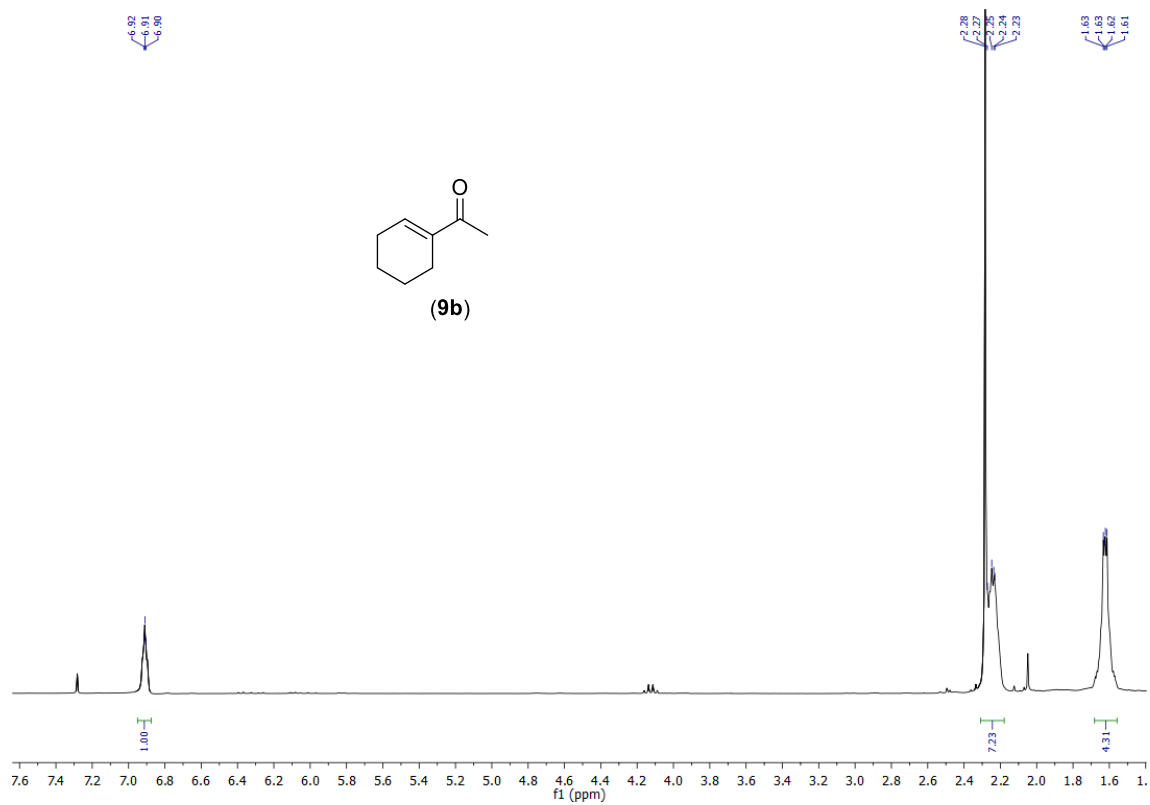


Figure S15. $^1\text{H-NMR}$ full chart for **9b** in CDCl₃.

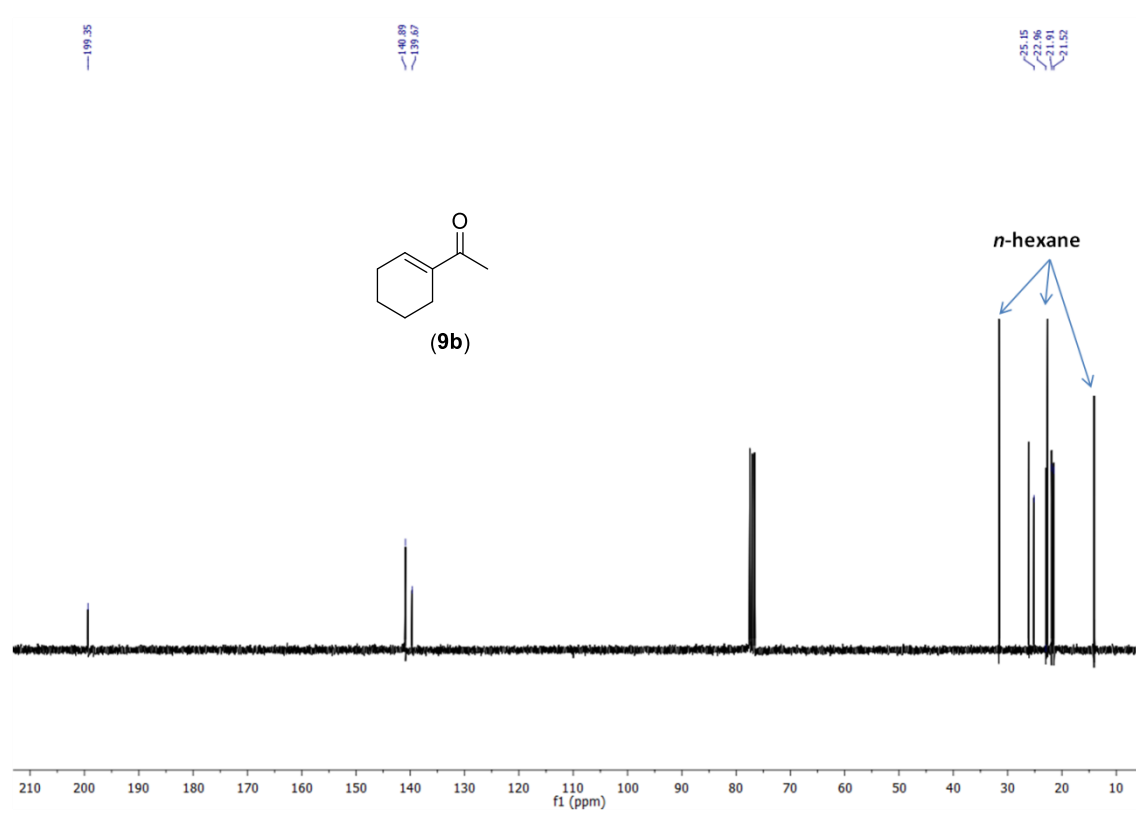


Figure S16. $^{13}\text{C}\{^1\text{H}\}$ -NMR full chart for **9b** in CDCl₃.

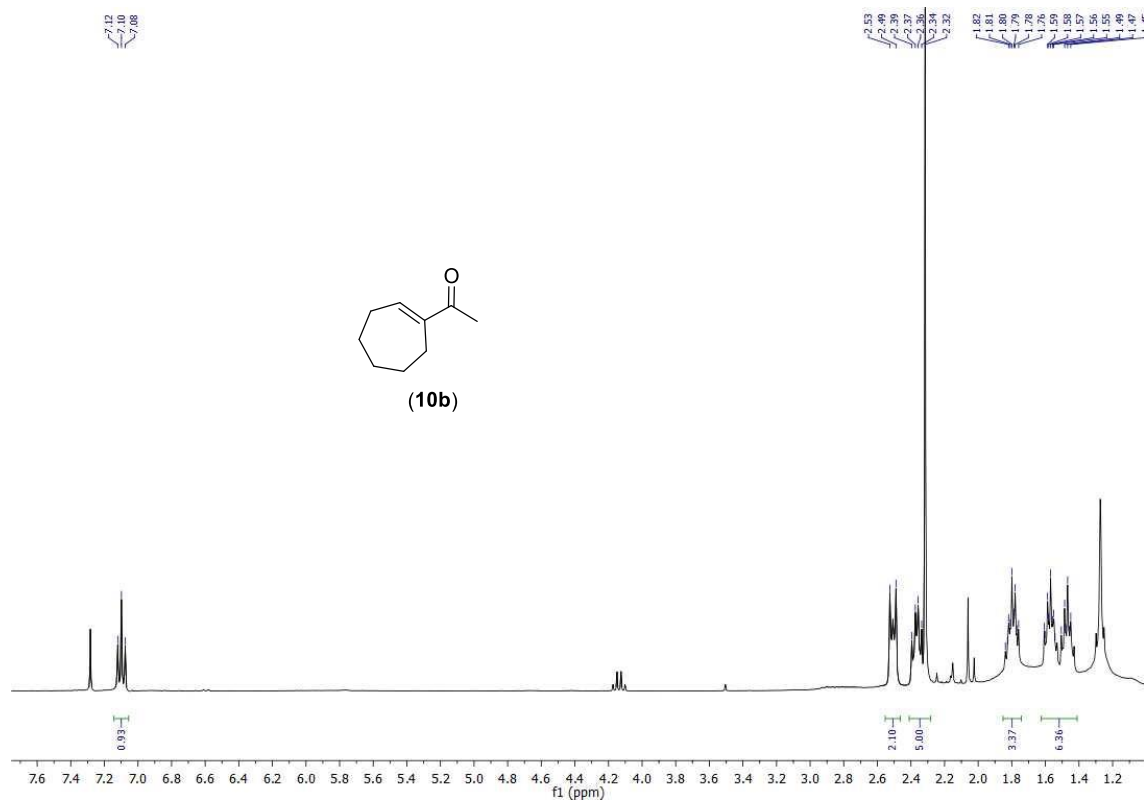


Figure S17. ¹H-NMR full chart for **10b** in CDCl₃.

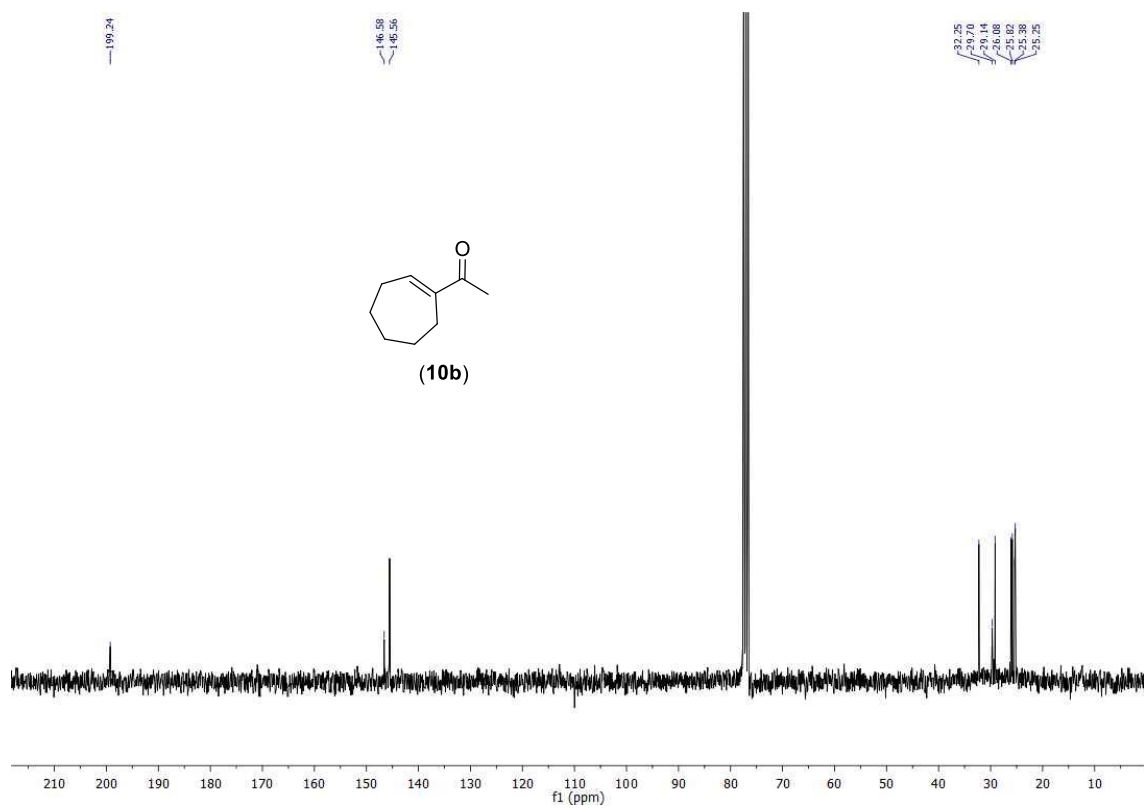


Figure S18. ¹³C{¹H}-NMR full chart for **10b** in CDCl₃.

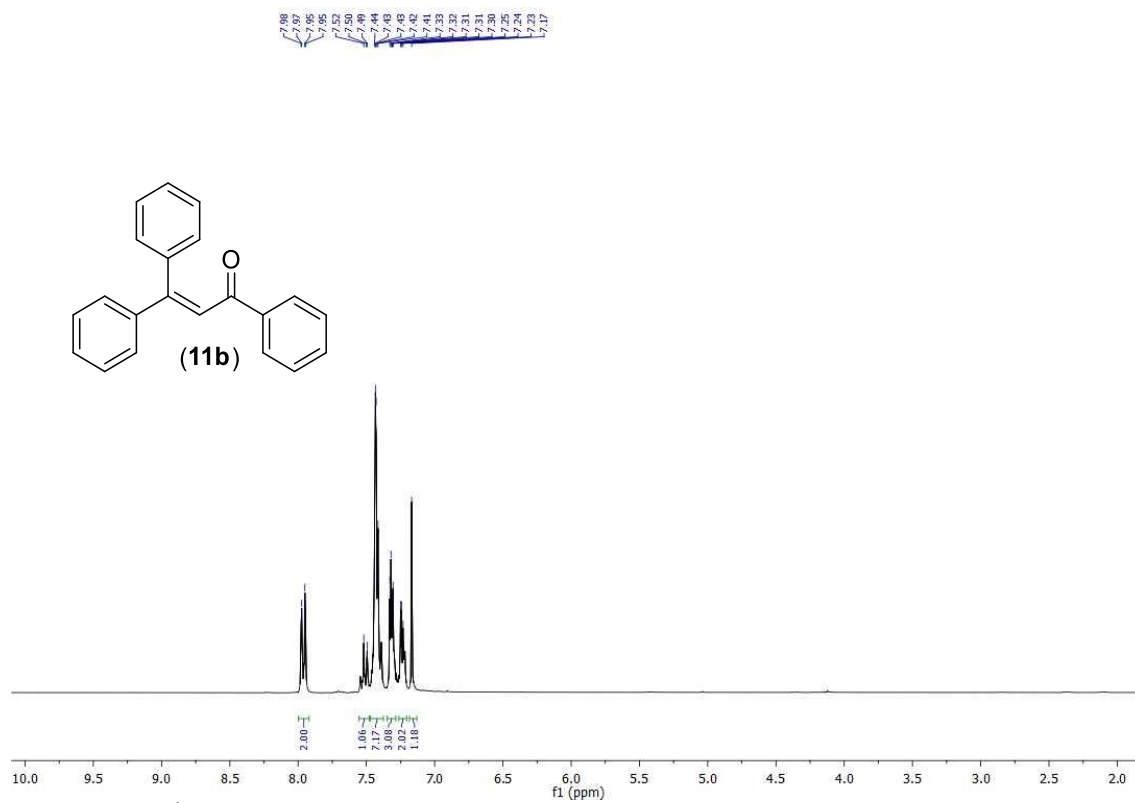


Figure S19. ¹H-NMR full chart for **11b** in CDCl₃.

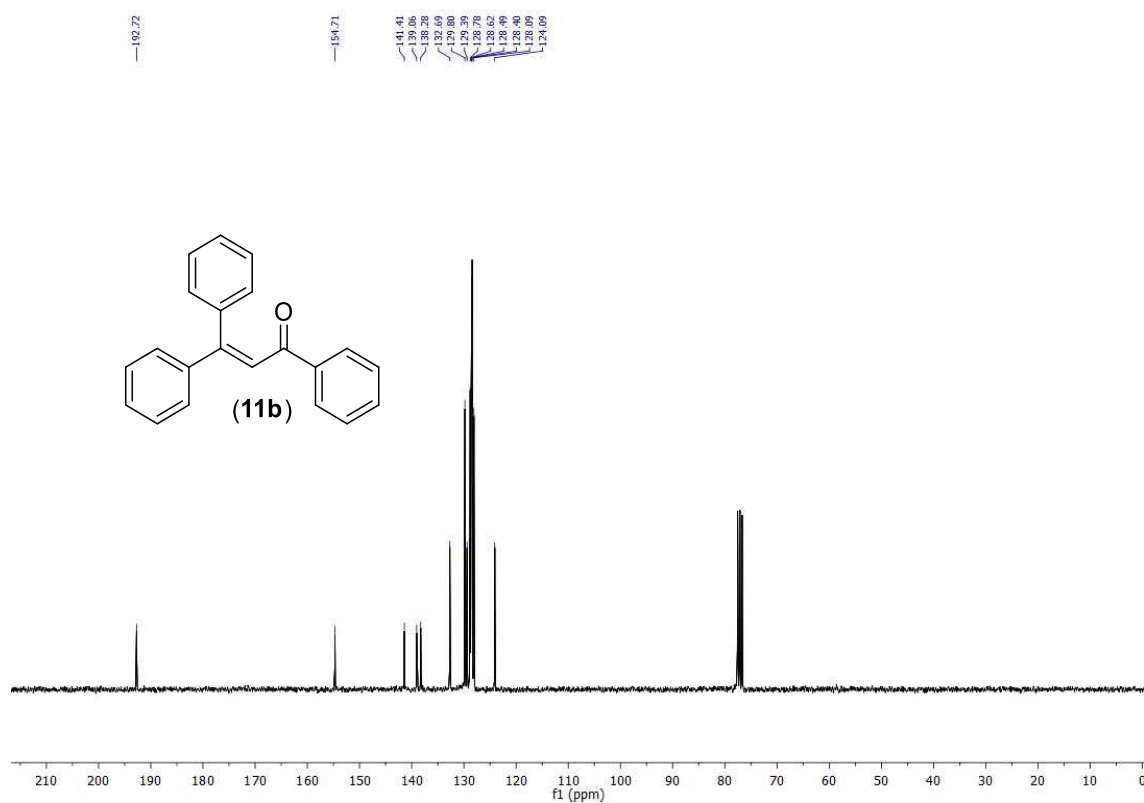


Figure S20. ¹³C{¹H}-NMR full chart for **11b** in CDCl₃.

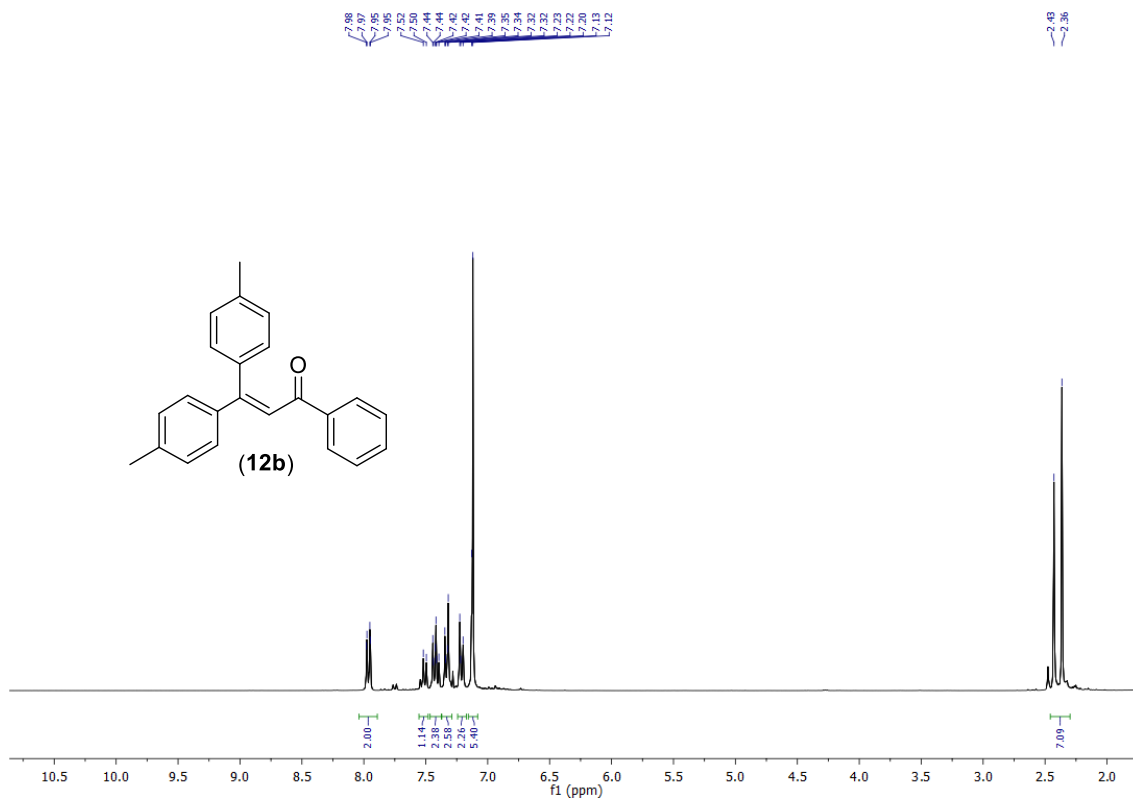


Figure S21. ¹H-NMR full chart for **12b** in CDCl₃.

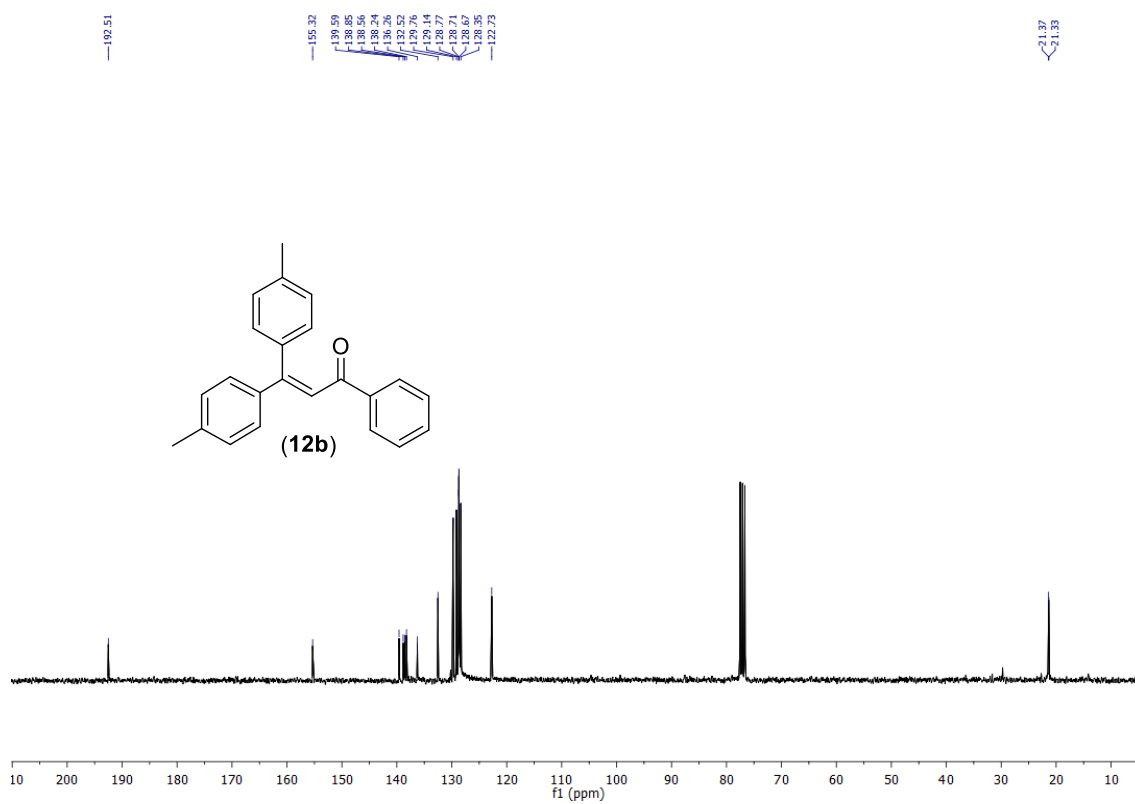


Figure S22. ¹³C{¹H}-NMR full chart for **12b** in CDCl₃.

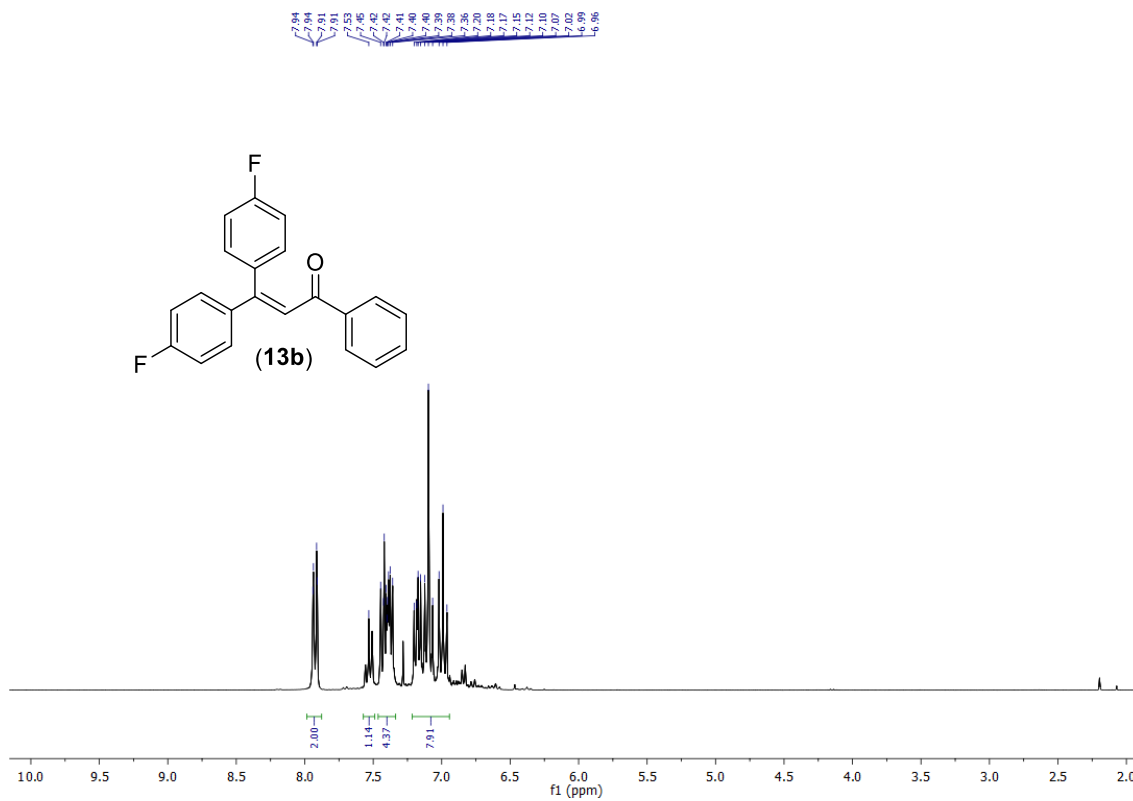


Figure S23. ¹H-NMR full chart for **13b** in CDCl₃.

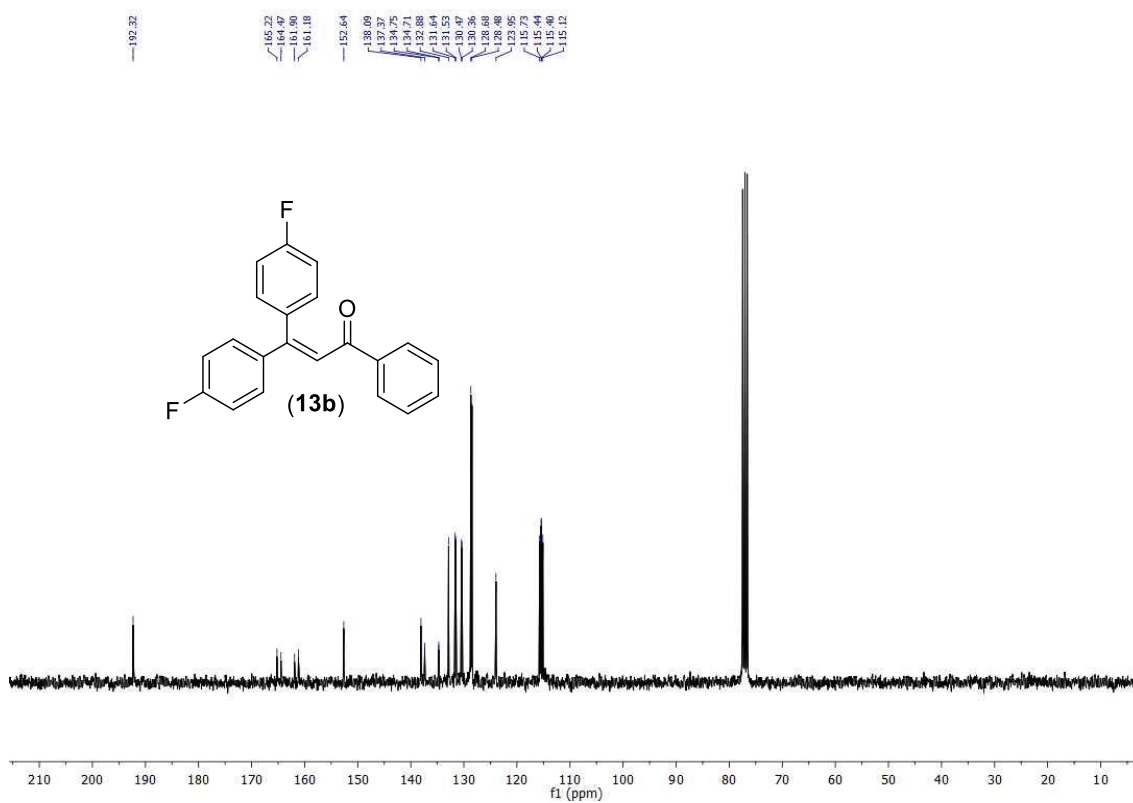


Figure S24. ¹³C{¹H}-NMR full chart for **13b** in CDCl₃.

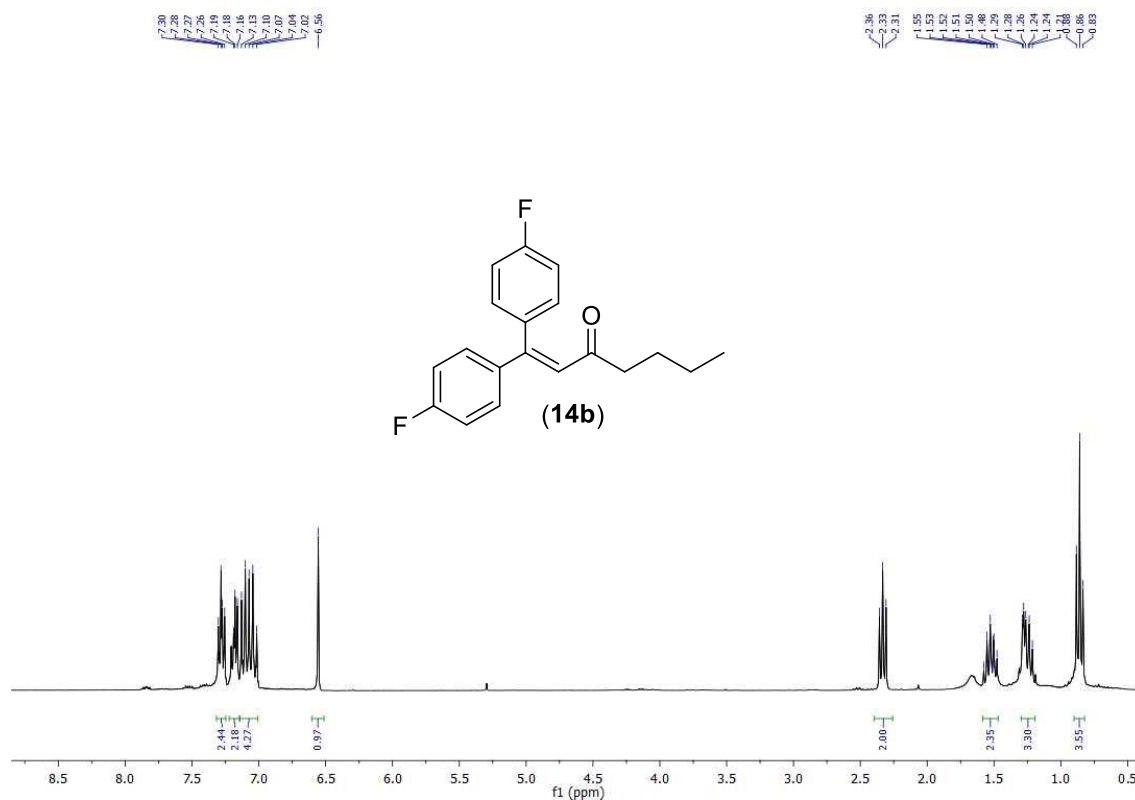


Figure S25. ¹H-NMR full chart for **14b** in CDCl₃.

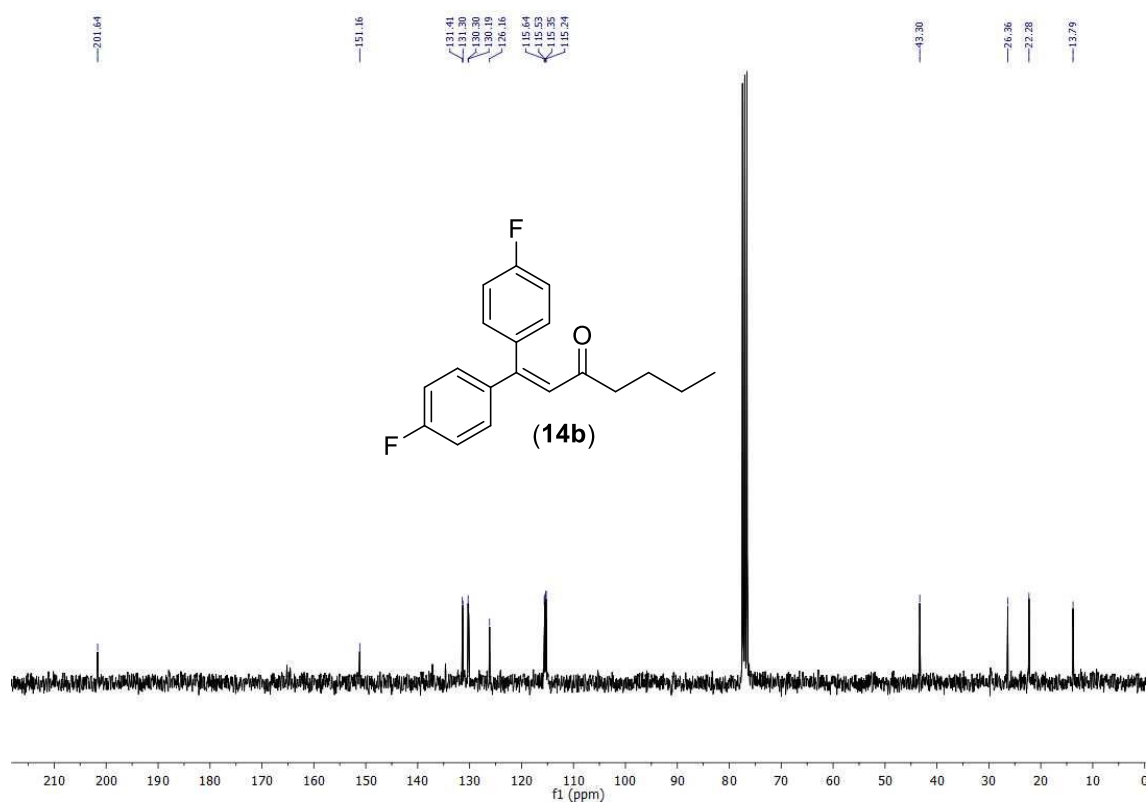


Figure S26. ¹³C{¹H}-NMR full chart for **14b** in CDCl₃.

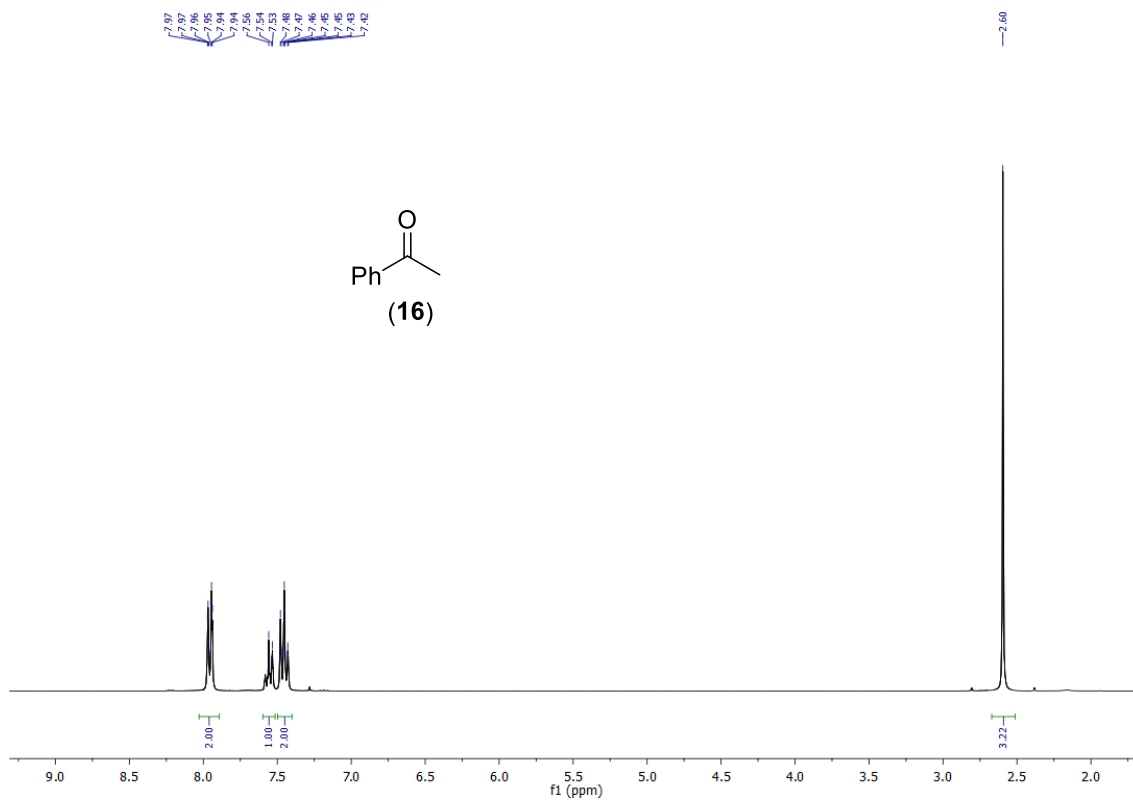


Figure S27. $^1\text{H-NMR}$ full chart for **16** in CDCl₃.

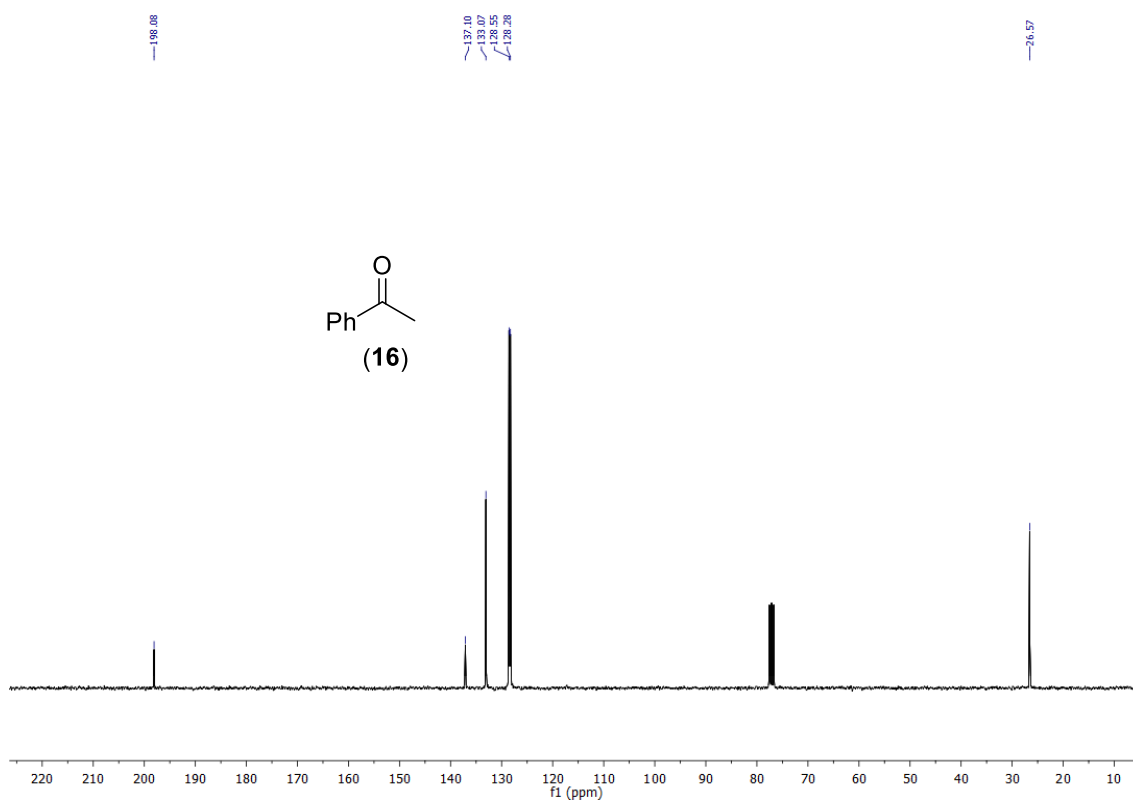


Figure S28. $^{13}\text{C}\{^1\text{H}\}$ -NMR full chart for **16** in CDCl₃.

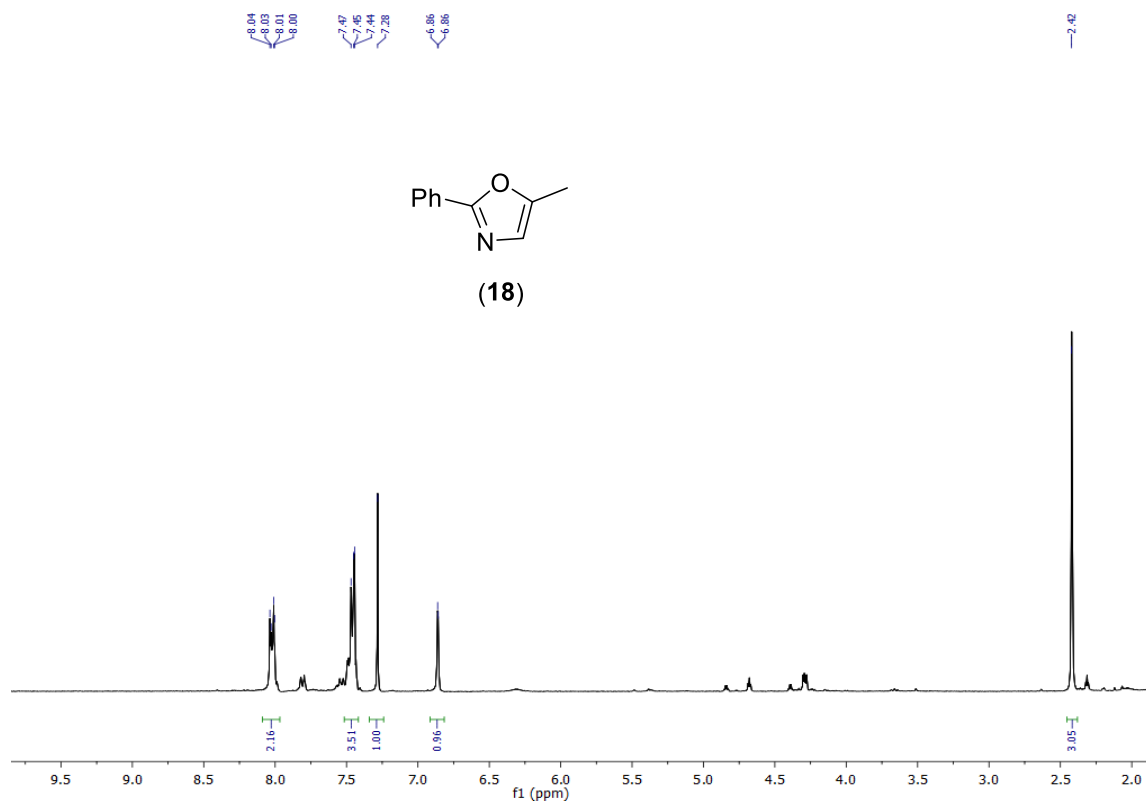


Figure S29. ¹H-NMR full chart for **18** in CDCl₃.

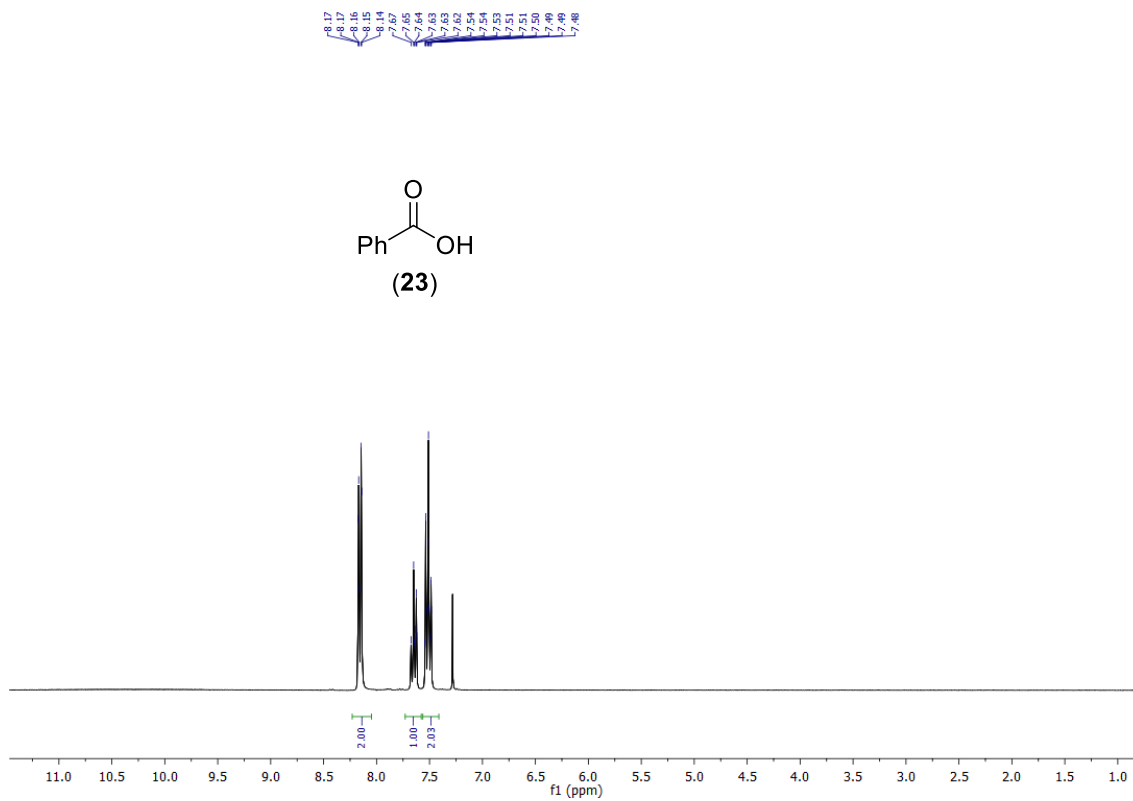


Figure S30. $^1\text{H-NMR}$ full chart for **23** in CDCl_3 .

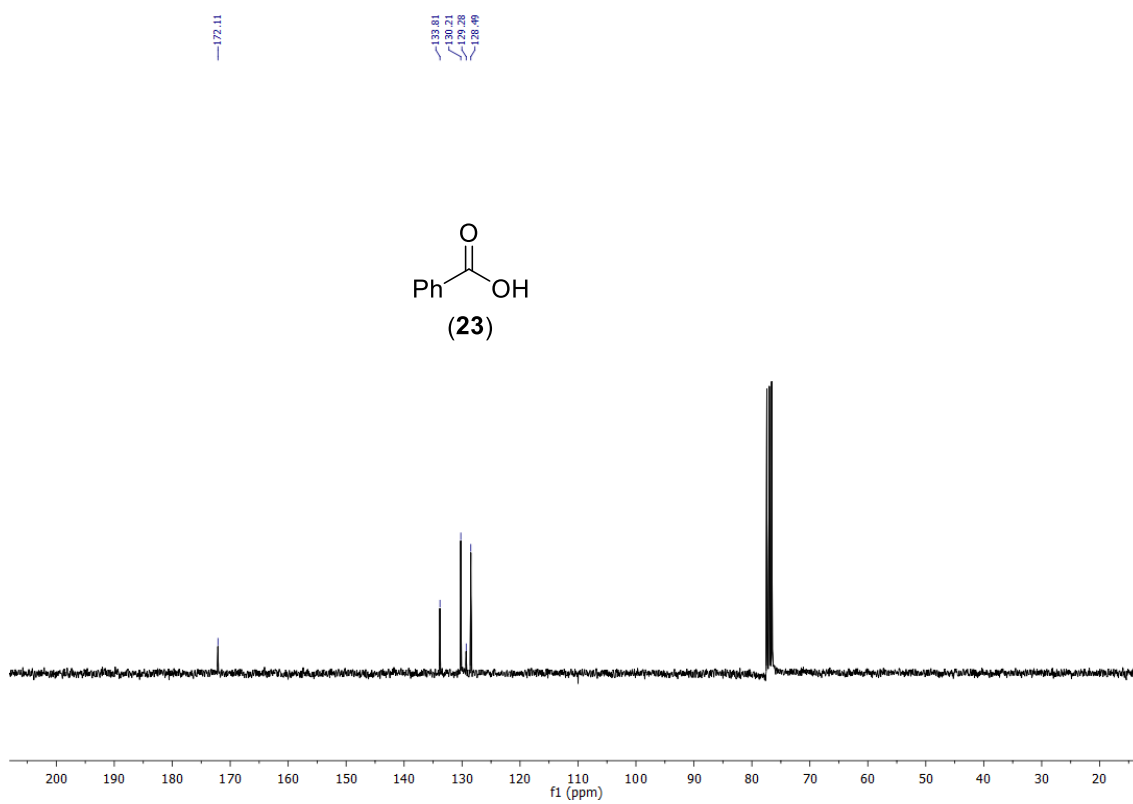


Figure S31. $^{13}\text{C}\{^1\text{H}\}$ -NMR full chart for **23** in CDCl_3 .

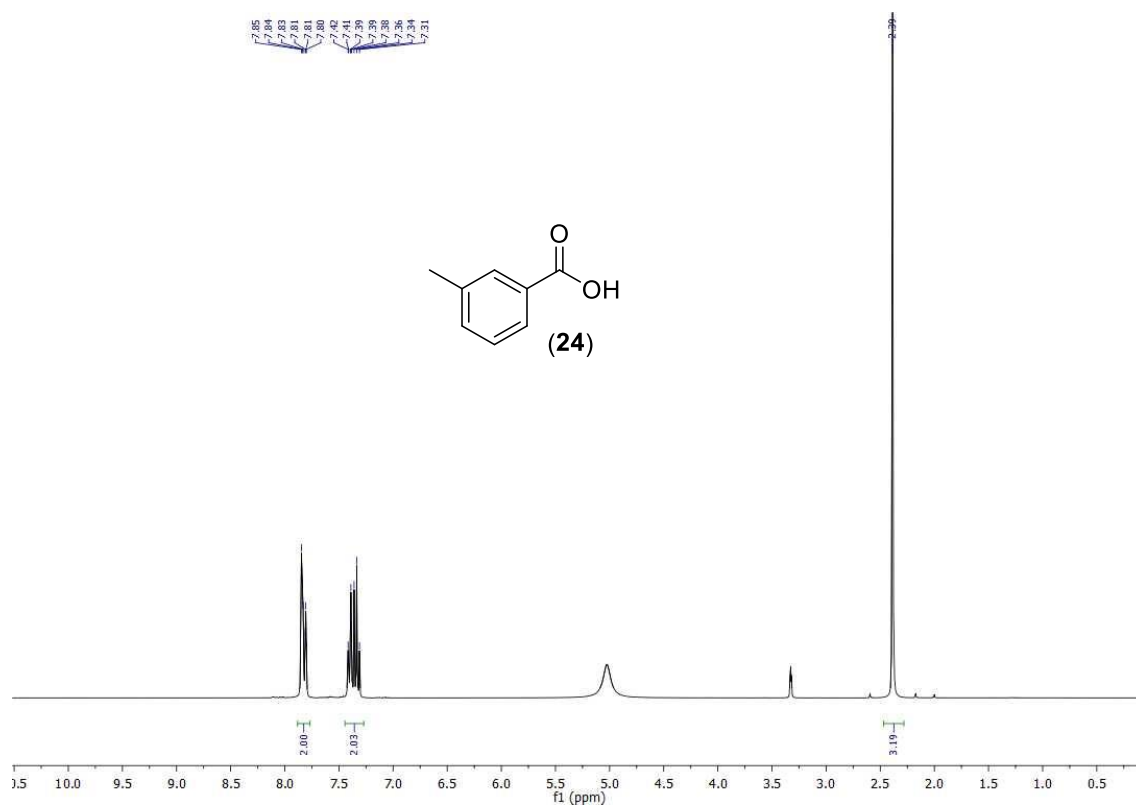


Figure S32. $^1\text{H-NMR}$ full chart for **24** in MeOD.

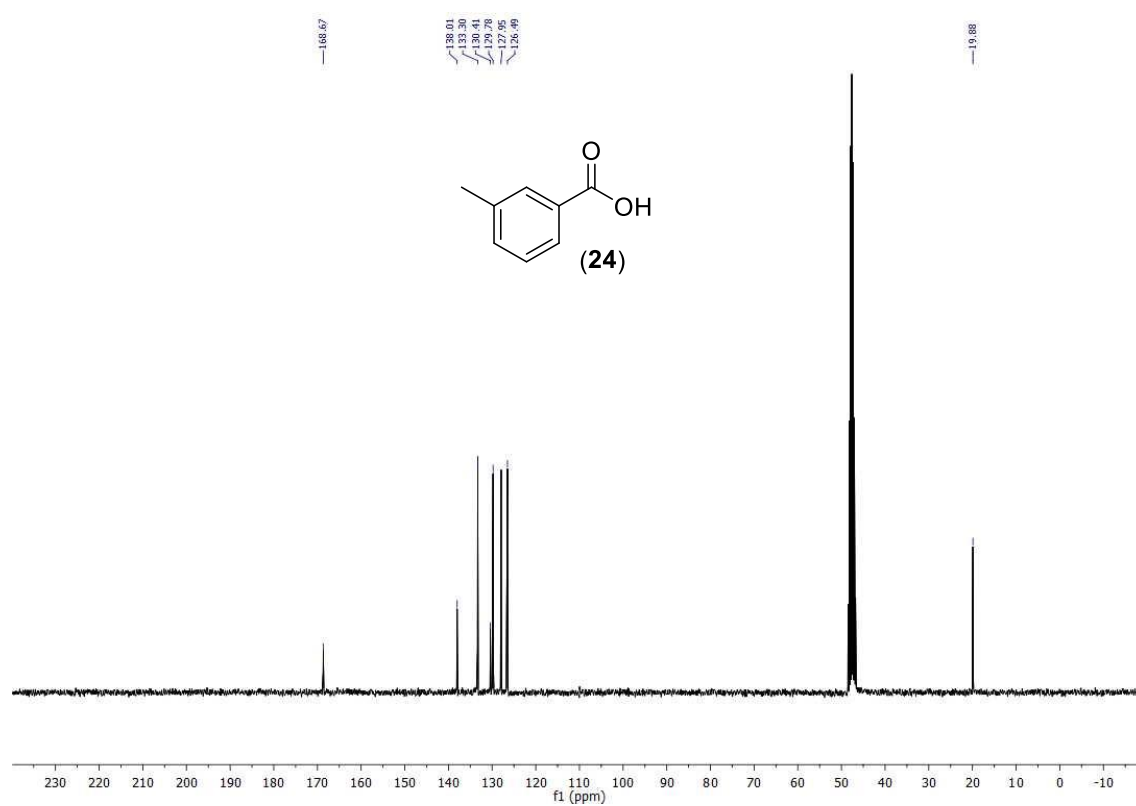


Figure S33. $^{13}\text{C}\{^1\text{H}\}$ -NMR full chart for **24** in MeOD.

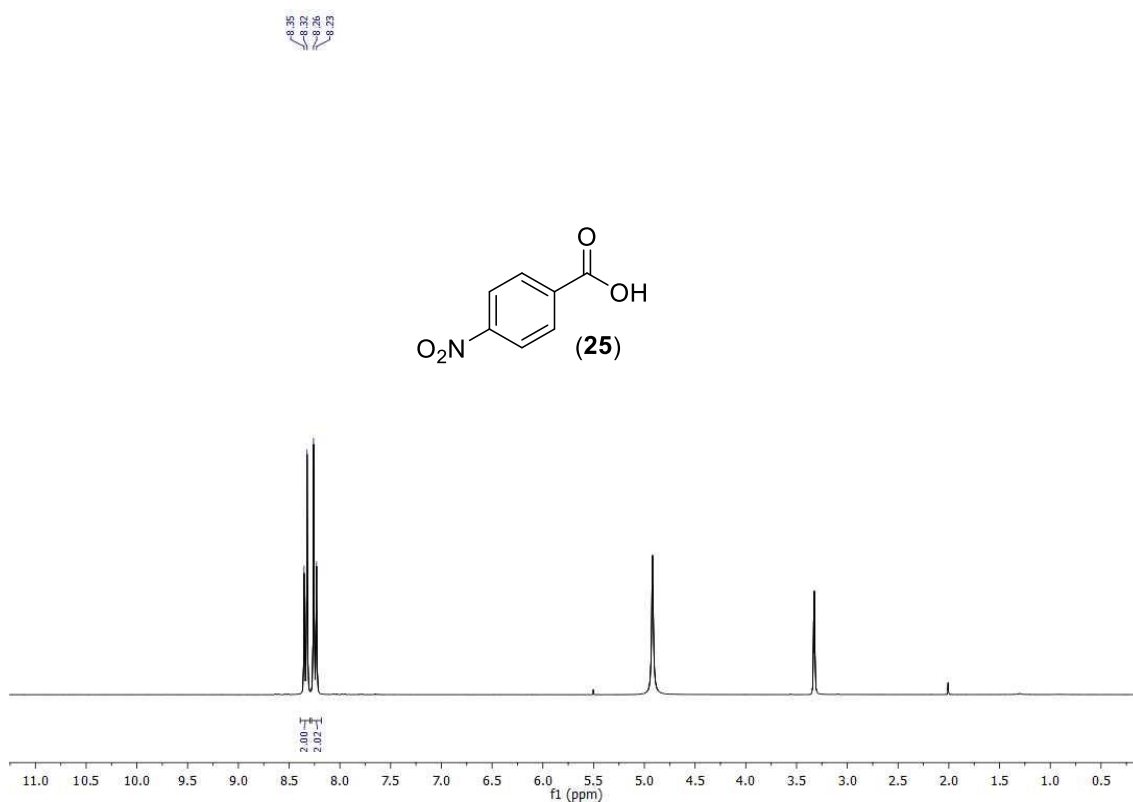


Figure S34. $^1\text{H-NMR}$ full chart for **25** in MeOD.

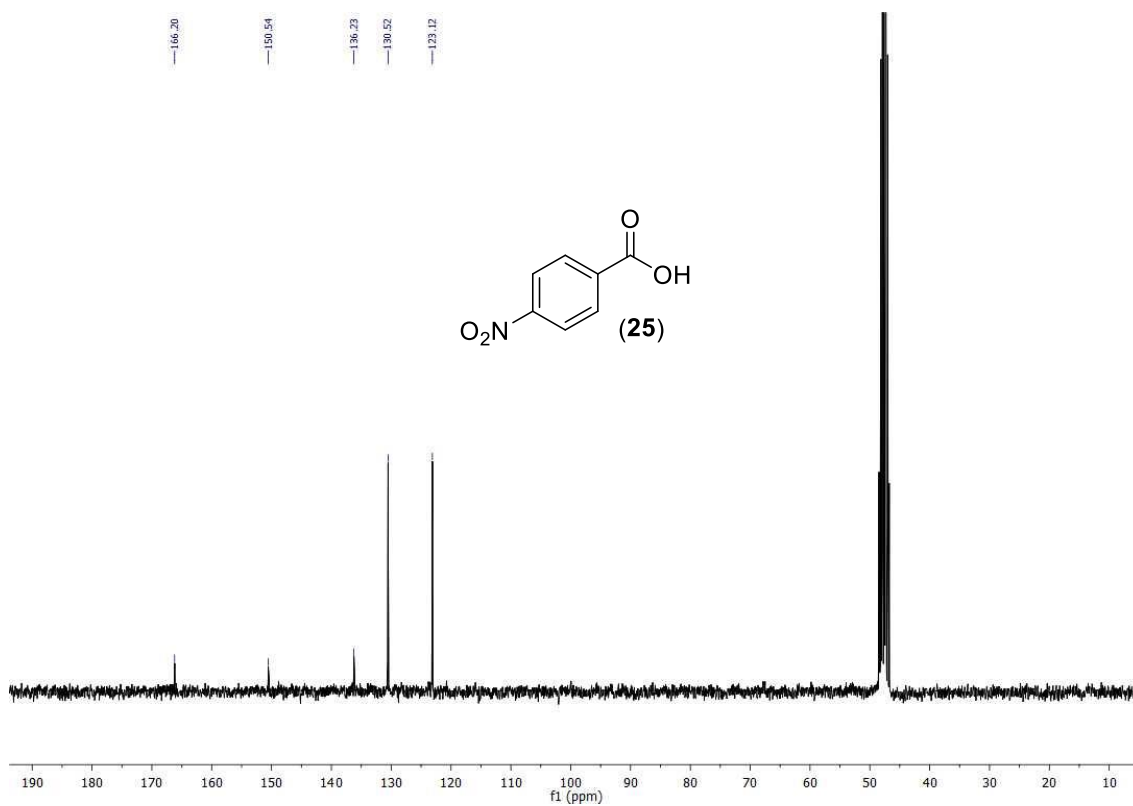


Figure S35. $^{13}\text{C}\{^1\text{H}\}$ -NMR full chart for **25** in MeOD.

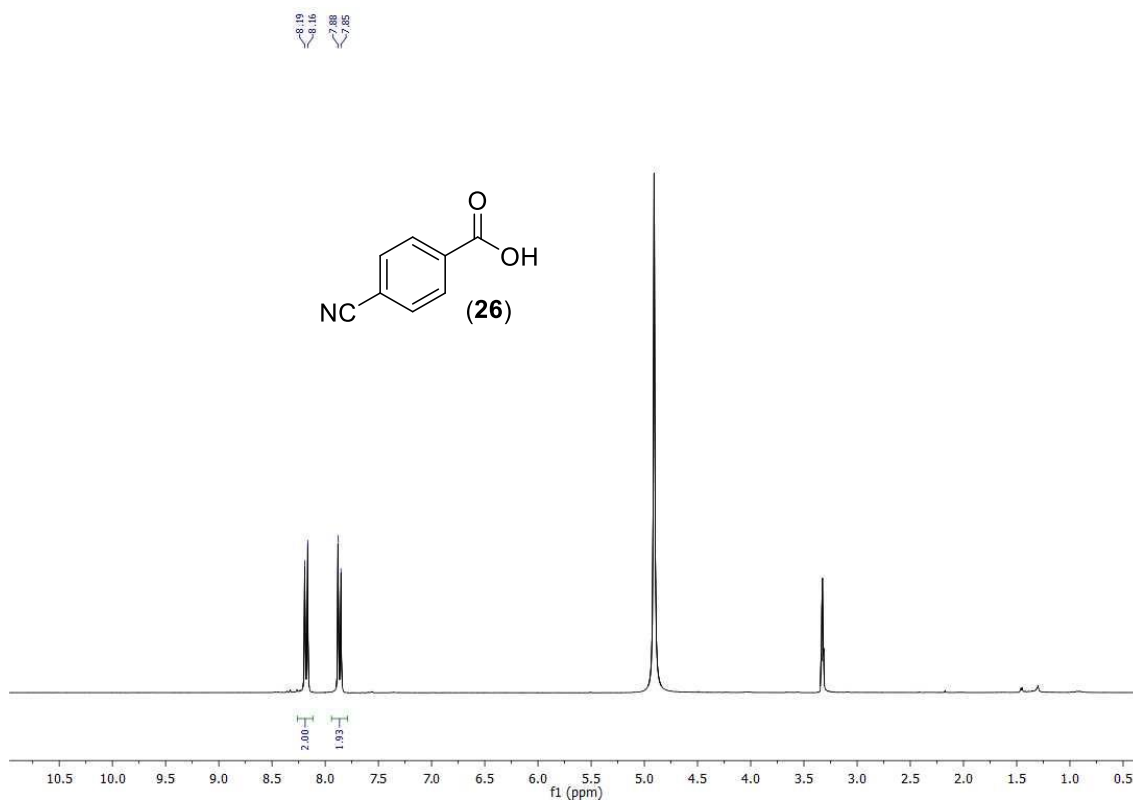


Figure S36. $^1\text{H-NMR}$ full chart for **26** in MeOD.

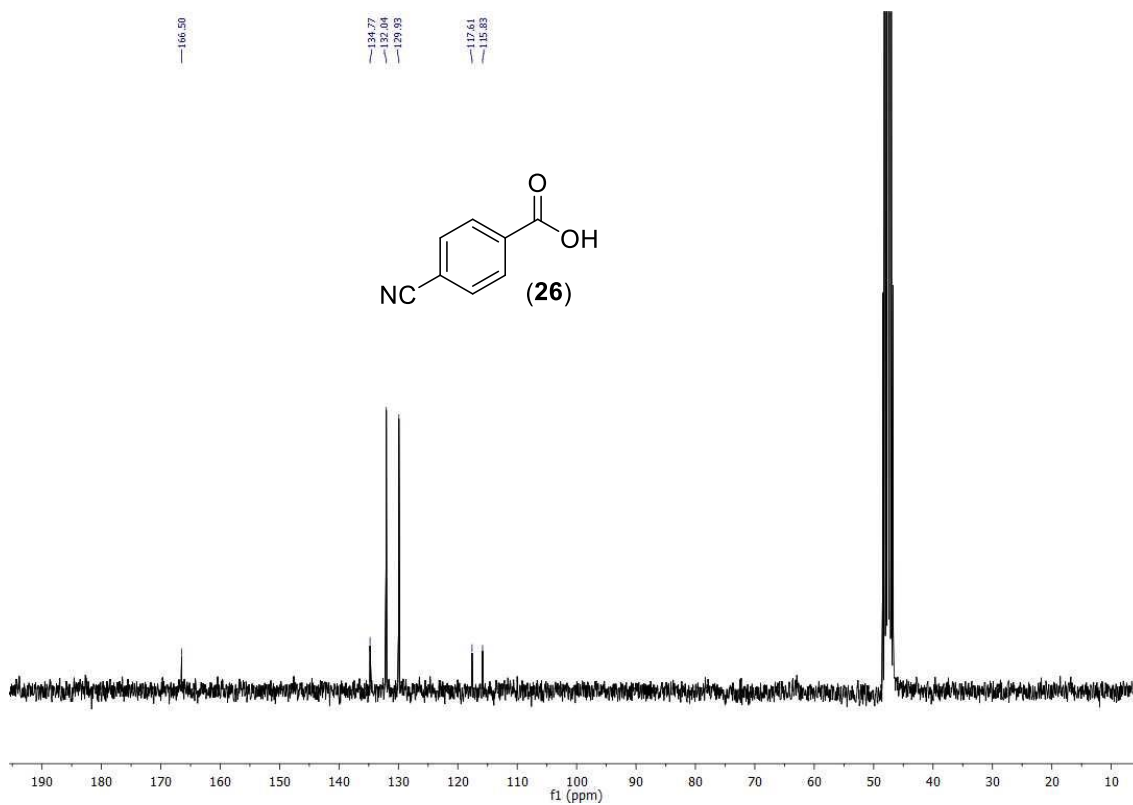


Figure S37. $^{13}\text{C}\{^1\text{H}\}$ -NMR full chart for **26** in MeOD.

6. HPLC analytical data

6.1. Analytical data for the determination of the degree of conversion (*c*) in Meyer Schuster and Rupe rearrangements

Apparent conversions of substrates **1a–14a** to products **1b–14b** were determined based on the % peak area of product and substrate. In the first instance, complete conversion was qualitatively assessed for all the reactions included in Table 2 by TLC. The propargylic alcohols **1a–14a** showed significant differences in R_f from the corresponding α,β -unsaturated carbonyl compounds **1b–14b**. Likewise, alcohols **1a–14a** underwent oxidation much more intensely than products when treated with KMnO_4 . After work up described in Section 2, the apparent conversion was established by HPLC. In all cases, and in good agreement with TLC analysis, complete disappearance of the starting product **1a–14a** was assessed. As a result, calibration experiments for determining the response factors of propargylic alcohols and α,β -unsaturated carbonyl compounds were discarded.

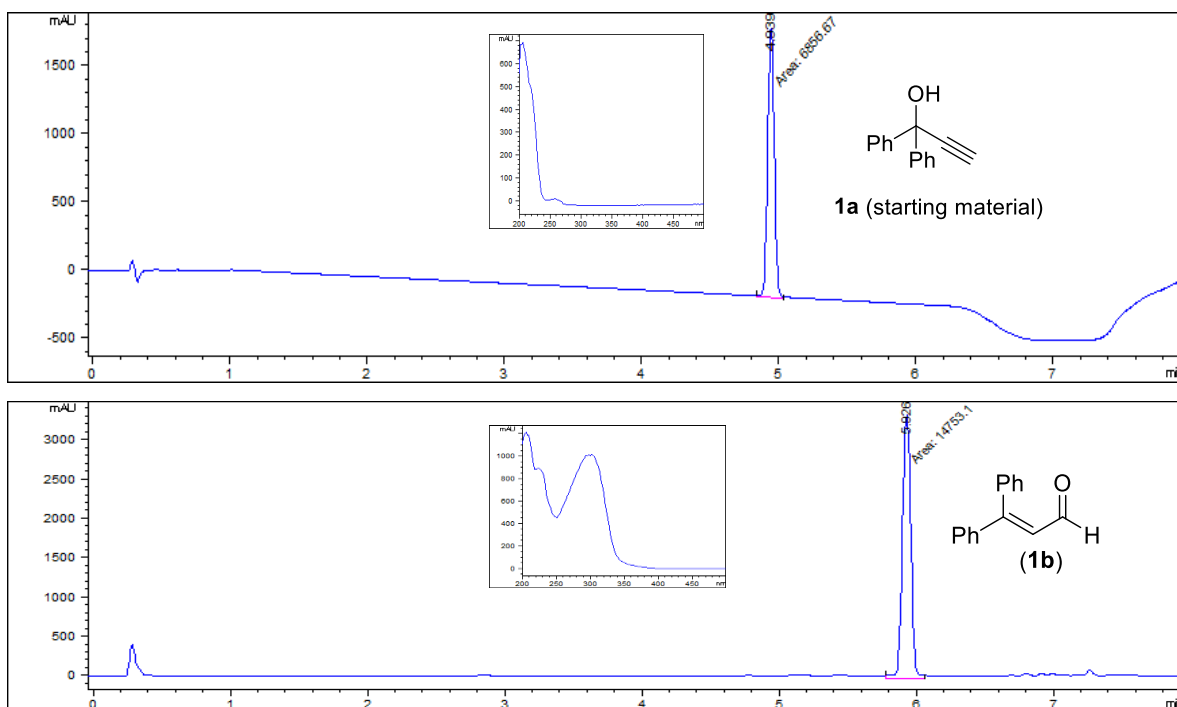
HPLC Method for **1a–14a**: HPLC analyses were carried out on an Agilent chromatographic system, using a reversed phase column (Zorbax Eclipse XDB-C18, RR, 1.8 μm , 4.6 x 50 mm, Agilent) and acetonitrile (MeCN) and 0.1% trifluoroacetic acid (TFA) in water as solvents. Samples were eluted with three linear gradients from 10% to 60% MeCN during 5.70 min, followed by another from 60% to 100% MeCN during 0.5 min and a third gradient from 100% to 10% MeCN during 1.90 min, at flow rate of 2 ml/min. Detection and spectral characterization of peaks were performed at 210 and 278 nm with a diode array detector and ChemStation Rev.B.03.01 software (Agilent).

Table S3. Analytical data for the determination of *c* (%) in Meyer Schuster and Rupe rearrangements.

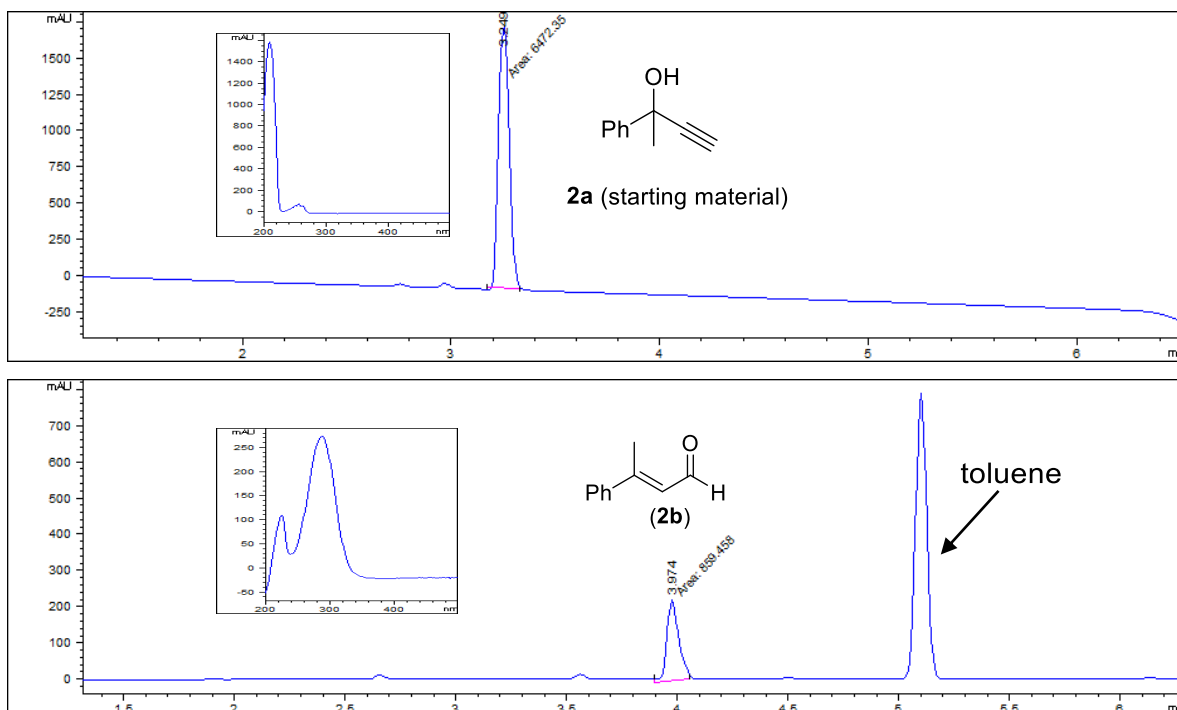
Retention time (<i>t_R</i>, min)			
Propargylic alcohol	<i>t_R</i>	Products	<i>t_R</i>
1a	4.9	1b	5.9
2a	3.2	2b	4.0
3a	2.5	3b	3.6
4a	6.3	4b	6.7
5a	6.4	5b	6.7
6a	4.8	6b	5.5
7a	6.7	6b	7.0
8a	4.5	7b	4.7
9a	2.7	9b	3.5
10a	3.3	10b	4.4
11a	6.5	11b	6.7
12a	6.8	12b	6.9
13a	6.6	13b	6.7
14a	6.7	14b	6.8

7. Copy of HPLC chromatograms

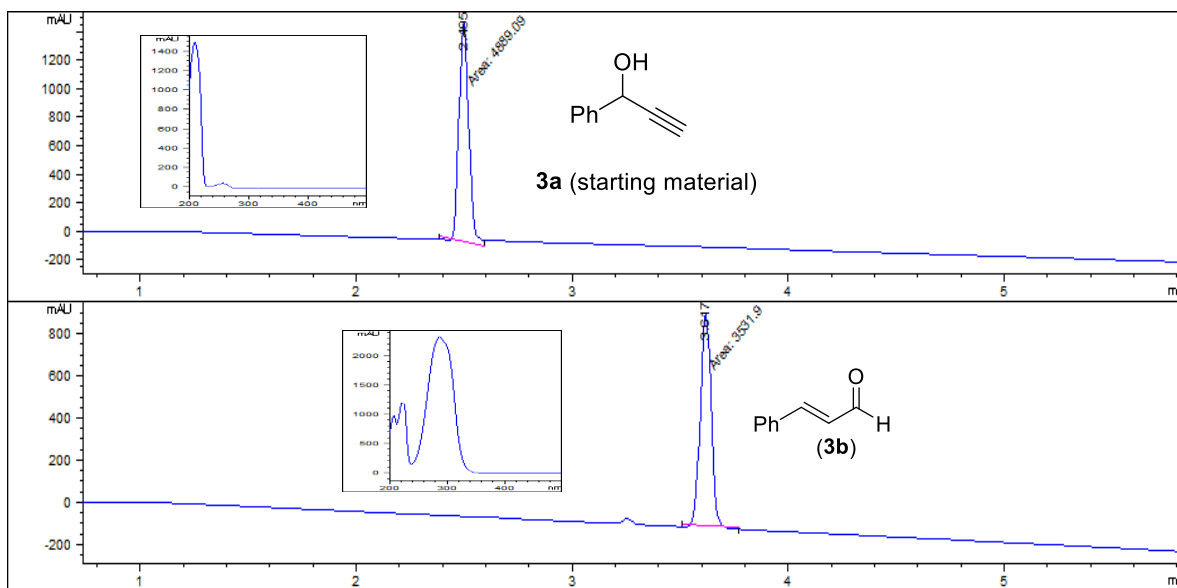
Attachment S1. In process HPLC monitoring for the isomerization of **1a** into **1b** (Table 2, entry 1)



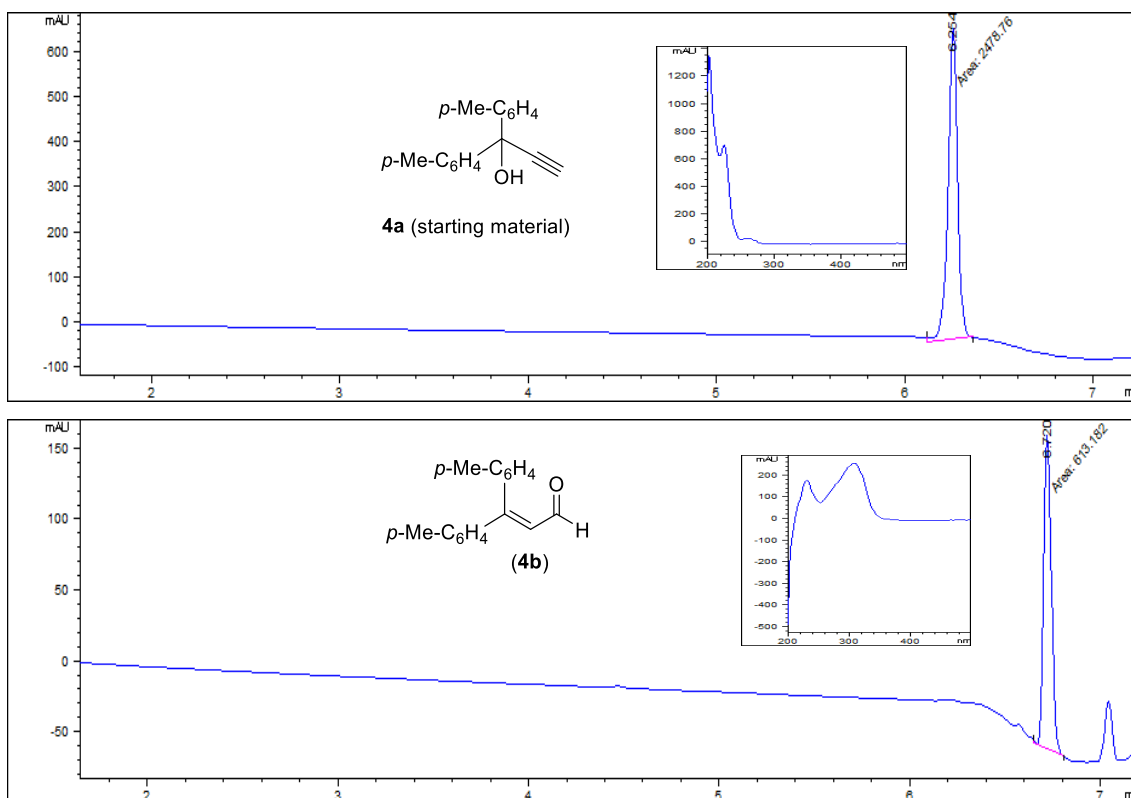
Attachment S2. In process HPLC monitoring for the isomerization of **2a** into **2b** (Table 2, entry 2)



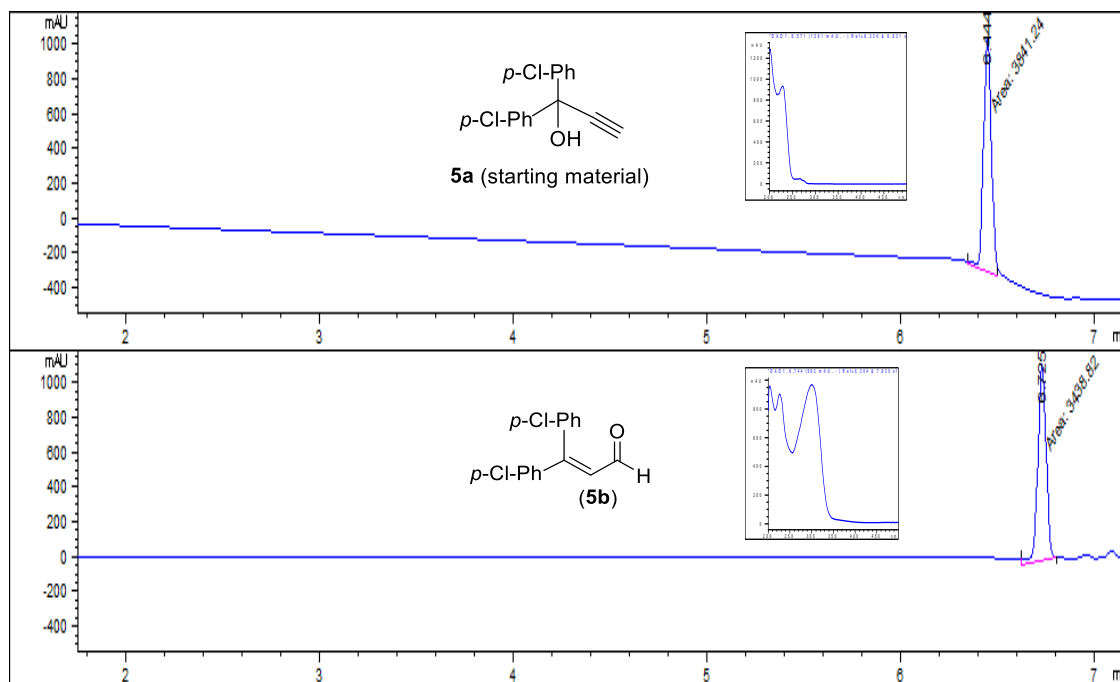
Attachment S3. In process HPLC monitoring for the isomerization of **3a** into **3b** (Table 2, entry 3)



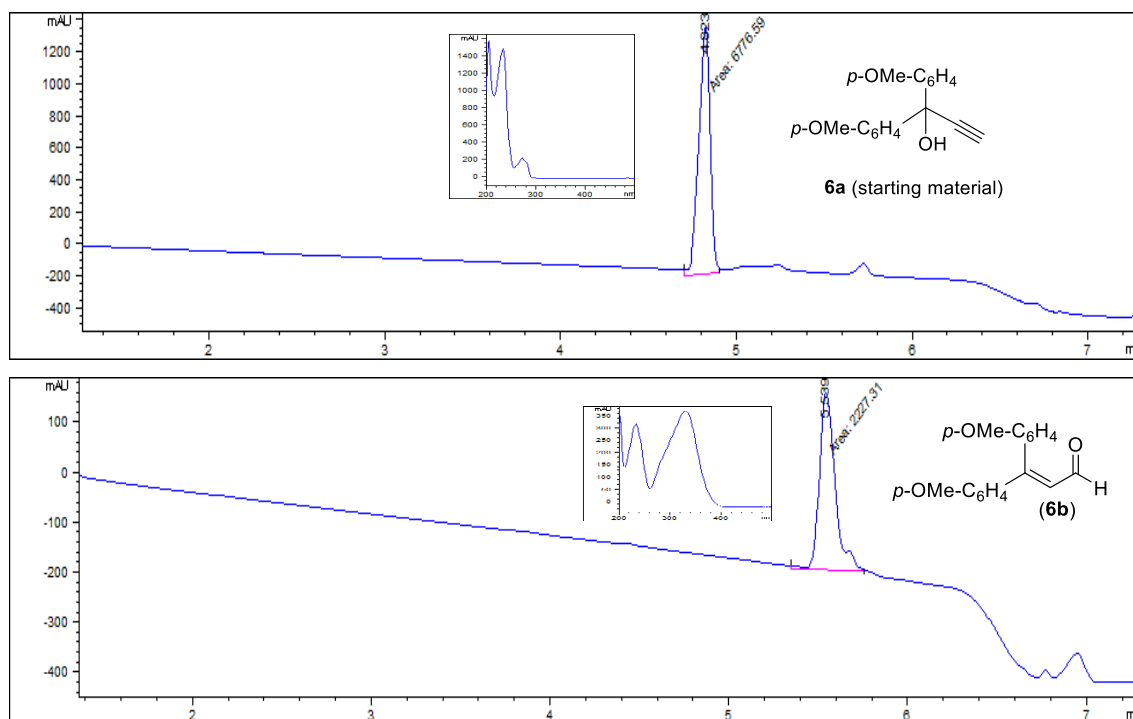
Attachment S4. In process HPLC monitoring for the isomerization of **4a** into **4b** (Table 2, entry 4)



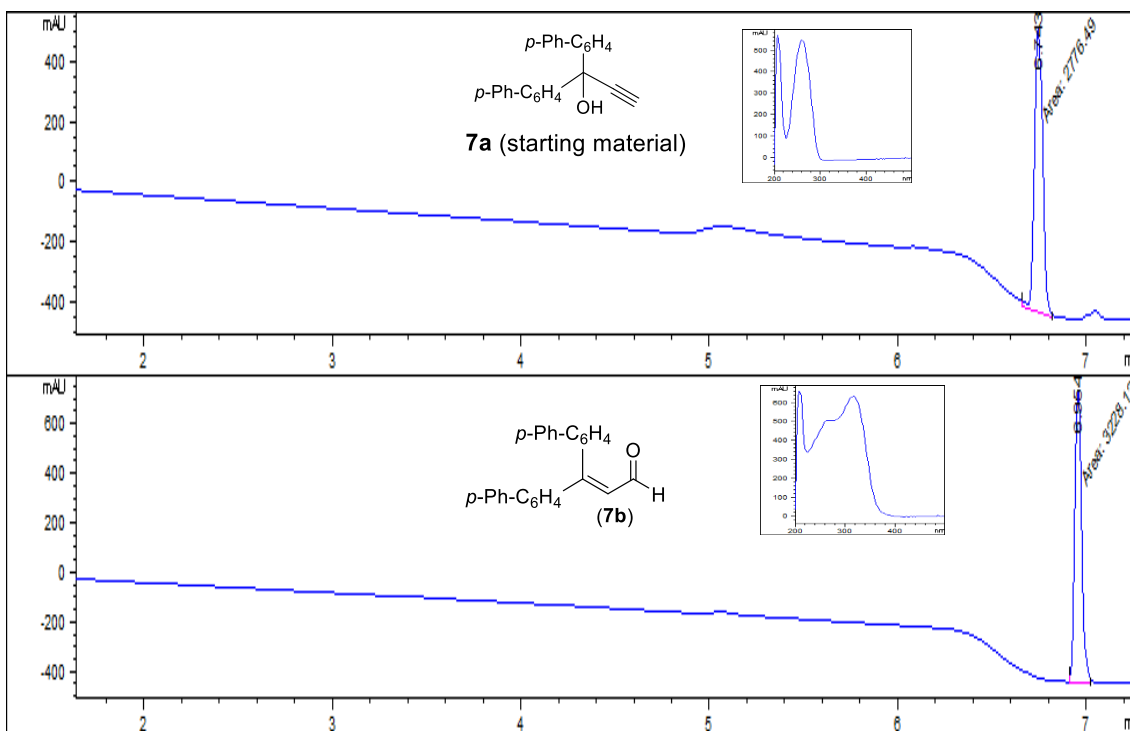
Attachment S5. In process HPLC monitoring for the isomerization of **5a** into **5b** (Table 2, entry 5)



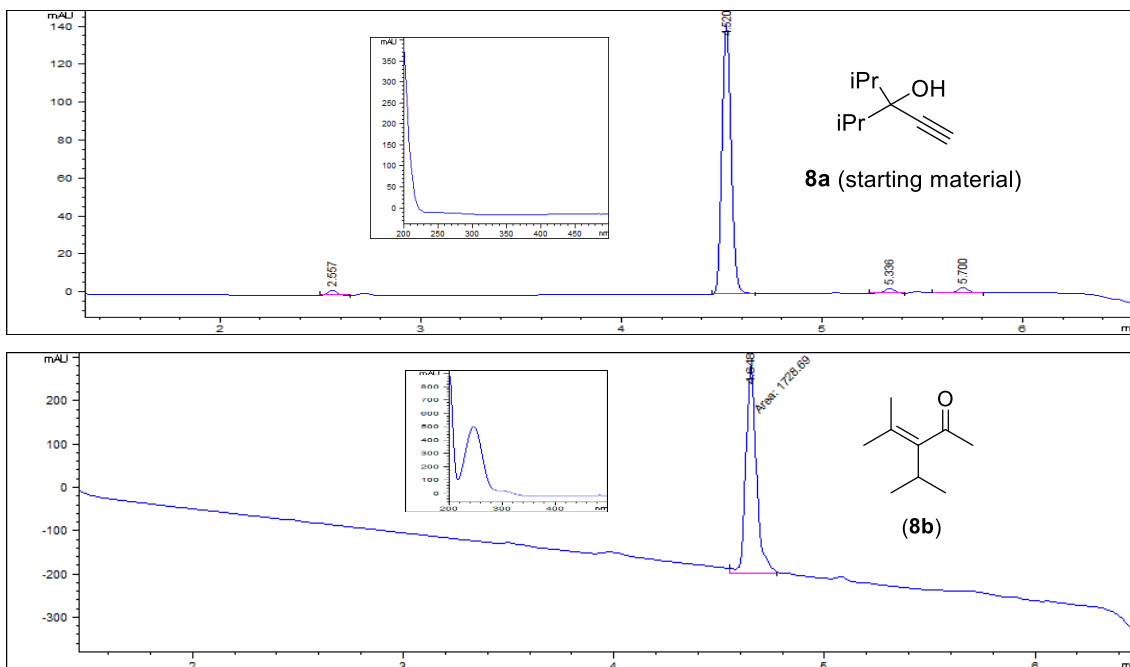
Attachment S6. In process HPLC monitoring for the isomerization of **6a** into **6b** (Table 2, entry 6)



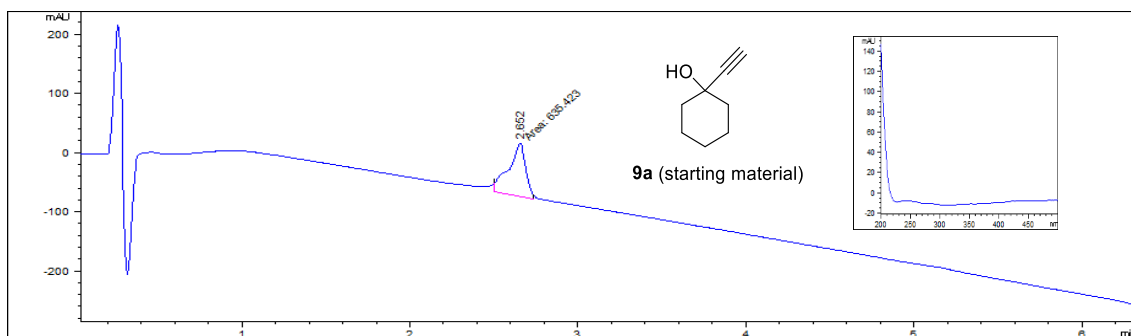
Attachment S7. In process HPLC monitoring for the isomerization of **7a** into **7b** (Table 2, entry 7)



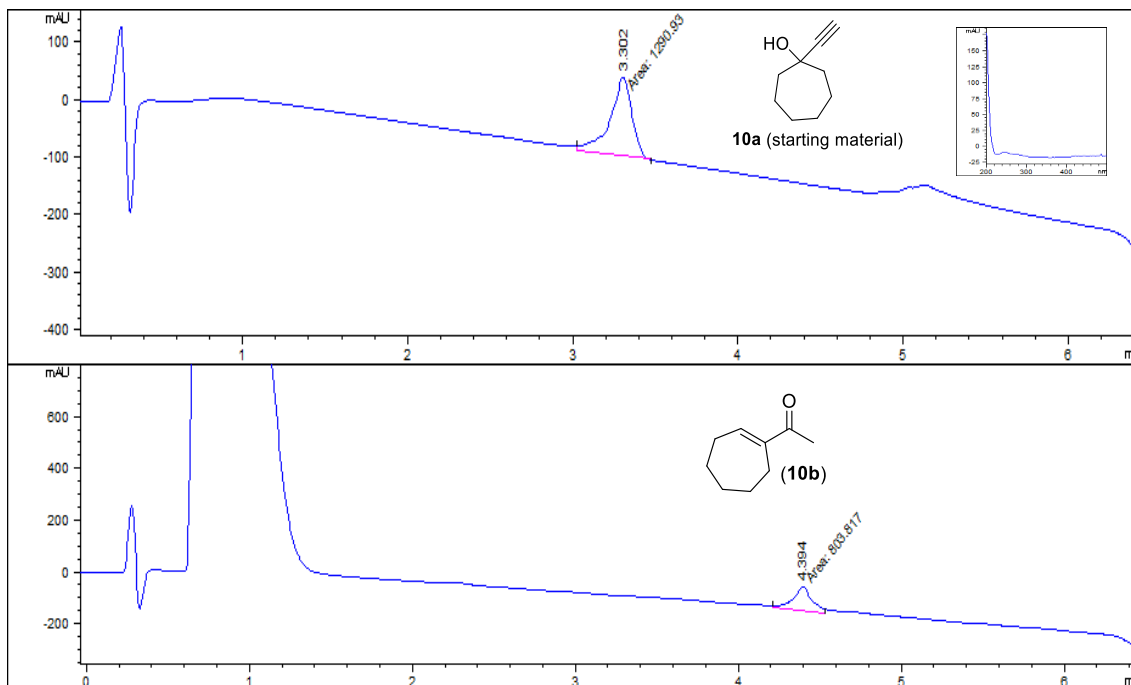
Attachment S8. In process HPLC monitoring for the isomerization of **8a** into **8b** (Table 2, entry 8)



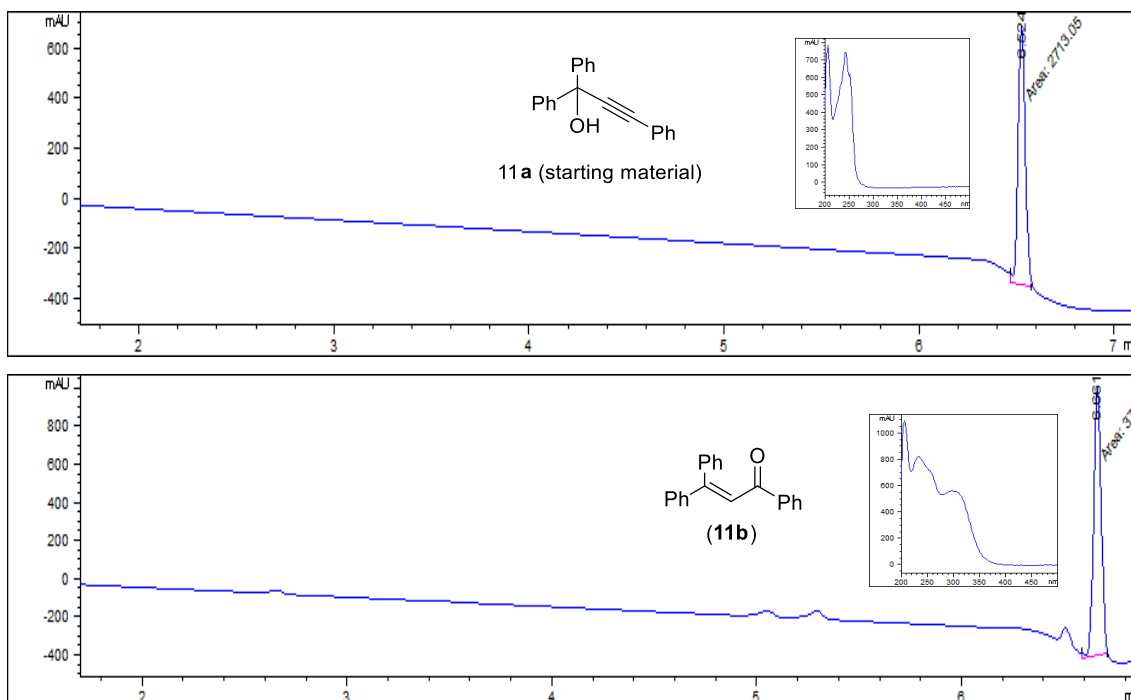
Attachment S9. In process HPLC monitoring for the isomerization of **9a** into **9b** (Table 2, entry 9)



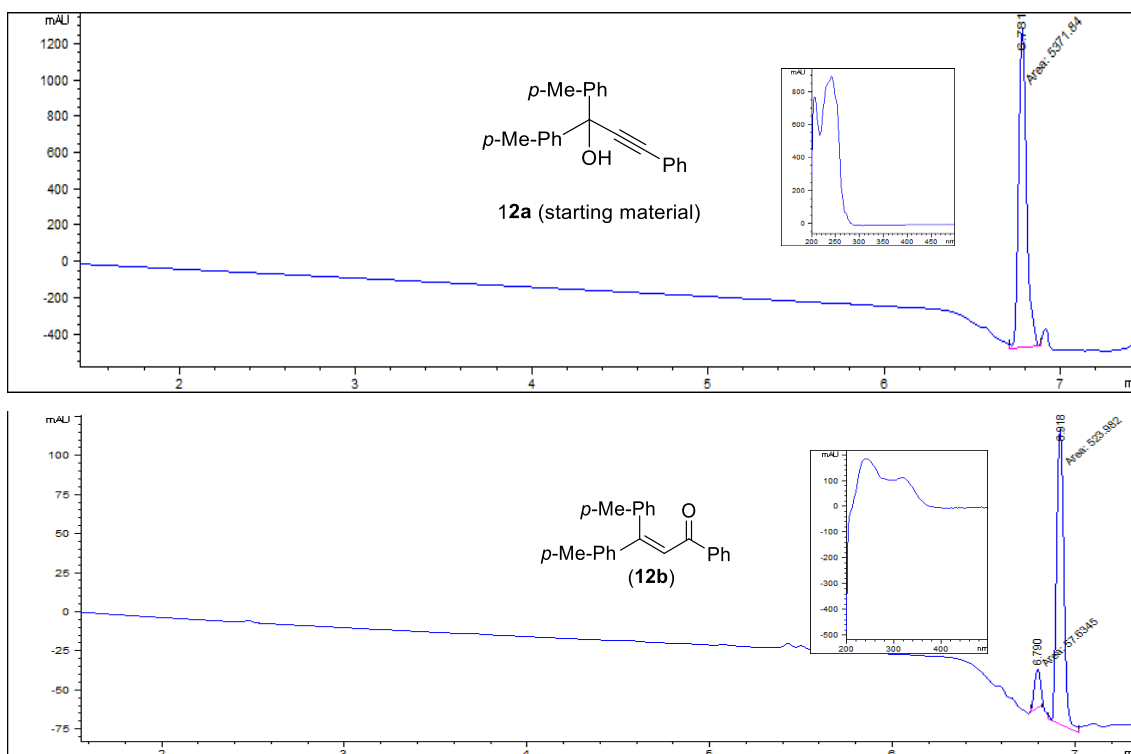
Attachment S10. In process HPLC monitoring for the isomerization of **10a** into **10b** (Table 2, entry 10).



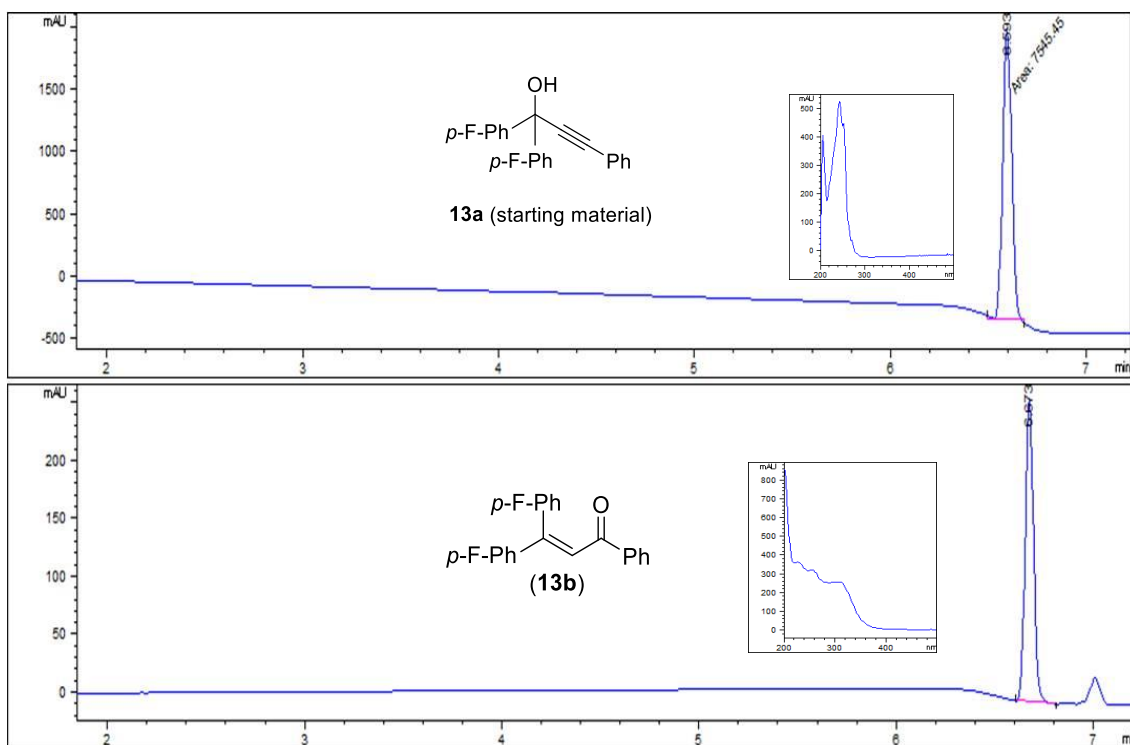
Attachment S11. In process HPLC monitoring for the isomerization of **11a** into **11b** (Table 2, entry 11).



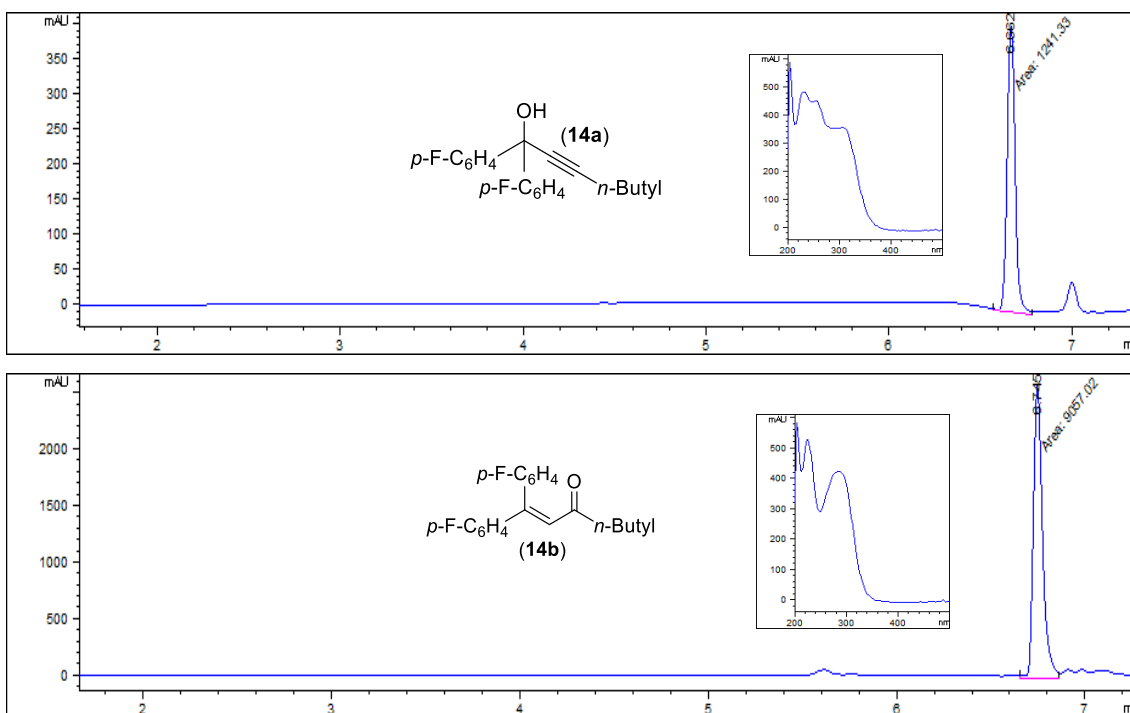
Attachment S12. In process HPLC monitoring for the isomerization of **12a** into **12b** (Table 2, entry 12)



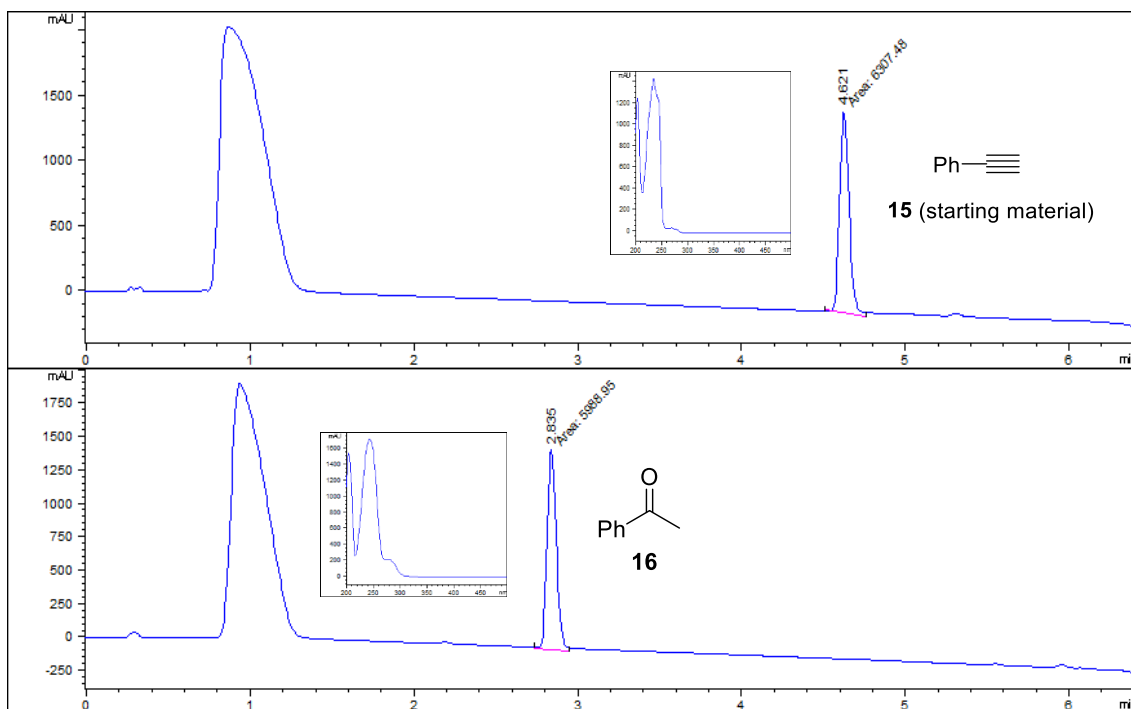
Attachment S13. In process HPLC monitoring for the isomerization of **13a** into **13b** (Table 2, entry 13)



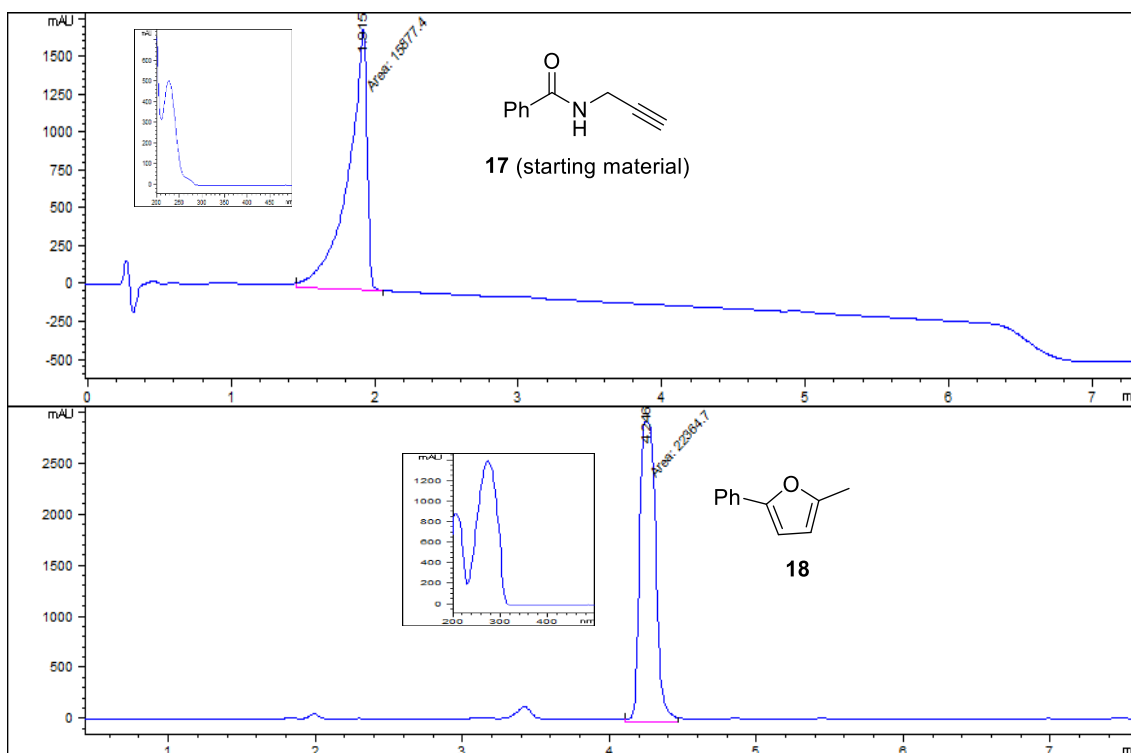
Attachment S14. In process HPLC monitoring for the isomerization of **14a** into **14b** (Table 2, entry 14)



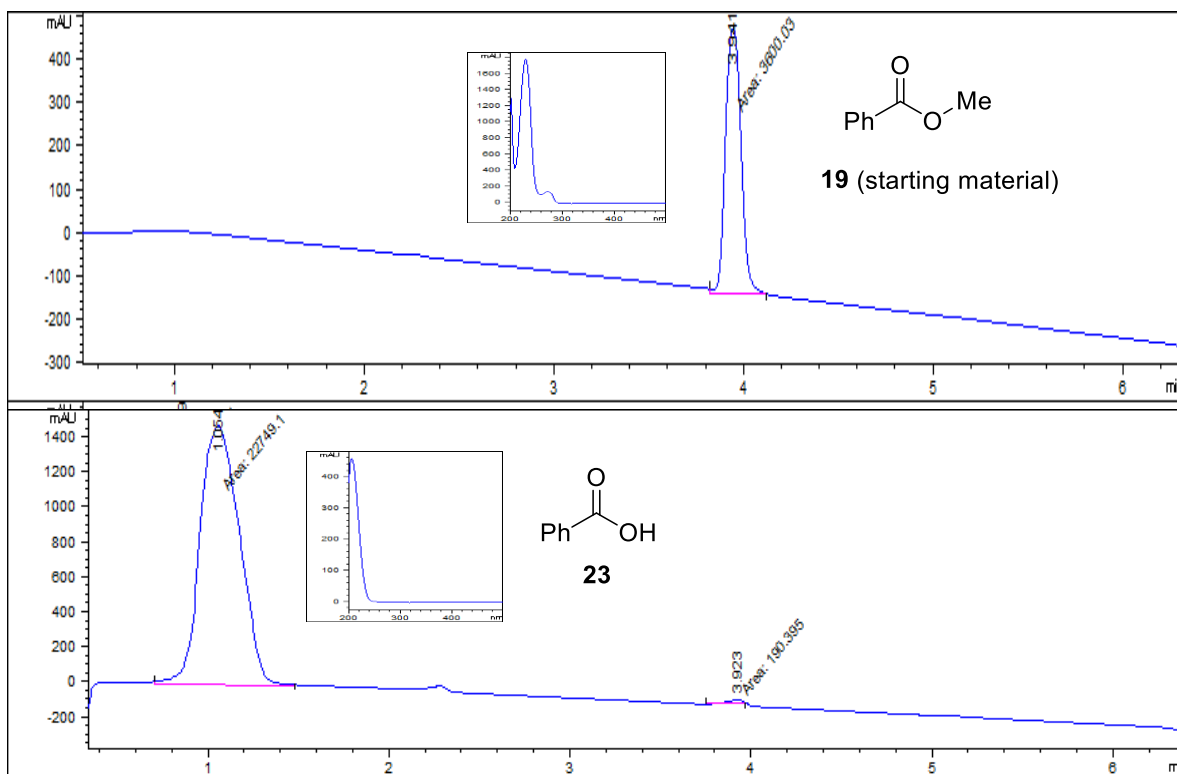
Attachment S15. In process HPLC monitoring for the hydration of **15** into **16** (Scheme 3)



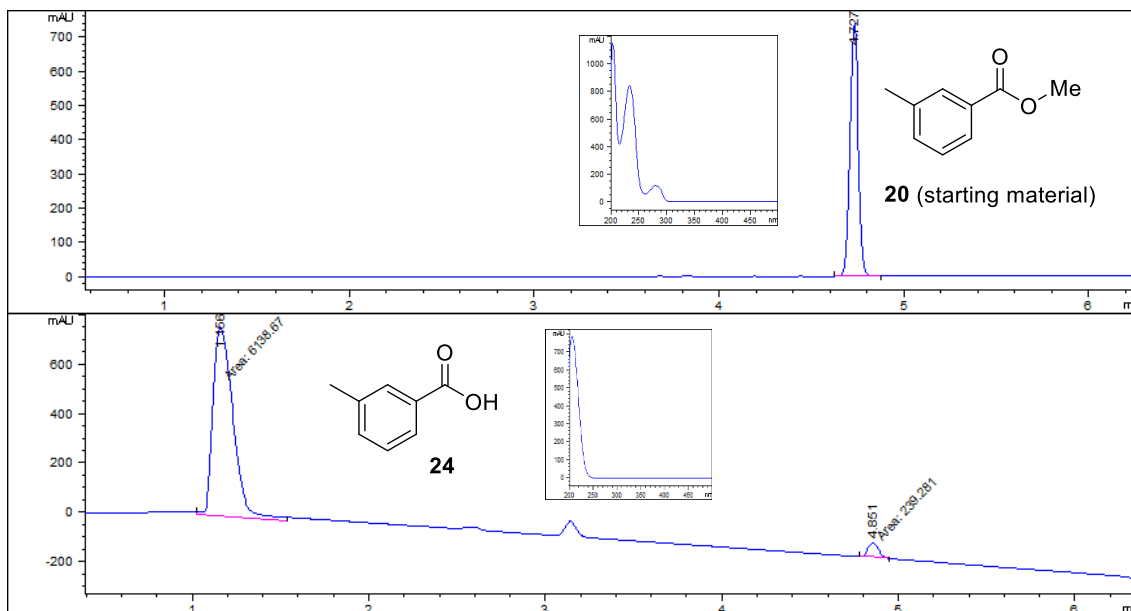
Attachment S16. In process HPLC monitoring for the cyclization of **17** into **18** (Scheme 3)



Attachment S17. In process HPLC monitoring for the hydrolysis of **19** into **23** (Scheme 3)



Attachment S18. In process HPLC monitoring for the hydrolysis of **20** into **24** (Scheme 3)



Attachment S19. In process HPLC monitoring for the isomerization of **11a** into **11b**. Recycling studies of *CDES* through extraction workup with cyrene.

