

Supporting Information for:
Chromatography-Free Wittig Reactions Using a Bifunctional
Polymeric Reagent

Peter Shu-Wai Leung, Yan Teng and Patrick H. Toy*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong,

P. R. of China

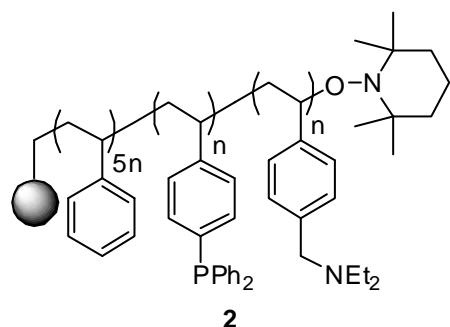
E-mail: phtoy@hku.hk

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General Experimental Procedures

All reagents were obtained from the Acros, Aldrich, or Lancaster chemical companies and were used as received. All moisture sensitive reactions were carried out in dry glassware under a N₂ atmosphere. Tetrahydrofuran was dried using a Solv-Tek purification system employing activated Al₂O₃. All reactions were carried out in dry glassware, and were monitored by TLC analysis using GF₂₅₄ silica gel coated plates. Merck silica gel 60 (230-400 mesh) was used for chromatography. ¹H- and ¹³C-NMR spectra were recorded in CDCl₃ on a Bruker DRX-400 or DRX-500 spectrometer operating at 400 MHz for ¹H and 100/125 MHz for ¹³C analysis. Gel-phase ³¹P-NMR analysis was performed on a Bruker DRX-400 spectrometer operating at 162 MHz. Chemical shift data is expressed in ppm with reference to TMS. Elemental analysis was performed at the Shanghai Institute of Organic Chemistry. HR/LR EI-MS data was recorded on a Finnigan MAT 96 mass spectrometer. The general morphology of the polymer beads was observed by SEM using a Hitachi S-4800 field emission scanning electron microscope. LC-MS data was recorded on a Waters 1525 high-performance liquid chromatography apparatus equipped with a Waters 3100 mass spectrometer and a Waters 2998 photodiode array detector.

Synthesis of RR-PPh₃-NBnEt₂ (2). A solution of sodium ascorbate (8.0 g, 40.4



mmol) in water (190 mL) was shaken with a solution of TEMPO (3.8 g, 24.3 mmol) in Et₂O (150 mL) until the organic layer became pale orange. The Et₂O layer was separated, dried over MgSO₄ and concentrated *in vacuo* to afford

an orange oil. The oil was then dissolved in dry DMF (30 mL) and added dropwise over 10 min to a stirred, septum-capped flask containing NaH (2.1 g, 53.5 mmol, 60% mineral oil dispersion) and DMF (30 mL) under N₂. After 1 h 4-vinylbenzylchloride (2.5 g, 16.2 mmol) was added, and the mixture was stirred for 12 h more at room temperature. The reaction mixture was diluted with Et₂O and washed with H₂O. The crude product was purified by silica gel chromatography (100% hexane) to afford 2,2,6,6-tetramethyl-1-((4-vinylbenzyl)oxy)-piperidine as a brown oil (3.7 g, 83%): ¹H-NMR (300 MHz, CDCl₃) δ 1.14-1.35 (m, 12H), 1.47-1.61 (m, 6H), 4.81 (s, 2H), 5.22 (d, 1H, *J* = 10.9 Hz), 5.73 (d, 1H, *J* = 17.6 Hz), 6.71 (dd, 1H, *J* = 17.6, 10.9 Hz), 7.30-7.40 (m, 4H).

A solution of acacia gum (4.0 g) and NaCl (2.5 g) in warm deionized water (45 °C, 100 mL) was placed in a 150-mL flanged reaction vessel that was equipped with a mechanical stirrer, and deoxygenated by purging with N₂ for 2 h. A solution of the JandaJel cross-linker (0.081 g, 0.3 mmol), 2,2,6,6-tetramethyl-1-((4-vinylbenzyl)oxy)-piperidine (3.7 g, 13.5 mmol), and AIBN (0.076g, 0.46 mmol) in chlorobenzene (4 mL) was injected into the rapidly stirred

aqueous solution. The resulting suspension was heated at 85 °C for 20 h. The crude polymer beads were collected, washed with hot water (3 × 100 mL) and then placed in a Soxhlet extractor and washed with refluxing THF for 24 h. The beads were then washed sequentially with methanol, diethyl ether, and hexanes, and dried *in vacuo* to afford **3** (2.8 g, 74%).

A suspension of **3** (0.6 g, 2 mmol), **5** (5.8 g, 20 mmol), **6** (3.8 g, 20 mmol) and **4** (10.4 g, 100 mmol) was heated at 130 °C under N₂ for 48 h. After cooling to room temperature, the resulting polymer was shaken with CH₂Cl₂ (25 mL) for about 5 min until the resin beads floated loosely. The resin was collected by filtration, placed in a Soxhlet extractor, and washed with refluxing THF for 24 h. The beads were then washed sequentially with methanol, diethyl ether, and hexanes, and dried *in vacuo* to afford **2** (12.4 g, 62%). Elemental analysis was used to determine the phosphine content (3.3%), nitrogen content (1.5%) and thus a loading level of 1.05 mmol PPh₃/g, 1.06 mmol NBnEt₂/g. Gel-phase ³¹P-NMR analysis of **2** confirmed the oxidation state. A single peak at δ -6 ppm was observed.

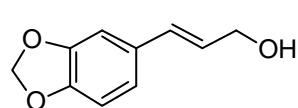
General Procedure for Wittig Reactions

To a solution of the aldehyde (0.5 mmol) and the alkyl halide (0.9 mmol) in CH₂Cl₂ (5 mL) was added **2** (1.0 g, 1.0 mmol). The reaction mixture was stirred at the required temperature until TLC analysis indicated that the aldehyde was completely consumed. The reaction mixture was then filtered through a plug of silica gel. After washing the polymer with CH₂Cl₂ (2 × 50 mL), the combined

filtrate was concentrated *in vacuo* to afford the desired product. All alkene products were characterized by ^1H -, ^{13}C -NMR and LR/HR mass spectroscopy. Stereoisomeric ratios were determined by ^1H -NMR spectroscopy.

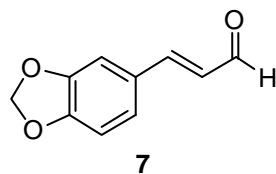
Procedures for the Synthesis of Piperine

(*E*)-3,4-(Methylenedioxy)cinnamyl alcohol.¹ To a solution of **Ba** (1.0 g, 4.5 mmol)



in dry THF (20 mL), was added dropwise diisobutylaluminium hydride (18 mL of 1.0 M solution in THF) at $-78\text{ }^\circ\text{C}$ over 1 h. The mixture was stirred at this temperature for 3 hours more and then it was then quenched by adding water. The reaction mixture was diluted with Et_2O and washed with H_2O . The organic layer was dried over MgSO_4 , filtered and concentrated *in vacuo*. The crude product was purified by silica gel chromatography (20% ethyl acetate/hexane) to afford (*E*)-3,4-(methylenedioxy)cinnamyl alcohol as a white solid (0.5 g, 60%): ^1H -NMR (400 MHz, CDCl_3) δ 1.69 (s, 1H), 4.28 (d, 2H, $J = 6.0$ Hz), 5.95 (s, 2H), 6.16-6.23 (m, 1H), 6.51 (d, 1H, $J = 16.0$ Hz), 6.74-6.82 (m, 2H), 6.92 (s, 1H); ^{13}C -NMR (100 MHz, CDCl_3) δ 63.6, 100.9, 105.6, 108.1, 121.0, 126.5, 130.8, 131.0, 147.2, 147.9; MS for $\text{C}_{10}\text{H}_{10}\text{O}_3$: calcd 178.2, found 178.1.

(E)-3',4'-(Methylenedioxy)cinnamaldehyde (7).¹ To a solution of

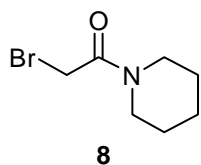


(E)-3,4-(methylenedioxy)cinnamyl alcohol (0.5 g, 2.7 mmol) in CH₂Cl₂ (20 mL) was added MnO₂ (1.5 g, 16.2 mmol) at room temperature. The mixture was stirred for 24 h, after

which the suspension was filtered through a plug of Celite. The filtrate was concentrated *in vacuo* and the crude product was purified by silica gel chromatography (10% ethyl acetate/hexane) to afford 7 as a white solid (0.5 g, 97%):

¹H-NMR (400 MHz, CDCl₃) δ 6.05 (s, 2H), 6.56 (dd, 1H, *J*₁ = 16.0 Hz, *J*₂ = 7.6 Hz), 6.86 (d, 1H, *J* = 8.8 Hz), 7.06-7.08 (m, 2H), 7.38 (d, 1H, *J* = 16.0 Hz), 9.65 (d, 1H, *J* = 7.6 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 101.9, 106.8, 108.8, 125.4, 126.9, 128.6, 148.6, 150.6, 152.7, 193.6; MS for C₁₀H₈O₃: calcd 176.2, found 176.1.

2-Bromo-1-(piperidin-1-yl)ethanone (8). To a solution of piperidine (0.5 mL, 5



mmol) and triethylamine (0.6 mL, 5 mmol) in CH₂Cl₂, bromoacetyl bromide (1.0 g, 5 mmol) was added dropwise at 0 °C. The mixture

was stirred at this temperature for 1 hour. The organic layer was

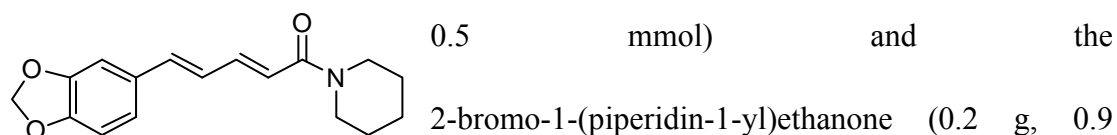
washed with water, saturated ammonium chloride and saturated sodium carbonate solution. Then the organic extracts were dried over MgSO₄. After filtration and

removal of the solvent, the crude product was purified by silica gel chromatography (100% ethyl acetate) to afford 2-bromo-1-(piperidin-1-yl)ethanone as a yellow oil (0.7

g, 65%): ¹H-NMR (400 MHz, CDCl₃) δ 1.57-1.66 (m, 6H), 3.45 (m, 2H), 3.56 (t, 2H, *J* = 5.2 Hz), 3.87 (s, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ 24.1, 25.2, 26.0, 43.1, 47.8,

164.9; MS for C₇H₁₂BrNO: calcd 205.1, found 205.0.

Piperine.¹ To a solution of the (*E*)-3,4-(methylenedioxy)cinnamaldehyde (0.1 g,



mmol) in propan-1-ol (5 mL), **2** (1.0 mmol) was added. The reaction mixture was stirred at the 80 °C for 24 hours, and then filtered through a plug of silica gel. After washing the polymer with CH₂Cl₂ (2 × 50 mL), the combined filtrate was concentrated in vacuo to afford piperine as a yellow solid (0.1 g, 94%): ¹H-NMR (400 MHz, CDCl₃) δ 1.58-1.66 (m, 6H), 3.52-3.63 (m, 4H), 5.96 (s, 2H), 6.43 (d, 1H, *J* = 14.8 Hz), 6.74-6.97 (m, 5H), 7.37-7.42 (m, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ 24.5, 25.5, 26.6, 43.1, 46.7, 101.1, 105.5, 108.3, 119.9, 122.3, 125.2, 130.8, 138.0, 142.3, 147.9, 148.0, 165.2; MS for C₁₇H₁₉NO₃: calcd 285.1, found 285.2.

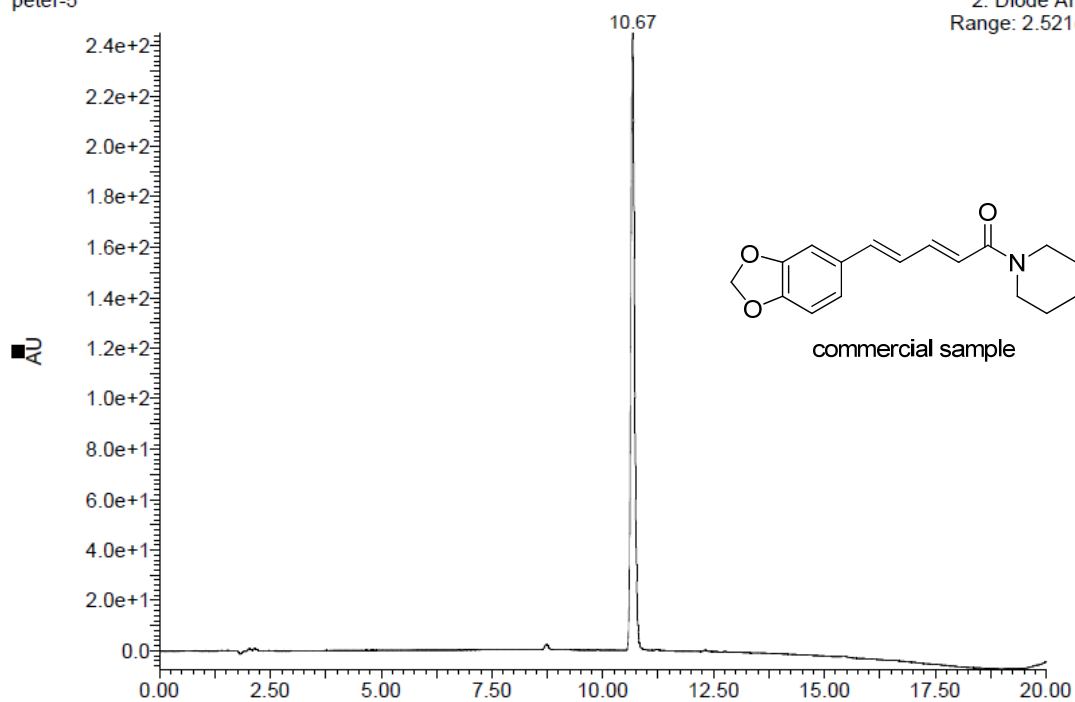
LC-MS Analysis of Synthetic Piperine

Solvent system

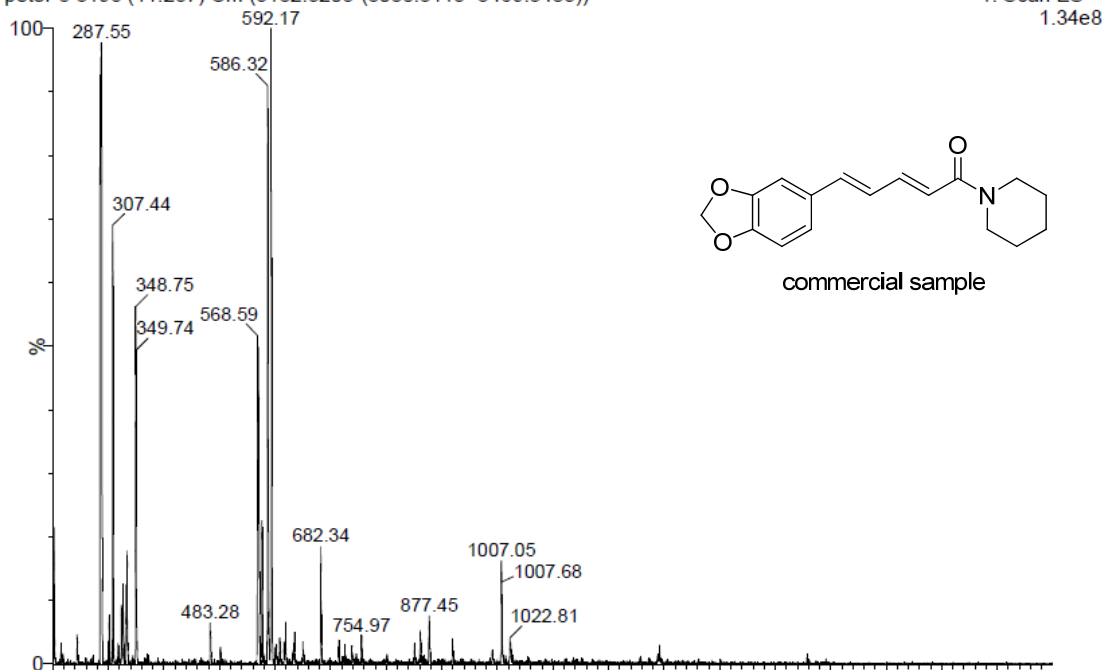
Time (min)	Acetonitrile ^a (%)	Water ^b (%)
0	50	50
15	95	5
20	50	50

^a0.05% TFA in acetonitrile. ^b0.05% TFA in water.

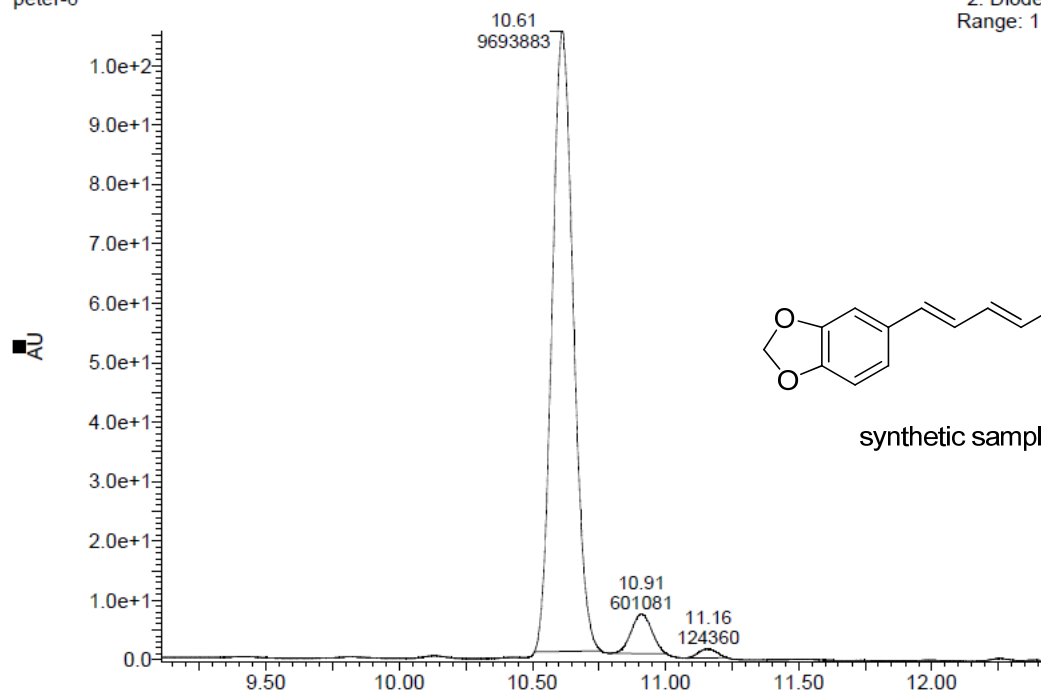
C18, sd
peter-5



C18, p
peter-5 3195 (11.237) Cm (3182:3205-(3088:3113+3469:3483))



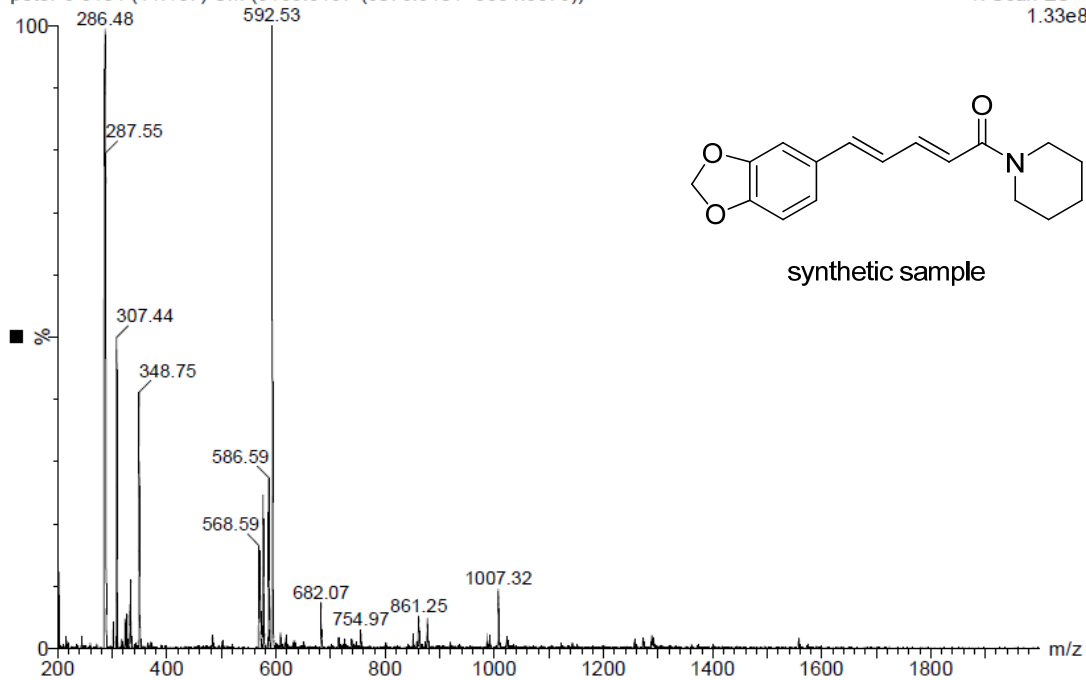
C18, p
peter-6



2: Diode Array
Range: 1.06e+2
Area

synthetic sample

peter-6 3181 (11.187) Cm (3163:3197-(3076:3101+3554:3579))



1: Scan ES+
1.33e8

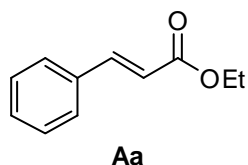
synthetic sample

Results:

Retention Time (min)	Integrated Area	Proportion (%)
10.61 (2 <i>E</i> , 4 <i>E</i>)	9693883	93
10.91 (2 <i>Z</i> , 4 <i>E</i>)	601081	6
11.16 (2 <i>E</i> , 4 <i>Z</i>)	124360	1

Wittig Reaction Product Characterization Data

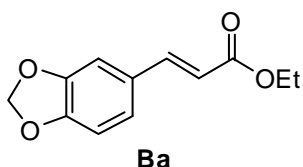
Ethyl cinnamate (Aa).² ¹H-NMR (400 MHz, CDCl₃) δ 1.34 (t, 3H, *J* = 7.2 Hz),



4.27 (q, 2H, *J* = 7.1 Hz), 6.40 (d, 1H, *J* = 16.0 Hz), 7.38-7.40 (m, 3H), 7.52-7.53 (m, 2H), 7.68 (d, 1H, *J* = 16.0 Hz); ¹³C-NMR (125 MHz, CDCl₃) δ 14.4, 60.5, 118.3, 128.1, 128.9, 130.3,

134.5, 144.6, 167.0; MS for C₁₁H₁₂O₂: calcd 176.1, found 176.1.

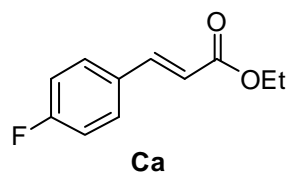
Ethyl 3-(benzo[d][1,3]dioxol-6-yl)acrylate (Ba).² ¹H-NMR (400 MHz, CDCl₃) δ



1.33 (t, 3H, *J* = 7.0 Hz), 4.25 (q, 2H, *J* = 7.2 Hz), 6.00 (s, 2H), 6.26 (d, 1H, *J* = 16.0 Hz), 6.80-6.82 (m, 1H), 7.00-7.03 (m, 2H), 7.57-7.61 (d, 1H, *J* = 16.0 Hz); ¹³C-NMR (100 MHz,

CDCl₃) δ 14.2, 60.3, 101.4, 106.3, 108.4, 116.1, 124.2, 128.7, 144.1, 148.3, 149.4, 167.0; MS for C₁₂H₁₂O₄: calcd 220.2, found 220.1.

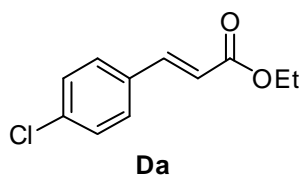
Ethyl 3-(4-fluorophenyl)acrylate (Ca).³ ¹H-NMR (400 MHz, CDCl₃) δ 1.34 (t, 3H,



J = 7.0 Hz), 4.27 (q, 2H, *J* = 7.2 Hz), 6.37 (d, 1H, *J* = 16.0 Hz), 7.06-7.10 (m, 2H), 7.50-7.54 (m, 2H), 7.65 (d, 1H, *J* = 16.0 Hz); ¹³C-NMR (125 MHz, CDCl₃) δ 14.4, 60.6, 116.1 (d,

*J*_{C-F} = 21.8 Hz), 118.2, 130.0 (d, *J*_{C-F} = 8.3 Hz), 130.8, 143.4, 164.0 (d, *J*_{C-F} = 249.6 Hz), 166.9; MS, for C₁₁H₁₁FO₂: calcd 194.2, found 194.1.

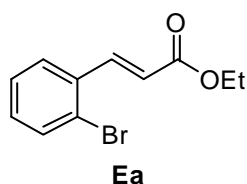
Ethyl 3-(4-chlorophenyl)acrylate (Da).³ ¹H-NMR (400 MHz, CDCl₃) δ 1.34 (t, 3H,



$J = 7.2$ Hz), 4.27 (q, 2H, $J = 7.1$ Hz), 6.41 (d, 1H, $J = 16.0$ Hz), 7.35-7.47 (dd, 4H, $J_1 = 38.4$ Hz, $J_2 = 8.4$ Hz), 7.63 (d, 1H, $J = 16.0$ Hz); ¹³C-NMR (125 MHz, CDCl₃) δ 14.4, 60.7,

119.0, 129.2, 129.3, 133.1, 136.2, 143.2, 166.8; MS for C₁₁H₁₁ClO₂: calcd 210.0, found 210.0.

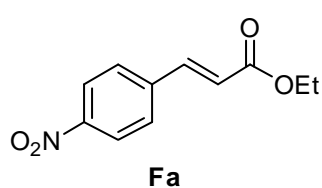
Ethyl 3-(2-bromophenyl)acrylate (Ea).² ¹H-NMR (400 MHz, CDCl₃) δ 1.34 (t, 3H,



$J = 7.2$ Hz), 4.28 (q, 2H, $J = 7.1$ Hz), 6.38 (d, 1H, $J = 16.0$ Hz), 7.21-7.31 (m, 2H), 7.58-7.61 (m, 2H), 8.04 (d, 1H, $J = 16.0$ Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 14.2, 60.6, 121.0, 125.1, 127.5,

127.6, 131.0, 133.3, 134.4, 142.7, 166.2; MS for C₁₁H₁₁BrO₂: calcd 255.1, found 254.0.

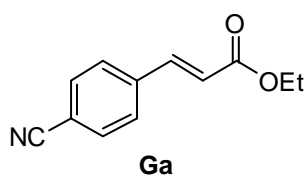
Ethyl 3-(4-nitrophenyl)acrylate (Fa).² ¹H-NMR (400 MHz, CDCl₃) δ 1.36 (t, 3H,



$J = 7.0$ Hz), 4.29 (q, 2H, $J = 7.1$ Hz), 6.55 (d, 1H, $J = 16.0$ Hz), 7.66-7.73 (m, 3H), 8.24-8.26 (m, 2H); ¹³C-NMR (125 MHz, CDCl₃) δ 14.2, 60.9, 122.5, 124.1, 128.6, 140.5,

141.5, 148.4, 165.9; MS for C₁₁H₁₁NO₄: calcd 221.1, found 221.1.

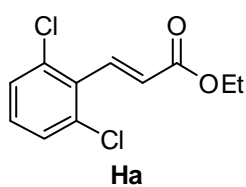
Ethyl 3-(4-cyanophenyl)acrylate (Ga).⁴ ¹H-NMR (400 MHz, CDCl₃) δ 1.34 (t, 3H,



$J = 7.2$ Hz), 4.28 (q, 2H, $J = 7.1$ Hz), 6.52 (d, 1H, $J = 16.0$ Hz), 7.60-7.69 (m, 5H); ¹³C-NMR (100 MHz, CDCl₃) δ 14.1, 60.8, 113.2, 118.2, 121.7, 128.2, 132.4, 138.6, 142.0, 166.0;

MS for C₁₂H₁₁NO₂: calcd 201.2, found 201.1.

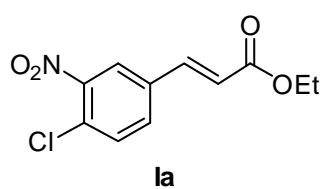
Ethyl 3-(2,6-dichlorophenyl)acrylate (Ha).⁵ ¹H-NMR (400 MHz, CDCl₃) δ 1.34 (t,



3H, $J = 7.0$ Hz), 4.28 (q, 2H, $J = 7.1$ Hz), 6.40 (d, 1H, $J = 16.0$ Hz), 7.26-7.54 (m, 3H), 7.99 (d, 1H, $J = 16.0$ Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 14.1, 60.7, 126.7, 128.6, 129.6, 131.9,

134.8, 137.9, 166.1.; MS for C₁₁H₁₀Cl₂O₂: calcd 245.1, found 244.0.

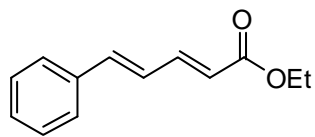
Ethyl 3-(4-chloro-3-nitrophenyl)acrylate (Ia).⁶ ¹H-NMR (400 MHz, CDCl₃) δ



1.34 (t, 3H, $J = 7.2$ Hz), 4.28 (q, 2H, $J = 7.1$ Hz), 6.50 (d, 1H, $J = 16.0$ Hz), 7.59-7.65 (m, 3H), 8.02 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ 14.1, 60.9, 121.7, 124.3,

128.0, 131.7, 132.3, 134.4, 139.2, 140.3, 165.7; HRMS for C₁₁H₁₀ClNO₄: calcd 255.0298, found 255.0292.

Ethyl 5-phenyl-2,4-pent-dienoate (Ja).⁷ ¹H-NMR (400 MHz, CDCl₃) δ 1.32 (t, 3H,

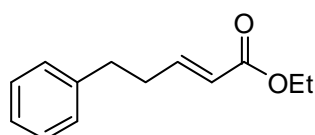


Ja

$J = 7.2$ Hz), 4.23 (q, 2H, $J = 7.1$ Hz), 5.99 (d, 1H, $J = 15.6$ Hz), 6.87-6.89 (m, 2H), 7.30-7.38 (m, 3H), 7.46-7.48 (m, 3H); ¹³C-NMR (125 MHz, CDCl₃) δ 14.3, 60.3, 121.3,

126.2, 127.2, 128.8, 129.0, 136.0, 140.3, 144.5, 167.0; MS for C₁₃H₁₄O₂: calcd 202.3, found 202.1.

Ethyl 5-phenyl-2-pentenoate (Ka).⁸ ¹H-NMR (400 MHz, CDCl₃) δ 1.28 (t, 3H, $J =$

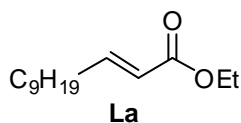


Ka

7.0 Hz), 2.50-2.56 (m, 2H), 2.80 (t, 2H, $J = 7.8$ Hz), 4.18 (q, 2H, $J = 7.1$ Hz), 5.84 (d, 1H, $J = 15.6$ Hz), 6.97-7.04 (m, 1H), 7.18-7.24 (m, 3H), 7.27-7.32 (m, 2H); ¹³C-NMR (100

MHz, CDCl₃) δ 14.1, 33.8, 34.2, 60.1, 121.7, 126.0, 128.2, 128.3, 140.7, 147.9, 166.4; MS for C₁₃H₁₆O₂: calcd 204.3, found 204.1.

Ethyl dodec-2-enoate (La).⁹ ¹H-NMR (400 MHz, CDCl₃) δ 0.88 (t, 3H, $J = 6.6$ Hz),

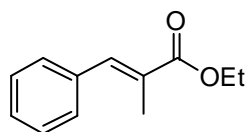


La

1.26-1.29 (m, 17H), 2.16-2.22 (m, 2H), 4.18 (q, 2H, $J = 7.1$ Hz), 5.80 (d, 1H, $J = 15.6$ Hz), 6.93-7.00 (m, 1H); ¹³C-NMR (100

MHz, CDCl₃) δ 14.1, 14.3, 22.7, 28.1, 29.2, 29.3, 29.4, 30.9, 31.9, 32.2, 60.2, 121.2, 149.6, 166.9; MS for C₁₄H₂₆O₂: calcd 226.4, found 227.2.

Ethyl 3-phenyl-2-methyl-2-propenoate (Ab).¹⁰ ¹H-NMR (400 MHz, CDCl₃) δ



Ab

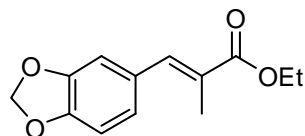
1.26 (t, 3H, *J* = 7.0 Hz), 2.03 (s, 3H), 4.19 (q, 2H, *J* = 7.2 Hz),

7.22-7.31 (m, 5H), 7.61 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ

13.9, 14.2, 60.7, 128.1, 128.2, 128.5, 129.5, 135.8, 138.5, 168.6;

MS for C₁₂H₁₄O₂: calcd 190.2, found 190.1.

Ethyl 3-(benzo[d][1,3]dioxol-6-yl)-2-methyl-2-propenoate (Bb).¹¹ ¹H-NMR (400



Bb

MHz, CDCl₃) δ 1.36 (t, 3H, *J* = 7.2 Hz), 2.13 (s, 3H), 4.27

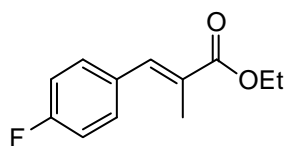
(q, 2H, *J* = 7.2 Hz), 6.00 (s, 2H), 6.75-6.95 (m, 3H), 7.61 (s,

1H); ¹³C-NMR (100 MHz, CDCl₃) δ 14.2, 14.5, 60.9, 101.4,

108.4, 109.7, 124.7, 127.1, 130.1, 138.5, 147.8, 168.9; MS for C₁₃H₁₄O₄: calcd 234.1,

found 234.2.

Ethyl 3-(4-fluorophenyl)-2-methyl-2-propenoate (Cb).¹² ¹H-NMR (400 MHz,



Cb

CDCl₃) δ 1.34 (t, 3H, *J* = 7.0 Hz), 2.10 (s, 3H), 4.26 (q, 2H, *J*

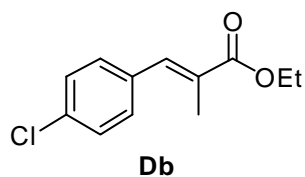
= 7.1 Hz), 7.05-7.09 (m, 2H), 7.36-7.39 (m, 2H), 7.64 (s, 1H);

¹³C-NMR (100 MHz, CDCl₃) δ 14.1, 14.4, 61.0, 115.6 (d, *J*_{C-F}

= 21.5 Hz), 128.6, 131.6 (d, *J*_{C-F} = 8.2 Hz), 132.1 (d, *J*_{C-F} = 3.4 Hz), 137.6, 162.5 (d,

*J*_{C-F} = 247.5 Hz), 168.7; MS for C₁₂H₁₃FO₂: calcd 208.2, found 208.1.

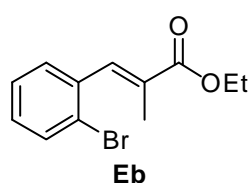
Ethyl 3-(4-chlorophenyl)-2-methyl-2-propenoate (Db).¹³ ¹H-NMR (400 MHz,



CDCl₃) δ 1.35 (t, 3H, *J* = 7.2 Hz), 2.09 (s, 3H), 4.27 (q, 2H, *J* = 7.1 Hz), 7.31-7.37 (m, 4H), 7.62 (s, 1H); ¹³C-NMR (125 MHz, CDCl₃) δ 13.9, 14.2, 60.8, 128.5, 129.1, 130.7, 134.0,

134.2, 137.1, 168.3; MS for C₁₂H₁₃ClO₂: calcd 224.1, found 224.1.

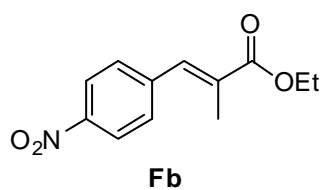
Ethyl 3-(2-bromophenyl)-2-methyl-2-propenoate (Eb).¹⁴ ¹H-NMR (400 MHz,



CDCl₃) δ 1.27 (t, 3H, *J* = 7.0 Hz), 1.89 (s, 3H), 4.20 (q, 2H, *J* = 6.9 Hz), 7.09-7.24 (m, 3H), 7.52 (d, 1H, *J* = 8.0 Hz), 7.62 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ 14.1, 14.4, 61.1, 124.3, 127.1,

129.6, 130.5, 130.6, 132.9, 136.5, 138.1, 168.2; MS for C₁₂H₁₃BrO₂: calcd 269.1, found 268.0.

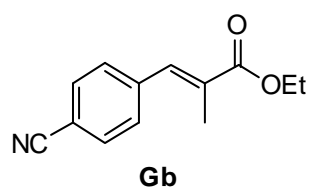
Ethyl 3-(4-nitrophenyl)-2-methyl-2-propenoate (Fb).¹⁵ ¹H-NMR (400 MHz,



CDCl₃) δ 1.36 (t, 3H, *J* = 7.2 Hz), 2.12 (s, 3H), 4.30 (q, 2H, *J* = 7.2 Hz), 7.53 (d, 2H, *J* = 8.8 Hz), 7.69 (s, 1H), 8.25 (d, 2H, *J* = 8.4 Hz); ¹³C-NMR (125 MHz, CDCl₃) δ 14.0, 14.1,

61.2, 123.5, 130.0, 132.2, 135.8, 142.4, 147.0, 167.7; MS for C₁₂H₁₃NO₄: calcd 235.2, found 235.1.

Ethyl 3-(4-cyanophenyl)-2-methyl-2-propenoate (Gb).¹⁶ ¹H-NMR (400 MHz,

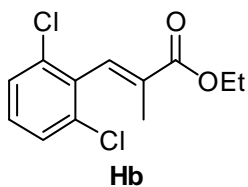


CDCl₃) δ 1.36 (t, 3H, *J* = 7.2 Hz), 2.11 (s, 3H), 4.29 (q, 2H, *J* = 7.1 Hz), 7.48 (d, 2H, *J* = 8.0 Hz), 7.66-7.70 (m, 3H);

¹³C-NMR (100 MHz, CDCl₃) δ 14.0, 14.1, 61.1, 111.5,

118.4, 129.9, 131.6, 132.0, 136.2, 140.4, 167.7; MS for C₁₃H₁₃NO₂: calcd 215.2, found 215.1.

Ethyl 3-(2,6-dichlorophenyl)-2-methyl-2-propenoate (Hb).¹⁷ ¹H-NMR (400 MHz,

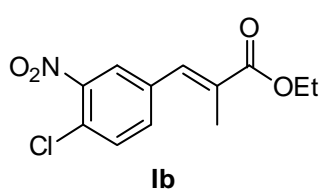


CDCl₃) δ 1.36 (t, 3H, *J* = 7.2 Hz), 1.98 (s, 3H), 4.28 (q, 2H, *J* = 7.2 Hz), 7.26-7.28 (m, 2H), 7.44 (s, 1H), 7.68 (s, 1H); ¹³C-NMR

(100 MHz, CDCl₃) δ 14.1, 14.3, 60.9, 127.8, 129.2, 132.0, 133.4,

133.8, 134.2, 167.2; HRMS for C₁₂H₁₂Cl₂O₂: calcd 258.0214, found 258.0215.

Ethyl 3-(4-chloro-3-nitrophenyl)-2-methyl-2-propenoate (Ib).¹⁸ ¹H-NMR (400

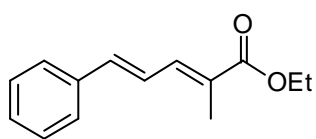


MHz, CDCl₃) δ 1.34 (t, 3H, *J* = 7.0 Hz), 2.10 (s, 3H), 4.27 (q, 2H, *J* = 6.8 Hz), 7.53-7.59 (m, 3H), 7.88 (s, 1H);

¹³C-NMR (100 MHz, CDCl₃) δ 13.9, 14.1, 61.2, 126.0,

126.3, 131.7, 131.9, 133.6, 134.4, 135.8, 147.7, 167.5; HRMS for C₁₂H₁₂ClNO₄: calcd 269.0455 found 269.0447.

Ethyl 2-methyl-5-phenyl-2,4-pent-dienoate (Jb).¹⁹ ¹H-NMR (400 MHz, CDCl₃) δ



Jb

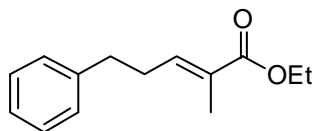
1.32 (t, 3H, *J* = 7.2 Hz), 2.04 (s, 3H), 4.22 (q, 2H, *J* = 7.1 Hz), 6.84 (d, 1H, *J* = 15.2 Hz), 7.01-7.08 (m, 1H),

7.31-7.35 (m, 4H), 7.45-7.47 (m, 2H); ¹³C-NMR (125 MHz,

CDCl₃) δ 12.8, 14.2, 60.5, 123.8, 126.9, 127.3, 128.5, 128.6, 136.5, 138.1, 138.8,

168.2; MS for C₁₄H₁₆O₂: calcd 216.3, found 216.1.

Ethyl 2-methyl-5-phenylpent-2-enoate (Kb).²⁰ ¹H-NMR (400 MHz, CDCl₃) δ



Kb

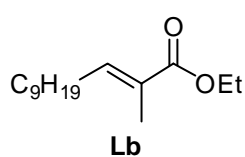
1.32 (t, 3H, *J* = 7.2 Hz), 1.82 (s, 3H), 2.52 (q, 2H, *J* = 7.6 Hz), 2.78 (t, 2H, *J* = 7.8 Hz), 4.21 (q, 2H, *J* = 7.2 Hz),

6.83-6.87 (m, 1H), 7.21-7.32 (m, 5H); ¹³C-NMR (125 MHz,

CDCl₃) δ 12.3, 14.3, 30.6, 34.8, 60.5, 126.1, 128.4, 128.5, 140.9, 141.3, 168.2; MS

for C₁₄H₁₈O₂: calcd 218.3, found 218.2.

Ethyl 2-methyldodec-2-enoate (Lb).²¹ ¹H-NMR (400 MHz, CDCl₃) δ 0.89 (s, 3H),



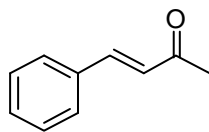
Lb

1.31 (m, 17H), 1.83 (s, 3H), 2.16-2.18 (m, 2H), 4.20 (q, 2H, *J* = 7.1 Hz), 6.77 (t, 1H, *J* = 7.0 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ

12.5, 14.2, 14.4, 22.8, 28.7, 28.8, 29.4, 29.5, 29.6, 29.7, 32.0,

60.5, 127.8, 142.6, 168.5; MS for C₁₅H₂₈O₂: calcd 240.2, found 240.2.

4-Phenylbut-3-en-2-one (Ac).²² ¹H-NMR (400 MHz, CDCl₃) δ 2.39 (s, 3H), 6.73



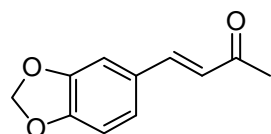
Ac

(d, 1H, $J = 16.4$ Hz), 7.40-7.42 (m, 3H), 7.51-7.57 (m, 3H);

¹³C-NMR (100 MHz, CDCl₃) δ 27.4, 127.0, 128.1, 128.8, 130.4,

134.3, 143.3, 198.3; MS for C₁₀H₁₀O: calcd 146.2, found 145.1.

4-(Benzo[d][1,3]dioxol-6-yl)-but-3-en-2-one (Bc).²³ ¹H-NMR (400 MHz, CDCl₃)



Bc

δ 2.33 (s, 3H), 5.99 (s, 2H), 6.53 (d, 1H, $J = 16.4$ Hz), 6.80 (d,

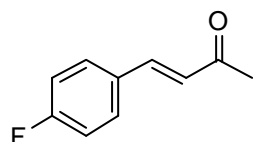
1H, $J = 8.0$ Hz) 6.99-7.03 (m, 2H), 7.40 (d, 1H, $J = 16.0$ Hz);

¹³C-NMR (100 MHz, CDCl₃) δ 27.3, 101.5, 106.3, 108.5,

124.7, 125.1, 128.6, 143.1, 148.3, 149.7, 198.1; MS for C₁₁H₁₀O₃: calcd 190.1, found

190.0.

4-(4-Fluorophenyl)but-3-en-2-one (Cc).²⁴ ¹H-NMR (400 MHz, CDCl₃) δ 2.40 (s,



Cc

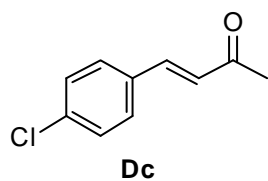
3H), 6.64 (d, 1H, $J = 16.0$ Hz), 7.06-7.10 (m, 2H), 7.46-7.55 (m,

3H); ¹³C-NMR (100 MHz, CDCl₃) δ 27.4, 116.0 (d, $J_{C-F} = 21.8$

Hz), 126.7, 130.0, (d, $J_{C-F} = 8.5$ Hz), 130.5 (d, $J_{C-F} = 3.2$ Hz),

142.0, 163.8 (d, $J_{C-F} = 250.2$ Hz), 198.1; MS for C₁₀H₉FO: calcd 164.2, found 164.1.

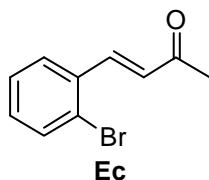
4-(4-Chlorophenyl)but-3-en-2-one (Dc).²⁴ ¹H-NMR (400 MHz, CDCl₃) δ 2.30 (s,



3H), 6.59 (d, 1H, *J* = 16.4 Hz), 7.27-7.29 (m, 2H), 7.35-7.40 (m, 3H); ¹³C-NMR (100 MHz, CDCl₃) δ 27.5, 127.3, 129.1, 129.2, 132.8, 136.3, 141.7, 198.0; MS for C₁₀H₉ClO: calcd 180.6,

found 180.1.

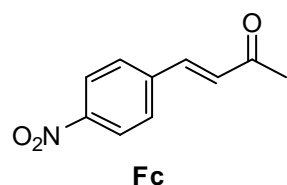
4-(2-Bromophenyl)but-3-en-2-one (Ec).²⁵ ¹H-NMR (400 MHz, CDCl₃) δ 2.42 (s,



3H), 6.62 (d, 1H, *J* = 16.4 Hz), 7.24-7.34 (m, 2H), 7.61 (m, 2H), 7.88 (d, 1H, *J* = 16.0 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 27.1, 125.4, 127.6, 127.7, 129.7, 131.3, 133.3, 134.3, 141.7, 198.1; MS

for C₁₀H₉BrO₂: calcd 224.0, found 226.0.

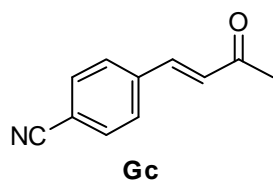
4-(4-Nitrophenyl)but-3-en-2-one (Fc).²⁶ ¹H-NMR (400 MHz, CDCl₃) δ 2.42 (s,



3H), 6.82 (d, 1H, *J* = 16.4 Hz), 7.53 (d, 1H, *J* = 16.4 Hz), 7.70 (d, 2H, *J* = 8.8 Hz), 8.23 (d, 2H, *J* = 8.8 Hz); ¹³C-NMR (125 MHz, CDCl₃) δ 28.1, 124.2, 128.8, 130.4, 140.1, 140.7, 148.6,

197.5; MS for C₁₀H₉NO₃: calcd 191.1, found 191.1.

4-(4-Cyanophenyl)but-3-en-2-one (Gc).²⁷ ¹H-NMR (400 MHz, CDCl₃) δ 2.40 (s,



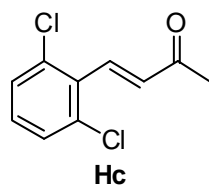
3H), 6.77 (d, 1H, *J* = 16.0 Hz), 7.48 (d, 1H, *J* = 16.4 Hz),

7.62-7.69 (m, 4H); ¹³C-NMR (100 MHz, CDCl₃) δ 28.0, 113.6,

118.3, 128.6, 129.8, 132.7, 138.8, 140.6, 197.6; MS for

C₁₁H₉NO₂: calcd 171.2, found 171.1.

4-(2,6-Dichlorophenyl)but-3-en-2-one (Hc).²⁸ ¹H-NMR (400 MHz, CDCl₃) δ 2.42



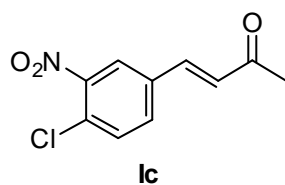
(s, 3H), 6.80 (d, 1H, *J* = 16.8 Hz), 7.18-7.22 (m, 1H), 7.36-7.38 (m,

2H), 7.60 (d, 1H, *J* = 16.8 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ 27.5,

128.7, 129.8, 131.9, 134.8, 134.9, 136.7, 198.0; HRMS for

C₁₀H₈Cl₂O: calcd 213.9952, found 213.9941.

4-(4-Chloro-3-nitrophenyl)but-3-en-2-one (Ic).²⁹ ¹H-NMR (400 MHz, CDCl₃) δ



2.41 (s, 3H), 6.77 (d, 1H, *J* = 16.0 Hz), 7.46 (d, 1H, *J* = 16.4

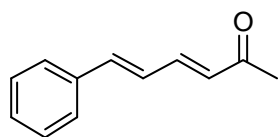
Hz), 7.58-7.61 (m, 1H), 7.66-7.68 (m, 1H), 8.04 (s, 1H);

¹³C-NMR (100 MHz, CDCl₃) δ 28.2, 124.7, 128.5, 129.6,

132.0, 132.3, 132.6, 134.7, 138.9, 197.2; HRMS for C₁₀H₈ClNO₃: calcd 225.0193,

found 225.0186.

6-Phenylhex-3,5-dien-2-one (Jc).³⁰ ¹H-NMR (400 MHz, CDCl₃) δ 2.34 (s, 3H),

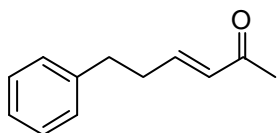


Jc

6.28 (d, 1H, $J = 15.6$ Hz), 6.91-7.00 (m, 2H), 7.28-7.39 (m, 4H), 7.48-7.57 (m, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ 27.4, 126.7, 127.3, 128.9, 129.2, 130.5, 136.0, 141.3, 143.5, 198.4;

MS for C₁₂H₁₂O: calcd 172.2, found 172.1.

6-Phenylhex-3-en-2-one (Kc).³⁰ ¹H-NMR (400 MHz, CDCl₃) δ 2.22 (s, 3H), 2.54

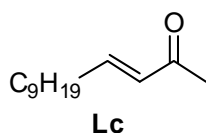


Kc

(q, 2H, $J = 7.1$ Hz), 2.78 (t, 2H, $J = 7.6$ Hz), 6.08 (d, 1H, $J = 16.0$ Hz), 6.78-6.85 (m, 1H), 7.17-7.30 (m, 5H); ¹³C-NMR (100 MHz, CDCl₃) δ 26.8, 34.0, 34.3, 126.1, 128.2, 128.4,

131.6, 140.5, 147.0, 198.4; MS for C₁₂H₁₄O: calcd 174.2, found 174.1.

Dodec-3-en-2-one (Lc).³¹ ¹H-NMR (400 MHz, CDCl₃) δ 0.88-0.90 (m, 3H), 1.28



Lc

(m, 16H), 2.26 (s, 3H), 6.09 (d, 1H, $J = 16.0$ Hz), 6.79-6.86 (m, 1H); ¹³C-NMR (125 MHz, CDCl₃) δ 14.1, 22.7, 26.9, 28.1, 29.4, 29.5,

29.7, 31.0, 31.9, 32.5, 131.3, 148.7, 198.8; HRMS for C₁₃H₂₄O: calcd 196.1827, found 196.1824.

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