Supporting Information

Substrate-selective C-H functionalization for the preparation of organosulfur compounds from crude oil-derived components

Konstantin V. Luzyanin,[1] Aleksei N. Marianov,[1] Pavel G. Kislitsin,[2] Valentine P. Ananikov[1,2*]

[1]*Saint Petersburg State University, Universitetsky Prospekt 26, Stary Petergof, 198504, Russia*

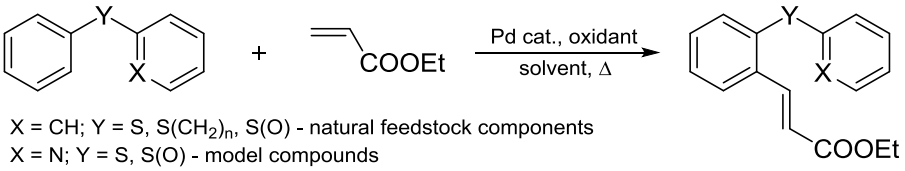
[2]*Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospekt 47, Moscow, 119991, Russia; e-mail: val@ioc.ac.ru*

Experimental Section

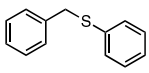
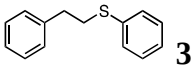
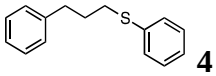
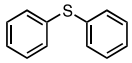
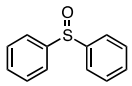
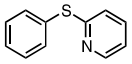
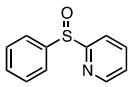
Materials and measurements. The substrates used in the alkenylation studies [i.e., 2-(phenylthio)pyridine, [1] 2-(phenylsulfinyl)pyridine, [2] benzyl(phenyl)sulfane, [3, 4] phenyl(2-phenylethyl)sulfane, [5] and phenyl(3-phenylpropyl)sulfane [6]] were prepared according to previously described protocols. The *cis*-$[PdCl_2(MeCN)_2]$ and *cis*-$[PdCl_2(CyNC)_2]$ complexes were synthesized via established procedures.[7] Electrospray ionization mass-spectra were obtained on either a BRUKER maXis (ESI-QTOF) or VARIAN 500-MS LC ion trap mass-spectrometer in either MeOH or MeCN. EI mass spectra of the organic product mixtures from the catalytic studies were acquired on a Shimadzu GCMS-QP2010 SE. The ^{1}H and ^{13}C spectra were recorded on Bruker Avance 400 MHz and Bruker DPX 300 MHz spectrometers at ambient temperature.

It should be noted that observed selectivity and yields can be greatly effected by the presence of thiols and other impurities in the substrates. To our experience, commercially available and synthesized sulfides may contain some impurities and careful control may be required. Catalyst poisoning by thiols is a well-known feature for sulfur species.[8]

Table S1. Comparative alkenylation of the individual substrates.[a]

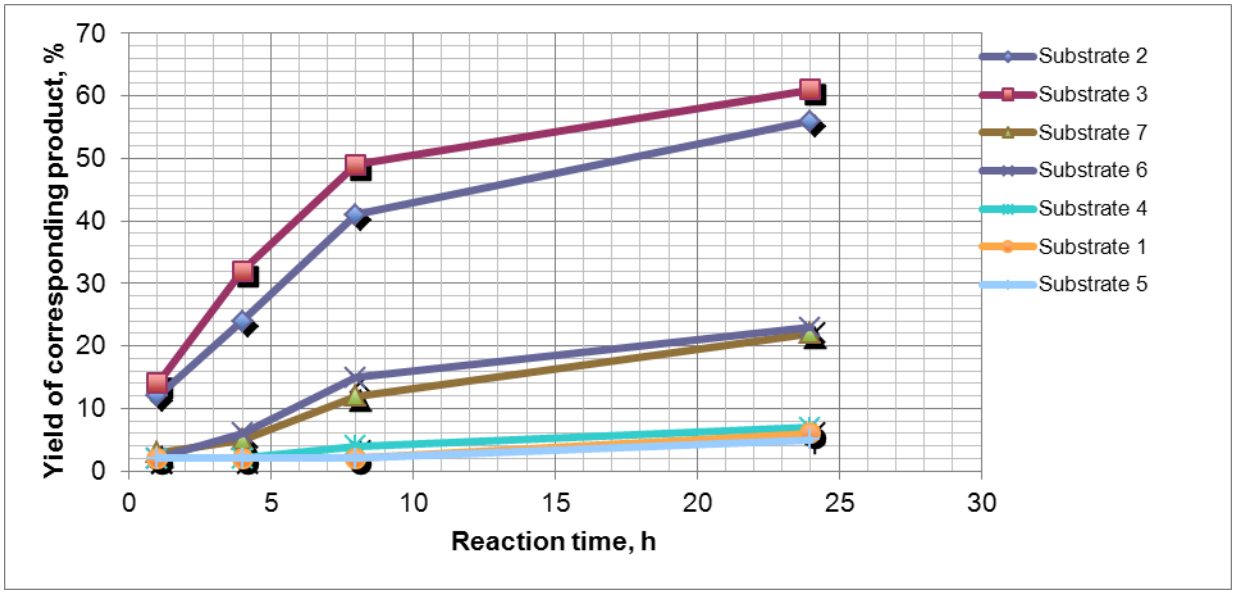


X = CH; Y = S, S(CH$_2$)$_n$, S(O) - natural feedstock components
X = N; Y = S, S(O) - model compounds

Entry	Substrate	Oxidant	T, °C	Solvent	Yields, [b] %
1	 **2**	$K_2S_2O_8$	110	DCE	NR
2		$PhI(OAc)_2$	110	DCE	NR
3		Oxygen	110	DCE	NR
4		AgOTFA	110[c]	DCE	53 (5:1)
5		AgOTFA + Oxygen[d]	130	DCE	56 (6:1)
6	 **3**	$K_2S_2O_8$	110	DCE	11
7		$PhI(OAc)_2$	110	DCE	15
8		Oxygen	110	DCE	5
9		AgOTFA	110[c]	DCE	56 (5:1)
10		AgOTFA + Oxygen[d]	130	DCE	61 (6:1)
11	 **4**	$K_2S_2O_8$	110	DCE	11[e]
12		$PhI(OAc)_2$	110	DCE	12[e]
13		Oxygen	110	DCE	NR
14		AgOTFA	110	DCE	6[e]
15		AgOTFA + Oxygen[d]	130	DCE	8[e]
16	 **1**	$K_2S_2O_8$	110	DCE	NR
17		$PhI(OAc)_2$	110	DCE	NR
18		Oxygen	110	DCE	NR
19		AgOTFA	110	DCE	NR
20		AgOTFA + Oxygen[d]	130	DCE	NR
21	 **5**	$K_2S_2O_8$	110	DCE	NR
22		$PhI(OAc)_2$	110	DCE	NR
23		Oxygen	110	DCE	NR
24		AgOTFA	110	DCE	NR
25		AgOTFA + Oxygen[d]	130	DCE	NR
26	 **6**	$K_2S_2O_8$	110	$MeNO_2$	42 (5:1)
27		$PhI(OAc)_2$	110	DCE	10
28		Oxygen	110	$MeNO_2$	11
29		AgOTFA	110	DCE	22 (5:1)
30		AgOTFA + Oxygen[d]	130	DCE	23 (5:1)
31	 **7**	$K_2S_2O_8$	110	$MeNO_2$	15
32		$PhI(OAc)_2$	110	DCE	57 (6:1)
33		Oxygen	110	$MeNO_2$	23 (5:1)
34		AgOTFA	110	DCE	NR
35		AgOTFA + Oxygen[d]	130	DCE	22 (5:1)

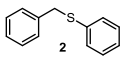
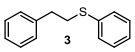
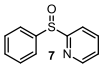
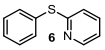
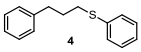
[a]Substrate (0.25 mmol), catalyst $Pd(OAc)_2$ (10 mol%; with *cis*-[$PdCl_2(MeCN)_2$] and *cis*-[$PdCl_2(CyNC)_2$] as catalysts, no formation of the olefin product was detected for any substrate), ethyl acrylate (0.50 mmol), oxidant (0.50 mmol) in 2 mL of solvent at 110 °C for 24 h; alkenylation of substrates **2**, **3**, **6** and **7** led to the products **11**, **9**, **12** and **13**, respectively. [b]Yields based on NMR integration; the values in parentheses are the mono:diolefination ratios (estimated for product yields higher than 20%). [c]Reaction time was 12 h. [d]Reaction vessel was sealed under oxygen. [e]Established by GC-MS only, and product was not isolated.

Figure S1. Comparative alkenylation of individual substrates followed by ^{1}H NMR.



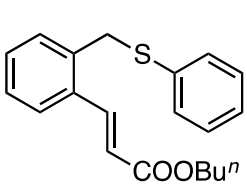
Similar kinetic curves were measured for substrates **2** and **3** in the individual transformation (one component as a substrate). These results indicate that the kinetic preference is not the primary factor that distinguishes the reactivity of these substrates in a binary mixture. Most likely, the primary factor is a thermodynamic factor that prefers coordination of the substrate to the catalyst active site. The same result was observed for the pairs of other substrates shown on the plot.

Table S2. Comparative alkenylation of individual substrates.

Substrates	**Time (h) and yields (%)**			
	1	4	8	24
	12	24	41	56
	14	32	49	61
	3	5	12	22
	2	6	15	23
	2	2	4	7
	2	2	2	2
	2	2	2	2

Conditions: substrate (0.25 mmol), catalyst $Pd(OAc)_2$ (10 mol%), ethyl acrylate (0.30 mmol; 0.50 mmol for pyridine-containing substrates), AgOTFA (0.50 mmol) in 2 mL of solvent at 110 °C; the reaction vessel was sealed under oxygen.

Spectral data for alkenylation products



8, (*E*)-butyl 3-(2-((phenylthio)methyl)phenyl)acrylate, yellowish oil. HRMS (ESI-MS), m/z: for $C_{20}H_{22}NaO_2S$ $[M + Na]^+$, calculated for: 349.1238, found 349.1241. ^{1}H NMR (400.13 MHz, $CDCl_3$), δ: 8.05 (d, J = 16.0 Hz, 1H), 7.59–7.57 (m, 1H), 7.36–7.30 (m, 2H), 7.29–7.23 (m, 6H), 6.37 (d, J = 16.0 Hz, 1H), 4.24–4.22 (m, 4H), 1.74–1.68 (m, 2H), 1.49–1.42 (m, 2H), 0.98 (t, J = 6.0 Hz, 3H). ^{13}C NMR (100.61 MHz, $CDCl_3$), δ: 166.9, 141.3, 136.5, 135.6, 133.8, 131.4, 130.8, 130.0, 129.0, 128.0, 127.1, 126.9, 120.4, 64.6, 37.5, 30.9, 19.3, 13.9.

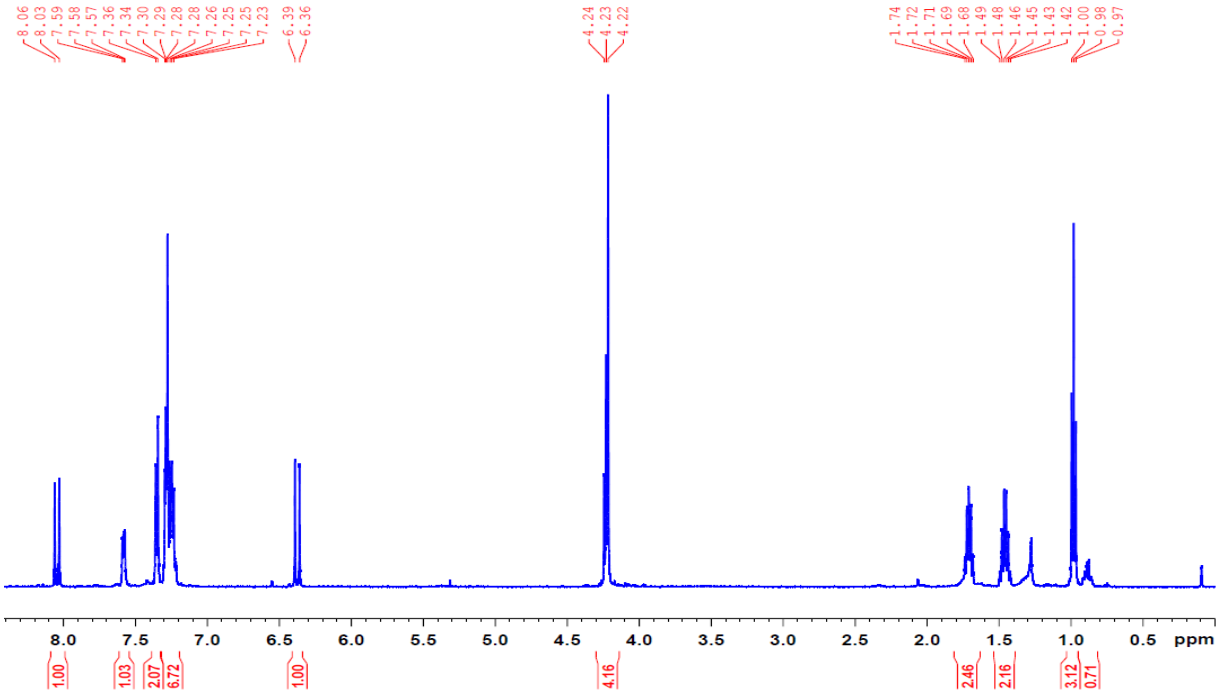


Figure S2. ^{1}H NMR spectrum of (*E*)-butyl 3-(2-((phenylthio)methyl)phenyl)acrylate.

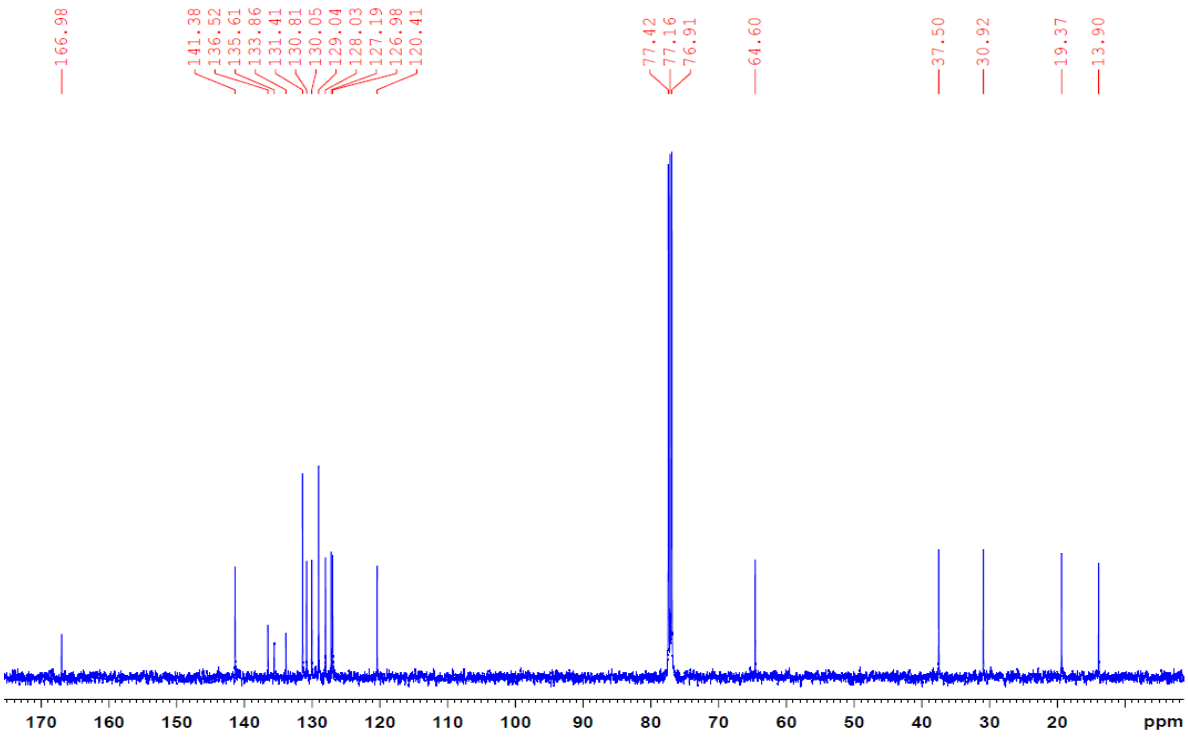
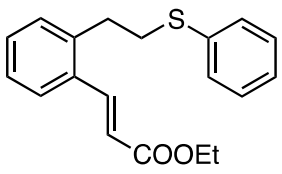


Figure S3. ^{13}C NMR spectrum of (*E*)-butyl 3-(2-((phenylthio)methyl)phenyl)acrylate.



9, (*E*)-ethyl-3-(2-(2-(phenylthio)ethyl)phenyl)acrylate, yellowish oil. HRMS (ESI-MS), m/z: for $C_{19}H_{21}O_2S$ $[M + H]^+$, calculated for: 313.1262, found 313.1251; for $C_{19}H_{20}NaO_2S$ $[M + Na]^+$, calculated: 335.1082, found 335.1083. ^{1}H NMR (400.13 MHz, $CDCl_3$), δ: 7.95 (d, J = 16.0 Hz, 1H), 7.56–7.54 (m, 1H) and 7.38–7.19 (m, 8H), 6.37 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 3.11–3.07 (m, 4H), 1.35 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100.61 MHz, $CDCl_3$), δ: 166.8, 141.5, 139.6, 136.0, 133.3, 130.3, 130.1, 129.3, 129.0, 127.2, 126.8, 126.1, 120.4, 60.6, 34.8, 33.2, 14.4.

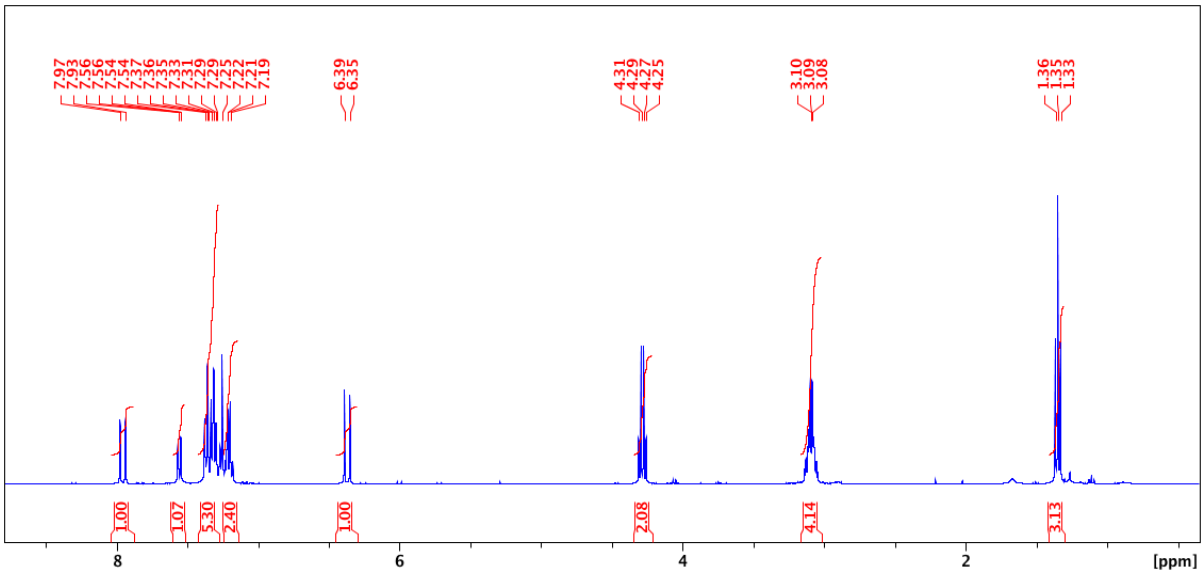


Figure S4. ^{1}H NMR spectrum of (*E*)-ethyl 3-(2-(2-(phenylthio)ethyl)phenyl)acrylate.

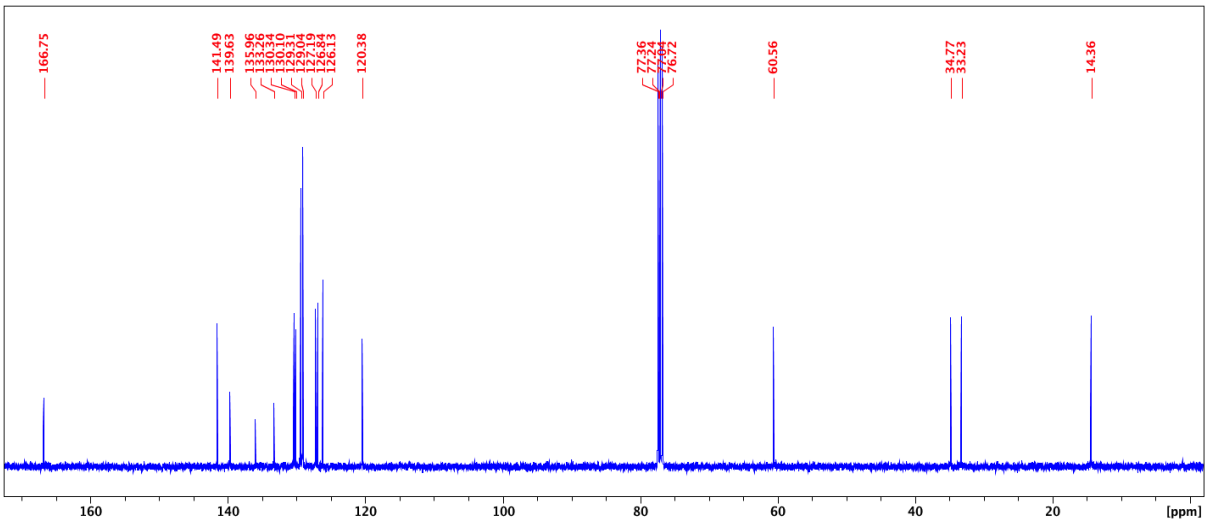
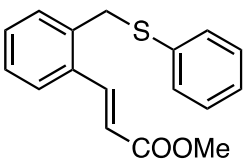
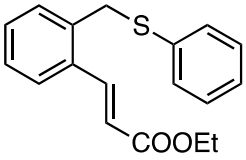


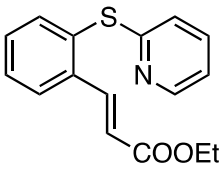
Figure S5. ^{13}C NMR spectrum of (*E*)-ethyl 3-(2-(2-(phenylthio)ethyl)phenyl)acrylate.



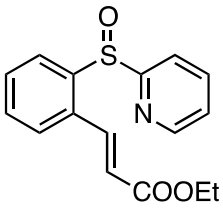
10, (E)-methyl -3-(2-((phenylthio)methyl)phenyl)acrylate, yellowish oil. Identified with spectral data.[3] HRMS (ESI-MS), m/z: for $C_{17}H_{16}NaO_2S$ $[M + Na]^+$, calculated: 307.0769, found 307.0777. ^{1}H NMR (400.13 MHz, $CDCl_3$), δ: 8.02 (d, J = 15.8 Hz, 1H), 7.33–7.31 (m, 1H), 7.26–7.24 (m, 2H), 7.28–7.20 (m, 6H), 6.35 (d, J = 15.8 Hz, 1H), 4.18 (s, 2H), 3.80 (s, 3H). ^{13}C NMR (100.61 MHz, $CDCl_3$), δ: 167.1, 141.5, 136.4, 135.4, 133.5, 131.2, 130.8, 129.9, 128.9, 127.9, 126.9, 126.7, 119.7, 51.7, 37.2.



(**11**) (E)-ethyl -3-(2-((phenylthio)methyl)phenyl)acrylate, yellowish oil. Identified with spectral data.[4] HRMS (ESI-MS), m/z: for $C_{18}H_{19}O_2S$ [M + H]$^+$, calculated for: 299.1106, found 299.1108; for $C_{18}H_{18}NaO_2S$ [M + Na]$^+$, calculated: 321.0925, found 321.0930. ^{1}H NMR (400.13 MHz, $CDCl_3$), δ: 8.05 (d, J = 15.8 Hz, 1H), 7.61–7.57 (m, 1H), 7.38–7.35 (m, 2H), 7.32–7.22 (m, 6H), 6.38 (d, J = 15.8 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 4.23 (s, 2H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100.61 MHz, $CDCl_3$), δ: 166.8, 141.3, 136.4, 135.5, 133.7, 131.3, 130.7, 129.9, 128.9, 127.9, 127.1, 126.9, 120.3, 60.5, 37.4, 14.3.



(**12**). (*E*)-ethyl 3-(2-(pyridin-2-ylthio)phenyl)acrylate, yellowish oil. Identified compared with spectral data.[9] HRMS (ESI-MS), m/z: for $C_{16}H_{16}NO_2S$ [M + H]$^+$, calculated for: 286.0902, found 286.0908; for $C_{16}H_{15}NNaO_2S$ [M + Na]$^+$, calculated: 308.0721, found 308.0718. ^{1}H NMR (400.13 MHz, $CDCl_3$), δ: 8.43 (d, J = 4.0 Hz, 1H), 8.23 (d, J = 16.0 Hz, 1H), 7.76 (d, J = 6.0 Hz, 1H), 7.69 (d, J = 6.0 Hz, 1H), 7.49 – 7.45 (m, 4H), 7.02 (m, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.41 (d, J = 16.0 Hz, 1 H), 4.23 (q, J = 7.0 Hz, 2H), 1.31 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100.61 MHz, $CDCl_3$), δ: 166.8, 160.3, 149.6, 142.3, 138.4, 137.1, 136.7, 131.6, 130.8, 130.0, 127.4, 121.2, 120.4, 120.0, 61.0, 14.5



(**13**). (*E*)-ethyl 3-(2-(pyridin-2-ylsulfinyl)phenyl)acrylate, orange oil. Identified with spectral data.[9] HRMS (ESI-MS), m/z: for $C_{16}H_{16}NO_3S$ [M + H]$^+$, calculated for: 302.0851, found 302.0857; for $C_{16}H_{15}NNaO_3S$ [M + Na]$^+$, calculated: 324.0670, found 324.0681. ^{1}H NMR (400.13 MHz, $CDCl_3$), δ: 8.50–8.46 (m, 2H), 8.05 (d, J = 8.0 Hz, 1H), 7.91–7.87 (m, 2H), 7.63 (d, J_2 = 2.0 Hz, 1H), 7.49–7.45 (m, 2H), 7.28 (m, 1H), 6.43 (d, J = 16.0 Hz, 1 H), 4.26 (m, 2H), 1.35 (m, 3H). ^{13}C NMR

(100.61 MHz, $CDCl_3$), δ: 166.5, 165.7, 150.1, 144.1, 139.9, 138.2, 134.6, 131.7, 130.9, 127.2, 125.7, 124.8, 122.0, 119.3, 61.0, 14.5.

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