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Perchloric Acid Impregnated on Silica Gel ($HClO_4/SiO_2$): A Versatile Catalyst for Michael Addition of Thiols to the Electron-Deficient Alkenes

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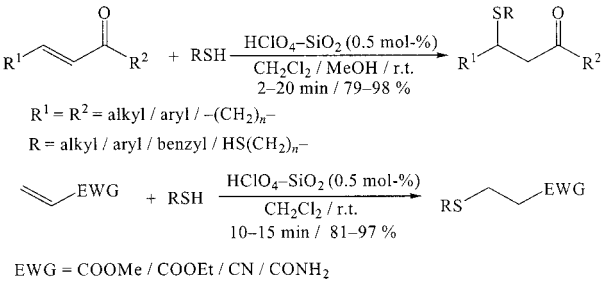
Keywords: Thiols / Electron-deficient alkenes / Michael addition / Silica-supported perchloric acid

Perchloric acid adsorbed on silica gel ($HClO_4/SiO_2$) has been found to be a highly efficient and versatile catalyst for the Michael addition of thiols to a wide variety of conjugated alkenes such as α,β-unsaturated ketones, carboxylic esters, nitriles, amides and chalcones in dichloromethane or methanol at room temperature. The reactions are completed within 2–20 min in high yields. Some of the additional advantages are: no aqueous work-up is necessary, and the catalyst is also reusable. Moreover, the solid product can be obtained without chromatographic separation.

Inltroduction

The addition of thiols to α,β-unsaturated carbonyl compounds is a very important process in carbon–sulfur bond formation.[1] By employing this process, the olefinic double bond of a conjugated carbonyl compound can selectively be protected, and deprotection can be easily done either by copper(I) induced elimination[2] or by oxidation followed by thermolytic elimination.[3] Thia-Michael addition product(s) of α,β-unsaturated carbonyl compounds are very important building blocks for the synthesis of bioactive compounds,[4] heterocycles,[5] and are also used as chiral auxiliary for the synthesis of optically active α-hydroxy aldehydes.[6] Therefore, the development of an efficient and selective catalyst for the construction of carbon–sulfur bond is of interest in organic synthesis. Thia-Michael reaction is classically carried out by employing a base under homogeneous conditions.[6a,7] Under heterogeneous conditions, various solid catalysts have been found to be useful. For example, natural phosphate or phosphate doped with potassium fluoride,[8] zeolite,[9] clay-supported $NiBr_2$ and $FeCl_3$,[10] Fluoroapatite,[11] polymer-supported Nafion® SAC-13[12] and dodecatungstophosphoric acid ($H_3PW_{12}O_{40}$).[13] Moreover, a wide variety of Lewis acid catalyst and other reagents have been used over the years for the similar transformation. Among them some of the reported catalysts are: $Hf(OTf)_4$,[14] $InBr_3$,[15] $InCl_3$,[16] $Bi(NO_3)_3$,[17] $Bi(OTf)_3$,[18] $Cu(BF_4)_2{\cdot}xH_2O$,[19] nickel(II) perchlorate,[20] [pmIm]Br,[21] [Bmim]PF_6/H_2O,[22] $RuCl_3$ in poly(ethyleneglycol),[23] molten tetrabutylammonium bromide,[24] chiral *N*,*N*′-dioxide–cadmium iodide,[25] I_2,[26] micellar solution of sodium dodecyl sulfate (SDS),[27] and azaphosphatrane nitrate salt.[28] Unfortunately, many of these procedures have one or the other disadvantages such as longer reaction time, use of excessive expensive catalyst, harsh reaction conditions, failure to provide addition product and tedious experimental procedure. Therefore, the development of an efficient and mild synthetic protocol is always in great demand to make the available procedures more convenient and simpler. Very recently, solid-supported reagents[29] have gained considerable interest in organic synthesis because of their unique properties of the reagents such as high efficiency due to more surface area, more stability and reusability, greater selectivity and ease of handling. In continuation of our ongoing research programme to develop better and newer synthetic methodologies, we perceived that $HClO_4/SiO_2$ might be a very useful catalyst for thia-Michael reaction. The catalyst, $HClO_4/SiO_2$ has been utilized so far by others for acetylation of phenols, thiols, alcohols and amines,[30] peracetylation of carbohydrates,[31] acetalization followed by acetylation,[32] glycosylation reaction[33] and for Ferrier rearrangement of glycals.[34] Very recently, we also noticed that the same catalyst is highly effective for the *gem* diacylation of aldehydes.[35] In this paper, we wish to report that $HClO_4/SiO_2$ is an efficient and valuable catalyst for the 1,4-



Scheme 1.

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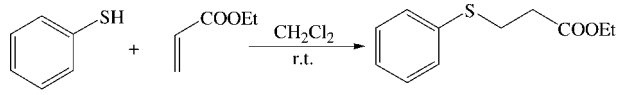
conjugate addition of thiols to a wide variety of conjugated alkenes such as α,β-unsaturated ketones, carboxylic esters, nitriles and amides as shown in Scheme 1.

Results and Discussion

For our investigations, $HClO_4/SiO_2$ was prepared according to the literature procedure.[30] To evaluate the better catalytic activity of $HClO_4/SiO_2$ over silica gel or aqueous perchloric acid, a model study was carried out with thiophenol and ethyl acrylate using various catalytic conditions, as shown in Scheme 2 and Table 1. From the study, it clearly demonstrated that the silica-supported perchloric acid is indeed an effective catalyst in terms of reaction time and yield.



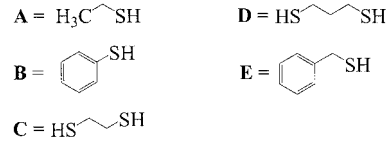
Scheme 2.

Table 1. The result of the reaction of ethyl acrylate (2 mmol) with thiophenol (2.2 mmol) under different catalytic conditions in dichloromethane at room temperature.

Run	Catalyst	Time	Yield [%][a,b]
I	No catalyst	24 h	52
II	SiO_2 (10 mg /mmol)	24 h	63
III	Aqueous $HClO_4$ (0.5 mol-%)	1 h	82
IV	$HClO_4/SiO_2$ (10 mg/mmol, 0.5 mol-%)	10 min	95

[a] Isolated yield. [b] All the compounds were characterized by recording IR, ^1H NMR, ^{13}C NMR and elemental analyses.

The thia-Michael reaction of 2-cyclopenten-1-one (**1**) with ethanethiol (**A**) using 0.5 mol-% of catalyst in dichloromethane at room temperature (run 1) proceeded within 5 min and the pure product 3-(ethylthio)cyclopentanone (**1a**) was isolated in 92% yield as a gummy liquid by filtration through a short silica gel column. The product was characterized by IR, ^1H NMR, ^{13}C NMR spectra and elemental analysis, and it was agreeable with the 1,4-addition product. Various thiols used for Michael addition are given in Scheme 3. The enone **1** also treated with thiophenol (**B**) in the presence of same catalyst under identical conditions to provide the desired addition product **1b** in 98% yield (run 2), in quicker time with better yield compared to the recently reported procedures.[15,22] Likewise, 1,2-ethanedithiol (**C**) on reaction with two molecules of the enone **1** smoothly provided the bis-Michael addition product **1c** within 5 min in good yield without any difficulty. By following identical reaction procedure, 2-cyclohexen-1-one (**2**) also treated with ethanethiol (**A**), thiophenol (**B**) and 1,3-propanedithiol (**D**) (run 4–6) to furnish the desired Michael addition products **2a**, **2b** and **2d**, respectively, in good yields. We observed that the present protocol is highly efficient in terms of mol-% of the catalyst used and yields, relative to a very recently reported procedure.[19] 4,4-Dimethyl-2-cyclohexen-1-one (**3**) was readily converted into **3b** on reaction with thiophenol (**B**) in good yields. The results are summarized in Table 2. Next, we were interested to see whether the same catalyst is useful for the Michael reaction of acyclic α,β-unsaturated ketones or not. Remarkably, an enone **4**, such as 16-dehydropregnenolone acetate (16-DPA), was also treated with ethanethiol (**A**) and thiophenol (**B**) independently to give the 1,4-addition products **4a** and **4b**, respectively, in fairly good yields using the same catalyst under similar reaction conditions. In addition, the use of methanol as the solvent, makes it possible to access the Michael addition products **5a** and **5b** from the corresponding chalcone (**5**) in very good yields. Notably, by employing our protocol, from naturally occurring α,β-unsaturated ketones such as (*S*)-(+)-carvone (**6**) and (*R*)-(+)-pulegone (**7**), we obtained the corresponding Michael addition products, **6a**, **7a** and **7e**, respectively, as a diastereomeric mixture on treatment with thiols under identical reaction conditions. It is noteworthy to point out that the addition reaction of (*R*)-(+)-pulegone (**7**) with phenylmethanethiol (**E**) took much longer reaction time under basic conditions.[6a] One more advantage of the present method is that the reaction does not need to be carried out under N_2.



Scheme 3.

All the final products were characterized by recording IR, ^1H NMR, ^{13}C NMR spectra and elemental analysis. The structure of compound **4b** was determined by X-ray crystallography. The ORTEP diagram is shown in Figure 1.

Each unit cell contains two identical molecules. The torsion angles between H^{32}–C^{16}–C^{17}–H^{46}, S^1–C^{16}–C^{17}–H^{46}, H^{32}–C^{16}–C^{17}–C^{20} and C^{20}–C^{17}–C^{16}–S^1 are 155.27°, 31.32°, 32.44° and 92.49°, respectively. These results are in accordance with the fact that H^{46} and H^{32} as well as C^{20} and S^1 are in an *anti* orientation as shown in Figure 2.

Moreover, by employing the present protocol, various α,β-unsaturated esters namely methyl acrylate (**8**), methyl methacrylate (**9**) and ethyl acrylate (**10**) furnished the desired Michael addition products **8b**, **9b** and **10b** respectively, on reaction with thiophenol (**B**) in good yields. Furthermore, our methodology can be extended for 1,4-conjugate addition reaction of thiols with acrylonitrile (**11**) and acrylamide (**12**) under identical conditions. We have also studied the recyclability of the catalyst by the following way. The reaction of acrylonitrile (100 mmol) with thiophenol (110 mmol) was carried out in the presence of $HClO_4/SiO_2$ (0.5 mol-%, 1 g). After completion, the catalyst was filtered off and activated by heating at 80 °C under vacuum for 1 hour and reused for thia-Michael reaction of a fresh lot of acrylonitrile (100 mmol) with thiophenol (110 mmol) affording 85% yield of the desired product after 20 min. Again, the catalyst was recovered, reactivated and reused repeatedly for three more consecutive times for thia-Michael reactions with acrylonitrile (100 mmol) affording

Table 2. Michael addition of thiols to conjugated alkenes catalyzed by silica-supported perchloric acid ($HClO_4/SiO_2$).

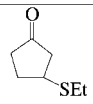
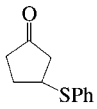
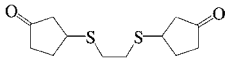
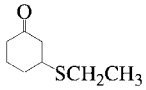
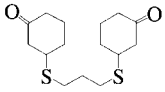
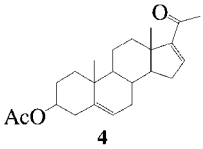
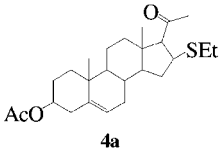
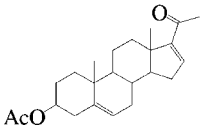
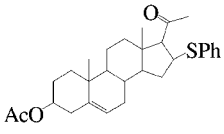
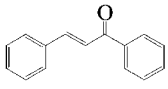
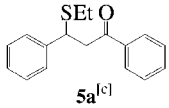
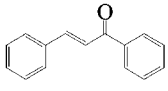
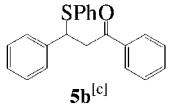
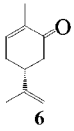
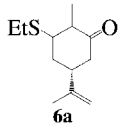
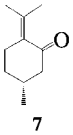
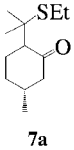
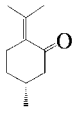
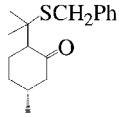
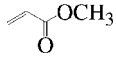
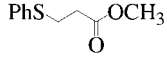
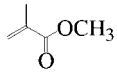
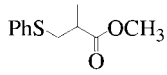
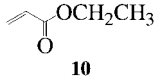
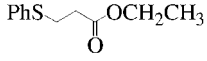
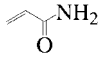
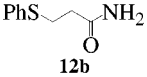
Run	Substrate	Time [min]	Product[a,b,c]	Yield[d] [%]
1	 **1**	5	 **1a**	92
2		2	 **1b**	98[26]
3		5	 **1c**	80[14]
4	 **2**	5	 **2a**	94[7c]
5		2	 **2b**	97[26]
6		5	 **2d**	81[14]
7	 **3**	20	 **3b**	82
8	 **4**	20	 **4a**	79
9		20	 **4b**	82
10	 **5**	15	 **5a**[c]	93
11		15	 **5b**[c]	95[15]
12	 **6**	10	 **6a**	95
13	 **7**	10	 **7a**	80

Table 2. (*Continued*).

Run	Substrate	Time [min]	Product[a,b,c]	Yield[d] [%]
14		10	 **7e**	86[6a]
15	 **8**	10	 **8b**	88
16	 **9**	10	 **9b**	91
17	 **10**	10	 **10b**	95
18	 **11**	10	 **11b**	97
19	 **12**	15	 **12b**	91

[a] All the compounds were characterized by recording IR, ^1H NMR, ^{13}C NMR and elemental analyses. [b] Isolated yield. [c] The reaction was carried out in methanol instead of dichloromethane. [d] The corresponding reference for spectroscopic data.

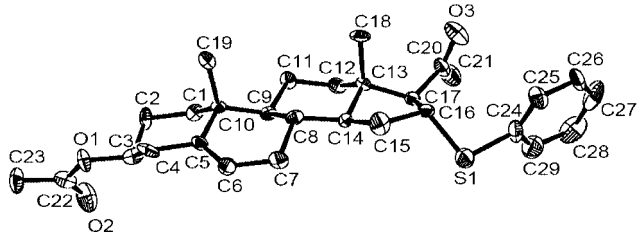


Figure 1. ORTEP plot of the molecule with atom numbering scheme; hydrogen atoms are omitted for clarity.

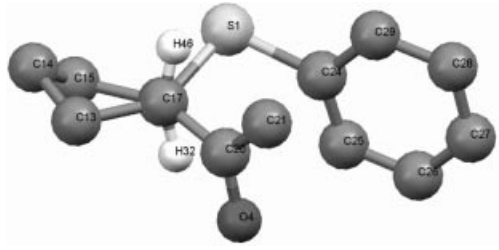


Figure 2. Front view of a selected portion.

81%, 76% and 70% yields respectively, in 25, 30 and 35 min. From this observation, it is clear that the reaction can be performed in a large scale as well as the catalyst can be reused although efficiency of the catalyst is lesser in further cycles. As the reaction took a longer time and gave lower yields during the reusability test, the following experiments were performed to rule out leaching of the actual catalyst perchloric acid. A reaction of ethyl acrylate

(2 mmol) and thiophenol (2.2 mmol) was carried out following the same experimental procedure. After completion of the reaction, the catalyst was removed by filtration through a Whatman 40 filter paper. To the filtrate was added another 2.2 mmol of thiophenol and 2 mmol of cyclohexenone and stirring was continued. A parallel reaction was performed with 2.2 mmol of thiophenol and 2 mmol of cyclohexenone in dichloromethane without any catalyst. The isolated yields of **2b** from the above two reactions were 30% and 27%, respectively, after five hours. From this observation, it is clear that no leaching has occurred during the experiment. But may be due to the poisoning of the surface of the catalyst, isolated yields are less and required longer reaction time in the recycling experiments.

Conclusion

In conclusion, the unique properties of silica-supported perchloric acid allowed us to demonstrate a new synthetic methodology for the thia-Michael addition reaction. The significant advantages of our protocol are: very good yields, mild conditions, short reaction times, non-aqueous work-up procedure and involvement of non-expensive reusable catalyst.

Experimental Section

Melting points were recorded with a Büchi B-545 melting point apparatus and were uncorrected. IR spectra were recorded in KBr or neat with a Nicolet Impact 410 spectrophotometer. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded either with a Jeol 300 MHz or Varian 400 spectrometer and Jeol 75 MHz or Varian 100 MHz, respectively, in $CDCl_3$ using TMS as internal reference. Elemental analyses were carried out in a Perkin–Elmer 2400 automatic carbon, hydrogen, nitrogen and sulfur analyzer. X-ray diffraction data were collected with a Bruker Apex II smart diffractometer with CCD area detectors using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Column chromatographic separations were done on SRL silica gel (60–120 mesh). CCDC-298160 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of $HClO_4/SiO_2$ Catalyst:[30] $HClO_4$ (1.8 g, 12.5 mmol, as a 70% aq. solution) was added to a suspension of SiO_2 (230–400 mesh, 23.7 g) in Et_2O (70.0 mL). The mixture was concentrated and the residue was heated at 100 °C for 72 hours under vacuum to furnish $HClO_4/SiO_2$ (0.5 mmol/g) as a free flowing powder (50 mg, 0.025 mmol of $HClO_4$).

Typical Experimental Procedure: To a magnetically stirred solution of 2-cyclohexene-1-one (**2**) (0.192 g, 2 mmol) and thiophenol (0.242 g, 2.2 mmol) in dichloromethane (2 mL) was added $HClO_4/SiO_2$ (20 mg, 0.5 mol-%). The reaction was instantly completed as checked by TLC. After completion of the reaction, the reaction mixture was directly passed through a silica gel column to obtain pure desired Michael addition product (**2b**) (0.400 g, 97%) as a colourless oily liquid. In case of solid product, it was obtained by removing the catalyst by filtration followed by recrystallization from the mixture of ethyl acetate/hexane (1:9) for compound **4a**, **4b**, and from methanol for compound **3b**, **5a**, **5b**, **12b**.

1a: Yield: 0.265 g, 92%. IR (neat): $\tilde{\nu}$ = 1748 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (t, J = 7.2 Hz, 3 $HSCH_2CH_3$), 1.89–1.98 (m, 1 H), 2.15–2.23 (m, 2 H), 2.30–2.48 (m, 2 H), 2.56–2.62 (m, 3 H), 3.46 (quin, J = 6.8 Hz, 1 H, $=CHSCH_2CH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.7, 25.1, 29.7, 36.9, 39.8, 45.5, 216.2 ppm. $C_7H_{12}OS$ (144.23): calcd. C 58.29, H 8.39, S 22.23; found C 58.08, H 8.35, S, 22.01.

3b: Yield: 0.385 g, 82%, m.p. 68 °C. IR (KBr): $\tilde{\nu}$ = 1711 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (s, 3 H), 1.23 (s, 3 H), 1.59–1.62 (m, 1 H), 1.82–1.86 (m, 1 H), 2.23–2.28 (m, 1 H), 2.37–2.41 (m, 1 H), 2.50–2.58 (m, 2 H), 3.11–3.15 (m, 1 H), 7.17–7.37 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 29.0, 34.6, 37.8, 38.6, 45.4, 57.6, 127.4, 129.1 (2 C), 132.7 (2 C), 134.6, 209.0 ppm. $C_{14}H_{18}OS$ (234.36): calcd. C 71.75, H 7.74, S 13.68; found C 71.49, H 7.67, S 13.45.

4a: Yield: 0.660 g, 79%, m.p. 126 °C (mixture of diastereomers, 1:1). IR (KBr): $\tilde{\nu}$ = 1731, 1706 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.62 (s, 3 H), 0.98–1.10 (m, 12 H), 1.01(s, 3 H), 1.02 (s, 3 H), 1.06 (s, 3 H), 1.23 (t, J = 7.2 Hz, 6 H), 1.49–1.58 (m, 16 H), 1.86 (d, J = 9.6 Hz, 2 H), 1.97 (d, J = 9.3 Hz, 2 H), 2.03 (s, 6 H), 2.16 (s, 3 H), 2.19 (s, 3 H), 2.32 (d, J = 9.6 Hz, 2 H), 2.41–2.62 (m, 4 H), 2.69 (d, J = 9.9 Hz, 2 H), 3.42–3.48 (m, 1 H), 3.72–3.76 (m, 1 H), 4.61 (m, 2 H), 5.37 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 14.2, 14.6, 14.7, 19.3 (2 C), 20.4, 20.8, 21.4 (2 C), 26.4, 27.7 (2 C), 28.0, 30.9, 31.4, 31.5, 31.7, 31.8, 34.8, 36.5, 36.6 (2 C), 36.9, 37.8, 38.0 (2 C), 38.5, 38.7, 40.5, 42.7, 42.8, 45.3 (2 C), 49.7, 50.1, 54.9, 55.8, 67.2, 72.1, 73.7, 73.8, 122.1 (2 C), 139.6, 139.9, 170.5 (2 C), 207.4 (2 C) ppm. $C_{25}H_{38}O_3S$ (418.64): calcd. C 71.73, H 9.15, S 7.66; found C 71.48, H 9.10, S 7.42.

4b: Yield: 0.765 g, 82%, m.p. 134 °C. IR (KBr): $\tilde{\nu}$ = 1731 (C=O), 1711 ($COCH_3$) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.66 (s, 3 H), 1.00 (s, 3 H), 0.92–1.02 (m, 5 H), 1.40–1.80 (m, 8 H), 1.82 (d, J = 10.8 Hz, 2 H), 1.83–1.97 (m, 4 H), 2.01 (s, 3 H), 2.29–2.32 (m, 1 H), 2.60 (d, J = 8.4 Hz, 1 H), 4.10–4.22 (m, 1 H), 4.55–4.62 (m, 1 H), 5.35–5.37 (m, 1 H), 7.10–7.20 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.2, 19.4, 20.9, 21.5, 27.8, 31.4, 31.7, 31.8, 34.7, 36.6, 36.9, 38.1, 38.9, 43.6, 45.4, 49.7, 54.9, 70.9, 73.9, 121.9, 126.4, 128.7 (2C), 130.8 (2C), 135.9, 139.4, 170.2, 206.4 ppm. $C_{29}H_{38}O_3S$ (466.68): calcd. C 74.64, H 8.21, S 6.87; found C 74.35, H 8.14, S 6.62.

5a: Yield: 0.503 g, 93%, m.p. 61–62 °C. IR (KBr): $\tilde{\nu}$ = 1693 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (t, J = 7.2 Hz, 3 H), 2.30–2.39 (m, 2 H), 3.52 (d, J = 7.6 Hz, 2 H), 4.57 (t, J = 7.2 Hz, 1 H), 7.18 (t, J = 7.2 Hz, 1 H), 7.28 (t, J = 8.0 Hz, 2 H), 7.38–7.43 (m, 4 H), 7.52 (t, J = 7.2 Hz, 1 H), 7.89 (d, J = 7.6 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.8, 25.9, 44.4, 45.8, 127.4, 128.0 (2 C), 128.3 (2 C), 128.7 (2 C), 128.8 (2 C), 133.4, 137.0, 142.4, 196.9 ppm. $C_{17}H_{18}OS$ (270.39): calcd. C 75.52, H 6.71, S 11.86; found C 75.18, H 6.63, S 11.58.

5b: Yield: 0.605 g, 95%, m.p. 114–115 °C. IR (KBr): $\tilde{\nu}$ = 1685 (C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.56 (dd, J = 6.0 Hz, J = 17.2 Hz, 1 H), 3.64 (dd, J = 8.4 Hz, J = 17.2 Hz, 1 H), 4.93 (dd, J = 6.0 Hz, J = 8.4 Hz, 1 H), 7.14–7.23 (m, 6 H), 7.28–7.31 (m, 4 H), 7.40 (t, J = 7.6 Hz, 2 H), 7.51 (t, J = 7.6 Hz, 1 H), 7.85 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.8, 48.3, 127.2, 127.4, 127.6 (2 C), 127.9 (2 C), 128.3 (2 C), 128.4 (2 C), 128.7 (2 C), 132.6 (2 C), 133.1, 134.1, 136.6, 141.0, 196.7 ppm. $C_{21}H_{18}OS$ (318.43): calcd. C 79.21, H 5.70, S 10.07; found C 78.95, H 5.65, S 9.87.

6a: (data for the major isomer), yield: 0.403 g, 95%. IR (neat): $\tilde{\nu}$ = 1711 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.15 (d, J = 7.2 Hz, 3 H), 1.24 (t, J = 7.6 Hz, 3 H), 1.76 (s, 3 H), 1.95–2.02 (m, 1 H), 2.15–2.25 (m, 2 H), 2.40–2.60 (m, 3 H), 2.76–2.84 (m, 1 H), 2.87–3.15 (m, 1 H), 3.42 (dd, J = 3.2 Hz, J = 8.4 Hz, 1 H), 4.73 (d, J = 20 Hz, 1 H), 4.81 (d, J = 15.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.7, 14.8, 20.9, 26.1, 35.9, 40.7, 46.0, 48.8, 49.2, 110.0, 146.9, 209.5 ppm. $C_{12}H_{20}OS$ (212.35): calcd. C 67.87, H 9.49, S 15.10; found C 67.55, H 9.40, S 14.95.

7a: (data for the major isomer), yield: 0.343 g, 80%. IR (neat): $\tilde{\nu}$ = 1718 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.00 (d, J = 6.0 Hz, 3 H), 1.21 (t, J = 7.6 Hz, 3 H, SCH_2CH_3), 1.36 (s, 3 H), 1.40–1.60 (m, 2 H), 1.52 (s, 3 H), 1.82–2.20 (m, 3 H), 2.27–2.30 (m, 1 H), 2.42 (dd, J = 3.6 Hz, J = 11.6 Hz, 1 H), 2.48–2.57 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5, 21.7, 22.3, 24.1, 28.0, 29.7, 34.8, 36.7, 46.9, 52.4, 58.1, 210.3, ppm. $C_{12}H_{22}OS$ (214.37): calcd. C 67.24, H 10.34, S 14.96; found C 67.01, H, 10.28, S 14.68.

8b: Yield: 0.345 g, 88%. IR (neat): $\tilde{\nu}$ = 1744 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.64 (t, J = 7.5 Hz, 2 H), 3.17 (t, J = 7.5 Hz, 2 H), 3.68 (s, 3 H), 7.19–7.39 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.0, 34.2, 51.8, 126.6, 129.0 (2 C), 130.1 (2 C), 135.1, 172.2 ppm. $C_{10}H_{12}O_2S$ (196.27): calcd. C 61.20, H 6.16, S 16.34; found C 61.01, H 6.12, S 16.12.

9b: Yield: 0.382 g, 91%. IR (neat): $\tilde{\nu}$ = 1742 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.27 (d, J = 6.9 Hz, 3 H), 2.70 (dd, J = 6.9 Hz, J = 13.8 Hz, 1 H), 2.93 (dd, J = 6.9 Hz, J = 13.2 Hz, 1 H), 3.27 (dd, J = 6.9 Hz, J = 13.2 Hz, 1 H), 3.67 (s, 3 H), 7.20–7.38 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.8, 37.4, 39.7, 51.9, 126.3, 128.8 (2 C), 129.8 (2 C), 135.5, 175.1 ppm. $C_{11}H_{14}O_2S$ (210.29): calcd: C 62.83, H 6.71, S 15.25; found C 62.61, H 6.68, S 14.95.

10b: Yield: 0.383 g, 95%. IR (neat): $\tilde{\nu}$ = 1743 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.24 (t, J = 7.2 Hz, 3 H), 2.61 (t, J = 7.2 Hz, 2 H), 3.15 (t, J = 7.2 Hz, 2 H), 4.13 (q, J = 7.2 Hz, 2 H), 7.18 (t, J = 7.6 Hz, 1 H), 7.27 (t, J = 7.6 H, 2 Hz), 7.34 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 29.0, 34.4, 60.6, 126.3, 128.8 (2 C), 129.8 (2 C), 135.0, 171.4 ppm. $C_{11}H_{14}O_2S$ (210.29): calcd. C 62.83, H 6.71, S 15.25; found C 62.66, H 6.62, S 14.99.

11b: Yield: 0.317 g, 97%. IR (neat): $\tilde{\nu}$ = 2250 (CN) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.58 (t, J = 7.2 Hz, 2 H), 3.12 (t, J = 7.2 H, 2 Hz), 7.26–7.34 (m, 3 H), 7.40 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.4, 30.4, 117.8, 127.6, 129.2 (2 C), 131.3 (2 C), 133.0 ppm. C_9H_9NS (163.24): calcd. C 66.22, H 5.56, N 8.58, S 19.64; found C 66.01, H 5.47, N 8.49, S 19.39.

12b: Yield: 0.330 g, 91%, m.p. 125 °C. IR (KBr): $\tilde{\nu}$ = 1657 ($CONH_2$) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.53 (t, J = 7.2 Hz, 2 H), 3.22 (t, J = 7.2 Hz, 2 H), 5.56 (br. s, 2 H), 7.20 (t, J = 8.4 Hz, 1 H), 7.29 (t, J = 8.8 Hz, 2 H), 7.36 (d, J = 8.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.2, 35.4, 126.3, 128.9 (2 C), 129.6 (2 C), 135.1, 173.2 ppm. $C_9H_{11}NOS$ (181.25): calcd. C 59.64, H 6.12, N 7.73, S 17.69; found C 59.40, H 6.04, N 7.59, S 17.51.

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