Tetrahedron Letters 51 (2010) 4627–4629

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Gold-catalyzed regiospecific intermolecular hydrothiolation of allenes

Menggenbateer [a], Meda Narsireddy [a], Giovanni Ferrara [a], Naoko Nishina [a], Tienan Jin [a,b,*], Yoshinori Yamamoto [a,b,*]

[a] Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan
[b] WPI-AIMR (WPI-Advanced Institute for Materials Research), Tohoku University, Sendai 980-8577, Japan

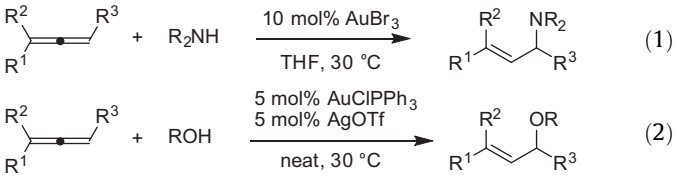
ARTICLE INFO

Article history:
Received 15 April 2010
Revised 14 June 2010
Accepted 25 June 2010
Available online 1 July 2010

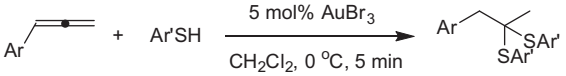
ABSTRACT

$AuBr_3$-catalyzed regiospecific intermolecular hydrothiolation of aromatic allenes and aromatic thiols afforded the corresponding dithioacetals in good yields at 0 °C in 5 min.

The use of gold catalysts in organic transformations has received much attention in recent years due to their unique electronic structure and soft carbophilic nature, which can activate unsaturated C–C bonds toward nucleophilic attack.[1] Among them, gold-catalyzed hydrofunctionalization, such as hydroamination[1,2] and hydroalkoxylation,[1,3] toward an unsaturated C–C bond, in both an intra- and intermolecular manner, represents an efficient and direct method for the synthesis of various heterocycles and heteroatom-containing compounds.[4] However, because of the high affinity of sulfur to transition metals, especially gold,[5] catalytic hydrothiolation has been explored to a lesser extent than hydroamination and hydroalkoxylation. Nonetheless, several novel metal catalytic hydrothiolations of alkynes and alkenes have been developed.[6] However, the metal-catalyzed hydrothiolation of allenes is rarely reported. Ogawa reported that palladium-catalyzed intermolecular addition of thiols to allenes gave vinyl sulfides,[7] and Krause reported the first gold-catalyzed intramolecular cycloisomerization of thioallenes.[8]

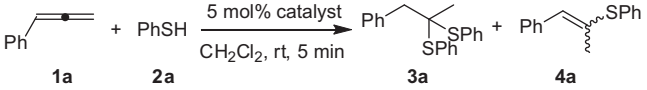


Recently, we reported the gold-catalyzed intermolecular hydroamination and hydroalkoxylation of allenes, which afforded allylic amines and allylic ethers, respectively, in high yields under mild reaction conditions (Eqs. 1 and 2).[9] In continuation of these investigations on gold catalysis, we report the gold-catalyzed regiospecific intermolecular hydrothiolation of aromatic allenes, in which the corresponding dithioacetals were obtained efficiently, under mild conditions (Eq. 3):



Initially, we focused on screening various gold catalysts for the hydrothiolation of phenylallene (**1a**) with 3 equiv of thiophenol (**2a**) in CH_2Cl_2 at room temperature (Table 1). When 5 mol % of $AuBr_3$ was used as the catalyst, the reaction reached completion in 5 min at room temperature, giving the corresponding dithioacetal **3a** in 80% yield along with a trace amount of vinyl sulfide **4a**

Table 1
Screening of the reaction conditions[a]



1a **2a** **3a** **4a**

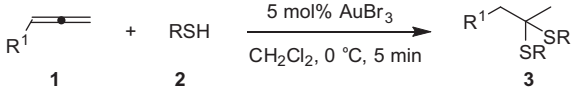
Entry	Catalyst	Yield[b] (%) **3a**	Yield[b,c] (%) **4a**	Yield[b] (%) **1a**
1	$AuBr_3$	80[d]	Trace	0
2	$AuBr_3$ (1 h)	32	47[e]	0
3	$AuBr_3$ (0 °C)	84[d]	0	0
4	$AuBr_3$ (−20 °C)	45	50	0
5	$AuBr_3$ (3 mol %)	19	67	0
6	$AuBr_3$ (1 mol %)	Trace	80	0
7	$AuCl_3$	Trace	37	41
8	AuCl	0	12	58
9	$AuClPPh_3/AgOTf$	14	15	45
10	$AuClPPh_3/AgBF_4$	0	13	60
11	$InBr_3$	16	15	51

[a] To a mixture of CH_2Cl_2 (2 mL, 0.2 M) and catalyst (5 mol %) were added **2a** (1.2 mmol) and **1a** (0.4 mmol) and the mixture was stirred at room temperature for 5 min.
[b] ^1H NMR yields determined using dibromomethane as an internal standard.
[c] A mixture of *E* and *Z* isomers.
[d] Isolated yield.
[e] *E*/*Z* ratio is 2:1.

* Corresponding authors. Tel.: +81 22 795 6582; fax: +81 22 795 6784 (Y.Y.).
E-mail addresses: tjin@m.tohoku.ac.jp (T. Jin), yoshi@m.tohoku.ac.jp (Y. Yamamoto).

0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2010.06.125

Table 2
$AuBr_3$-catalyzed intermolecular hydrothiolation of allenes **1** with thiols **2**[a]

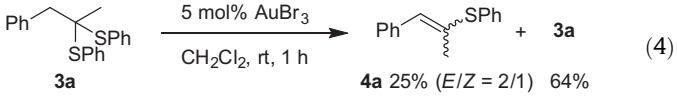


1 2 3

Entry	R^1		R		Product	Yield[b] (%)
1	4-F–C_6H_4	(**1b**)	Ph	(**2a**)	**3b**	76
2	4-Cl–C_6H_4	(**1c**)	Ph	(**2a**)	**3c**	71
3	4-Me–C_6H_4	(**1d**)	Ph	(**2a**)	**3d**	66
4	4-Me–C_6H_4	(**1d**)	3-Me–C_6H_4	(**2b**)	**3e**	61
5	Ph	(**1a**)	4-Me–C_6H_4	(**2c**)	**3f**	80
6	Ph	(**1a**)	3-Me–C_6H_4	(**2b**)	**3g**	66
7	Ph	(**1a**)	4-Br–C_6H_4	(**2d**)	**3h**	67
8	Ph	(**1a**)	3-Cl–C_6H_4	(**2e**)	**3i**	76
9	Ph	(**1a**)	Cyclohexyl	(**2f**)	**3j**	0
10	Cyclohexyl	(**1e**)	Ph	(**2a**)	**3k**	0

[a] To a mixture of CH_2Cl_2 (2 mL, 0.2 M) and $AuBr_3$ (5 mol %) were added **2** (1.2 mmol) and **1** (0.4 mmol) and the mixture was stirred at 0 °C for 5 min.
[b] Isolated yield.

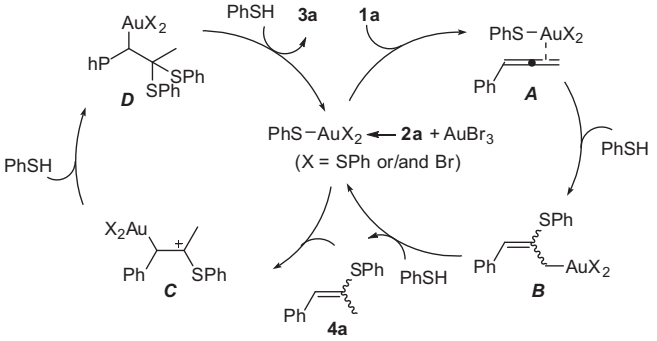
(entry 1). It is noteworthy that, when the reaction was carried out for 1 h at room temperature, a mixture of **3a** and **4a** (E/Z = 2/1)[10] was obtained (entry 2). As expected, treatment of the dithioacetal **3a** with 5 mol % of $AuBr_3$ produced a mixture of **3a** and **4a**, which indicated that **3a** and **4a** must be in equilibrium under the reaction conditions at higher temperatures (Eq. 4). Consequently, the reaction was carried out at a lower temperature. For example, the reaction at 0 °C afforded the corresponding dithioacetal **3a** in 84% yield in 5 min without detection of **4a**, although at −20 °C a mixture of **3a** and **4a** was obtained (entries 3 and 4). The results suggest that the reaction may proceed through the initial formation of vinyl sulfide **4a**. The use of lower amounts of $AuBr_3$ (3 mol % and 1 mol %) gave the vinyl sulfide **4a** as the major product (entries 5 and 6). Other catalysts, such as $AuCl_3$, AuCl, $AuClPPh_3$/AgOTf, $AuClPPh_3$/$AgBF_4$, and $InBr_3$,[6g] were ineffective (entries 7–11). The results indicate unambiguously that $AuBr_3$ was the best catalyst for this catalytic hydrothiolation.



3a **4a** 25% (E/Z = 2/1) 64% (4)

The scope of the $AuBr_3$-catalyzed hydrothiolation of allenes **1** is summarized in Table 2.[11] All the reactions were carried out in the presence of 5 mol % of $AuBr_3$ in CH_2Cl_2 at 0 °C for 5 min. The reactions of thiophenol (**2a**) with mono-substituted allenes having an electron-withdrawing aromatic ring at R^1 (**1b** and **1c**) gave the corresponding dithioacetals **3b** and **3c** in 76% and 71% yields, respectively (entries 1 and 2). Allene **1d**, substituted with an electron-donating aromatic ring at the allenyl terminus, reacted with arylthiols **2a** and **2b**, affording the desired products **3d** and **3e** in good yields (entries 3 and 4). We also investigated the reactivity of substituted thiophenols. The reaction of phenylallene (**1a**) with substituted arylthiols **2** bearing an electron-donating or an electron-withdrawing group on the benzene ring afforded the corresponding dithioacetals **3f–i** in good yields (entries 5–8). The electronic characteristics of the aromatic ring did not exert a significant influence on the yield of **3**. However, the reaction of phenylallene (**1a**) with cyclohexyl thiol (**2f**) and the reaction of cyclohexyl allene (**1e**) with **2a** resulted in no reaction and the starting allenes were recovered (entries 10 and 11). It is also noteworthy that reactions of 1,1- or 1,3-disubstituted allenes with **2a** did not produce any of the desired products. Thus, aryl allenes and aryl thiols proved to be suitable substrates for the present hydrothiolation.

A proposed reaction mechanism is shown in Scheme 1. (1) The gold sulfide complex is formed in situ through ligand exchange between $AuBr_3$ and PhSH along with concomitant formation of HBr. (2) Coordination of the allene double bond, having higher electron density, to the gold complex affords the intermediate **A**. (3) Both *syn*- and *anti*-addition of PhS to the central carbon of the allene would give a (σ-allyl)gold intermediate **B**. (4) Protonation of **B** by PhSH produces a mixture of *E* and *Z* isomers of **4a** with regeneration of the gold catalyst. (5) Further coordination of the gold catalyst to the electron-rich vinyl sulfide forms a stable carbocation **C**. (6) Addition of PhSH to **C** produces the dithioacetal intermediate **D**, which is followed by immediate protonation to give **3a**.



Scheme 1. Proposed mechanism.

In summary, we have developed an efficient $AuBr_3$-catalyzed regiospecific intermolecular hydrothiolation of aryl allenes with aryl thiols under mild reaction conditions. In contrast to our previously reported hydroamination and hydroalkoxylation, the present hydrothiolation took place selectively at the central carbon of allenes to produce the dithioacetal products. Further investigation of the mechanistic details and gold-catalyzed hydrofunctionalization are in progress.

General procedure for hydrothiolation of an allene: To a CH_2Cl_2 (0.2 M, 2 mL) solution of $AuBr_3$ (5 mol %, 8.7 mg) were added thiophenol (**2a**) (1.2 mmol, 0.123 mL) and phenylallene (**1a**) (0.4 mmol, 46.4 mg) under an Ar atmosphere. The reaction mixture was stirred at 0 °C for 5 min then filtered through a short Florisil pad using Et_2O as the eluent. After evaporation, the residue was purified by column chromatography to give **3a** in 84% yield (113 mg).

Acknowledgment

We thank the faculty members of the Instrumental Analysis Center at Tohoku University for the measurement of NMR and mass spectra.

References and notes

1. For recent selected reviews on gold catalysis, see: (a) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896–7936; (b) Gorin, D. J.; Toste, F. D. *Nature* **2007**, *446*, 395; (c) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180–3211; (d) Widenhoefer, R. A. *Chem. Eur. J.* **2008**, *14*, 5382; (e) Arcadi, A. *Chem. Rev.* **2008**, *108*, 3266–3325; (f) Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351–3378; (g) Patil, N. T.; Yamamoto, Y. *Chem. Rev.* **2008**, *108*, 3395–3442; (h) Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239–3265.
2. For recent selected examples of gold-catalyzed hydroamination, see: (a) Aikawa, K.; Kojima, M.; Mikami, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 6073–6077; (b) Zeng, X.; Soleilhavoup, M.; Bertrand, G. *Org. Lett.* **2009**, *11*, 3166–3169; (c) Manzo, A. M.; Perboni, A. D.; Broggini, G.; Rigamonti, M. *Tetrahedron Lett.* **2009**, *50*, 4696–4699; (d) Duan, H.; Sengupta, S.; Petersen, J. L.; Akhmedov, N. G.; Shi, X. *J. Am. Chem. Soc.* **2009**, *131*, 12100–12102; (e) Han, Z.-Y.; Xiao, H.; Chen, X.-H.; Gong, L.-Z. *J. Am. Chem. Soc.* **2009**, *131*, 9182–9183; (f) Zeng, X.; Frey, G. D.; Kinjo, R.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2009**, *131*, 8690–8696; (g) Kramer, S.; Dooleweerdt, K.; Lindhardt, A. T.; Rottländer, M.; Skrydstrup, T. *Org. Lett.* **2009**, *11*, 4208–4211; (h) Liu, X.-Y.; Che, C.-M. *Org. Lett.* **2009**, *11*, 4204–4207; (i) Zhang, Z.; Lee, S. D.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2009**, *131*, 5372–5373; (j) Iglesias, A.; Muñiz, K. *Chem. Eur. J.* **2009**, *15*, 10563–10569.

3. For recent selected examples of gold-catalyzed hydroalkoxylation, see: (a) Barluenga, J.; Fernández, A.; Diéguez, A.; Rodríguez, F.; Fañanás, F. J. *Chem. Eur. J.* **2009**, *15*, 11660–11667; (b) Diéguez-Vázquez, A.; Tzschucke, C. C.; Crecente-Campo, J.; McGrath, S.; Ley, S. V. *Eur. J. Org. Chem.* **2009**, 1698–1706; (c) Hirai, T.; Hamasaki, A.; Nakamura, A.; Tokunaga, M. *Org. Lett.* **2009**, *11*, 5510–5513; (d) Cui, D.-M.; Zheng, Z.-L.; Zhang, C. *J. Org. Chem.* **2009**, *74*, 1426–1427; (e) Zhang, Z.; Widenhoefer, R. A. *Org. Lett.* **2009**, *11*, 2079–2081; (f) Paton, R. S.; Maseras, F. *Org. Lett.* **2009**, *11*, 2237–2240; (g) Hadfield, M. S.; Lee, A.-L. *Org. Lett.* **2010**, *12*, 484–487; (h) Horino, Y.; Takata, Y.; Hashimoto, K.; Kuroda, S.; Kimura, M.; Tamaru, Y. *Org. Biomol. Chem.* **2008**, *6*, 4105–4107; (i) Cui, D.-M.; Yu, K.-R.; Zhang, C. *Synlett* **2009**, 1103–1106.
4. For our previous Pd-catalyzed hydrofunctionalizations of alkynes, see: (a) Kadota, I.; Shibuya, A.; Lutete, M. L.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 4570–4571; (b) Lutete, M. L.; Kadota, I.; Shibuya, A.; Yamamoto, Y. *Heterocycles* **2002**, *58*, 347–357; (c) Lutete, L. M.; Kadota, I.; Yamamoto, Y. *J. Am. Chem. Soc.* **2004**, *126*, 1622–1623; (d) Patil, N. T.; Wu, H.; Kadota, I.; Yamamoto, Y. *J. Org. Chem.* **2004**, *69*, 8745–8750; (e) Patil, N. T.; Pahadi, N. K.; Yamamoto, Y. *Tetrahedron Lett.* **2005**, *46*, 2101–2103; (f) Kadota, I.; Shibuya, A.; Gyoung, Y. S.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 10262–10263; (g) Patil, N. T.; Kadota, I.; Shibuya, A.; Gyoung, Y. S.; Yamamoto, Y. *Adv. Synth. Catal.* **2004**, *346*, 800–804; (h) Patil, N. T.; Yamamoto, Y. *J. Org. Chem.* **2004**, *19*, 6478–6481; (i) Kadota, I.; Lutete, M. L.; Shibuya, A.; Yamamoto, Y. *Tetrahedron Lett.* **2001**, *42*, 6207–6210; (j) Patil, N. T.; Khan, N. F.; Yamamoto, Y. *Tetrahedron Lett.* **2004**, *45*, 8497–8499; (k) Patil, N. T.; Lutete, L. M.; Wu, H.; Pahadi, N. K.; Gridnev, I. D.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 4270–4279; (l) Patil, N. T.; Huo, Z.; Bajracharya, G. B.; Yamamoto, Y. *J. Org. Chem.* **2006**, *71*, 3612–3614; (m) Bajracharya, G. B.; Huo, Z.; Yamamoto, Y. *J. Org. Chem.* **2005**, *70*, 4883–4886; (n) Huo, Z.; Patil, N. T.; Jin, T.; Pahadi, N. K.; Yamamoto, Y. *Adv. Synth. Catal.* **2007**, *349*, 680–684.
5. (a) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533–1554; (b) Gronbeck, H.; Curioni, A.; Andreoni, W. *J. Am. Chem. Soc.* **2000**, *122*, 3839–3842; (c) Fujita, K.; Nakamura, N.; Ohno, H.; Leigh, B. S.; Niki, K.; Gray, H. B.; Richards, J. H. *J. Am. Chem. Soc.* **2004**, *126*, 13954–13961.
6. (a) Kondo, T.; Mitsudo, T. *Chem. Rev.* **2000**, *100*, 3205–3220; (b) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079–3159; (c) Han, L.-B.; Zhang, C.; Yazawa, H.; Shimada, S. *J. Am. Chem. Soc.* **2004**, *126*, 5080–5081; (d) Cao, C.; Fraser, L. R.; Love, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 17614–17615; (e) Kondoh, A.; Takami, K.; Yorimitsu, H.; Oshima, K. *J. Org. Chem.* **2005**, *70*, 6468–6473; (f) Brouwer, C.; Rahaman, R.; He, C. *Synlett* **2007**, 1785–1789; (g) Yadav, J. S.; Reddy, B. V. S.; Ravindar, A. R. K.; Baishy, G. *Chem. Lett.* **2007**, *36*, 1474–1475; (h) Weiss, C. J.; Wobser, S. D.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 2062–2063.
7. (a) Ogawa, A.; Kawakami, J.; Sonoda, N.; Hirau, T. *J. Org. Chem.* **1996**, *61*, 4161–4163; (b) Kodama, S.; Nomoto, A.; Kajitani, M.; Nishinaka, E.; Sonoda, M.; Ogawa, A. *J. Sulfur Chem.* **2009**, *30*, 309–318.
8. Morita, N.; Krause, N. *Angew. Chem., Int. Ed.* **2006**, *45*, 1894–1899.
9. (a) Nishina, N.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 3314–3317; (b) Nishina, N.; Yamamoto, Y. *Synlett* **2007**, 1767–1770; (c) Nishina, N.; Yamamoto, Y. *Tetrahedron Lett.* **2008**, *49*, 4908–4911; (d) Nishina, N.; Yamamoto, Y. *Tetrahedron* **2009**, *65*, 1799–1808.
10. The *E*/*Z* isomers of **4a** were identified by comparison with the literature, see: Silveira, C. C.; Perin, G.; Braga, A. L.; Dabdoub, M. J.; Jacob, R. G. *Tetrahedron* **1999**, *55*, 7421–7432.
11. Compound **3a**: White solid; mp 103.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61–7.65 (m, 4H), 7.24–7.42 (m, 11H), 3.19 (s, 2H), 1.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.8, 136.3, 132.1, 131.2, 128.9, 128.5, 127.7, 126.7, 63.7, 48.1, 27.7; IR (neat) 1471, 1451, 1303, 1085, 1022, 746, 701, 690 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{20}S_2Na$ (M+Na) 359.0899. Found 359.0897.
Compound **3b:** White solid; mp 75 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60–7.64 (m, 4H), 7.32–7.42 (m, 6H), 7.18–7.24 (m, 2H), 6.94–7.00 (m, 2H), 3.15 (s, 2H), 1.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.8 (J = 235 Hz), 136.8, 132.6 (J = 8.3 Hz), 131.9 (J = 3.3 Hz), 131.8, 129.0, 128.5, 114.5 (J = 21.6 Hz), 63.5, 47.3, 27.6; IR (neat) 1506, 1471, 1436, 1220, 1056, 854, 774, 703, 691 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{19}FS_2Na$ (M+Na) 377.0804. Found 377.0803.
Compound **3c:** White solid; mp 93.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58–7.64 (m, 4H), 7.32–7.42 (m, 6H), 7.23–7.25 (m, 2H), 7.16–7.22 (m, 2H), 3.12 (s, 2H), 1.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.8, 134.7, 132.7, 132.4, 131.8, 129.1, 128.6, 127.8, 63.4, 47.4, 27.6; IR (neat) 1487, 1469, 1435, 1092, 845, 801, 754, 702, 691 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{19}ClS_2Na$ (M+Na) 393.0509. Found 393.0507.
Compound **3d:** White solid; mp 92 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60–7.66 (m, 4H), 7.22–7.40 (m, 6H), 7.08–7.18 (m, 4H), 3.15 (s, 2H), 2.35 (s, 3H), 1.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.8, 136.3, 133.2, 132.1, 131.0, 128.9, 128.5, 128.4, 63.8, 47.7, 27.7, 21.2; IR (neat) 1510, 1470, 1435, 1064, 1022, 754, 702, 690 cm^{-1}. HRMS (ESI) Calcd for $C_{22}H_{22}S_2Na$ (M+Na) 373.1055. Found 373.1054.
Compound **3e:** Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36–7.46 (m, 4H), 7.06–7.24 (m, 8H), 3.12 (s, 2H), 2.35 (s, 9H), 1.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.1, 137.4, 136.2, 133.8, 133.4, 131.9, 131.1, 129.7, 128.4, 128.2, 63.6, 47.9, 27.7, 21.3, 21.2; IR (neat) 1572, 1473, 1444, 1056, 806, 779, 693 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{26}S_2Na$ (M+Na) 401.1368. Found 401.1365.
Compound **3f:** White solid; mp 133.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45–7.55 (m, 4H), 7.21–7.30 (m, 5H), 7.10–7.17 (m, 4H), 3.15 (s, 2H), 2.38 (s, 6H), 1.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.1, 136.9, 136.5, 131.2, 129.3, 128.6, 127.6, 126.7, 63.4, 48.0, 27.5, 21.4; IR (neat) 1489, 1450, 1063, 1017, 815, 754, 704, 679 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{24}S_2Na$ (M+Na) 387.1212. Found 387.1210.
Compound **3g:** White solid; mp 66 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36–7.46 (m, 4H), 7.10–7.30 (m, 9H), 3.20 (s, 2H), 2.32 (s, 6H), 1.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.2, 137.4, 136.5, 133.9, 131.8, 131.2, 129.7, 128.2, 127.6, 126.7, 63.5, 48.3, 27.7, 21.3; IR (neat) 1590, 1473, 1080, 881, 853, 789, 751, 694 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{24}S_2Na$ (M+Na) 387.1212. Found 387.1211.
Compound **3h:** White solid; mp 112 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20–7.50 (m, 13H), 3.12 (s, 2H), 1.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.1, 135.8, 131.7, 131.1, 130.9, 127.8, 127.0, 123.9, 63.9, 48.2, 27.6; IR (neat) 1580, 1471, 1435, 1303, 1062, 1022, 746, 702, 690 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{18}Br_2S_2Na$ (M+Na) 514.9109. Found 514.9108.
Compound **3i:** Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55–7.60 (m, 2H), 7.47–7.53 (m, 2H), 7.35–7.40 (m, 2H), 7.20–7.35 (m, 7H), 3.17 (s, 2H), 1.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.1, 135.7, 134.7, 134.1, 133.7, 131.1, 129.6, 129.3, 127.8, 127.0, 64.3, 48.4, 27.7; IR (neat) 1573, 1561, 1459, 1070, 881, 776, 700, 680 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{18}Cl_2S_2Na$ (M+Na) 427.0119. Found 427.0118.