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Ag(I)-catalyzed C–H borylation of terminal alkynes

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ABSTRACT

An efficient Ag(I)-catalyzed borylation method of terminal alkynes is reported. The obtained borylated alkynes are shown to engage in C–Br, C–CN, C–N, and C–C bond formation with various reaction partners. Meanwhile the Ag(I) catalyst could be regenerated in the presence of PPh_3 and BF_3.

1. Introduction

Boronic acids and borate esters are useful intermediates in organic synthesis,[1] particularly, for reactions involving carbon–carbon bond formation through the palladium-catalyzed Suzuki–Miyaura cross-coupling reaction, the chemistry of which has been developed extensively in the past decade. Prevalent methods for the formation of carbon–boron bonds involve the metal-catalyzed borylation of aryl halides[2,3] or the addition of aryllithium or magnesium species to borates.[1] Recently, transition metal (Ir, Rh, Pd, Cu)-catalyzed C(sp^2, sp^3)–H borylation methods are reported more.[4–9] However, to our knowledge, most of borylated alkynes were synthesized with an equivalent strong base,[10] such as *n*-BuLi, and Ir-catalyzed C(sp)–H borylation of terminal alkynes are currently under development.[11] Due to the expensive price of Ir-species, there is a need to develop other methods for this synthesis. Herein, a Ag(I)-catalyzed borylation method of terminal alkynes is reported. The obtained borylated alkynes are shown to engage in C–Br, C–CN, C–N, and C–C bond formation with various reaction partners. Meanwhile the Ag(I) catalyst could be regenerated in the presence of PPh_3 and BF_3.

2. Results and discussion

Inspired by Lu's work,[12] which use AgI as catalyst affording carboxylation of terminal alkynes, we attempt to use the similar Ag(I) to achieve C(sp)–H borylation (Scheme 1). We began our investigation by reacting PhC≡CH **1a** and $B(O^iPr)pin$ ($pin{=}Me_4C_2O_2$) in the presence of different silver salts, bases, and solvents to optimize the reaction conditions. The catalytic system using 1 mol % of AgI as catalyst and Cs_2CO_3 as base gave an encouraging yield of 38% for **2a** (entry 1). Other Ag(I) salt could also afford some amount product (**2a**), but AgCl establishing the best activity increased the yield to 51% (entries 1–5). Further reaction with other bases led no significant improvement on the yield (entries 6–8). To our surprise, an additive ligand helped increasing the yield to 83% (entries 9–12). Notably, the mixed ligands of PPh_3 and $\mathbf{L_1}$ gave the best yield to 92% (entry 13). Increasing the amount of catalyst and ligand did not improve the yield (entry 15). Very poor yield of **2a** was detected either without AgCl or without base (entries 16 and 17).

With the optimized reaction conditions (Table 1, entry 13), the substrate scope was then examined (Table 2). Substrates bearing various aryl-substituted terminal alkynes could afford the corresponding borate esters in good to excellent yields (Table 2). Both electron-withdrawing and electron-donating substitutions on the aromatic ring were successfully borylated with $B(O^iPr)pin$ (Table 2, **2a**–**2i**). More importantly, a variety of alkyl-substituted terminal alkynes could also be borylated in good yield under the normal conditions (Table 2, **2j**–**2o**).

Additionally, to demonstrate the utility of this borylation method, we conducted the reaction on gram scale, which proved **2a** in 68% yield. Subsequently, we also showed that **2a** could be converted to a wide range of desirable synthons in good yields using known conversion such as halogenation,[13] cyanation,[13] amination,[14] and homocoupling[15] with itself (Scheme 2).

Finally, we try to recycled the Ag-catalyst. All silver species after the reaction could be recycled conveniently by reacting with 1 equiv PPh_3 and 2 equiv BF_3, then recrystallized by CH_3OH and

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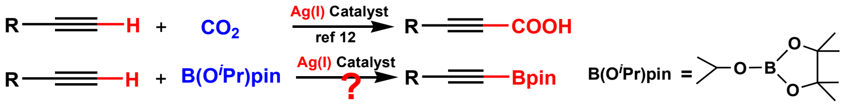
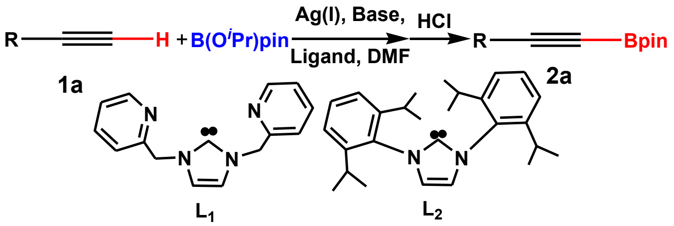


Scheme 1. The C–H bond functionalization of terminal alkynes.

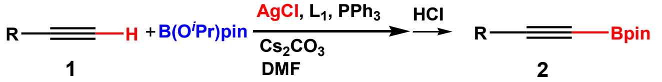
Table 1
Borylation of PhC≡CH

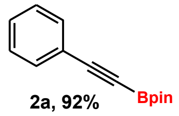
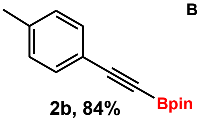
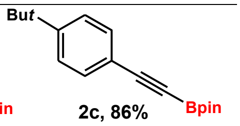
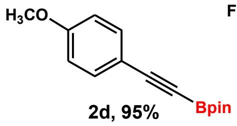
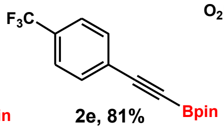
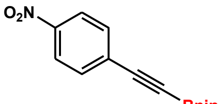
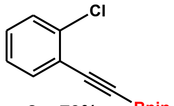
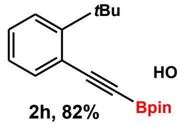
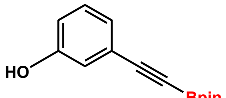
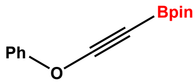
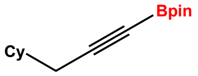
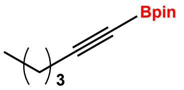
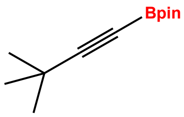
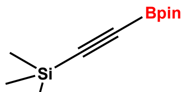
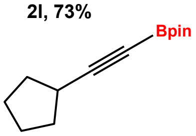


Entry[a]	Cat: Ag(I) (1 mol %)	Base	Ligand	Yield[c] (%)
1	AgI	Cs_2CO_3	No	38
2	AgF	Cs_2CO_3	No	45
3	AgCl	Cs_2CO_3	No	51
4	AgBr	Cs_2CO_3	No	41
5	AgOAc	Cs_2CO_3	No	25
6	AgCl	K_2CO_3	No	12
7	AgCl	K_3PO_4	No	29
8	AgCl	KO^{t}Bu	No	<5
9	AgCl	Cs_2CO_3	PPh_3	60
10	AgCl	Cs_2CO_3	Py	43
11	AgCl	Cs_2CO_3	L_1	83
12	AgCl	Cs_2CO_3	L_2	68
13	AgCl	Cs_2CO_3	PPh_3+L_1	92
14	AgCl	Cs_2CO_3	PPh_3+L_2	81
15[b]	AgCl	Cs_2CO_3	PPh_3+L_1	90
16	AgCl	No	PPh_3+L_1	<5
17	No	Cs_2CO_3	PPh_3+L_1	0

[a] Reaction conditions: **1a** (0.5 mmol), B(O^{i}Pr)pin (0.75 mmol), base (1.1 mmol), ligand (1 mol %), catalyst (1 mol %), 5 mL DMF, 50 °C, 24 h.
[b] The same condition as (a) except for ligand (2 mol %), catalyst (2 mol %).
[c] Isolated yield.

Table 2
Scope of substrates under standard conditions (Table 1, entry 13)



 **2a, 92%**	 **2b, 84%**	 **2c, 86%**
 **2d, 95%**	 **2e, 81%**	 **2f, 78%**
 **2g, 79%**	 **2h, 82%**	 **2i, 70%**
 **2j, 85%**	 **2k, 83%**	 **2l, 73%**
 **2m, 68%**	 **2n, 88%**	 **2o, 75%**

H_2O, giving cubane-like $(PPh_3AgCl)_4$[16] and the precursor of *N*-heterocyclic carbenes **L'_1** (Fig. 1). Single crystal X-ray diffraction analysis reveals that **L'_1** contains one imidazolium cation, two $[BF_4]^-$ anion, and one additional H_2O molecule. The unique structure feature for compound (**L'_1**) is the hydrogen bonding interaction between the imidazolium cation and the fluorine atoms of $[BF_4]^-$ anion. Mixing $(PPh_3AgCl)_4$ and **L'_1** could also catalyze this borylation again in good yield (**2a**, 88%) under standard conditions.

3. Conclusions

In summary, we have developed a Ag(I)-catalyzed terminal alkynes borylation method, which can afford the target products on gram scale. Meanwhile, **2a** as an example can be converted to a wide range of desirable synthons in good yield. The Ag-catalyst can be recovered conveniently after the reaction.

4. Experiment

4.1. General

*4.1.1. Synthesis of **2a**–**2o**.* A mixture of **1** (0.5 mmol), B(O^{i}Pr)pin (0.75 mmol), PPh_3+L_1+AgCl (1 mol %), and Cs_2CO_3 (1.1 mmol) in DMF (5 mL) was stirred at 50 °C under Ar atmosphere for 24 h. The reaction mixture was acidified by 1 M solution of hydrochloric acid in an ice water bath, and the aqueous phase was extracted with ethyl acetate (three times). The combined organic layer was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to give the corresponding products.

Note: The carbine ligand (**L_1**) was prepared by mixing the corresponding imidazolidinium salt (1,3-di(2-picolyl)imidazolium chloride) with *n*-LiBu (1 equiv) for 2 h at −78 °C, then adding the other starting materials.

*4.1.2. Synthesis of **3**.* A mixture of **2a** (0.05 mmol), $CuBr_2$ (0.05 mmol) in H_2O, and CH_3OH (1 mL for each) was stirred at 80 °C under Ar atmosphere for 24 h. The combined organic layer was washed with brine, extracted with ethyl acetate, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to give the corresponding products.

*4.1.3. Synthesis of **4**.* A mixture of **2a** (0.05 mmol), CuCN (0.05 mmol), and K_2CO_3 (0.15 mmol) in DMF (1 mL) was stirred at 60 °C under Ar atmosphere for 4 h. The combined organic layer was washed with brine, extracted with ethyl acetate, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to give the corresponding products.

*4.1.4. Synthesis of **5**.* A mixture of **2a** (0.05 mmol), 2-oxozolidinone (0.1 mmol), $Cu(NO_3)_2$ (TEMEDA) (10 mol %), and K_2CO_3 (0.15 mmol) in CH_3OH (1 mL) was stirred in rt under Ar atmosphere for 48 h. The combined organic layer was washed with brine, extracted with ethyl acetate, dried over Na_2SO_4, and evaporated under reduced

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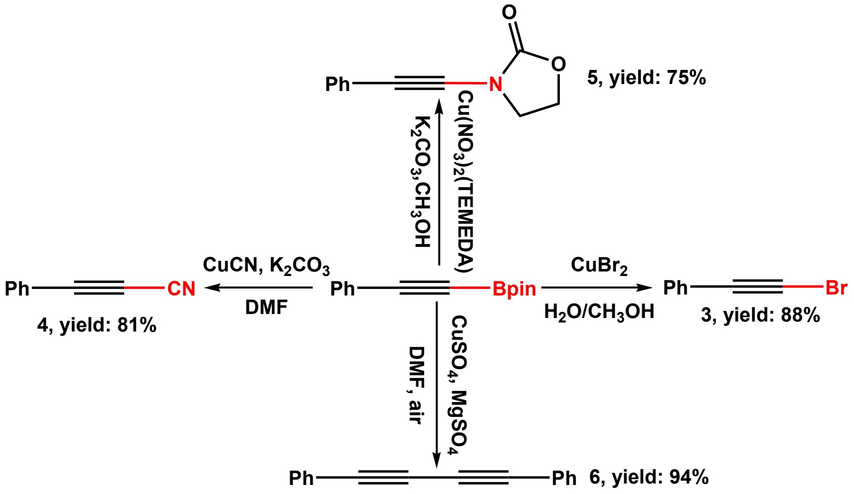

Scheme 2. Versatile transformations of the borylated products.

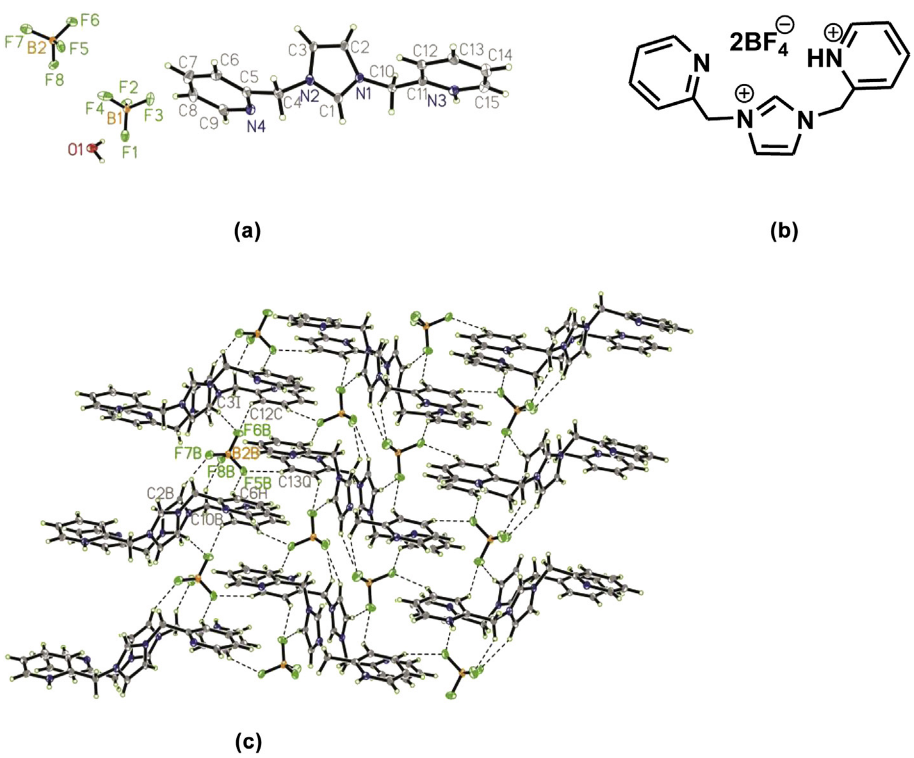

Fig. 1. (a) Molecular structure of $\mathbf{L}'_1$; (b) chemical structure of $\mathbf{L}'_1$; (c) view of the two-dimensional network formed by C–H···F hydrogen bonds.

pressure. The crude product was purified by silica gel column chromatography to give the corresponding products.

*4.1.5. Synthesis of **6***. A mixture of **2a** (0.05 mmol), $CuSO_4$ (0.02 mmol), $MgSO_4$ (0.1 mmol) in DMF (1 mL) was stirred at 60 °C under air atmosphere for 24 h. The combined organic layer was washed with brine, extracted with ethyl acetate, dried over Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography to give the corresponding products.

4.2. Characterization data

*4.2.1. Compound **2a***.[11] Yield 92%. ^1H NMR (500 MHz, $CDCl_3$): δ 7.40 (m, 2H), 6.86 (m, 3H), 1.03 (s, 12H); ^{11}B NMR (128 MHz, $CDCl_3$): δ 24.5; $[M]^+$: HRMS for $C_{14}H_{17}BO_2$ calcd 228.0946, found 228.0945.

*4.2.2. Compound **2b***.[11] Yield 84%. ^1H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, J=7.5 Hz, 2H), 7.10 (d, J=7.5 Hz, 2H), 2.35 (s, 3H), 1.28 (s, 12H); ^{11}B NMR (128 MHz, $CDCl_3$): δ 23.9; $[M]^+$: HRMS for $C_{15}H_{19}BO_2$ calcd 242.1212, found 242.1209.

*4.2.3. Compound **2c***. Yield 86%. Colorless oil, ^1H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, J=8.6 Hz, 2H), 7.32 (d, J=8.6 Hz, 2H), 1.32 (s, 9H), 1.24 (s, 12H); ^{11}B NMR (128 MHz, $CDCl_3$): δ 23.5; ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.5, 131.3, 129.8, 119.1, 108.3 (br), 85.0, 29.8, 25.2, 19.8; $[M]^+$: HRMS for $C_{18}H_{25}BO_2$ calcd 284.2009, found 284.2010.

*4.2.4. Compound **2d***. Yield 95%. Colorless oil, ^1H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, J=8.2 Hz, 2H), 6.75 (d, J=8.2 Hz, 2H), 3.78 (s, 3H), 1.18 (s, 12H); ^{11}B NMR (128 MHz, $CDCl_3$): δ 23.1; ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.3, 133.6, 131.8, 123.2, 101.5 (br), 85.4, 25.9, 18.3; [M]$^+$: HRMS for $C_{15}H_{19}BO_3$ calcd 258.1206, found 258.1210.

4.2.5. Compound ***2e***. Yield 81%. Mp 63–65 °C, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (m, 4H), 1.27 (s, 12H); ^{11}B NMR (128 MHz, $CDCl_3$): δ 25.3; ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.2, 135.1, 134.5, 128.2, 107.9 (br), 86.1, 27.4, 21.5; [M]$^+$: HRMS for $C_{15}H_{16}BF_3O_2$ calcd 296.0925, found 296.0922.

4.2.6. Compound ***2f***. Yield 78%. Mp 68–69 °C, ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (d, J=8.6 Hz, 2H), 7.64 (d, J=8.6 Hz, 2H), 1.23 (s, 12H); ^{11}B NMR (128 MHz, $CDCl_3$): δ 25.8; ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.2, 133.8, 131.6, 129.7, 109.3 (br), 84.8, 22.3; [M]$^+$: HRMS for $C_{14}H_{16}BNO_4$ calcd 273.0921, found 273.0920.

4.2.7. Compound ***2g***. Yield 79%. Mp 48–50 °C, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (m, 4H), 1.16 (s, 12H); ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.9; ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.5, 135.8, 133.8, 131.6, 129.7, 127.5, 109.3 (br), 85.2, 21.8; [M]$^+$: HRMS for $C_{14}H_{16}BClO_2$ calcd 262.5396, found 262.5399.

4.2.8. Compound ***2h***. Yield 82%. Colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (m, 4H), 1.31 (s, 9H), 1.08 (s, 12H); ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.5; ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.8, 135.4, 132.9, 130.3, 128.5, 126.3, 103.9 (br), 84.9, 29.6, 24.3, 20.5; [M]$^+$: HRMS for $C_{18}H_{25}BO_2$ calcd 284.2009, found 284.1006.

4.2.9. Compound ***2i***. Yield 70%. Mp 53–55 °C, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11 (m, 4H), 1.07 (s, 12H); ^{11}B NMR (128 MHz, $CDCl_3$): δ 23.3; ^{13}C NMR (125 MHz, $CDCl_3$): δ 130.8, 129.4, 127.6, 125.0, 123.5, 118.9, 105.1 (br), 84.6, 20.1; [M]$^+$: HRMS for $C_{14}H_{17}BO_3$ calcd 244.0940, found 244.0939.

4.2.10. Compound ***2j***. Yield 85%. Colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (m, 5H), 1.02 (s, 12H); ^{11}B NMR (128 MHz, $CDCl_3$): δ 23.8; ^{13}C NMR (125 MHz, $CDCl_3$): δ 130.8, 123.5, 121.6, 118.4, 105.8 (br), 83.9, 19.6; [M]$^+$: HRMS for $C_{14}H_{17}BO_3$ calcd 244.0940, found 244.0942.

4.2.11. Compound ***2k***. Yield 83%. Colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.75 (m, 1H), 2.00–1.63 (m, 10H), 0.92 (s, 12H); ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.5; ^{13}C NMR (125 MHz, $CDCl_3$): δ 101.2 (br), 85.5, 29.8, 25.5, 24.9, 22.6, 18.7; [M]$^+$: HRMS for $C_{15}H_{25}BO_2$ calcd 248.1688, found 248.1685.

4.2.12. Compound ***2l***.[11] Yield 73%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.25 (t, J=7.0 Hz, 2H), 1.48 (m, 2H), 1.39 (m, 2H), 1.25 (s, 12H), 0.85 (t, J=7.5 Hz, 3H); ^{11}B NMR (128 MHz, $CDCl_3$): δ 23.5; [M]$^+$: HRMS for $C_{12}H_{21}BO_2$ calcd 208.1049, found 208.1050.

4.2.13. Compound ***2m***. Yield 68%. Colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.33 (s. 9H), 1.01 (s, 12H); ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.2; ^{13}C NMR (125 MHz, $CDCl_3$): δ 101.9 (br), 84.1, 28.3, 21.9, 19.8; [M]$^+$: HRMS for $C_{12}H_{21}BO_2$ calcd 208.1049, found 208.1045.

4.2.14. Compound ***2n***.[11] Yield 88%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.95 (s, 12H), 0.08 (s, 9H); ^{11}B NMR (128 MHz, $CDCl_3$): δ 23.5; [M]$^+$: HRMS for $C_{11}H_{21}BO_2Si$ calcd 224.1797, found 224.1795.

4.2.15. Compound ***2o***. Yield 75%. Colorless oil, ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.73 (m, 1H), 1.92–1.60 (m. 8H), 0.99 (s, 12H); ^{11}B NMR (128 MHz, $CDCl_3$): δ 22.1; ^{13}C NMR (125 MHz, $CDCl_3$): δ 100.5 (br), 82.8, 28.5, 26.4, 22.1, 19.3; [M]$^+$: HRMS for $C_{13}H_{21}BO_2$ calcd 220.1156, found 220.1155.

4.2.16. Compound ***3***.[17] Yield 88%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (m, 2H), 7.25 (m, 3H); [M]$^+$: HRMS for C_8H_5Br calcd 181.0293, found 181.0290.

4.2.17. Compound ***4***.[18] Yield 81%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, J=7.5 Hz, 2H), 7.53 (t, J=7.4 Hz, 1H), 7.42 (t, J=7.4 Hz, 2H); [M]$^+$: HRMS for C_9H_5N calcd 127.1427, found 127.1428.

4.2.18. Compound ***5***.[19] Yield 75%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (m, 2H), 7.30 (m, 3H), 4.48 (t, J=7.8 Hz, 2H), 4.01 (t, J=7.8 Hz, 2H); [M]$^+$: HRMS for $C_{11}H_9NO_2$ calcd 187.1947, found 187.1948.

4.2.19. Compound ***6***.[15] Yield 94%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (m, 4H), 7.29 (m, 6H); [M]$^+$: HRMS for $C_{16}H_{10}$ calcd 202.2506, found 202.2505.

Acknowledgements

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Supplementary data

Experimental procedures and crystallographic data and structural refinement details (SD-Table 1); CCDC-998979 ($\mathbf{L}_1'$) contain 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. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.06.033.

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