

A Simple and Facile Carboxylation Method and Its Application for Synthesis of Liquid Crystals

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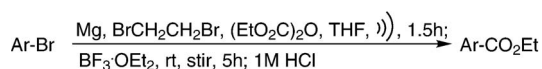
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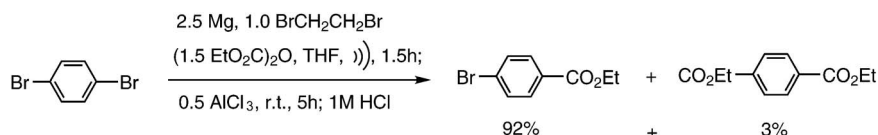
Abstract: Sonication of a mixture of magnesium powder, 1,2-dibromoethane, aryl bromide and diethyl dicarbonate in THF followed by treatment with $\text{BF}_3 \cdot \text{OEt}_2$ at room temperature afforded aryl ester with reasonable yield. A series of aryl bromides were investigated and transformed to their corresponding aryl esters under the reaction conditions.

Key words: carboxylation, Barbier reaction, diethyl dicarbonate, Lewis acid, liquid crystal

Synthesis of carboxylic esters from alkyl or aryl halide usually requires two-step reaction such as carboxylation reaction with Grignard reagent followed by esterification with alcohols. The addition of organometallic reagents to carbon dioxide (dry ice) is the most direct method for the synthesis of carboxylic acids but generally the yields are not very high.^{1,2} Aryl acids or esters have been prepared by the carboxylation reactions of organometallics of bismuth,³ lithium,^{4,5} magnesium,^{6–9} with dry ice or methyl chloroformate or by palladium-mediated carbonylation reactions.^{10,11} Our previous studies showed that organostannane could be prepared from aryl bromides under sonochemical Barbier reaction condition.¹² Thus, we investigated the carboxylation reaction of aromatic bromides under similar sonochemical Barbier reaction condition. Herewith, we wish to report a sonochemical Barbier carboxylation reaction in the presence of Lewis acid, which leads to the synthesis of ethyl aryl esters (Scheme 1).



Scheme 1




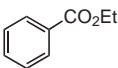
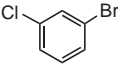
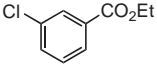
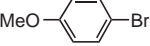
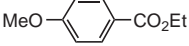
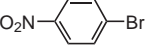
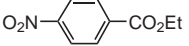
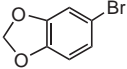
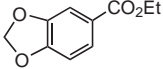



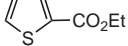
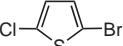
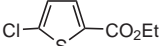

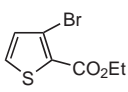

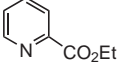
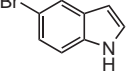
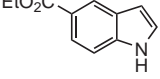
Scheme 2

According to our previous studies for the in situ generation of Grignard reagent under sonication conditions,¹³ we first investigated the carboxylation reactions of 2-bromothiophene with ethyl chloroformate or triethyl orthoformate under sonochemical Barbier reaction conditions. No expected ethyl thiophenyl ester was obtained under the reaction condition. We next investigated that 2-bromothiophene reacted with diethyl dicarbonate instead of ethyl chloroformate under this sonochemical Barbier reaction condition and ethyl thiophenyl ester was produced with 47% yield. Interestingly, the yield of ethyl thiophenyl ester was improved dramatically to 83% when Lewis acid such as $\text{BF}_3 \cdot \text{OEt}_2$ was introduced after sonication. We also observed that the highest yield of thiophenyl ester was obtained when the exact amount of Lewis acid (half molar ratio to substrate) was used. The Lewis acids such as AlCl_3 , TiCl_4 and BBr_3 were also investigated and all can improve the carboxylation yield. The results showed that $\text{BF}_3 \cdot \text{OEt}_2$ is the best choice of promoter producing the least amount of byproducts. Thus, a series of aryl bromides were carboxylated under the typical reaction condition and the results are shown in Table 1.

The experimental results showed that aryl bromides bearing electron-withdrawing groups were less reactive or were completely inert to the reaction conditions (Table 1, entries 2 and 4). It should be noted that indole underwent carboxylation without protection of the relatively acidic proton under this reaction condition (Table 1, entry 11).

The phenyl- and thiophene-based derivatives have potential applications as organic materials such as liquid crystal^{14–16} and organic light-emitting diode.^{17–19} Therefore, we investigated this carboxylation reaction of 1,4-dibromobenzene under the typical reaction condition and the results showed that monocarboxybenzene was obtained as the major product (Scheme 2).

Table 1 Carboxylation of a Series of Aryl Bromides Under the Typical Reaction Condition

Entry	Substrate	Product	Yield ^a
1			91%
2			81%
3			72%
4			N.R. ^b
5			74%
6			80%
7			88%
8			83%
9			28% 46% ^c (40%) ^d
10			N.R. ^b
11			43% (39%) ^d

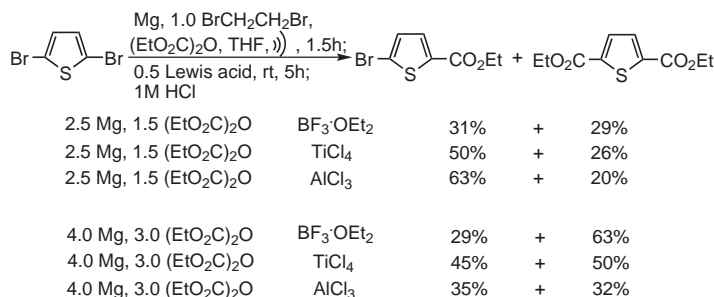
^a The yields were determined after chromatographic purification.

^b No reaction and recovery of starting material.

^c The TiCl_4 was used instead of BF_3 .

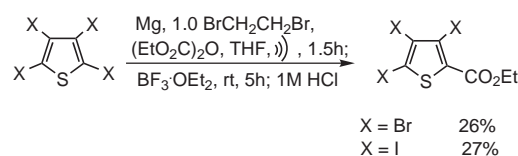
^d The recovered yield of starting material.

We further investigated this carboxylation reaction for 2,5-dibromothiophene and the experimental results showed that nearly equal amount of monoester and diester were obtained (Scheme 3). To improve the selectivity for monoester formation, 2,5-dibromothiophene was treated with different amounts of carboxylating reagents under

**Scheme 3**

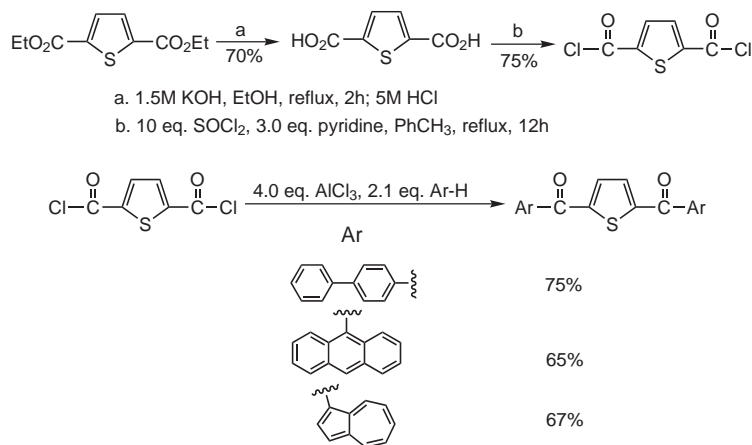
the reaction conditions. However, a mixture of monocarboxylation and dicarboxylation product was produced irrespective of the fact whether equivalent or excess reagents were used under the reaction conditions. The results showed that a mixture of monoester and diester was obtained no matter what kind of Lewis acid was introduced.

The reactivity towards carboxylation was decreased when more electron-withdrawing group was attached to substrate. We also investigated this carboxylation reaction for polyhalothiophene and the results are shown in Scheme 4. Monocarboxylthiophene was obtained as the only product even when excess amounts of magnesium and diethyl dicarbonate were used.

**Scheme 4**

In conclusion, this Lewis acid promoted sonochemical Barbier reaction condition provides a simple and facile method for the synthesis of aryl esters. This procedure features in situ activation of Mg metal to generate Grignard reagent under sonication, which is reacted with diethyl dicarbonate in the presence of Lewis acid to form ethyl aryl ester. In addition, our investigations showed that aryl bromide bearing electron-withdrawing groups were less reactive or even inert to this reaction condition. These results lead us to apply this Lewis acid promoted Barbier reaction for synthesis of potentially phenyl and thiophene-based organic material such as liquid crystal. Thiophene-2,5-dicarboxylic acid ethyl ester was hydrolyzed to its corresponding dicarboxylic acid with 70% yield under basic reaction condition²⁰ (Scheme 5).

Dicarboxylic acid was transformed to diacyl chloride in 75% yield by treatment with thionyl chloride and NEt_3 .²¹ Thiophene-based 2,5-diaryl ketones were synthesized by the Friedel–Crafts acylation reactions²² of 2,5-diacyl chloride with aromatic compounds such as biphenyl, anthracene and azulene. These thiophene-based diketones did not exhibit any efficient light emitting or any liquid crystal properties.



Scheme 5

These results lead us to apply this Lewis acid promoted Barbier reaction for synthesis of thiophene-based liquid crystal materials. 5-Bromo-thiophene-2-acyl chloride was prepared by the above acylation method. 5-Bromo-thiophene-2-acyl chloride was reacted with biphenylethyne under palladium catalyzed coupling reaction²³ (Scheme 6).

Dialkyne was obtained as the major product (35%) by the self-coupling reaction of biphenylethyne and the expected propargyl ketone was obtained in 11% yield. This new type of thiophene-based propargyl ketone was found to exhibit smectic A phase (124.6–132.2 °C) as evidenced by the fan-shaped texture (Figure 1) under polarized optical microscope. With the new preparative methodology, the synthesis of related mesogenic oligo-thiophene derivatives are underway.

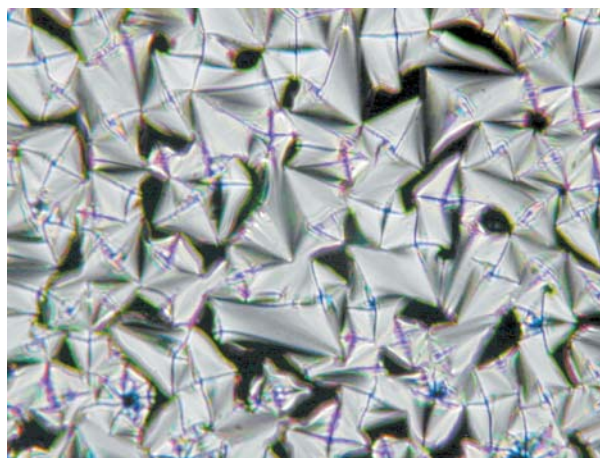
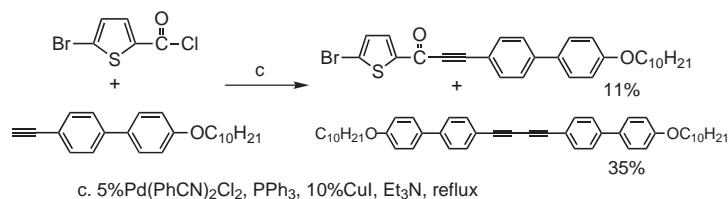


Figure 1

All experiments were carried out under a nitrogen atmosphere, which was dried primarily by passing through a column of KOH layered with CaSO₄. All reagents (Table 1, Schemes 2– 6) were purchased and used directly without further purification. The ¹H NMR and ¹³C NMR spectra were recorded on Bruker-AC300P with CDCl₃ as the solvent and the internal standard. Chemical shifts are reported in ppm and resonance patterns are reported with the notations of s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet). Coupling constants (*J*) are reported in Hz. Mass spectra (MS) were recorded on JOEL SX-102A and VG 70-250S spectrophotometers and are reported in *m/z* units for the most abundant peaks. IR spectra were recorded on a BIO-RAD FTS-40 infrared spectrophotometer as a liquid film (neat) or a Nujol mull. Polystyrene was used as a standard, and the spectra are reported in reciprocal centimeters (cm⁻¹). UV spectra were recorded on a Shimadzu 3101PC spectrophotometer in the indicated solvent, and are reported in nm.

Carboxylation Reaction; General Procedure

A reaction mixture of aryl bromide (1.0 mmol), Mg powder (2.5 mmol), 1,2-dibromoethane (1.0 mmol) and diethyl dicarbonate (1.5 mmol) in anhyd THF (5 mL) was sonicated for 1.5 h in cleaning bath (Elmar, 50 kHz; the bath should be filled with water containing 5% detergent. In our laboratory, we used Decon 90 which permits much more even cavitations in bath water). BF₃·OEt₂ (0.5 mmol) was added to the reaction mixture at r.t. without sonication and then stirred at r.t. for 5 h. Aqueous HCl (1 M, 10 mL) was added to the reaction mixture and stirred at r.t. for 5 min. The reaction mixture was extracted with EtOAc (3 × 10 mL) and the combined organic layer was washed with brine, dried over MgSO₄ and then organic solvent was removed directly under reduced pressure. Further purification was achieved on a flash chromatograph with EtOAc–hexane as eluant.



Scheme 6

Benzoic Acid Ethyl Ester (Table 1, entry 1)

$^1\text{H NMR}$: $\delta = 1.40$ (t, $J = 7.1$ Hz, 2 H), 4.38 (q, $J = 7.1$ Hz, 3 H), 7.41 (m, 2 H), 7.55 (m, 1 H), 8.05 (m, 2 H).

$^{13}\text{C NMR}$: $\delta = 14.3, 60.9, 128.3, 129.5, 130.6, 132.8, 166.6$.

MS: $m/z = 150$ (47) [M], 122 (60), 106 (14), 105 (base), 78 (6), 77 (67), 51 (19).

HRMS: m/z calcd for $\text{C}_9\text{H}_{10}\text{O}_2$: 150.0681; found: 150.0687.

4-Chloro-benzoic Acid Ethyl Ester (Table 1, entry 2)

IR: 3063 (w), 2983 (w), 1723 (s), 1292 (s), 1256 (s), 1131 (m), 1021 (m), 894 (s), 748 (w) cm^{-1} .

$^1\text{H NMR}$: $\delta = 1.40$ (t, $J = 7.2$ Hz, 2 H), 4.39 (q, $J = 7.2$ Hz, 3 H), 7.38 (t, m, 1 H), 7.52 (m, 1 H), 7.93 (m, 1 H), 8.02 (t, m, 1 H).

$^{13}\text{C NMR}$: $\delta = 14.3, 61.4, 127.7, 129.6, 132.3, 132.8, 134.5, 165.4$.

MS: $m/z = 186$ (10), 184 (34) [M], 158 (16), 156 (65), 141 (48), 139 (base), 113 (13), 111 (46), 75 (19).

HRMS: m/z calcd for $\text{C}_9\text{H}_9\text{ClO}_2$: 184.0289; found: 184.0291.

3-Methoxy-Benzoic Acid Ethyl Ester (Table 1, entry 3)

$^1\text{H NMR}$: $\delta = 1.38$ (t, $J = 7.2$ Hz, 2 H), 3.86 (s, 3 H), 4.35 (q, $J = 7.2$ Hz, 3 H), 6.91 (d, $J = 8.1$ Hz, 2 H), 8.00 (d, $J = 8.1$ Hz, 2 H).

$^{13}\text{C NMR}$: $\delta = 14.2, 61.3, 127.6, 129.6, 132.3, 132.8, 134.5, 165.4$.

MS: $m/z = 180$ (25) [M], 152 (20), 139 (6), 136 (10), 135 (base), 107 (10), 92 (9), 77 (14).

HRMS: m/z calcd for $\text{C}_{10}\text{H}_{12}\text{O}_3$: 180.0787; found: 180.0805.

Benzo[1,3]dioxole-5-carboxylic Acid Ethyl Ester (Table 1, entry 5)

IR: 2983 (w), 1713 (s), 1442 (s), 1258 (s), 1158 (s), 1105 (m), 1037 (m), 761 (s) cm^{-1} .

$^1\text{H NMR}$: $\delta = 1.37$ (t, $J = 7.1$ Hz, 2 H), 4.34 (q, $J = 7.1$ Hz, 3 H), 6.03 (s, 2 H), 6.83 (d, $J = 8.2$ Hz, 1 H), 7.47 (d, $J = 1.7$ Hz, 1 H), 7.65 (dd, $J = 8.2, 1.7$ Hz, 1 H).

$^{13}\text{C NMR}$: $\delta = 14.3, 60.9, 101.7, 107.9, 109.5, 124.6, 125.2, 147.7, 151.5, 166.0$.

MS: $m/z = 194$ (42) [M], 166 (24), 165 (18), 150 (13), 149 (base), 121 (21), 65 (10), 63 (12).

HRMS: m/z calcd for $\text{C}_{10}\text{H}_{10}\text{O}_4$: 194.0579; found: 194.0592.

Naphthalene-1-carboxylic Acid Ethyl Ester (Table 1, entry 6)

$^1\text{H NMR}$: $\delta = 1.47$ (t, $J = 7.1$ Hz, 2 H), 4.49 (q, $J = 7.1$ Hz, 3 H), 7.56 (m, 2 H), 7.60 (m, 1 H), 7.90 (m, 1 H), 8.02 (m, 1 H), 8.19 (m, 1 H), 8.91 (m, 1 H).

$^{13}\text{C NMR}$: $\delta = 14.3, 61.0, 124.4, 125.8, 126.1, 127.5, 127.6, 128.5, 130.0, 131.3, 133.1, 133.8, 167.6$.

MS: $m/z = 200$ (52) [M], 172 (17), 156 (33), 155 (base), 128 (30), 127 (72), 126 (15), 111 (60), 77 (15).

HRMS: m/z calcd for $\text{C}_{13}\text{H}_{12}\text{O}_2$: 200.0837; found: 200.0845.

Thiophene-2-carboxylic Acid Ethyl Ester (Table 1, entry 7)

$^1\text{H NMR}$: $\delta = 1.38$ (t, $J = 7.0$ Hz, 2 H), 4.36 (q, $J = 7.0$ Hz, 3 H), 7.09 (dd, $J = 5.0, 3.8$ Hz, 1 H), 7.54 (dd, $J = 5.0, 1.3$ Hz, 1 H), 7.80 (dd, $J = 3.8, 1.3$ Hz, 1 H).

$^{13}\text{C NMR}$: $\delta = 14.3, 61.1, 127.6, 132.1, 133.2, 134.1, 162.3$.

MS: $m/z = 156$ (25) [M], 141 (3), 128 (26), 112 (10), 111 (base), 83 (5), 57 (3).

HRMS: m/z calcd for $\text{C}_7\text{H}_8\text{O}_2\text{S}$: 156.0245; found: 156.0259.

5-Chloro-thiophene-2-carboxylic Acid Ethyl Ester (Table 1, entry 8)

IR: 2982 (w), 1711 (s), 1426 (s), 1279 (s), 1254 (s), 1090 (s), 1060 (s), 747 (s) cm^{-1} .

$^1\text{H NMR}$: $\delta = 1.36$ (t, $J = 7.3$ Hz, 2 H), 4.33 (q, $J = 7.3$ Hz, 3 H), 6.92 (d, $J = 4.0$ Hz, 1 H), 7.58 (d, $J = 4.0$ Hz, 1 H).

$^{13}\text{C NMR}$: $\delta = 14.2, 61.4, 127.2, 132.2, 132.8, 137.1, 161.3$.

MS: $m/z = 192$ (12), 190 (36) [M], 164 (11), 162 (33), 147 (39), 145 (base), 75 (4), 73 (12).

HRMS: m/z calcd for $\text{C}_7\text{H}_7\text{ClO}_2\text{S}$: 189.9856; found: 189.9873.

3-Bromo-thiophene-2-carboxylic Acid Ethyl Ester (Table 1, entry 9)

IR: 3120 (w), 2985 (w), 2940 (w), 2905 (w), 1720 (s), 1515 (m), 1416 (s), 1279 (m), 1245 (s), 1090 (m), 1080 (m), 767 (m) cm^{-1} .

$^1\text{H NMR}$: $\delta = 1.39$ (t, $J = 7.2$ Hz, 2 H), 4.37 (q, $J = 7.2$ Hz, 3 H), 7.09 (d, $J = 5.4$ Hz, 1 H), 7.45 (d, $J = 5.4$ Hz, 1 H).

MS: $m/z = 236$ (12), 234 (12) [M], 208 (15), 206 (15), 191 (11), 189 (38), 147 (36), 86 (17), 69 (26), 57 (base), 56 (51).

HRMS: m/z calcd for $\text{C}_7\text{H}_7\text{BrO}_2\text{S}$: 233.9350; found: 233.9347.

1H-Indole-5-carboxylic Acid Ethyl Ester (Table 1, entry 11)

IR: 2982 (w), 1741 (s), 1450 (s), 1378 (s), 1342 (s), 1324 (s), 1241 (s), 1084 (m), 1046 (m), 761 (s) cm^{-1} .

$^1\text{H NMR}$: $\delta = 1.46$ (t, $J = 7.2$ Hz, 2 H), 4.48 (q, $J = 7.2$ Hz, 3 H), 6.50 (d, $J = 3.5$ Hz, 1 H), 7.40 (d, $J = 8.8$ Hz, 1 H), 7.59 (d, $J = 3.5$ Hz, 1 H), 7.67 (d, $J = 2.1$ Hz, 1 H), 8.02 (dd, $J = 8.8, 2.1$ Hz, 1 H).

$^{13}\text{C NMR}$: $\delta = 14.3, 63.4, 107.8, 123.5, 126.6, 127.1, 132.1, 133.9, 150.6$.

5-Bromo-thiophene-2-carboxylic Acid Ethyl Ester (Scheme 3)

IR: 3095 (w), 2980 (m), 1710 (s), 1526 (m), 1417 (s), 1322 (m), 1278 (s), 1246 (s), 1081 (w), 808 (w), 744 (m) cm^{-1} .

$^1\text{H NMR}$: $\delta = 1.36$ (t, $J = 7.1$ Hz, 2 H), 4.33 (q, $J = 7.1$ Hz, 3 H), 7.06 (d, $J = 4.0$ Hz, 1 H), 7.54 (d, $J = 4.0$ Hz, 1 H).

$^{13}\text{C NMR}$: $\delta = 14.2, 61.4, 120.0, 130.8, 133.4, 135.2, 137.1, 161.1$.

MS: $m/z = 236$ (35), 234 (34) [M], 208 (36), 206 (35), 191 (base), 189 (98), 163 (5), 161 (4), 119 (5), 117 (5), 82 (20).

HRMS: m/z calcd for $\text{C}_7\text{H}_7\text{BrO}_2\text{S}$: 233.9349; found: 233.9350.

Thiophene-2,5-dicarboxylic Acid Ethyl Ester (Scheme 3)

IR: 2985 (m), 1713 (s), 1644 (w), 1455 (w), 1369 (w), 1246 (s), 1089 (m), 1051 (w), 1012 (w), 749 (m) cm^{-1} .

$^1\text{H NMR}$: $\delta = 1.38$ (t, $J = 7.2$ Hz, 4 H), 4.37 (q, $J = 7.2$ Hz, 6 H), 7.71 (s, 2 H).

$^{13}\text{C NMR}$: $\delta = 14.2, 61.7, 132.8, 139.1, 161.6$.

MS: $m/z = 228$ (35) [M], 213 (9), 200 (25), 184 (15), 183 (base), 172 (40), 156 (20), 155 (99), 111 (17).

HRMS: m/z calcd for $\text{C}_{10}\text{H}_{12}\text{O}_4\text{S}$: 228.0456; found: 228.0459.

[5-(Biphenyl-4-carbonyl)-thiophen-2-yl]-biphenyl-4-yl-methanone (Scheme 5)

$^1\text{H NMR}$: $\delta = 7.40$ – 7.52 (m, 6 H), 7.66 (d, $J = 8.2$ Hz, 4 H), 7.74– 7.77 (m, 6 H), 8.02 (d, $J = 8.2$ Hz, 4 H).

$^{13}\text{C NMR}$: $\delta = 127.3, 128.3, 129.0, 130.0, 133.6, 135.9, 139.7, 145.8, 148.5, 187.5$.

MS: $m/z = 444$ (3) [M], 256 (9), 250 (10), 224 (10), 167 (12), 149 (17), 127 (13), 125 (21), 111 (35), 97 (51), 83 (52), 71 (63), 57 (base).

UV (CH_2Cl_2): λ_{max} (ϵ) = 322 (12500) nm.

[5-(Anthracene-9-carbonyl)-thiophen-2-yl]-anthracen-9-yl-methanone (Scheme 5)

$^1\text{H NMR}$: δ = 7.02 (s, 2 H), 7.43–7.52 (m, 8 H), 7.81–7.84 (m, 4 H), 8.04–8.08 (m, 4 H), 8.57 (m, 2 H).

$^{13}\text{C NMR}$: δ = 124.9, 125.6, 126.9, 128.1, 128.7, 129.2, 130.6, 133.1, 134.7, 151.6, 192.4.

MS: m/z = 492 (8) [M], 316 (8), 308 (17), 281 (24), 280 (base), 252 (44), 250 (34), 179 (19), 178 (40), 126 (27), 125 (29), 83 (21), 69 (38), 57 (35).

HRMS: m/z calcd for $\text{C}_{34}\text{H}_{20}\text{O}_2\text{S}$: 492.1185; found: 429.1174.

UV (CH_2Cl_2): λ_{max} (ϵ) = 254 (11100) nm.

[5-(Azulene-1-carbonyl)-thiophene-2-yl]-azulene-1-yl-methanone (Scheme 5)

$^1\text{H NMR}$: δ = 7.34 (d, J = 4.2 Hz, 2 H), 7.52 (t, J = 9.8 Hz, 2 H), 7.63 (t, J = 9.8 Hz, 2 H), 7.78 (s, 2 H), 7.86 (t, J = 9.8 Hz, 2 H), 8.43 (d, J = 4.2 Hz, 2 H), 8.52 (d, J = 9.8 Hz, 2 H), 9.7 (d, J = 9.8 Hz, 2 H).

$^{13}\text{C NMR}$: δ = 118.1, 124.7, 127.8, 129.2, 132.0, 138.8, 139.2, 139.9, 141.1, 141.6, 145.4, 150.4, 183.4.

MS: m/z = 392 (57) [M], 238 (48), 237 (33), 155 (base), 128 (38), 127 (39).

HRMS: m/z calcd for $\text{C}_{26}\text{H}_{16}\text{O}_2\text{S}$: 392.0871; found: 392.0874.

UV (CH_2Cl_2): λ_{max} (ϵ) = 414 (12600), 288 (19400) nm.

UV (CH_2Cl_2): λ_{max} (ϵ) = 226 (21800) nm.

1-(5-Bromo-thiophen-2-yl)-3-(4-decyloxy-biphenyl-4-yl)-propynone (Scheme 6)

$^1\text{H NMR}$: δ = 0.89 (d, J = 6.5 Hz, 3 H), 1.26–1.54 (m, 14 H), 1.81 (m, 2 H), 4.01 (t, J = 6.5 Hz, 2 H), 6.99 (d, J = 8.7 Hz, 2 H), 7.17 (d, J = 4.1 Hz, 1 H), 7.55 (d, J = 8.7 Hz, 2 H), 7.61 (d, J = 8.7 Hz, 2 H), 7.69 (d, J = 8.7 Hz, 2 H), 7.76 (d, J = 4.1 Hz, 1 H).

$^{13}\text{C NMR}$: δ = 14.1, 22.6, 26.0, 29.3, 29.7, 31.8, 68.1, 86.5, 92.9, 115.0, 117.5, 124.1, 126.7, 128.2, 131.5, 131.8, 133.6, 134.8, 143.5, 146.2, 159.5, 169.0.

MS: m/z = 526 (3), 525 (10), 524 (32), 522 (30) [M], 384 (31), 382 (31), 356 (14), 354 (13), 256 (16), 236 (13), 221 (13), 185 (16), 183 (20), 171 (12), 155 (26), 129 (31), 98 (29), 97 (51), 83 (59), 69 (83), 57 (base).

HRMS: m/z calcd for $\text{C}_{29}\text{H}_{31}\text{BrO}_2\text{S}$: 522.1229; found: 522.1222.

UV (CH_2Cl_2): λ_{max} (ϵ) = 356 (24400), 337 (26500) nm.

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