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TETRAHEDRON

Preparation of Push-Pull Type Chromophores via Nitrothiophene Induced Michael Type Reaction of Alkynes

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Abstract: Nitrothiophene activates a neighboring alkyne to undergo Michael addition with dialkylamines and methanol to afford push-pull type chromophores. These compounds exhibit a large positive solvatochromism. The olefinic moiety in (*Z*)-(((5-nitrothien-2-yl)methylene)-(ferrocenyl)methyl)diethylamine (**14**) can be converted to an α-diketone.

Keywords: Michael reactions, Thiophenes, Nitro compounds

INTRODUCTION

In the past fifteen years organic compounds for nonlinear optics have been actively investigated.[1] Recently there has great interest in interposing a thiophene moiety in the conjugation chain of NLO-phores because thiophene has reduced aromaticity compared to benzene (stabilization energy: benzene, 36 KCal mol^{-1}; thiophene, 29 KCal mol^{-1})[2] which allows better electron delocalization.[3] Indeed, several organic chromophores with an end-capping nitrothienyl moiety have been found to possess a much larger second-order response than those with an end-capping nitrophenyl moiety.[4] It is well documented that an electron withdrawing group such as an ester, ketone, aldehyde, nitrile, or sulfone can activate an alkyne toward Michael addition.[5] Conceptually the products thus formed are candidates for second-order nonlinear optical chromophores since they contain donor and acceptor substituents linked through an intervening π-backbone. We felt that the electron withdrawing power of the nitrothienyl moiety would suffice to activate a neighboring alkyne to undergo Michael addition with suitable nucleophiles and afford useful second-order nonlinear optical chromophores. We report here the Michael addition of 5-nitro-2-alkynylthiophene towards secondary amines.

RESULTS AND DISCUSSION

New nitrothienylalkynes **3-8** were synthesized in good yields from terminal alkynes and 2-bromo-5-nitrothiophene via Sonogashira coupling[6] catalyzed by $PdCl_2(PPh_3)_2$ and CuI. Table 1 illustrates the results of

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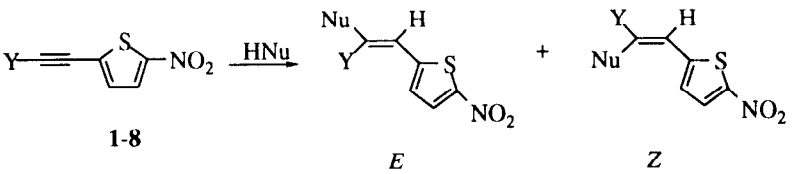
Table 1. Michael Addition of 5-Nitro-2-alkynylthiophenes



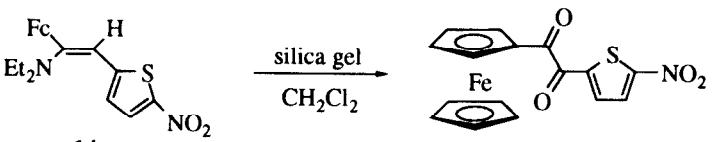
1-8 *E* *Z*

reagent	product	Y	Nu	condition	*E*/*Z* (%)	% yield	λmax (nm)[a]
1	**9**	H	A	25 °C/18 h	100/0	92	521
1	**10**	H	B	25 °C/18 h	50/50[b]	80	406
2	**11**	phenyl	C	70 °C/48 h	100/0	71	510
3	**12**	4-pyridyl	A	55 °C/18 h	100/0	63	510
4	**13**	4-styryl	A	55 °C/48 h	100/0	73	529
5	**14**	ferrocenyl	A	55 °C/24 h	0/100	70	567, 475
6	**15**	4-ethynylphenyl	A	55 °C/24 h	100/0	34	524
7	**16**	4-ethynyl-4'-biphenyl	A	55 °C/48 h	100/0	10	529
8	**17**	4-(*N*,*N*-dimethylamino)phenyl	A	100 °C/24 h (sealed tube)	100/0	85	545

[a] in CH_2Cl_2; [b] not separated; A = NEt_2; B = OMe; C = $N(CH_2CH_2OH)_2$

Michael addition of these alkyne as well as **1** and **2** towards heteronucleophiles. Most of the reactions can also be conducted at lower temperature with a reduced rate. The somewhat low yields of **15** and **16** are due to the limited solubility of **6** and **7** in Et_2NH, and most of **6** and **7** remained unreacted. The strongly electron releasing substituent, 4-dimethylaminophenyl, seems to greatly retard the reaction. Although **17** was obtained in high yield from the reaction of **8** with diethylamine under forcing conditions (100 °C in a scaled tube), **8** was recovered nearly quantitatively if the reaction was performed at 55 °C for 86 h. It is important to note that similar Michael addition does not occur if the nitrothienyl moiety in **1-8** is replaced by a *p*-nitrophenyl moiety. While the strong electron withdrawing ability of nitrothiophene plays a decisive role in activating the alkyne moiety, the other substituent of the alkyne as well as the incoming nucleophile seem to direct the stereoselectivity of the Michael addition both sterically and electronically: (a) except for the ferrocenyl substituent (vide infra), addition of secondary amines gave exclusively the (*E*)-isomer which is consistent with literature reports;[7] (b) both (*E*)- and (*Z*)- isomers were obtained when the terminal alkyne was allowed to react with the sterically less demanding nucleophile, methanol; (c) for compound **14**, the steric bulk of the ferrocenyl moiety forces the diethylamino moiety to be in a *trans* position to the nitrothienyl moiety. The stereochemistry of **14** was also confirmed by 2-D NOESY spectroscopy.[8] Although **14** is stable enough to be isolated after being chromatographed through alumina (Merck, neutral, activity I, 70-230 mesh), it is readily converted to 2-

ferrocenyloxalyl-5-nitrothiophene (**18**) (Scheme 1) on silica gel (Macherey-Nagel GmbH & Co., 230-400 mesh). The structure of **18** was also characterized by single crystal X-ray diffraction (Fig. 1).



14 **18**

Fc = ferrocenyl

Scheme 1

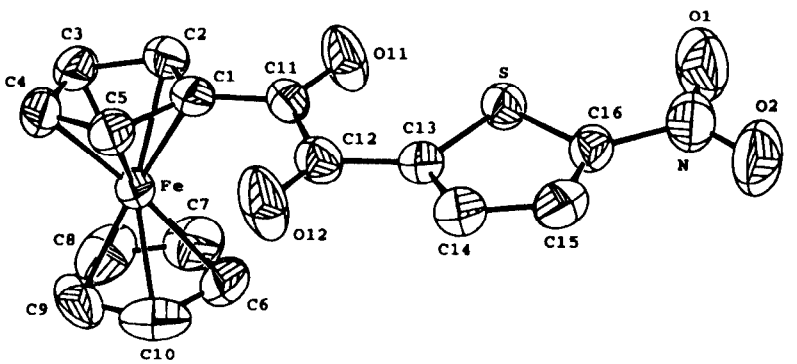


Figure 1. ORTEP Drawing of **18**.

It is interesting to note that there is a close intramolecular nonbonded contact[9] between S···O11 of 2.680(2) Å and between S···O1 of 2.860(2) Å (cf. the van der Waals radii of sulfur and oxygen which are 1.80 and 1.40 Å, respectively). Such an interaction helps to lock a planar conformation of the α-diketone with the thiophene ring or the nitro group with the thiophene ring (the dihedral angle between the plane O11-C11-C12-O12 and the plane S-C13-C14-C15-C16 is 3.4(1)°, and that between the plane of S-C13-C14-C15-C16 and O1-N2-O2 is 5.6(2)°). The detailed mechanism for the formation of **18** from **14** is not known at present. Such two-step formation of an α-diketone from internal alkyne is, to our knowledge, unprecedented, although several oxidizing agents, including RuO_4, $KMnO_4$, SeO_2/H_2SO_4, I_2-Me_2SO, and $Tl(NO_3)_3$ were reported to oxidize internal alkynes to α-diketones.[10]

The structure of **11** was determined by single crystal X-ray diffraction (Fig. 2). Reasonably good coplanarity of the dialkylamino, vinylthiophene and nitro moieties[11] would allow easy charge-transfer from the amine electron donor to the nitro electron acceptor. Indeed, the charge-transfer absorption band of **11** exhibits a large positive solvatochromism (λ_{max}: 546 nm in DMSO; 523 nm in CH_3CN; 510 nm in CH_2Cl_2; 488 nm in benzene). It is obvious that a stronger electron donor, either *syn* or *anti* to the nitrothiophene, results in a lower charge-transfer absorption energy, and therefore a larger λ_{max}. For instance, λ_{max} (in CH_2Cl_2) of **9** (521 nm, donor = NEt_2) is larger than that of **10** (406 nm, donor = OMe), and λ_{max} of **14** (567 nm, donor = ferrocenyl (*anti*); NEt_2 (*syn*)) > λ_{max} of **17** (545 nm, donor = NEt_2 (*anti*); $C_6H_4NMe_2$-4 (*syn*)) > λ_{max} of **13** (529 nm, donor

= NEt_2 (*anti*); 4-styryl (*syn*)) > λ_{max} of **12** (510 nm, donor = NEt_2 (*anti*); 4-pyridyl (*syn*)). There is only a small increment (24 nm) in λ_{max} from **9** (*syn* group = H) to **17** (*syn* group = $C_6H_4NMe_2$-4). Apparently, steric congestion prevents the aryl ring assuming coplanarity with the thiophene ring and hampers the resonance delocalization of π-electrons between the two. Such a conformation has been confirmed by structural determination on **12**, **15**, and **17**.[12]

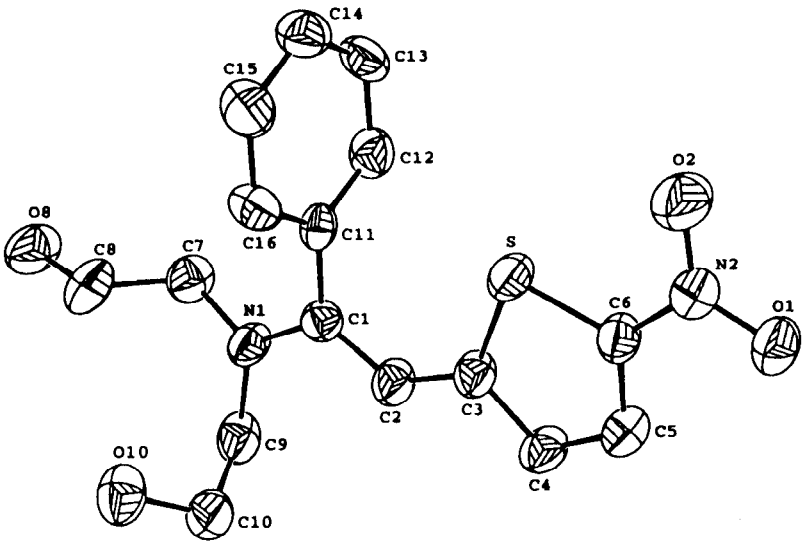
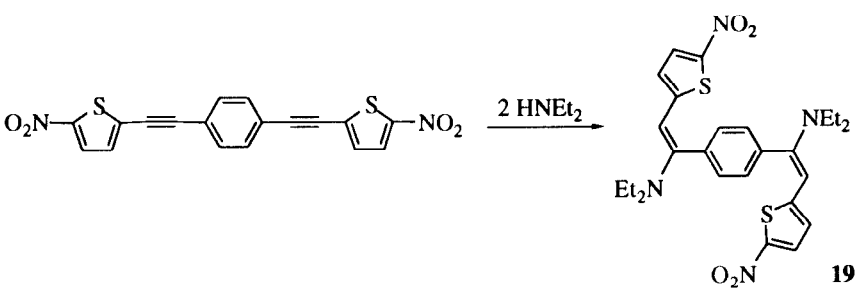


Figure 2. ORTEP Drawing of **11**.

Compound **11** and analogues are potential candidates for polymeric NLO materials since chromophores possessing the diol moiety have been found to be very useful precursors for the construction of nonlinear optical polymers, such as polyesters, polyimides, and polyurethanes.[13] Both internal alkynes of 1,4-bis((5-nitro-2-thienyl)ethynyl)benzene can react with diethylamine to give 1,4-bis(1-(diethylamino)-2-(5-nitrothien-2-yl)vinyl)benzene (**19**) (Scheme 2).[14] Compound **19** and its 1,3,5-trisubstituted benzene congener appear to be interesting for study relevant to dipolar two-dimensional NLO-phores[15] and octopolar NLO-phores,[16] and will be the subject of future publication.



Scheme 2

EXPERIMENTAL SECTION

General. All reactions and manipulations were carried out under N_2 with the use of standard inert-atmosphere and Schlenk techniques. Solvents were dried by standard procedures. All column chromatography was performed with use of silica gel (Macherey-Nagel GmbH & Co., 230-400 mesh) or alumina (Merck, neutral, activity I, 70-230 mesh) as the stationary phase in a column 35 cm in length and 2.5 cm in diameter. The NMR spectra were measured by using Bruker AMX500 (^{1}H), AC200 (^{1}H), and AC300 (^{1}H, ^{13}C) spectrometers. Electronic absorption spectra was obtained on a Perkin-Elmer Lambda 9 spectrometer or a Varian Cary 50 UV-Vis spectrophotometer. Mass spectra were collected on a VG 70-250S mass spectrometer. Decomposition temperatures of the complexes were determined by thermogravimetric analysis on a Perkin Elmer TGA7 thermal analyzer, and the samples were heated at 10 °C/min in air. Melting points were determined on a Yamato MP-21 melting point apparatus. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. $PdCl_2(PPh_3)_2$,[17] 2-bromo-5-nitrothiophene,[18] 4-ethynylpyridine,[19] 1-ethynyl-4-vinylbenzene,[20] 2-ethynyl-5-nitrothiophene (**1**),[21] ferrocenylacetylene,[22] 1,4-diethynylbenzene,[23] 4,4'-diethynylbiphenyl,[24] 2-nitro-5-phenylethynylthiophene (**2**),[25] and *N,N*-dimethyl-4-(1-ethynyl)aniline[26] were prepared following the published methods with modifications.

General Procedure for Preparation of 2-nitro-5-(4-pyridylethynyl)-thiophene (3), 2-nitro-5-((4-vinylphenyl)ethynyl)thiophene (4), 2-ferrocenylethynyl-5-nitrothiophene (5), 2-(4-ethynylphenylethynyl)-5-nitrothiophene (6), 4-((5-nitrothien-2-yl)ethynyl)-4'-ethynylbiphenyl (7), and (4-(2-(5-nitrothien-2-yl)ethynyl)phenyl)dimethylamine (8). Similar procedures were followed for the syntheses of **3**-**8**. Only the preparation of **3** will be described in detail.

Compound 3. To a flask containing 2-bromo-5-nitrothiophene (4.16 g, 20.0 mmol), 4-ethynylpyridine (2.06 g, 20.0 mmol), $Pd(PPh_3)_2Cl_2$ (175 mg, 1.2 mol%), and CuI (70 mg, 1.8 mol%) was added 120 mL of $^iPr_2NH$, and the solution was heated at 75-80 °C for 19 h. The solvent was removed *in vacuo*, and the residue was extracted with CH_2Cl_2/H_2O. The CH_2Cl_2 layer was transfer to a flask containing $MgSO_4$ to remove H_2O and filtered. The filtrate was pumped dry and the residue was chromatographed (silica gel, 230-400 mesh, Macherey-Nagel GmbH & Co.). Elution with CH_2Cl_2/THF (12:1) afforded a dark red band which was collected. The solvent was removed and the residue was washed with hexane to provide dark red powdery **3** in 79% yield (3.64 g). mp. 90-91 °C; T_d 170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (d, J = 5.7 Hz, 2 H), 8.05 (d, J = 4.3 Hz, 1 H), 7.54 (d, J = 5.7 Hz, 2 H), 7.51 (d, J = 4.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.8, 150.0, 132.2, 129.4, 129.1, 128.4, 125.2, 94.5, 84.8; UV-vis (CH_2Cl_2) λ_{max} 362 nm (ε = 37660); EIMS *m/z* 230 (M^+). Anal. Calcd for $C_{11}H_6N_2O_2S$: C, 57.38; H, 2.63; N, 12.17. Found: C, 57.45; H, 2.61; N, 11.95.

Compound 4. 1-ethynyl-4-vinylbenzene was utilized to synthesize **4**. Yield: 80%. Yellow powder. mp. 69-70 °C; T_d 185 °C; ^{1}H NMR ($CDCl_3$) δ 7.81 (d, J = 4.2 Hz, 1 H), 7.48 (d, J = 8.5 Hz, 2 H), 7.41 (d, J = 8.5 Hz, 2 H), 7.13 (d, J = 4.2 Hz, 1 H), 6.70 (dd, J = 17.5, 11.0 Hz, 1 H), 5.80 (d, J = 17.5 Hz, 1 H), 5.34 (d, J = 11.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 150.5, 138.9, 135.9, 132.0, 131.0, 130.8, 128.6, 126.3, 120.4, 115.8, 98.3, 81.8; UV-vis (CH_2Cl_2) λ_{max} 392 nm (ε = 26880); EIMS *m/z* 255 (M^+). Anal. Calcd for $C_{14}H_9NO_2S$: C, 65.87; H, 3.55; N, 5.49. Found: C, 65.80; H, 3.41; N, 5.25.

Compound 5. Ferrocenylacetylene was utilized to synthesize **5**. Yield: 61%. Dark red powder. mp. 190-191 °C (decomp); T_d 184 °C; ^{1}H NMR (acetone-d_6) δ 7.98 (d, J = 4.4 Hz, 1 H), 7.30 (d, J = 4.4 Hz, 1 H), 4.62 (t, J = 1.8 Hz, 2 H), 4.42 (t, J = 1.8 Hz, 2 H), 4.29 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 149.7, 132.1, 129.9, 128.7, 99.4,

77.9, 71.9, 70.3, 69.9, 62.7; UV-vis (CH_2Cl_2) λ_{max} 514 nm (ε = 3470), 377 nm (ε = 13330); FABMS *m/z* 337 (M^+). Anal. Calcd for $C_{16}H_{11}NO_2SFe$: C, 56.99; H, 3.29; N, 4.15. Found: C, 56.92; H, 3.40; N, 3.98.

Compound 6. 1,4-diethynylbenzene was utilized to synthesize **6**. Yield: 60%. Yellow powder. mp. 184-185 °C; T_d 186 °C; ^1H NMR ($CDCl_3$) δ 7.82 (d, J = 4.3 Hz, 1 H), 7.48 (d, J = 8.6 Hz, 2 H), 7.48 (d, J = 8.6 Hz, 2 H), 7.15 (d, J = 4.3 Hz, 1 H), 3.21 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 151.0, 132.2, 131.6, 131.1, 130.4, 128.5, 123.4, 121.6, 97.3, 82.8, 82.8, 79.9; UV-vis (CH_2Cl_2) λ_{max} 388 nm (ε = 28740); EIMS *m/z* 253 (M^+). Anal. Calcd for $C_{14}H_7NO_2S$: C, 66.39; H, 2.79; N, 5.53. Found: C, 66.19; H, 2.75; N, 5.30.

Compound 7. 4,4'-diethynylbiphenyl was utilized to synthesize **7**. Yield: 71%. Yellow powder. mp. 210-211 °C (decomp); T_d 196 °C; ^1H NMR ($CDCl_3$) δ 7.83 (d, J = 4.2 Hz, 1 H), 7.60 (s, 4 H), 7.56 (s, 4 H), 7.16 (d, J = 4.2 Hz, 1 H), 3.14 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 152.5, 142.6, 141.3, 132.6, 132.2, 131.3, 130.8, 128.4, 127.0, 126.8, 120.5, 118.7, 97.8, 87.0, 82.0, 78.2; UV-vis (CH_2Cl_2) λ_{max} 391 nm (ε = 31760); EIMS *m/z* 329 (M^+). Anal. Calcd for $C_{20}H_{11}NO_2S$: C, 72.93; H, 3.37; N, 4.25. Found: C, 72.63; H, 3.31; N, 4.15.

Compound 8. *N,N*-dimethyl-4-(1-ethynyl)aniline was utilized to synthesize **8**. Yield: 70%. Orange powder. mp. 144-145 °C; T_d 211 °C; ^1H NMR ($CDCl_3$) δ 7.79 (d, J = 4.3 Hz, 1 H), 7.39 (d, J = 7.5 Hz, 2 H), 7.03 (d, J = 4.3 Hz, 1 H), 6.64 (d, J = 7.5 Hz, 2 H), 3.01 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 151.0, 149.5, 133.2, 132.8, 129.5, 128.8, 111.7, 107.5, 101.1, 80.2, 40.0; UV-vis (CH_2Cl_2) λ_{max} 463 nm (ε = 21590); EIMS *m/z* 272 (M^+). Anal. Calcd for $C_{14}H_{12}N_2O_2S$: C, 61.75; H, 4.44; N, 10.29. Found: C, 61.51; H, 4.39; N, 10.01.

Preparation of (*E*)-(2-(5-nitrothien-2-yl)vinyl)diethylamine (9), methyl-(2-(5-nitrothien-2-yl)vinyl)ether (10), (*E*)-((((5-nitrothien-2-yl)methyl-ene)phenylmethyl)(hydroxyethyl)amino)ethanol (11), (*E*)-(((5-nitrothien-2-yl)methylene)(4-pyridyl)methyl)diethylamine (12), (*E*)-(((5-nitrothien-2-yl)methylene)(4-styryl)methyl)diethylamine (13), (*Z*)-(((5-nitrothien-2-yl)methylene)(ferrocenyl)methyl)diethylamine (14), (*E*)-(((5-nitrothien-2-yl)methylene)(4-ethynylphenyl)methyl)diethylamine (15), (*E*)-(((5-nitrothien-2-yl)methylene)(4-ethynyl-4'-biphenyl)methyl)di-ethylamine (16), and (*E*)-(((5-nitrothien-2-yl)methyl-ene)(4-(dimethyl-amino)phenyl)methyl)diethylamine (17). Compounds **9-17** were synthesized by similar procedures, and only the preparation of **11** will be described in detail. Except for the preparation of **11**, neat nucleophiles (MeOH or Et_2NH) were used without addition of other solvents.

Compound 11. Diethanolamine (4 mL, 41.7 mmol) was added to a THF solution (40 mL) of **2** (1.60 g, 7.0 mmol), and the resulting solution was refluxed for 48 h. The solvent was removed *in vacuo*, and the residue was chromatographed. Elution with THF/hexane (1:3) provided three bands, and the dark purple third band was collected. Removal of the solvent and recrystallization of the residue from CH_2Cl_2/hexane provided dark purple powdery **11** in 71% yield (1.66 g, 4.97 mmol). mp. 124-125 °C; T_d 194 °C; ^1H NMR (acetone-d_6) δ 7.61-7.55 (m, 4 H), 7.36-7.31 (m, 2 H), 6.44 (d, J = 4.6 Hz, 1 H), 5.96 (s, 1 H), 4.09 (t, J = 5.6 Hz, 2 H), 3.74 (m, 4 H), 3.46 (t, J = 5.8 Hz, 4 H); ^{13}C NMR (acetone-d_6) δ 157.4, 156.0, 143.5, 135.6, 130.9, 130.8, 130.3, 128.5, 121.9, 94.8, 60.2, 53.9; UV-vis (CH_2Cl_2) λ_{max} = 510 nm (ε = 32500); EIMS *m/z* 334 (M^+). Anal. Calcd for $C_{16}H_{18}N_2O_4S$: C, 57.47; H, 5.43; N, 8.38. Found: C, 57.25; H, 5.19; N, 8.14.

Compound 9. The reaction of **1** with Et_2NH was performed at room temperature for 18 h. Yield: **92%**. Purple powder. mp. 64-65 °C; T_d 170 °C; ^1H NMR ($CDCl_3$) δ 7.70 (d, J = 4.4 Hz, 1 H), 7.50 (d, J = 13.3 Hz, 1 H), 6.41 (d, J = 4.4 Hz, 1 H), 5.29 (d, J = 13.3 Hz, 1 H), 3.23 (q, J = 7.1 Hz, 4 H), 1.19 (t, J = 7.1 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 157.3, 154.6, 142.6, 134.5, 130.3, 130.2, 130.0, 128.9, 120.8, 93.0, 44.1, 13.2; UV-vis (CH_2Cl_2) λ_{max} 521 nm (ε = 38770); EIMS *m/z* 226 (M^+). Anal. Calcd for $C_{10}H_{14}N_2O_2S$: C, 53.08; H, 6.24; N, 12.38. Found: C, 53.10; H, 6.08; N, 12.05.

Compound 10. The reaction of **1** with MeOH was performed at room temperature for 18 h. The *cis* and *trans* isomers of **10** were inseparable. Yield: 80%. Orange powder. mp. 80-81 °C; T_d 134 °C; ^{1}H NMR ($CDCl_3$) δ 7.78 (d, J = 4.3 Hz, 1 H), 6.78 (d, J = 4.3 Hz, 1 H), 6.40 (d, J = 6.1 Hz, 1 H), 5.65 (d, J = 6.1 Hz, 1 H), 3.93 (s, 3 H) cis; 7.74 (d, J = 4.2 Hz, 1 H), 7.18 (d, J = 12.7 Hz, 1 H), 6.69 (d, J = 4.2 Hz, 1 H), 5.87 (d, J = 12.7 Hz, 1 H), 3.72 (s, 3 H) trans; ^{13}C NMR ($CDCl_3$) δ 152.9, 150.9, 146.8, 128.7, 123.4, 100.1, 61.4; UV-vis (CH_2Cl_2) λ_{max} 406 nm (ε = 37670); EIMS *m/z* 185 (M^+). Anal. Calcd for $C_7H_7NO_3S$: C, 45.40; H, 3.81; N, 7.56. Found: C, 45.55; H, 4.01; N, 7.28.

Compound 12. Compound **12** was prepared from **3** and diethylamine at 55 °C for 18 h. Yield: 63%. Dark red powder. mp. 188-189 °C; T_d 223 °C; ^{1}H NMR (acetone-d_6) δ 8.83 (d, J = 6.0 Hz, 2 H), 7.60 (d, J = 4.7 Hz, 1 H), 7.40 (d, J = 6.0 Hz, 2 H), 6.46 (d, J = 4.7 Hz, 1 H), 5.89 (s, 1 H), 3.27 (q, J = 6.9 Hz, 4 H), 1.15 (t, J = 6.9 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 154.3, 151.4, 150.7, 143.7, 143.2, 129.7, 124.2, 121.3, 93.3, 40.0, 12.9; UV-vis (CH_2Cl_2) λ_{max} 510 nm (ε = 26710); EIMS *m/z* 303 (M^+). Anal. Calcd for $C_{15}H_{17}N_3O_2S$: C, 59.38; H, 5.65; N, 13.85. Found: C, 58.91; H, 5.69; N, 13.62.

Compound 13. Compound **13** was prepared from **4** and diethylamine at 55 °C for 48 h. Yield: 73%. Reddish brown crystals. mp. 108-109 °C; T_d 197 °C; ^{1}H NMR ($CDCl_3$) δ 7.57 (d, J = 4.5 Hz, 1 H), 7.57 (d, J = 8.2 Hz, 2 H), 7.20 (d, J = 8.2 Hz, 2 H), 6.78 (dd, J = 17.6, 10.9 Hz, 1 H), 6.27 (d, J = 4.5 Hz, 1 H), 5.86 (d, J = 17.6 Hz, 1 H), 5.38 (d, J = 10.9 Hz, 1 H), 5.66 (s, 1 H), 3.19 (q, J = 7.1 Hz, 4 H), 1.17 (t, J = 7.1 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 156.3, 153.7, 140.2, 139.4, 136.0, 133.6, 130.0, 129.2, 127.9, 121.0, 115.6, 93.9, 44.2, 13.1; UV-vis (CH_2Cl_2) λ_{max} 529 nm (ε = 48750); EIMS *m/z* 328 (M^+). Anal. Calcd for $C_{18}H_{20}N_2O_2S$: C, 65.83; H, 6.14; N, 8.53. Found: C, 65.70; H, 6.02; N, 8.44.

Compound 14. Compound **14** was prepared from **5** and diethylamine at 55 °C for 24 h. The crude product was chromatographed through alumina (Merck, neutral, activity I, 70-230 mesh) and was eluted with CH_2Cl_2/hexane (1:5). Compound **14** was isolated as a purple powder in a yield of 70%. mp. 107-108 °C; T_d 177 °C; ^{1}H NMR (acetone-d_6) δ 7.84 (d, J = 4.2 Hz, 1 H), 7.12 (s, 1 H), 7.03 (d, J = 4.2 Hz, 2 H), 4.59 (t, J = 1.8 Hz, 2 H), 4.41 (t, J = 1.8 Hz, 1 H), 4.20 (s, 5 H), 3.17 (q, J = 7.1 Hz, 4 H), 1.13 (t, J = 7.1 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 154.6, 149.7, 147.2, 129.0, 123.4, 113.4, 81.3, 70.3, 69.7, 69.5, 47.3, 13.8; UV-vis (CH_2Cl_2) λ_{max} 567 nm (ε = 25210), 475 nm (ε = 18500); FABMS *m/z* 411 ($(M + 1)^+$). Anal. Calcd for $C_{20}H_{22}N_2O_2SFe$: C, 58.54; H, 5.40; N, 6.83. Found: C, 58.18; H, 5.26; N, 6.66.

Compound 15. Compound **15** was prepared from **6** and diethylamine at 55 °C for 24 h. Yield: 34%. Dark purple powder. mp. 135-136 °C; T_d 195 °C; ^{1}H NMR ($CDCl_3$) δ 7.64 (d, J = 8.1 Hz, 2 H), 7.55 (d, J = 4.6 Hz, 1 H), 7.22 (d, J = 8.1 Hz, 2 H), 6.17 (d, J = 4.6, 1 H), 5.62 (br, 1 H), 3.19 (s, 1 H), 3.16 (q, J = 7.1 Hz, 4 H), 1.12 (t, J = 7.1 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 156.0, 153.3, 143.2, 135.1, 135.1, 130.0, 129.2, 124.1, 120.9, 93.2, 82.8, 79.1, 44.1, 13.1; UV-vis (CH_2Cl_2) λ_{max} 524 nm (ε = 42780); EIMS *m/z* 326 (M^+). Anal. Calcd for $C_{18}H_{18}N_2O_2S$: C, 66.23; H, 5.56; N, 8.58. Found: C, 66.37; H, 5.45; N, 8.50.

Compound 16. Compound **16** was prepared from **7** and diethylamine at 55 °C for 48 h. Yield: 10%. Dark purple powder. mp. 188-189 °C; T_d 199 °C; ^{1}H NMR ($CDCl_3$) δ 7.75 (d, J = 8.1 Hz, 2 H), 7.64 (d, J = 8.4 Hz, 2 H), 7.58 (d, J = 8.4 Hz, 2 H), 7.55 (d, J = 4.5, 1 H), 7.31 (d, J = 8.1, 2 H), 6.23 (d, J = 4.5 Hz, 1 H), 5.69 (br, 1 H), 3.21 (q, J = 7.0 Hz, 4 H), 3.14 (s, 1 H), 1.16 (t, J = 7.0 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 156.1, 153.4, 143.3, 142.1, 140.2, 133.6, 132.6, 129.9, 129.6, 128.7, 127.1, 121.6, 121.1, 94.1, 83.3, 78.1, 44.3, 13.1; UV-vis (CH_2Cl_2) λ_{max} 529 nm (ε = 49330); EIMS *m/z* 402 (M^+). Anal. Calcd for $C_{24}H_{22}N_2O_2S$: C, 71.61; H, 5.51; N, 6.96. Found: C, 71.73; H, 5.45; N, 6.96.

Compound 17. The reaction of **8** with Et_2NH was performed in a sealed tube at 100 °C for 24 h. Yield: 85%. Purple powder. mp. 165-166 °C; T_d 223 °C; ^1H NMR ($CDCl_3$) δ 7.56 (d, J = 4.5 Hz, 1 H), 7.00 (d, J = 9.0 Hz, 2 H), 6.77 (d, J = 9.0 Hz, 2 H), 6.24 (d, J = 4.5 Hz, 1 H), 5.62 (s, 1 H), 3.20 (q, J = 7.0 Hz, 4 H), 3.02 (s, 6 H), 1.11 (t, J = 7.0 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 158.0, 155.7, 151.0, 142.7, 130.2, 130.0, 120.6, 113.9, 113.1, 93.9, 44.1, 40.7, 13.2; UV-vis (CH_2Cl_2) λ_{max} 545 nm (ε = 36940); EIMS *m/z* 345 (M^+). Anal. Calcd for $C_{18}H_{23}N_3O_2S$: C, 62.58; H, 6.71; N, 12.16. Found: C, 62.74; H, 6.56; N, 12.03.

Ferrocenyl(5-nitrothien-2-yl)ethanedione (18). A solution of **14** (200 mg, 0.49 mmol) in CH_2Cl_2 (30 mL) was soaked with 2 g of silica gel (230-400 mesh, Macherey-Nagel GmbH & Co.) and pumped dry. It was then carefully placed on the top of the column packed with silica/hexane and chromatographed in the air. Elution with CH_2Cl_2/hexane (1:1) afforded a red-purple band, which was collected and pumped dry to provide **18** as a dark purple powder in a yield of 80% (155 mg). mp. 101-102 °C; ^1H NMR (300 MHz, acetone-d_6) δ 8.13 (d, J = 4.4 Hz, 1 H), 8.04 (d, J = 4.4 Hz, 1 H), 5.09 (t, J = 1.8 Hz, 2 H), 4.91 (t, J = 1.8 Hz, 2 H), 4.29 (s, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.3, 181.4, 158.3, 140.7, 133.8, 127.7, 75.3, 73.5, 71.4, 70.8; UV-vis (CH_2Cl_2) λ_{max} 568 nm (ε = 1468), 323 nm (ε = 15794); FABMS *m/z* 369 (M^+). Anal. Calcd for $C_{16}H_{11}NO_4SFe$: C, 52.05; H, 3.00; N, 3.79. Found: C, 52.00; H, 3.27; N, 3.67.

X-ray Structure Determination of 11 and 18. Crystals of **11** and **18** were grown by slowly diffusing hexane into a concentrated solution of relevant compounds in CH_2Cl_2. Crystals were mounted on a glass fiber covered with epoxy. Data were collected at 293 K on an Enraf-Nonius CAD4 diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) with the θ-2θ scan mode. Unit cells were determined by centering 25 reflections in the suitable 2θ range. The structure was solved by direct method and refined by full-matrix least squares using NRCVAX.[27] All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were placed in idealized positions with $d_{C\text{-}H}$ = 1.00 Å. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Crystal data for **11**: $C_{16}H_{18}N_2O_4S$, f_w = 334.39, T = 293 K, crystal size 0.06 x 0.12 x 0.02 mm; monoclinic, $P2_1/c$, a = 9.018(2) Å, b = 22.322(3) Å, c = 9.0703(8) Å, β = 118.99(1)°, V = 1596.9(5) Å^3, Z = 4, $\rho_{calc.}$ = 1.391 g cm^{-3}, $F(000)$ = 704, μ = 2.136 cm^{-1}, R = 0.039, R_w = 0.040 for 1318 reflections with $I > 2\sigma(I)$ and 208 parameters among 2810 unique reflections in the θ range 0 - 25 °, GOF = 1.24.

Crystal data for **18**: $C_{16}H_{11}NO_4SFe$, f_w = 369.17, T = 293 K, crystal size 0.44 x 0.13 x 0.25 mm; monoclinic, $P2_1/n$, a = 6.3871(3) Å, b = 25.022(3) Å, c = 9.3214(4) Å, β = 94.995(4)°, V = 1484.1(2) Å^3, Z = 4, $\rho_{calc.}$ = 1.652 g cm^{-3}, $F(000)$ = 752, μ = 11.67 cm^{-1}, R = 0.026, R_w = 0.036 for 1677 reflections with $I > 2\sigma(I)$ and 208 parameters among 1933 unique reflections in the θ range 0 - 25 °, GOF = 2.04.

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