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Convenient Synthesis of Ferrocene Conjugates Mediated by Benzyltriethylammonium Tetrathiomolybdate in a Multi-Step Tandem Process

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The synthesis of a wide range of ferrocene-derived sulfur-linked mono- and disubstituted Michael adducts and conjugates mediated by benzyltriethylammonium tetrathiomolybdate (**1**) in a tandem process is reported. New route to access acryloylferrocene (**4**) and 1,1′-diacryloylferrocene (**5**) is discussed. Conjugation of amino acids to ferrocene is established via their *N* and *C* termini and also via side chains employing conjugate addition as key step to furnish mono- and divalent conjugates. This methodology has also been extended to access several ferrocene–carbohydrate conjugates. The electrochemical behavior of some selected ferrocene conjugates was studied by cyclic voltammetry.

Introduction

Conjugates of ferrocene with various biomolecules which makes them redox-active have been shown to have potential applications in developing chemical and biosensors and new drugs.[1] Therefore, engineering new methods for covalent attachment of redox-active molecules like ferrocene to biomolecules would contribute enormously to study various biological processes employing diverse analytical methods. Labeling of amino acids, peptides and carbohydrates has been reported in the literature mostly through amide,[2] ester,[3] alkylation[4] or reductive amination[5] strategies. Some labeling strategies are more specific either to the synthesis of carbohydrate[6] or amino acid conjugates.[7] Recently, the "click reaction" has been used for labelling of amino acids, carbohydrates and PNA oligomers with ferrocene in an elegant manner.[11,18f,18g] Conjugate addition was employed only in a few cases for labeling of biomolecules with ferrocene.[8] Glutathione has been labeled with ferrocene employing ferrocenylethyl maleimide as a Michael acceptor.[8a] A related maleimide derivative has also been used to label the hexapeptide Ac-Arg-Arg-Ala-Ser-Leu-Cys-OH which was used for the detection of serine phosphorylation by protein kinase A by electrochemical method.[8b] Exploration of the utility of benzyltriethylammonium tetrathiomolybdate $[BnEt_3N]_2[MoS_4]$ (**1**) for the synthesis of many novel sulfur-containing molecules has been the prime focus in our laboratory for many years.[9] The tetrathiomolybdate **1** not only acts as a sulfur transfer agent but can also cleave the resulting disulfide in situ when present in excess which can be trapped with various electrophiles like Michael acceptors,[9c] epoxides[9d] and aziridines.[10] Recently, we have reported a "click chemistry" inspired synthesis of ferrocene amino acid, peptide conjugates.[11a] In our continued interest towards new labeling protocols, we report herein a simple and high-yielding synthesis of ferrocene conjugates involving conjugate addition of in situ generated thiolates ranging from simple thiolates to diverse substituted amino acids and carbohydrate derivatives to acryloylferrocene **4** and 1,1′-diacryloylferrocene **5** furnishing diverse functionalized sulfur-linked Michael adducts and conjugates respectively. A few conjugates were characterized by cyclic voltammetry.

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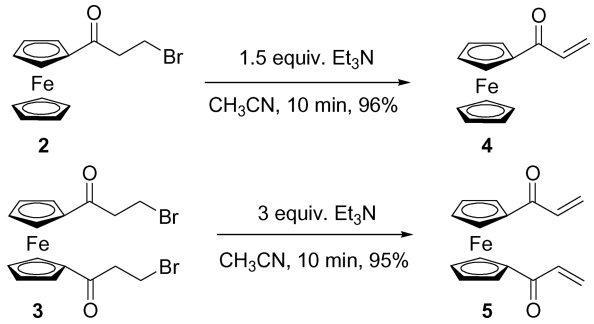
Results and Discussion

Synthesis of Acryloylferrocene (4) and 1,1′-Diacryloylferrocene (5)

To the best of our knowledge, there is no report on the synthesis of diacryloylferrocene **5** and conjugate addition of nucleophiles to it (Scheme 1). Acryloylferrocene **4** is accessed via various routes in the literature and some of them are not straightforward.[12] We wanted to access acryloylferrocene (**4**) and 1,1′-diacryloylferrocene (**5**) in bulk quantities employing simple procedure to carry out further reactions with them.

We anticipated that base-promoted elimination of HBr from (bromopropionyl)ferrocene **2** and 1,1′-bis(bromopropionyl)ferrocene would furnish acryloylferrocene and diacryloylferrocene, respectively. For this purpose, we easily accessed **2** and **3** from ferrocene via Friedel–Crafts acylation of ferrocene with bromopropionyl chloride.[13] Reaction of (bromopropionyl)ferrocene (**2**) with Et_3N (1.5 equiv., CH_3CN, 28 °C, 10 min) led to the formation of **4** in 96% yield. Similarly, treatment of dibromide **3** with Et_3N (3.0 equiv., CH_3CN, 28 °C, 10 min) gave **5** in excellent



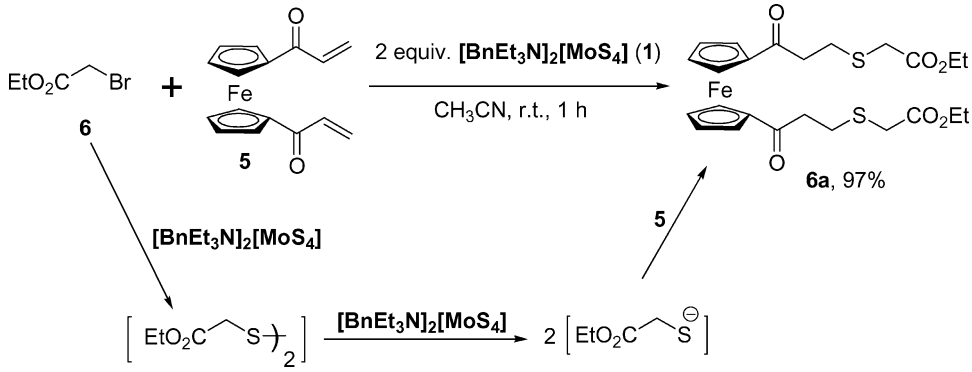
Scheme 1. Synthesis of acryloylferrocene **4** and 1,1′-diacryloylferrocene (**5**).

yield. In the absence of solvent compound **5** polymerised readily (Scheme 2). However, when stored in solution (dichloromethane, 0 °C) it was found to be stable.

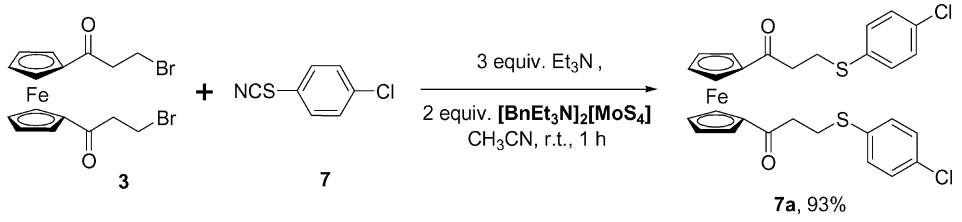
With both compounds **4** and **5** available in quantity, we attempted the Michael addition with diverse thiolates generated in situ by employing benzyltriethylammonium tetrathiomolybdate (**1**). Initially, treatment of ethyl bromoacetate **6** (1 equiv.) with diacryloylferrocene (0.5 equiv.) and tetrathiomolybdate (**1**) (CH_3CN, room temp. 1 h) furnished the disubstituted Michael adduct **6a** in 97% yield. We then wanted to accomplish two reactions, i.e., synthesis of the Michael acceptor and Michael addition with in situ generated thiolates in one pot in a tandem fashion. In this way, isolation and storage of **5**, which is prone to thermal polymerization, can be circumvented. To test this, we initially treated ferrocene-derived dibromide **3** with Et_3N in CH_3CN. After 15 min *p*-chlorothiocyanate **7** dissolved in acetonitrile and tetrathiomolybdate (**1**) were added. The reaction proceeded smoothly at room temp. in 1 h to furnish the disubstituted Michael adduct **7a** in 93% yield (Scheme 3).

Encouraged by this result, diverse functionalized thiolates generated in situ were added to **4** and **5** in a tandem fashion (Scheme 4) and in all cases Michael adducts and conjugates derived from **4** and **5** were isolated in excellent yields.

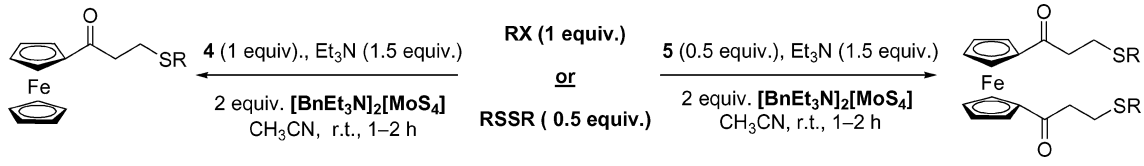
Cinnamyl chloride (**8**), the chloroacetamide **9**, *N*-tosylbenzylaziridine (**10**) and *N*-(chloroacetyl)phenylalaninol (**11**) were subjected to reaction with **4** in the presence of **1** as described in Scheme 4 to furnish the corresponding Michael adducts **8a**–**11a**. Similar reactions of **8**–**11** with **5** in the presence of **1** afforded the disubstituted Michael adducts **8b**–**11b** in excellent yield (Table 1). In all these cases initially the corresponding disulfides were formed, which were cleaved with excess tetrathiomolybdate (**1**) present to generate thiolates in situ. The thiolates underwent facile



Scheme 2. Michael addition of bromoethyl acetate **6** to diacryloylferrocene (**5**).



Scheme 3. One pot synthesis of disubstituted Michael adduct **7a** in a tandem fashion.



Scheme 4. General scheme for the synthesis of mono- and disubstituted Michael adducts.

Table 1. Conjugate addition of simple in situ generated thiolates to **4** and **5**.

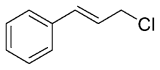
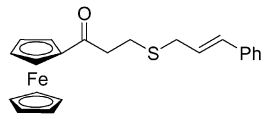
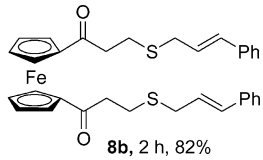
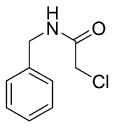
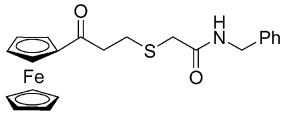
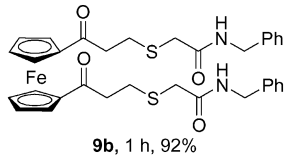
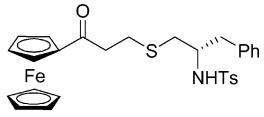
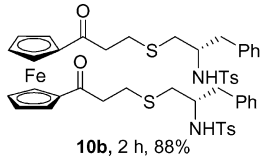
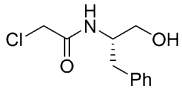
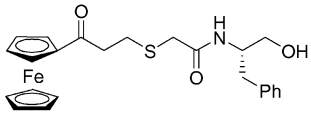
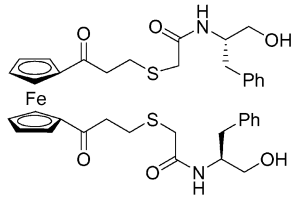
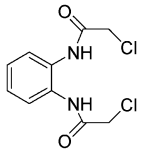
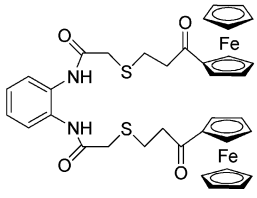
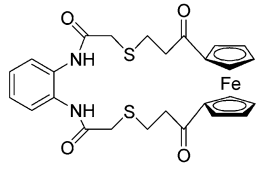
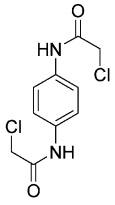
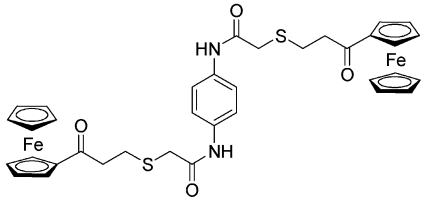
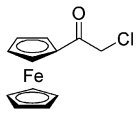
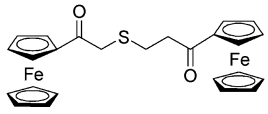
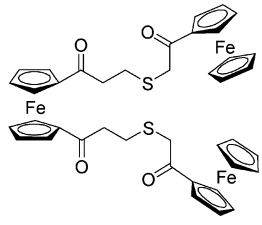
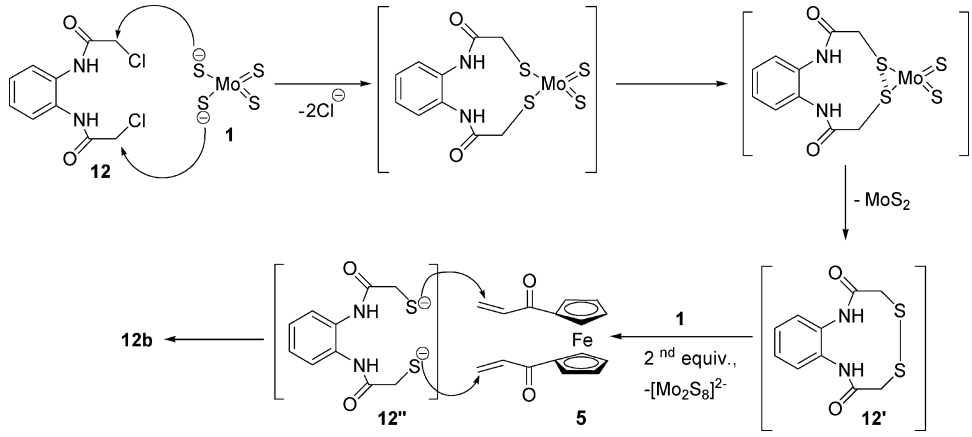
Substrate	Monosubstituted Michael adduct	Disubstituted Michael adduct
 **8**	 **8a**, 2 h, 85%	 **8b,** 2 h, 82%
 **9**	 **9a,** 1 h, 94%	 **9b,** 1 h, 92%
 **10**	 **10a,** 2 h, 90%	 **10b,** 2 h, 88%
 **11**	 **11a,** 1 h, 94%	 **11b,** 1 h, 92%

Table 2. Conjugate addition of diverse chloroacetyl derivatives **12**–**14** to **4** and **5**.

Substrate	Monosubstituted Michael adduct	Disubstituted Michael adduct
 **12**	 **12a**, 2 h, 70%	 **12b**, 3 h, 35%
 **13**	 **13a**, 2 h, 80%	—
 **14**	 **14a**, 2 h, 81%	 **14b**, 3 h, 75%



Scheme 5. Tentative mechanism for the formation of ferrocenophane **12b**.

Michael addition with **4** or **5** to furnish the corresponding Michael adducts (according to the pathway shown in Scheme 2).

It has been possible to synthesize ferrocene-tagged chiral amine derivatives **10a** and **10b** by ring opening of optically pure aziridine **10** derived from phenylalanine. The initially formed *N*-tosylsulfonamido disulfide[9e] and thiolate derived from the cleavage of this disulfide was trapped with **4** and **5** to furnish **10a** and **10b**. In the case of chloroacetamides **9** and **11** the reaction proceeded faster than for **8** and **10** indicating that they were more reactive substrates towards tetrathiomolybdate (**1**). In the present method both the Michael acceptor and the thiolate are generated in the same reaction vessel and then they undergo conjugate addition. As further extension of this methodology, we decided to study the reactivity of the bis(chloroacetamides) **12** and **13** derived from 1,2- and 1,4-diaminobenzenes with **4** and **5** in the presence of **1** (Table 2). The reaction of **12** (1 equiv.) with tetrathiomolybdate (**1**) (2 equiv.) along with acryloylferrocene (2 equiv., CH_3CN, 2 h) furnished the dimetallic compound **12a** in good yield. Similarly, when **12** was treated with **1** (2 equiv.) and **5** (1 equiv.) under high dilution conditions for 3 h, the ferrocenophane **12b** was obtained in moderate yield. The formation of **12b** proceeds via the formation of cyclic disulfide **12′** (Scheme 5). Initially, displacement of chlorine by **1** occurs followed by intramolecular disulfide bond formation to furnish **12′** which undergoes reduction of the disulfide bond in the presence of second equivalent of **1** to form thiolate **12′′** in situ which finally undergoes 1,4-addition to Michael acceptor **5** to form the macrocycle **12b**.

In a similar fashion, when the *para*-substituted bis(chloroacetamide) **13** was treated with **1** and **4** in acetonitrile the dimetallic compound **13a** was obtained in good yield, possibly via an intermolecular disulfide-bridged dimer. However, treatment of **13** under similar conditions with diacryloylferrocene failed to furnish any product, even under very high dilution conditions. Similarly, the reaction of (chloroacetyl)ferrocene **14** with **4** and **5** in the presence of **1** resulted in the formation of the novel ferrocene-derived dimetallic product **14a** and trimetallic compound **14b** in very good yield.

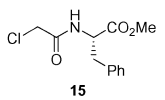
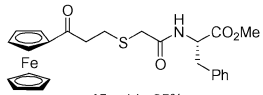
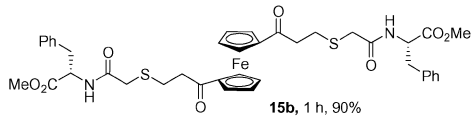
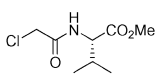
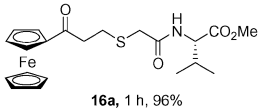
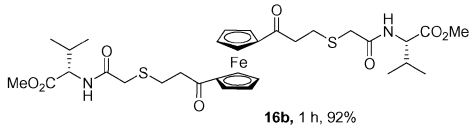
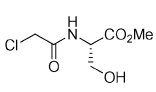
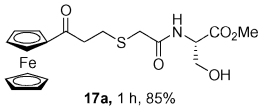
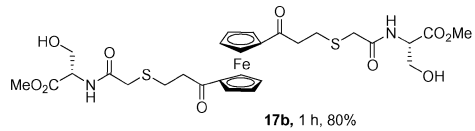
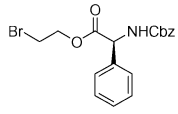
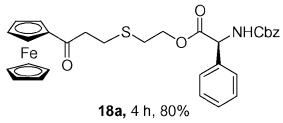
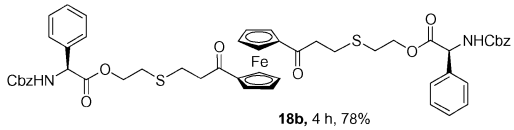
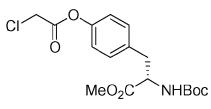
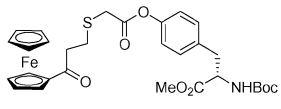
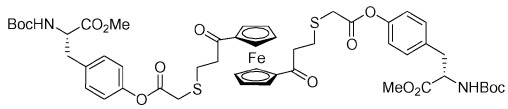
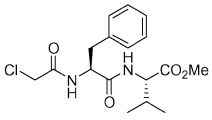
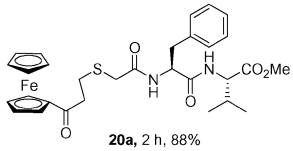
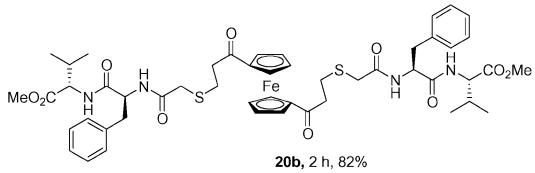
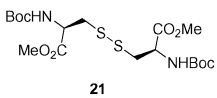
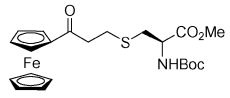
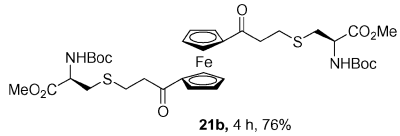
Synthesis of Ferrocene–Amino Acid Conjugates

Our next goal was to synthesize amino acid and peptide conjugates of ferrocene using our protocol via *N* and *C* termini and via side chains of amino acids. Initially, for conjugation of amino acids and peptides via their *N*-terminus we synthesized chloroacetamides of L-phenylalanine (**15**), valine (**16**) and the dipeptide **20**.[14] When these were treated with **4** and **5** (Scheme 4) we could conveniently isolate monovalent (**15a**, **16a** and **20a**) and divalent conjugates (**15b**, **16b** and **20b**) in very good yields (Table 3). Further, the bromoethyl ester **17** of phenyl glycine[15] and chloroacetyl esters **18** of L-serine and tyrosine **19** were synthesized for conjugation of the *C*-terminus and side chain of the amino acids. Reaction with **4** and **5** furnished the monovalent conjugates **17a**–**19a** and divalent conjugates **17b**–**19b**. Subsequently the Boc-protected cystine methyl ester **21** was treated with **4** and **5** along with tetrathiomolybdate to furnish the cysteine conjugates **21a**–**21b** in good yields. It is worth mentioning that a cysteine conjugate similar to **21a** was obtained by a circuitous route.[16]

Synthesis of Ferrocene–Carbohydrate Conjugates

To demonstrate the generality of our methodology, conjugation of carbohydrate derivatives onto the ferrocene backbone was envisaged. Towards this, diverse substrates derived from carbohydrates were employed. Several anomeric bromides **22** and **24** derived from D-glucose, **23** from D-glucosamine and **25** from D-xylose were treated with **1** to form the corresponding anomeric disulfides[17a], which were subsequently cleaved in situ with excess of tetrathiomolybdate to yield the corresponding thiolates. The latter undergo Michael addition reactions[17b] with **4** and **5** to furnish the corresponding monovalent and divalent carbohydrate conjugates **22a**–**25a** and **22b**–**25b**, respectively. D-Glucosamine was also conjugated through its chloroacetamide **26** to furnish adducts **26a** and **26b**. The reaction of the D-ribose-derived chloroacetyl ester **27** with **4** and **5** gave the conjugates **27a** and **27b** in excellent yields (Table 4). All the conjugates were extensively characterized using NMR, IR and

Table 3. Synthesis of monovalent and divalent ferrocene–amino acid conjugates **15a**–**21a** and **15b**–**21b**, respectively.

Substrate	Monovalent amino acid conjugates	Divalent amino acid conjugates
 **15**	 **15a,** 1 h, 95%	 **15b,** 1 h, 90%
 **16**	 **16a,** 1 h, 96%	 **16b,** 1 h, 92%
 **17**	 **17a,** 1 h, 85%	 **17b,** 1 h, 80%
 **18**	 **18a,** 4 h, 80%	 **18b,** 4 h, 78%
 **19**	 **19a,** 1 h, 95%	 **19b,** 1 h, 92%
 **20**	 **20a,** 2 h, 88%	 **20b,** 2 h, 82%
 **21**	 **21a,** 4 h, 85%	 **21b,** 4 h, 76%

mass spectroscopic techniques. Interestingly, in the ^{1}H NMR of the disubstituted ferrocene conjugate **23b** each ferrocene ring proton gives rise to different shift values as a result of the chiral environment introduced by the appended carbohydrate moieties. ^{1}H NMR measurements of **23b** at different temperatures between 22–55 °C in $CDCl_3$ did not reveal any change in the peak patterns indicating that there is only one distinguishable form present.[18f]

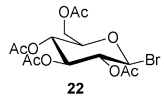
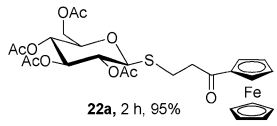
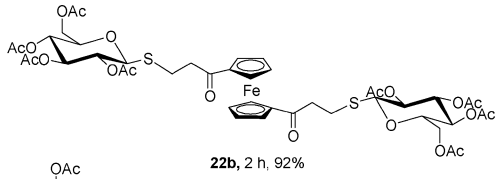
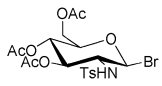
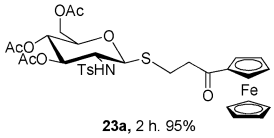
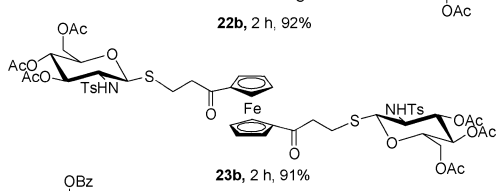
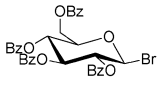
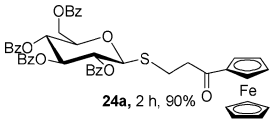
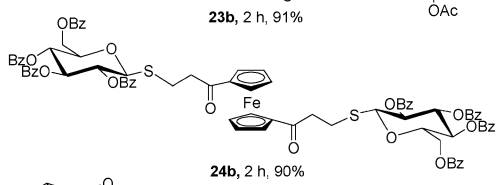
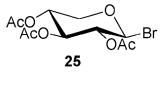
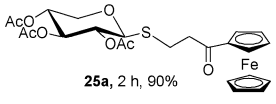
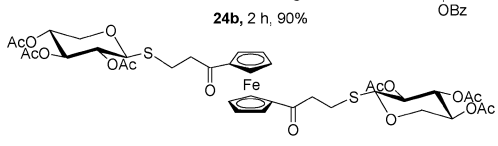
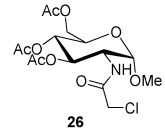
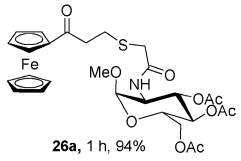
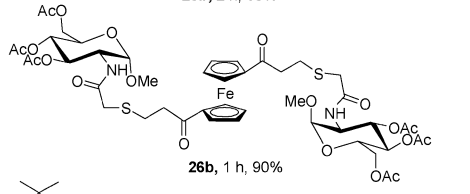
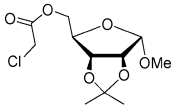
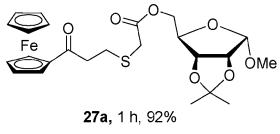
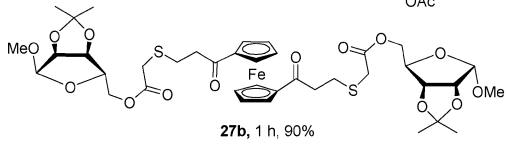
Electrochemical Characterization

Cyclic voltammetric studies were carried out to understand the effect of substituents attached to the Cp rings on the susceptibility of ferrocenyl moiety to get oxidized. The voltammograms obtained for the amino acid conjugates **15a** and **15b** and a set of carbohydrate conjugates **24a** and **24b** are given in Figures 1 and 2. The voltammograms were recorded in CH_3CN with Bu_4NPF_6 as the supporting electrolyte (0.1 M). The reference electrode potential was calibrated against the internal ferrocene/ferrocenium redox couple.

The voltammograms revealed highly reversible redox behavior for the ferrocene moiety with almost equal peak currents for the forward and reverse directions. Earlier reports have demonstrated that the susceptibility of Fe^{II} in ferrocene to oxidation depends on the electronic nature of substituents attached.[11,18] Electron-withdrawing groups produce an increase in the formal potential as compared to unsubstituted ferrocene, whereas electron-donating groups have the opposite trend.

As evident from the formal potential values, ferrocene moieties in **15b** and **24b** are less prone to oxidation than the ferrocene units present in **15a** and **24a**. This is likely to be due to the difference in the electronic environment of the

Table 4. Synthesis of monovalent and divalent ferrocene carbohydrate conjugates **22a**–**27a** and **22b**–**27b**, respectively.

Substrate	Monovalent carbohydrate conjugates	Divalent carbohydrate conjugates
 **22**	 **22a,** 2 h, 95%	 **22b,** 2 h, 92%
 **23**	 **23a,** 2 h. 95%	 **23b,** 2 h, 91%
 **24**	 **24a,** 2 h, 90%	 **24b,** 2 h, 90%
 **25**	 **25a,** 2 h, 90%	 **25b,** 2 h, 88%
 **26**	 **26a,** 1 h, 94%	 **26b,** 1 h, 90%
 **27**	 **27a,** 1 h, 92%	 **27b,** 1 h, 90%

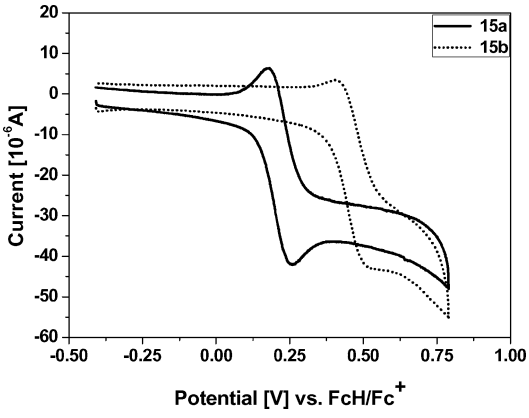


Figure 1. Cyclic voltammogramms of 1 mM each of amino acid conjugates **15a** and **15b** on glassy carbon electrode in CH_3CN containing Bu_4NPF_6 (scan rate: 20 mV/s).

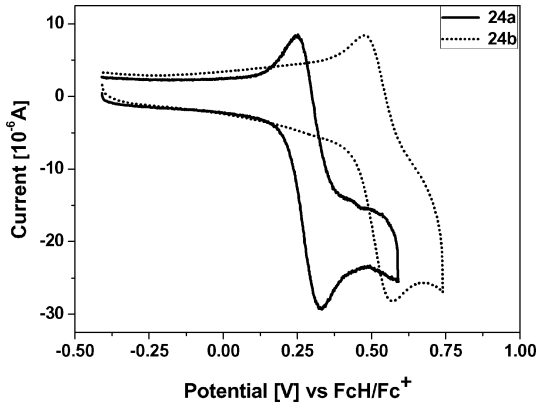


Figure 2. Cyclic voltammograms of 1 mM each of carbohydrate conjugates **24a** and **24b** on glassy carbon electrode in CH_3CN containing Bu_4NPF_6 (scan rate: 20 mV/s).

ferrocene moieties, as both Cp rings of ferrocene in **15b** and **24b** are covalently attached to carbonyl group whereas in **15a** and **24a**, only one of the Cp rings is attached to the carbonyl group. The formal potentials ($E°_f$) and peak separation values ($E_p^{anodic} - E_p^{cathodic}$) for the ferrocene conjugates are listed in Table 5.

Table 5. $E°_f$ (midpoint of oxidation and reduction peaks) and the difference between the anodic and cathodic peak potentials ΔE_{a-c} for the compounds listed above.

Entry	Compound	$E°_f$ (± 3mV vs Fc/Fc^+)	ΔE_{a-c}(mV)
1	**15a**	218	83
2	**15b**	462	109
3	**24a**	289	84
4	**24b**	523	93

Conclusion

In conclusion, diverse functionalized mono- and bis-sulfur-linked Michael adducts and conjugates were synthesized in one pot in a tandem fashion. Short reaction times, high yields, mildness of the method, operational simplicity makes it useful and attractive for the synthesis of Michael adducts and conjugates of amino acids and carbohydrates onto the ferrocene backbone.

Experimental Section

Physical Properties and Spectral Measurements: All glassware was oven-dried before starting a reaction. Solvents like CH_3CN and CH_2Cl_2 were purified according to literature procedures.[19] Analytical TLC was performed on commercial plates coated with silica gel GF_{254} (0.25 mm). Silica gel (230–400 mesh) was used for column chromatography. Melting points determined are uncorrected. ^1H and ^{13}C NMR spectra were recorded on 300 MHz (^1H: 300 MHz, ^{13}C: 75 MHz) or 400 MHz NMR spectrometers (^1H: 400 MHz, ^{13}C: 100 MHz). Chemical shifts (δ) are reported in parts per million (ppm) downfield from the internal reference, tetramethylsilane for ^1H and $CDCl_3$ for ^{13}C. IR spectra were recorded on a FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Micromass Q-TOF mass spectrometer.

Synthesis of Acryloylferrocene (4): To a well-stirred solution of (bromopropionyl)ferrocene (1 mmol) in CH_3CN (10 mL), triethylamine (1.5 mmol) was added and stirred for 10 min. CH_3CN was evaporated under vacuum and to the residue DCM (20 mL) was added and washed with water. DCM layer was filtered through anhydrous sodium sulfate followed by evaporation of solvent provided **4** (230 mg, 96%).

Synthesis of 1,1′-Diacryloylferrocene (5): To a well-stirred solution of 1,1′-(bromopropionyl)ferrocene (1 mmol) in CH_3CN (10 mL), triethylamine (3 mmol) was added and stirred for 10 min. CH_3CN was evaporated under vacuum and to the residue DCM (25 mL) was added and washed with water. DCM layer was filtered through anhydrous sodium sulfate followed by concentration gave **5** (279 mg, 95%). Red gummy solid. ^1H NMR (300 MHz, $CDCl_3$, 28 °C): δ = 6.75 (dd, J_1 = 16.8, J_2 = 10.2 Hz, 1 H), 6.47 (dd, J_1 = 17.1, J_2 = 2.1 Hz, 1 H), 5.78 (dd, J_1 = 10.5, J_2 = 1.8 Hz, 1 H), 4.84 (t, J = 1.8 Hz, 2 H), 4.56 (t, J = 1.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 28 °C): δ = 192.1, 132.5, 127.5, 80.8, 74.4, 71.2 ppm. IR (neat): $\tilde{\nu}$ = 3100, 1660, 1609, 1456, 1257, 1076 cm^{-1}. HRMS: *m*/*z*: calcd. for $C_6H_{14}FeO_2$ [M + Na]: 317.0241, found 317.0245;

General Procedure for the Synthesis of Mono-Michael Adducts 8–27a and Conjugates in a Tandem Fashion: To a well-stirred solution of (bromopropionyl)ferrocene (1 mmol) in CH_3CN (10 mL), triethylamine (1.5 mmol) was added and stirred for 10 min. To this solution substrate (1 mmol) and tetrathiomolybdate (2 mmol) were added, the mixture was stirred for the required time (1–4 h). CH_3CN was evaporated and to this DCM and ether (1:2) (15 mL × 3) were added and filtered through a sintered funnel. The filtrate was evaporated and the crude product was purified by flash chromatography.

Conjugate 24a: (EtOAc/hexane, 4:6), (766 mg, 90%), orange solid; m.p. 120 °C. ^1H NMR (300 MHz, $CDCl_3$, 28 °C): δ = 8.05–7.80 (m, 5 H), 7.56–7.23 (m, 15 H), 5.97 (t, J = 9.6 Hz, 1 H), 5.72 (t, J = 9.6 Hz, 1 H), 5.60 (t, J = 9.9 Hz, 1 H), 5.0 (d, J = 10.2 Hz, 1 H), 4.73–4.71 (m, 2 H), 4.66 (dd, J_1 = 12.6, J_2 = 3 Hz, 1 H), 4.49 (dd, J_1 = 12.6, J_2 = 5.1 Hz, 1 H), 4.44 (t, J = 1.8 Hz, 2 H), 4.25–4.14 (m, 6 H), 3.16–3.05 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 28 °C): δ = 201.9, 166.1, 165.7, 165.1 (2 C), 133.4, 133.3, 133.2, 133.1, 129.9, 129.8, 129.7, 129.6, 129.5, 129, 128.7, 128.6, 128.4 (2 C), 128.3, 128.2, 84.7, 78.4, 76.3, 74.0, 72.3, 70.6, 69.8, 69.4, 69.2, 69.1, 63.2, 40.5, 24.7 ppm. IR (neat): $\tilde{\nu}$ = 2959, 1733, 1664, 1452, 1266, 1090, 1026, 709 cm^{-1}. HRMS: *m*/*z*: calcd. for $C_{47}H_{40}FeO_{10}S$ [M + Na]: 875.1589, found 875.1586. $[\alpha]_D^{23}$ = –23.0 (*c* = 2, $CHCl_3$).

General Procedure for the Synthesis of Bis Michael Adducts 6a, 7a and 8–27b and Conjugates in a Tandem Fashion: To a well-stirred solution of 1,1′-(bromopropionyl)ferrocene (0.5 mmol) in CH_3CN (10 mL), triethylamine (1.5 mmol) was added and stirred for 10 min. To the resulting solution substrate (1 mmol) and tetrathiomolybdate (2 mmol) were added, then the mixture was stirred for the required time (1–4 h). CH_3CN was evaporated and dichloromethane (DCM) and diethyl ether (1:2) (15 mL × 3) were added to the residue. The resulting solution was filtered through a sintered funnel. The solvent was then evaporated and the residue purified by flash chromatography.

Conjugate 24b: EtOAc/hexane, 6:4; yield 683 mg, 90%; orange gummy liquid. ^1H NMR (300 MHz, $CDCl_3$, 28 °C): δ = 8.04–7.80 (m, 8 H), 7.54–7.22 (m, 12 H), 5.98 (t, J = 9 Hz, 1 H), 5.73 (t, J = 9.9 Hz, 1 H), 5.60 (t, J = 9.6 Hz, 1 H), 5.08 (d, J = 9.9 Hz, 1 H), 4.72–4.64 (m, 3 H), 4.48 (dd, J_1 = 12, J_2 = 4.8 Hz, 1 H), 4.39 (br. s, 2 H), 4.27–4.24 (m, 1 H), 3.18–3.01 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 28 °C): δ = 201.3, 166.0, 165.7, 165.2, 165.1, 133.4, 133.2, 133.1, 129.8, 129.7, 129.6, 129.5, 128.9, 128.7, 128.6, 128.4, 128.3, 128.2, 84.5, 79.5, 76.2, 74.0, 73.6, 73.5, 70.7, 70.5, 70.4, 69.4, 63.1, 40.9, 24.4 ppm. IR (neat): $\tilde{\nu}$ = 3062, 2883, 1730, 1670, 1601, 1452, 1268, 1089, 709 cm^{-1}. HRMS: *m*/*z*: calcd. for $C_{84}H_{70}FeO_{20}S_2$ [M + Na]: 1541.3149, found 1541.3120. $[\alpha]_D^{23}$ = 18.0 (*c* = 2, $CHCl_3$).

Electrochemical Measurements: Cyclic voltammetric studies were carried out using an electrochemical system consisting of a potentiostat and galvanostat (EG&G 273A, Princeton Applied Research, USA). All experiments were carried out in de-aerated CH_3CN containing 0.1 M Bu_4NPF_6 as the supporting electrolyte. Glassy carbon (0.2 cm^2) was used as the working electrode and a large-area Pt foil (2 cm^2) was used as the counter electrode. The surface of the glassy carbon electrode was polished with various grades of SiC (emery) sheets and subsequently ultrasonicated in distilled water for 15 min. The platinum foil counter electrode was cleaned in boiling nitric acid, washed with copius amounts of water and subsequently flamed to obtain a clean surface. The reference electrode used was Ag/AgCl/0.1 M Bu_4NPF_6 in acetonitrile. An internal reference of ferrocene/ferrocenium redox couple (FcH/Fc^+) in the same electrolyte was used in all the experiments and the voltammograms are represented with reference to this couple. All the voltammograms were recorded at a scan rate of 20 mV/s. The

formal potential of ferrocene/ferrocenium redox couple is 0.409 V (vs. Ag/AgCl/0.1 M Bu_4NPF_6) under the conditions employed. The concentration of the analytes was kept at 1 mM in all the experiments.

Supporting Information (see also the footnote on the first page of this article): Spectroscopic and analytical data of all the new compounds.

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