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Synthesis of Functionalized Tetracyanocyclopentadienides from Tetracyanothiophene and Sulfones

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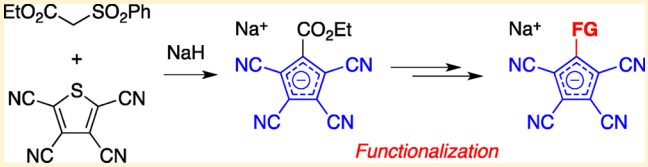
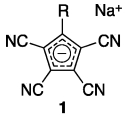
Supporting Information

ABSTRACT: Tetracyanothiophene and tetracyano-1,4-dithiin react with a leaving group substituted carbon nucleophile such as ethyl benzenesulfonylacetate to afford substituted tetracyanocyclopentadienyl sodium derivatives in moderate to high yields through a putative condensation and desulfurization pathway. Subsequent functional-group transformation reactions on the Cp anion ring provided various $C_5R(CN)_4^-$ derivatives.



INTRODUCTION

Superacid conjugate bases are employed in many useful organometallic and organic catalysts[1] as weakly coordinating anionic species, which are mainly involved in ionic bonds with catalysts. The roles of these bases are usually considered only for increasing the cationic character and reactivity of catalysts. Therefore, superacid conjugate bases have been excluded from mechanistic discussions. The importance of superacid anion modification was reported in a study of the carba-*closo*-dodecaborate anion ($CB_{11}H_{12}^-$); many derivatives have subsequently been demonstrated to have use in numerous applications.[2] On the other hand, functionalization of representative superacid anions such as OTf^-, BF_4^-, and ClO_4^- are typically difficult. We therefore focused on tetracyanocyclopentadienyl anions ($C_5R(CN)_4^-$) (Figure 1) as another class of functionalized possible superacid anions.



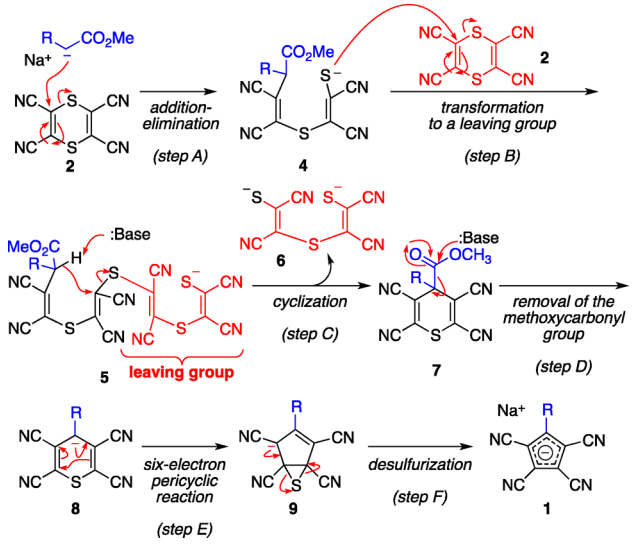
1a	R = H	**1g**	R = CO_2Ph
1b	R = CN	**1h**	R = COPh
1c	R = CO_2Me	**1i**	R = CONMe(OMe)
1d	R = CO_2Et	**1j**	R = Ph
1e	R = CO_2Menthyl	**1k**	R = CH_2CH_2OBn
1f	R = CO_2t-Bu	**1l**	R = CH_2CH_2OTBS

Figure 1. Sodium salts of $C_5R(CN)_4$ anions **1**.

The $C_5R(CN)_4$ anions **1a** (R = H) and **1b** (R = CN), originally reported by Webster as potential superacid conjugate bases,[3] have proton affinities weaker than that of ClO_4^-, which is indicated by their pK_a values (in CH_3CN) of their conjugate acids (H−$C_5H(CN)_4$, 0.2; H−$C_5(CN)_5$, <−2; H−ClO_4, 1.83)[4] and the ν(NH) values of their tri-*n*-octylammonium salts ($C_5H(CN)_4^-$, 3054 cm^{-1}; $C_5(CN)_5^-$, 3097 cm^{-1}; ClO_4^-, 3049 cm^{-1}).[5] Previous related studies of $C_5R(CN)_4$ salts have been conducted mainly with pentacyanocyclopentadienide (R = CN) in the areas of structural[6] and computational chemistry;[7] however, an efficient synthetic method for $C_5R(CN)_4$ salts has yet to be established. Webster described the synthesis of **1a,b** via cyclization of disodium hexacyanobutenediide, which was prepared from tetracyanoethane.[3,8] Simmons reported another method using tetracyanodithiin (**2**) as a starting material; this protocol requires more than 2 equiv of **2** for the synthesis of **1b,c** and other $C_5R(CN)_4$ salts (R = OCH_3, NO_2).[9] Thus, the development of a new synthetic method is crucial for preparing functionalized derivatives of **1**.

A proposed mechanism for the Simmons method toward $C_5R(CN)_4$ salts is shown in Scheme 1. Attack of a methyl ester enolate on tetracyanodithiin **2** affords the open-chain thiolate anion **4** (step A). Nucleophilic attack of **4** on another 1 equiv of dithiin **2** affords the dimeric product **5**, whereby the thiolate anion moiety of **5** becomes a *leaving group* (step B). Deprotonation of the α proton of ester **5** and concomitant

Scheme 1. Mechanism Proposed by Simmons[9]



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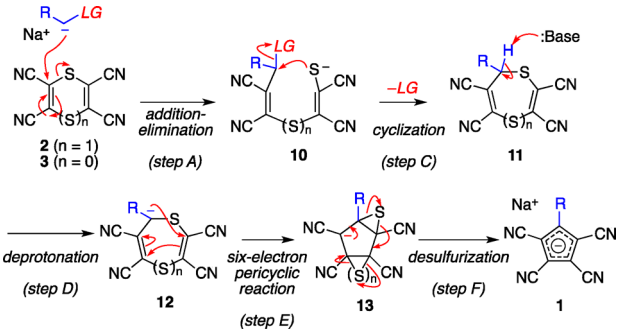
cyclization provides **7**, accompanied by elimination of dithiolate **6** (step C). Base-mediated dealkoxycarbonylation of the methoxycarbonyl group of **7** affords anion **8** (step D). Electrocyclic ring closure followed by desulfurization finally provides tetracyanocyclopentadienide **1** (steps E and F). Thus, because a second molecule of **2** is consumed as a reagent at step B, the amount of **2** used in the reaction cannot be reduced to less than 2 equiv.[10]

We therefore designed the synthesis of **1** based on the mechanism shown in Scheme 2, where a leaving group (LG) is

Scheme 2. Presumed Mechanism for the Synthesis of 1



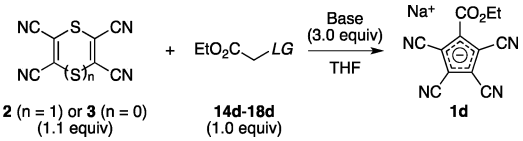
included in the nucleophile.[11] An LG-substituted nucleophile attacks tetracyanodithiin (**2**; n = 1) or tetracyanothiophene (**3**; n = 0) to give thiolate anion **10** (step A). Intramolecular LG displacement of **10** provides compound **11**, which, following deprotonation, affords anion **12** (step C). A six-electron pericyclic reaction of **12** and subsequent desulfurization of **13** affords the $C_5R(CN)_4$ salt **1** (steps E and F). In contrast to the mechanism in Scheme 1, only 1 equiv of **2** (or **3**) is theoretically necessary, as step B is avoided. We herein report a practical synthesis of **1** based on this strategy.

RESULTS AND DISCUSSION

Initially, the LG substituent of the nucleophile was examined (Table 1). The first substrate examined was ethyl diazoacetate (**14d**), which has a good leaving group (N_2) and potentially anionic nature at the α-position; however, simple mixing of **14d** with **2** in THF at room temperature was insufficient in promoting the reaction (entry 1). Deprotonation of **14d** with NaH and subsequent addition of **2** provided **1d** in low yield because of generation of a pyrazolium side product (**19**), which possibly formed via the [3 + 2]-type cycloaddition of **14d** with **2** (entry 2). We therefore decided to modify the leaving group to halogens. Treatment of a mixture of ethyl bromoacetate (**15d**) and **2** with NaH gave **1d** in 53% yield (entry 3). When tetracyanothiophene (**3**) was used instead of **2**,[9,12] the yield of **1d** was increased to 73% (entry 4). Other bases such as LiHMDS, NaHMDS, KO-*t*-Bu, and DBU gave a lower product yield than did NaH (entries 5−8). Reactions using ethyl chloroacetate and iodoacetate (**16d** and **17d**) resulted in almost comparable yields (entries 9 and 10). These results show that the leaving ability of halogen atoms did not greatly influence the yield of **1d**. We then focused on the phenylsulfonyl group, which could play the role of both leaving group and anion-stabilizing group. Product **1d** was obtained in 79% yield at 0 °C upon reaction of **3** with ethyl (phenylsulfonyl)acetate (**18d**; entry 11). The highest yield (91%) was achieved with **3** and **18d** when the reaction was performed at −40 °C (entry 12). It is worth mentioning that **1d** dissolves in a variety of organic solvents and can be purified by silica gel column chromatography, despite its strongly ionic nature. The R_f value of **1d** by TLC was about 0.2 (eluent EtOAc).

We next examined the substrate scope of sulfones (**18**) in the formation of $C_5R(CN)_4$ with tetracyanothiophene **3** (Table 2). Methyl, menthyl, and *tert*-butyl (arylsulfonyl)acetates (**18c,e,f**) provided **1c,e,f** in good yields, respectively (entries 1−3). However, phenyl (tolylsulfonyl)acetate (**18g**) gave **1g** in very low yield (entry 4). (Tolylsulfonyl)acetonitrile (**18b**) gave $NaC_5(CN)_5$ (**1b**) in excellent yield. The reaction using

Table 1. Screening of Leaving Groups and Bases



entry	2/3	14d−18d	LG	base	temp (°C)	time (min)	yield (%)
1	**2** (n = 1)	**14d**[b]	N_2^+		27	60	0
2[a]	**2** (n = 1)	**14d**[b]	N_2^+	NaH	27	60	25[c]
3	**2** (n = 1)	**15d**	Br	NaH	0	20	53
4	**3** (n = 0)	**15d**	Br	NaH	0	40	73
5	**3** (n = 0)	**15d**	Br	NaHMDS	0	60	45[d]
6	**3** (n = 0)	**15d**	Br	LiHMDS	0	30	59[d]
7	**3** (n = 0)	**15d**	Br	KO*t*-Bu	0	120	*d,e*
8	**3** (n = 0)	**15d**	Br	DBU	0	120	13[d]
9	**3** (n = 0)	**16d**	Cl	NaH	0	20	55
10	**3** (n = 0)	**17d**	I	NaH	0	40	64
11	**3** (n = 0)	**18d**	SO_2Ph	NaH	0	40	79
12	**3** (n = 0)	**18d**	SO_2Ph	NaH	−40	40	91

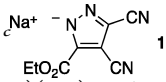
[a]1.2 equiv of **14c** and NaH were used for 1.0 equiv of **2**. [b]Ethyl diazoacetate. [c]  **19** (61%) [d]Isolated as an Ag salt after an ion-exchange reaction with $AgNO_3$ in MeOH. [e]A 31/69 inseparable mixture of $AgC_5(CO_2Et)(CN)_4$ and $AgC_5(CO_2$-*t*-Bu$)(CN)_4$ was obtained in 66% yield.

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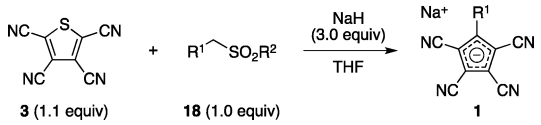
Table 2. Sulfone Substrate Scope of Reaction



entry	18	R^1	R^2	temp (°C)	time (min)	1	yield (%)
1	**18c**	CO_2Me	Ph	−40	40	**1c**	59
2	**18e**	CO_2Menthyl	Tol	0	40	**1e**	83
3	**18f**	CO_2t-Bu	Tol	0	60	**1f**	78
4	**18g**	CO_2Ph	Tol	0	180	**1g**	22
5	**18b**	CN	Tol	−40	40	**1b**	96
6	**18h**	COPh	Ph	−40 to reflux	60	**1h**	0
7	**18i**	CONMe(OMe)	Tol	−40	35	**1i**	86
8	**18m**	Ph	Ph	−40	120	**1j**	15
9	**18j**	Ph	CF_3	−40	30	**1j**	71
10	**18k**	CH_2CH_2OBn	CF_3	−40	90	**1k**	61
11[a]	**18l**	CH_2CH_2OTBS	CF_3	−40	60	**1l**	51

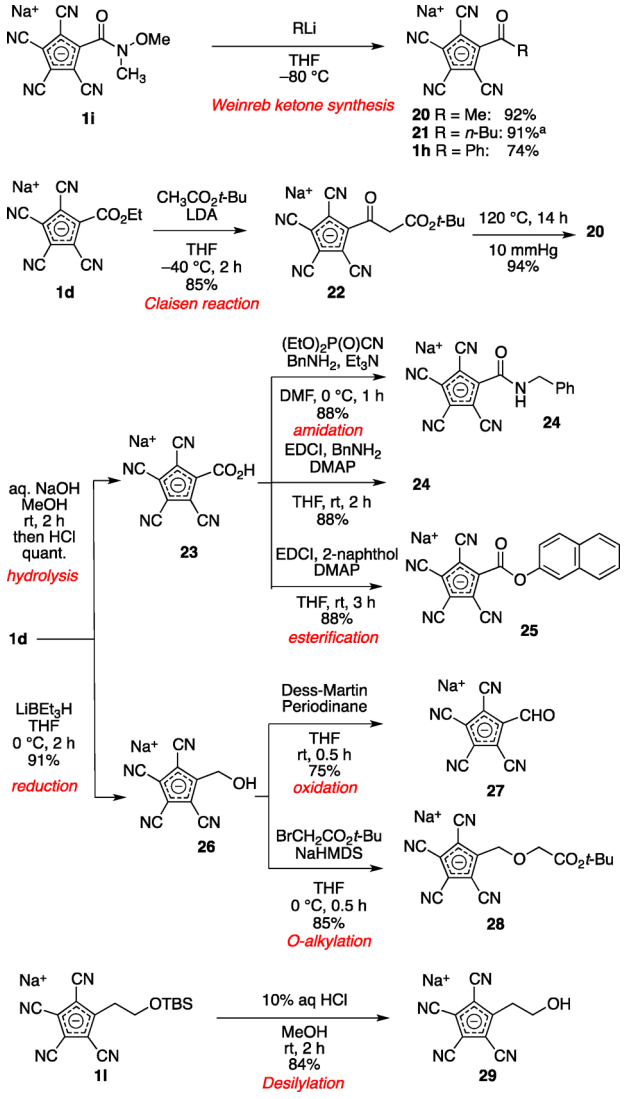
[a]THF/DMF (12/1) cosolvent system was used instead of THF.

(phenylsulfonyl)acetophenone (**18h**) did not proceed below 0 °C and provided a complex mixture at elevated temperatures (entry 6). Other ketones such as aliphatic (methyl, *tert*-butyl) and brominated ketones as well as 2-(trifluoromethylsulfonyl)-acetophenone also did not give any of the target compounds. Instead, the Weinreb amide derivative, a potent ketone precursor, could be used (**18i**) to afford **1i** in 86% yield (entry 7). Introduction of phenyl or alkyl groups on the Cp anion ring was achieved by using a trifluoromethanesulfonyl leaving group (entries 9−11). When benzyl phenyl sulfone (**18m**) was employed instead of trifluoromethyl benzyl sulfone (**18j**, entry 9), only 15% of the expected product was obtained (entry 8).

Numerous $C_5R(CN)_4$ salts (**1**) were successfully synthesized from **3** and **18**. We then explored functional group interconversions of the newly introduced substituents, which could not be obtained directly from **3** and **18**, including ketones and aryl esters (Scheme 3).[13] Tetracyanocyclopentadienyl ketones **20**, **21**, and **1h** were directly synthesized by the reaction of Weinreb amide **1i** with the corresponding alkyllithium reagents. Treatment of **1i** with methyl- and phenyllithium afforded methyl and phenyl ketones **20** and **1h**, respectively. In contrast, *n*-BuLi afforded an inseparable mixture of diketones generated by *n*-butyl addition to the nitrile groups. This was circumvented by employing methylmagnesium bromide as an additive to afford butyl ketone derivative **21** in 91% yield.[14] A second synthesis of ketone **20** was achieved by a Claisen reaction of **1d** with an ester enolate and subsequent vacuum pyrolysis of the *β*-keto ester **22** at 120 °C.

Hydrolysis of ethyl ester **1d** with NaOH followed by acidification with aqueous HCl afforded the corresponding carboxylic acid **23** in quantitative yield. It is worth noting that protonation occurred only at the carboxylate anion and not at the $C_5R(CN)_4^-$ anion and that carboxylic acid **23** could be extracted with EtOAc (see the Supporting Information). Amidation of **23** with benzylamine was then examined. Acyl chloride formation by an oxalyl chloride−DMF system failed, giving a complex mixture, while formation of a mixed anhydride with pivaloyl chloride succeeded on the basis of TLC monitoring. However, subsequent nucleophilic attack by benzylamine was not selective and gave a ca. 1/1 mixture of

Scheme 3. Substitution Modification Reactions of 1



[a]*n*-BuLi (3.6 equiv) and MeMgBr (1.3 equiv) were used.

24 and **23**. On the other hand, the condensation agents diethyl phosphorocyanidate[15] and 1-ethyl-3-(3-(dimethylamino)-propyl)carbodiimide hydrochloride (EDCI) gave amide **24** in good yield. Esterification of **23** with 2-naphthol was also achieved with an EDCI−*N*,*N*-DMAP system to provide aryl ester **25**, which was not obtained in satisfactory yield by the direct method using **18** and **3** (Table 2, entry 4).

Super-Hydride reduction of ethyl ester **1d** interestingly provided alcohol **26** in high yield with all four cyano groups remaining intact. The starting ester **1d** was recovered when DIBAL was employed. Oxidation of **26** to aldehyde **27** was also achieved using Dess−Martin periodinane. An O-alkylation reaction with *tert*-butyl bromoacetate mediated by NaHMDS gave ether **28**.

We also attempted to remove the O-protecting groups of **1k**,**l**. The TBS group of **1l** was removed under mildly acidic conditions to afford alcohol **29** in good yield. Surprisingly, the benzyl group of **1k** was not removed by hydrogenation using standard Pd or Pt catalysts. Even with a large excess of catalyst under high pressures and temperatures, the starting benzyl ether **1k** was recovered unchanged along with a trace amount of

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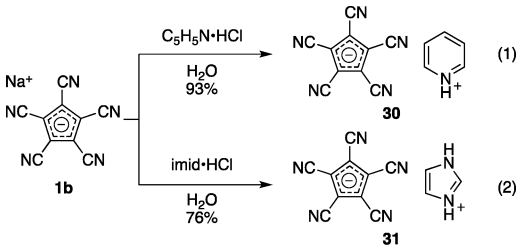
product **29**. This low reactivity toward hydrogenation implies that $C_5R(CN)_4$ anion acts as a catalyst poison.

Finally, a counterion-exchange reaction was performed to prepare $C_5(CN)_5$ salts of nitrogen-containing heteroaromatics. Addition of pyridinium or imidazolium hydrochloride to an aqueous solution of sodium salt **1b** led to precipitation of the corresponding $C_5(CN)_5$ salts **30** and **31**, respectively, in good yield (eqs 1 and 2).



CONCLUSION

We have developed a new efficient synthetic method for a variety of $C_5R(CN)_4$ salts from tetracyanothiophene **3** and sulfones **18** and have demonstrated further functionalization reactions on the Cp anion ring. Recently, the importance of modified phosphonate or sulfonate anions is increasingly being recognized in the field of organocatalysis.[16] Further study on this new class of functionalized potential superacid anion is in progress.

EXPERIMENTAL SECTION

General Considerations. All air- and moisture-sensitive reactions were carried in dry solvent under an argon atmosphere. Flash chromatography was carried out with silica gel (spherical, neutral, 40−50 mm). Melting points are uncorrected. Chemical shifts are reported in ppm relative to solvent signal (δ 1.94 ppm for CD_3CN, δ 3.31 ppm for CD_3OD) or internal TMS (δ 0.00 ppm for $CDCl_3$) for ^{1}H NMR spectra and to the solvent signals (δ 1.39 ppm for CD_3CN, δ 77.0 ppm for $CDCl_3$, δ 49.15 ppm for CD_3OD, 39.51 ppm for DMSO-d_6) for ^{13}C NMR spectra. Coupling constants (J) are reported in hertz. Data are reported as follows: integration, chemical shift, and multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). The low- and high-resolution mass spectra were recorded on magnetic sector FAB and EI mass spectrometers. Unless otherwise noted, $C_5R(CN)_4$ salts were dried overnight at 120 °C/10 mmHg to remove solvent and water from the products, both (1) after purification by flash chromatography and (2) before functionalization reactions.

Tetracyanothiophene (3). Tetracyanothiophene (**3**) was prepared via **2** according to Simmons's method[12] modified by Reed et al.,[6c] except for the purification procedure of **2**.

To a suspension of NaCN (23.5 g, 480 mmol) in DMF (160 mL) was added dropwise CS_2 (28.8 mL, 36.3 g, 480 mmol) via an addition funnel over 1 h, and the mixture was stirred for 3 h. The reaction mixture was then poured into 1400 mL of water, and the resulting mixture was allowed to stand for 12 h. The resulting sulfur precipitate was removed by filtration, and the filtrate was transferred into a round-bottomed flask.

A solution of ammonium persulfate (109.5 g, 480 mmol) in water (210 mL) was added to the filtrate dropwise over 40 min, and the reaction mixture was stirred for 15 min at room temperature. The resulting precipitate containing tetracyanodithiin (**2**) was collected by filtration, washed well with water, and thoroughly dried under vacuum. The precipitate was suspended in MeCN (1400 mL) and filtered. The filtrate was concentrated to give 19.5 g of tetracyanodithiin (**2**), which was used in the next step without further purification.

A solution of tetracyanodithiin (**2**; 19.5 g) in 1,2-dichlorobenzene (100 mL) was degassed by three freeze−pump−thaw cycles at −196 °C (0.5 mmHg) and then stirred at 200 °C for 2 h. After it was cooled to room temperature, *n*-hexane (300 mL) was added to the dark brown solution, and the resulting precipitate was collected by filtration. The dark brown solid was dissolved in AcOEt (300 mL), and the solution was passed through a short silica plug and then concentrated. The obtained brown solid was reprecipitated with AcOEt/*n*-hexane to provide 13.1 g (59%) of tetracyanothiophene (**3**) as a pale brown powder: mp 205−206 °C; IR (KBr) 2240, 1153 cm^{-1}; ^{13}C NMR (CD_3CN, 125 MHz) δ 126.2, 122.7, 110.8, 110.5.

(1*R*,3*R*,4*S*)-Menthyl (*p*-Toluenesulfonyl)acetate (18e). A mixture of (1*R*,3*R*,4*S*)-menthyl bromoacetate[17] (276 mg, 1.0 mmol, 1.0 equiv), sodium *p*-toluenesulfinate (715 mg, 4.0 mmol, 4.0 equiv), and DMF (20 mL) was stirred at room temperature for 24 h. After addition of water (20 mL), the resulting mixture was extracted with EtOAc, and the organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (20% EtOAc/*n*-hexane) afforded 415 mg (96%) of **18e** as a colorless solid: mp 93−94 °C; $[\alpha]^{23}_D$ −45.0 (c 1.01, $CHCl_3$); IR (KBr) 2960, 2870, 1735, 1324, 1294, 1148, 1087 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82 (2H, d, J = 8.3 Hz), 7.37 (2H, d, J = 8.3 Hz), 4.66 (1H, td, J = 11.0, 4.4 Hz), 4.09 (2H, s), 2.46 (3H, s), 1.88 (1H, dddd, J = 11.9, 4.4, 3.4, 2.1 Hz), 1.75 (1H, sept-d, J = 6.9, 2.6 Hz), 1.68−1.63 (2H, m), 1.42 (1H, tqt, J = 12.0, 6.4, 3.4 Hz), 1.33 (1H, dddd, J = 12.1, 11.0, 3.3, 2.6 Hz), 1.00 (1H, tdd, J = 13.5, 12.0, 3.9 Hz), 0.90 (1H, ddd, J = 12.1, 12.0, 11.9 Hz), 0.89 (3H, d, J = 6.4 Hz), 0.844 (3H, d, J = 6.9 Hz), 0.836 (1H, tdd, J = 13.5, 12.0, 3.9 Hz), 0.69 (3H, d, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.0, 145.2, 135.8, 129.8, 128.6, 76.7, 61.2, 46.6, 40.3, 34.0, 31.3, 25.8, 23.1, 21.9, 21.7, 20.7, 16.0; HRFABMS m/z calcd for $C_{19}H_{27}O_4S$ $[M - H]^-$ 351.1630, found 351.1633.

***t*-Butyl (*p*-Toluenesulfonyl)acetate[18] (18f).** A mixture of *tert*-butyl bromoacetate (0.310 mL, 0.41 g, 2.0 mmol), sodium *p*-toluenesulfinate (1.43 g, 8.0 mmol, 4.0 equiv), and DMF (40 mL) was stirred at room temperature for 24 h. After addition of water (40 mL), the resulting mixture was extracted with EtOAc, and the organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (20% EtOAc/80% *n*-hexane) afforded 568 mg (quantitative) of **18f** as a colorless solid: mp 57−58 °C; IR (KBr) 2981, 2938, 1731, 1321, 1292, 1157 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82 (2H, d, J = 8.3 Hz), 7.37 (2H, d, J = 8.3 Hz), 4.02 (2H, s), 2.45 (3H, s), 1.38 (9H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.4, 145.2, 136.0, 129.7, 128.5, 83.5, 62.2, 27.6, 21.6.

Phenyl (*p*-Toluenesulfonyl)acetate (18g). A mixture of phenyl bromoacetate (0.285 mL, 0.43 g, 2.0 mmol), sodium *p*-toluenesulfinate (1.43 g, 8.0 mmol, 4.0 equiv), and DMF (40 mL) was stirred at room temperature for 24 h. After addition of water (40 mL), the resulting mixture was extracted with EtOAc, and the organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (20% EtOAc/80% *n*-hexane) afforded 206 mg (35%) of **18g** as a colorless solid: mp 79−80 °C; IR (KBr) 3003, 2937, 1759, 1596, 1488, 1328, 1267, 1143, 1084 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.88 (2H, d, J = 8.0 Hz), 7.39−7.35 (4H, m), 7.24 (1H, m), 7.02 (2H, d, J = 8.0 Hz), 4.33 (2H, s), 2.45 (3H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.1, 150.0 145.7, 135.7, 130.0, 129.5, 128.6, 126.5, 121.0, 61.2, 21.7; HRFABMS m/z calcd for $C_{15}H_{15}O_4S$ $[M + H]^+$ 291.0691, found 291.0718.

***N*-Methoxy-*N*-methyl-2-(*p*-toluenesulfonyl)acetamide (18i).** A mixture of 2-chloro-*N*-methoxy-*N*-methylacetamide (1.00 g, 7.3 mmol, 1.0 equiv), sodium *p*-toluenesulfinate (1.43 g, 8.0 mmol, 1.1 equiv), and DMF (6 mL) was stirred at room temperature for 18 h. After addition of water (7 mL), the resulting mixture was extracted with EtOAc, and the organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (30% acetone/70% *n*-hexane) afforded 1.64 g (88%) of **18i** as a colorless oil: IR ($CHCl_3$) 3024, 2944, 1665, 1325, 1162 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (2H, d, J = 8.3 Hz), 7.36 (1H, d, J = 8.3 Hz), 4.32 (2H, s), 3.80 (3H, s), 3.18 (3H, s), 2.45 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.5, 145.2, 136.3, 129.7, 128.7, 61.7,

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57.9, 32.1, 21.6; HRFABMS m/z calcd for $C_{11}H_{14}O_4NS$ $[M - H]^-$ 256.0644, found 256.0651.

3-Benzyloxy-1-propyl Trifluoromethyl Sulfone (18k). A mixture of 3-benzyloxy-1-propyl bromide (456 mg, 2.0 mmol, 1.0 equiv), sodium trifluoromethanesulfinate (406 mg, 2.6 mmol, 1.3 equiv), and DMF (1 mL) was stirred at 120 °C for 24 h. After it was cooled to room temperature, the mixture was diluted with 5 mL of water and then extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (60% CH_2Cl_2/40% *n*-hexane) afforded 353 mg (63%) of **18k** as a colorless oil: IR (KBr) 2867, 1366, 1199, 1122 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.39−7.29 (5H, m), 4.52 (2H, s), 3.61 (2H, t, J = 5.7 Hz), 3.38(2H, t, J = 7.8 Hz), 2.21 (2H, tt, J = 7.8, 5.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.6, 128.6, 128.0, 127.8, 119.5 (q, J_{C-F} = 325 Hz), 73.1, 66.9, 47.0, 21.6; HREIMS m/z calcd for $C_{11}H_{13}O_3F_3S$ $[M^+]$ 282.0537, found 282.0530.

3-(*tert*-Butyldimethylsilyl)oxy-1-propyl Trifluoromethyl Sulfone (18l). A mixture of (3-bromopropoxy)-*tert*-butyldimethylsilane (506 mg, 2.0 mmol, 1.0 equiv), sodium trifluoromethanesulfinate (406 mg, 2.6 mmol, 1.3 equiv), and DMF (1 mL) was stirred at 120 °C for 12 h. After it was cooled to room temperature, the mixture was diluted with 5 mL of water and then extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography (50% CH_2Cl_2/50% *n*-hexane) afforded 324 mg (53%) of **18l** as a colorless oil: IR (KBr) 2956, 2932, 2860, 1369, 1198, 1124, 837 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.75 (2H, t, J = 5.7 Hz), 3.38 (2H, t, J = 7.7 Hz), 2.21 (2H, tt, J = 7.7, 5.7 Hz), 0.89 (9H, s), 0.07 (6H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 119.5 (q, J_{C-F} = 325 Hz), 60.1, 46.8, 25.7, 24.3, 18.1, −5.6; HRFABMS m/z calcd for $C_{10}H_{22}O_3F_3SiS$ $[M + H]^+$ 307.1012, found 307.0992.

General Procedure for the Synthesis of Sodium Tetracyanocyclopentadienides. *Sodium 1,2,3,4-Tetracyano-5-(ethoxycarbonyl)cyclopentadienide (1d) (Table 1, Entry 12).* To a suspension of NaH (60% dispersion in mineral oil, 54 mg, 1.4 mmol, 3.0 equiv) in THF (0.5 mL) was added a solution of sulfone **18d** (0.45 mmol, 1.0 equiv) in THF (1.2 mL) dropwise at 0 °C, and the reaction mixture was stirred at 0 °C for 0.5 h. After the mixture was cooled to −40 °C, a solution of tetracyanothiophene (**3**; 91 mg, 0.50 mmol, 1.1 equiv) in THF (1.3 mL) was added, and the reaction mixture was stirred for 0.7 h. Brine (5 mL) was added, and the reaction mixture was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, and then concentrated. Flash chromatography (0 → 10% MeCN/AcOEt) afforded 102 mg (91%) of **1d** as a yellow solid: R_f = 0.2 (AcOEt); mp 351−367 °C dec; IR (KBr) 2223, 1698, 1485, 1278 cm^{-1}; ^1H NMR (CD_3CN, 500 MHz) δ 4.29 (2H, q, J = 7.1 Hz), 1.33 (3H, t, J = 7.1 Hz); ^{13}C NMR (CD_3CN, 125 Hz) δ 162.3, 124.2, 116.0 115.2, 103.6, 101.1, 61.8, 14.5; HRFABMS m/z calcd for $C_{12}H_5N_4O_2$ $[M - Na]^-$ 237.0418, found 237.0421.

Sodium 1,2,3,4-Tetracyano-5-(methoxycarbonyl)cyclopentadienide (1c) (Table 2, Entry 1). According to the general procedure, **1c** was synthesized with methyl phenylsulfonylacetate (**18c**; 74 μL, 96 mg, 0.45 mmol, 1.0 equiv) at −40 °C for 0.7 h. Flash chromatography (0 → 10% MeCN/AcOEt) afforded 65 mg (59%) of **1c** as a pale brown solid: R_f = 0.5 (10% MeCN/AcOEt); mp 350−360 °C dec; IR (KBr) 2966, 2224, 1712, 1489, 1280, 1126 cm^{-1}; ^1H NMR (CD_3CN, 500 MHz) δ 3.82 (3H, s); ^{13}C NMR (CD_3CN, 125 MHz) δ 162.7, 123.9, 115.9, 115.2, 103.7, 101.1, 52.4; HRFABMS m/z calcd for $C_{11}H_3N_4O_2$ $[M - Na]^-$ 223.0256, found 223.0235.

Sodium 1,2,3,4-Tetracyano-5-((1R,3R,4S)-menthoxycarbonyl)cyclopentadienide (1e) (Table 2, Entry 2). According to the general procedure, **1e** was synthesized with (1*R*,3*R*,4*S*)-menthyl (*p*-toluenesulfonyl)acetate (**18e**; 159 mg, 0.45 mmol, 1.0 equiv) at 0 °C for 1 h. Flash chromatography (0 → 10% MeCN/AcOEt) afforded 138 mg (83%) of **1e** as a pale brown solid: R_f = 0.6 (10% MeCN/AcOEt); mp 206−207 °C; $[\alpha]^{23}_D$ −69.9 (*c* 0.25, MeOH); IR (KBr) 2958, 2928, 2223, 1691, 1482, 1276, 1125 cm^{-1}; ^1H NMR (CD_3CN, 500 MHz) δ 4.87 (1H, td, J = 11.0, 4.6 Hz), 2.06 (1H, dddd, J = 12.2, 4.3, 3.6, 2.1 Hz), 2.01 (1H, spt-d, J = 6.9, 2.5 Hz), 1.74−1.69 (2H, m), 1.58−1.50 (2H, m), 1.124 (1H, qd, J = 12.8, 3.4 Hz), 1.115 (1H, td, J = 12.2, 11.0 Hz), 0.94 (1H, dddd, J = 13.8, 13.0, 11.9, 4.1 Hz), 0.93 (3H, d, J = 6.6 Hz), 0.91 (3H, d, J = 6.9 Hz), 0.77 (1H, d, J = 6.9 Hz); ^{13}C NMR (CD_3CN, 125 MHz) δ 161.8, 124.3, 116.0, 115.3, 103.7, 101.2, 75.6, 48.0, 41.9, 35.0, 32.3, 27.1, 24.1, 22.4, 21.2, 16.6; HRFABMS m/z calcd for $C_{20}H_{19}N_4O_2$ $[M - Na]^-$ 347.1508, found 347.1520.

Sodium 1-(tert-Butoxycarbonyl)-2,3,4,5-tetracyanocyclopentadienide (1f) (Table 2, Entry 3). According to the general procedure, **1f** was synthesized with *tert*-butyl (*p*-toluenesulfonyl)acetate (**18f**; 122 mg, 0.45 mmol, 1.0 equiv) at 0 °C for 1 h. Flash chromatography (0 → 10% MeCN/AcOEt) afforded 102 mg (78%) of **1f** as a pale brown solid: R_f = 0.5 (10% MeCN/AcOEt); mp 290−300 °C dec; IR (KBr) 2979, 2929, 2225, 1691, 1487, 1290, 1119 cm^{-1}; ^1H NMR (CD_3CN, 500 MHz) δ 1.54 (9H, s); ^{13}C NMR (CD_3CN, 125 MHz) δ 161.5, 125.8, 116.1, 115.4, 103.3, 101.0, 82.7, 28.4; HRFABMS m/z calcd for $C_{14}H_9N_4O_2$ $[M - Na]^-$ 265.0726, found 265.0700.

Sodium 1,2,3,4-Tetracyano-5-(phenoxycarbonyl)cyclopentadienide (1g) (Table 2, Entry 4). According to the general procedure, **1g** was synthesized with phenyl (*p*-toluenesulfonyl)acetate (**18g**; 122 mg, 0.45 mmol, 1.0 equiv) at 0 °C for 1 h. Flash chromatography (0 → 10% MeCN/AcOEt) afforded 30 mg (22%) of **1g** as a brown solid: R_f = 0.6 (10% MeCN/AcOEt); mp 220−223 °C; IR (KBr) 2223, 1716, 1619, 1473, 1362, 1256, 1191 cm^{-1}; ^1H NMR (CD_3CN, 500 MHz) δ 7.46−7.43 (2H, m), 7.31−7.25 (3H, m); ^{13}C NMR (CD_3CN, 125 MHz) δ 160.5, 151.7, 130.6, 127.0, 122.8, 122.7, 115.8, 115.0, 104.2, 101.9; HRFABMS m/z calcd for $C_{16}H_5N_4O_2$ $[M - Na]^-$ 285.0413, found 285.0392.

Sodium Pentacyanocyclopentadienide (1b) (Table 2, Entry 5).[6e] According to the general procedure, **1b** was synthesized with phenyl (*p*-toluenesulfonyl)acetonitrile (**18b**; 88 mg, 0.45 mmol, 1.0 equiv) at 0 °C for 1 h. Flash chromatography (0 → 10% MeCN/AcOEt) afforded 92 mg (96%) of **1b** as a pale brown solid: R_f = 0.4 (10% MeCN/AcOEt); mp >380 °C; IR (KBr) 2248, 2225, 1468 cm^{-1}; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 113.0, 101.7.

Sodium 1,2,3,4-Tetracyano-5-(N-methoxy-N-methylcarbamoyl)cyclopentadienide (1i) (Table 2, Entry 7). According to the general procedure, **1i** was synthesized with NaH (60% dispersion in mineral oil, 120 mg, 3.0 mmol, 3.0 equiv), *N*-methoxy-*N*-methyl-2-(*p*-toluenesulfonyl)acetamide (**18i**; 228 mg, 1.0 mmol, 1.0 equiv), and tetracyanothiophene (**3**; 203 mg, 1.1 mmol, 1.1 equiv) at −40 °C for 0.5 h. Flash chromatography (0 → 10% MeCN/AcOEt) afforded 236 mg (86%) of sodium tetracyanocyclopentadienide (**1i**) as a pale brown solid: R_f = 0.2 (AcOEt); mp 335−339 °C dec; IR (KBr) 2236, 2217, 1621, 1499, 1463, 1076, 999 cm^{-1}; ^1H NMR (CD_3CN, 400 MHz) δ 3.55 (3H, s), 3.28 (3H, s); ^{13}C NMR (CD_3CN, 100 MHz) δ 164.0, 128.9, 116.2, 115.7, 102.2, 99.0, 62.0, 34.5; HRFABMS m/z calcd for $C_{12}H_6N_5O_2$ $[M - Na]^-$ 252.0521, found 252.0532.

Sodium 1,2,3,4-Tetracyano-5-phenylcyclopentadienide (1j) (Table 2, Entry 9). According to the general procedure, **1j** was synthesized with benzyl trifluoromethyl sulfone (**18j**;[19] 101 mg, 0.45 mmol, 1.0 equiv) at 0 °C for 1 h. Flash chromatography (0 → 10% MeCN/AcOEt) afforded 84 mg (78%) of **1j** as a pale brown solid: R_f = 0.6 (10% MeCN/AcOEt); mp 300−320 °C dec; IR (KBr) 3064, 2924, 2208, 1637, 1464 cm^{-1}; ^1H NMR (CD_3CN, 500 MHz) δ 7.60 (2H, m), 7.47 (2H, m), 7.38 (1H, m); ^{13}C NMR (CD_3CN, 125 MHz) δ 137.4, 133.5, 128.8, 128.2, 128.0, 116.5, 115.1, 100.9, 95.4; HRFABMS m/z calcd for $C_{15}H_5N_4$ $[M - Na]^-$ 241.0514, found 252.0524.

Sodium 1-(2-Benzyloxyethyl)-2,3,4,5-tetracyanocyclopentadienide (1k) (Table 2, Entry 10). According to the general procedure, **1k** was synthesized with 3-benzyloxy-1-propyl trifluoromethyl sulfone (**18k**; 124 mg, 0.44 mmol, 1.0 equiv) at −40 °C for 1.5 h. Flash chromatography (0 → 10% MeCN/AcOEt) afforded 87 mg (61%) of **1k** as a reddish brown amorphous solid: R_f = 0.2 (AcOEt); IR (KBr) 2211, 1636, 1467, 1095 cm^{-1}; ^1H NMR (CD_3CN, 400 MHz) δ 7.34−7.26 (5H, m), 4.48 (2H, s), 3.65 (2H, t, J = 6.7 Hz), 2.91 (2H, t, J = 6.7 Hz); ^{13}C NMR (CD_3CN, 100 MHz) δ 139.9, 137.8, 129.4, 128.6, 128.5, 117.1, 116.4, 100.2, 97.7, 73.2, 70.5, 29.2; HRFABMS m/z calcd for $C_{18}H_{11}ON_4$ $[M - Na]^-$ 299.0933, found 299.0929.

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Sodium 1-(2-(tert-Butyldimethylsilyl)oxyethyl)-2,3,4,5-tetracyanocyclopentadienide (1l) (Table 2, Entry 11). To a suspension of NaH (60% dispersion in mineral oil, 54 mg, 1.35 mmol, 3.0 equiv) in THF (0.5 mL) and DMF (0.25 mL) was added a solution of 3-(*tert*-butyldimethylsilyl)oxy-1-propyl trifluoromethyl sulfone (**18l**; 138 mg, 0.45 mmol, 1.0 equiv) in THF (1.25 mL) dropwise at 0 °C. The mixture was stirred at 0 °C for 1.0 h and then cooled to −40 °C. A solution of tetracyanothiophene (**3**; 91 mg, 0.5 mmol, 1.1 equiv) in THF (1.25 mL) was added, and the reaction mixture was stirred at −40 °C for 1.0 h. Brine (5 mL) was added, and the resulting mixture was extracted with EtOAc. The organic layer was washed with brine (5 mL), dried over Na_2SO_4, and then concentrated. Flash chromatography (20 → 50% CH_3CN/CH_2Cl_2) afforded 80 mg (51%) of **1l** as a brown amorphous solid: R_f = 0.2 (AcOEt); IR (KBr) 2955, 2929, 2858, 2214, 1467, 1092, 837 cm^{-1}; ^1H NMR (CD_3CN, 400 MHz) δ 3.79 (2H, t, J = 6.6 Hz), 2.78 (2H, t, J = 6.6 Hz), 0.83 (9H, s), −0.04 (6H, s); ^{13}C NMR (CD_3CN, 100 MHz) δ 138.0, 117.2, 116.5, 100.0, 97.9, 63.9, 32.3, 26.3, 18.9, −5.2; HRFABMS m/z calcd for $C_{17}H_{19}ON_4Si$ $[M - Na]^-$ 323.1328, found 323.1305.

*Reaction of **14d** with **2** in the Presence of NaH (Table 1, Entry 2).* To a suspension of NaH (60% dispersion in mineral oil, 22 mg, 0.55 mmol, 1.2 equiv) in THF (1 mL) was added a solution of ethyl diazoacetate (**14d**; 67 μL, 63 mg, 0.55 mmol, 1.2 equiv) in THF (1.25 mL) dropwise at 0 °C. The mixture was stirred for 0.5 h at room temperature. A solution of tetracyanodithiin (**2**; 100 mg, 0.46 mmol, 1.0 equiv) in THF (1 mL) was added, and the reaction mixture was stirred at room temperature for 1.0 h. Brine (5 mL) was added, and the resulting mixture was extracted with EtOAc. The organic layer was washed with brine (5 mL), dried over Na_2SO_4, and then concentrated. Flash chromatography (0 → 30% CH_3CN/AcOEt) afforded 29 mg (25%) of **1d** and 64 mg (66%) of **19**.

Sodium 4,5-dicyano-3-ethoxycarbonylpyrazolide (**19**): brown amorphous solid; R_f = 0.1 (10% MeCN/AcOEt); IR (KBr) 2238, 2193, 2066, 1702, 1627 1560, 1458, 1259 cm^{-1}; ^1H NMR (CD_3CN, 600 MHz) δ 4.40 (2H, q, J = 6.9 Hz), 1.35 (3H, t, J = 6.9 Hz); ^{13}C NMR (CD_3CN, 125 Hz) δ 164.5, 146.0, 130.0 114.8, 114.0, 97.3, 63.2, 14.5; HRFABMS m/z calcd for $C_8H_5N_4O_2$ $[M - Na]^-$ 189.0413, found 189.0417.

Sodium 1-Acetyl-2,3,4,5-tetracyanocyclopentadienide (20). To a solution of Weinreb amide **1i** (48.8 mg, 0.18 mmol) in THF (1 mL) was added MeLi (1.14 M Et_2O solution, 0.800 mL, 0.9 mmol, 5.0 equiv) over 3 min at −80 °C, and the reaction mixture was stirred at −80 °C for 1 h. The reaction was quenched with saturated aqueous NH_4Cl solution, and the resulting mixture was extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated: R_f = 0.6 (20% MeOH/CH_2Cl_2). Flash chromatography (20% MeOH/80% CH_2Cl_2) afforded 38.0 mg (92%) of ketone **20** as a pale yellow solid: mp 259−262 °C dec; IR (KBr) 2925, 2853, 2766, 2218, 1667, 1467, 1250, 1100, 983 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 2.53 (3H, s); ^{13}C NMR (100 MHz, CD_3CN) δ 192.0, 133.5, 116.9, 115.2, 104.4, 100.4, 29.0; HRFABMS calcd for $C_{11}H_3ON_4$ $[M - Na]^-$ 207.0312, found 207.0323.

Sodium 1,2,3,4-Tetracyano-5-pentanoylcyclopentadienide (21). To a solution of Weinreb amide **1i** (50.4 mg, 0.18 mmol) in THF (1 mL) at −80 °C were added MeMgBr (3.0 M Et_2O solution, 0.080 mL, 0.24 mmol, 1.3 equiv) over 2 min and then *n*-BuLi (1.65 M hexane solution, 0.40 mL, 0.66 mmol, 3.6 equiv) over 2 min. The reaction mixture was stirred at −80 °C for 50 min. The reaction was quenched with saturated aqueous NH_4Cl solution, and the resulting mixture was extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (15% MeOH/85% CH_2Cl_2) afforded 44.8 mg (91%) of ketone **21** as a pale yellow solid: R_f = 0.5 (15% MeOH/CH_2Cl_2); mp 149−152 °C; IR (KBr) 2961, 2237, 1662, 1468, 1386, 1201, 1042 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 2.93 (2H, t, J = 7.3 Hz), 1.64 (2H, quintet, J = 7.3 Hz), 1.38 (2H, septet, J = 7.3 Hz), 0.92 (3H, t, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_3CN) δ 194.2, 133.4, 117.0, 115.4, 104.2, 100.1, 40.9, 27.2, 23.1, 14.3; HRFABMS calcd for $C_{14}H_9ON_4$ $[M-Na]^-$ 249.0781, found 249.0771.

Sodium 1-Benzoyl-2,3,4,5-tetracyanocyclopentadienide (1h). To a solution of Weinreb amide **1i** (49 mg, 0.18 mmol) in THF (1 mL) at −80 °C was added dropwise PhLi (1.08 M cyclohexane−Et_2O, 0.830 mL, 0.898 mmol) over 5 min, and the reaction mixture was stirred at −80 °C for 2.5 h. The reaction was quenched with saturated aqueous NH_4Cl solution, and the resulting mixture was extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (12.5 → 50% MeOH/Et_2O) afforded 41 mg (78%) of ketone **1h** as a pale yellow solid: R_f = 0.3 (15% MeOH/Et_2O); mp 297−301 °C; IR (KBr) 2987, 2929, 2762, 2221, 1717, 1636, 1466, 1378, 1271, 1043, 741, 698, 649 cm^{-1}; ^1H NMR (500 MHz, CD_3CN) δ 7.76−7.34 (5H, m); ^{13}C NMR (125 MHz, CD_3CN) δ 189.8, 139.3, 133.8, 133.0, 130.4, 129.4, 116.0, 115.3, 103.9, 101.3; HRFABMS calcd for $C_{16}H_5ON_4$ $[M - Na]^-$ 269.0469, found 269.0449.

Sodium 1-(3-(*tert*-Butoxy)-3-oxopropanoyl)-2,3,4,5-tetracyanocyclopentadienide (22). To a solution of diisopropylamine (0.145 mL, 1.03 mmol, 5.4 equiv) in THF (1 mL) was added *n*-BuLi (1.58 M hexane solution, 0.65 mL, 1.03 mmol, 5.4 equiv) over 4 min at −80 °C. After 0.5 h, a solution of *tert*-butyl acetate (0.140 mL, 1.03 mmol, 5.4 equiv) in THF (1 mL) was added, and the mixture was stirred at −80 °C for 0.5 h. A solution of ethyl ester **1d** (50 mg, 0.192 mmol, 1.0 equiv) in THF (1 mL) was added, and the reaction mixture was stirred at −40 °C for 2 h. The reaction was quenched with 10% aqueous citric acid solution, and the resulting mixture was extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was dissolved in MeOH, and the solution was passed through an Amberlyst 15 (Na form) column (15 cm height, 2.0 cm i.d.). The eluted solution was concentrated and purified by flash chromatography (10% MeOH/90% Et_2O) to afford 54 mg (85%) of **22** as a yellow solid: R_f = 0.3 (10% MeOH/Et_2O); mp 95−128 °C dec; IR (KBr) 2982, 2936, 2222, 1723, 1661, 1469, 1149 cm^{-1}; ^1H NMR (CD_3CN, 500 MHz) δ 3.87 (2H, s), 1.43 (9H, s); ^{13}C NMR (CD_3CN, 125 MHz) δ 186.7, 167.9, 132.2, 116.4, 115.0, 104.6, 100.6, 82.7, 48.8, 28.2; HRFABMS m/z calcd for $C_{16}H_{11}N_4O_3$ $[M - Na]^-$ 307.0837, found 307.0829. Because of the low decomposition point of **22**, the sample was dried overnight at 50 °C/10 mmHg.

Methyl Ketone 20 from 22. Keto ester **22** (54 mg, 0.164 mmol) was heated at 120 °C under vacuum (10 mmHg) for 14 h. Flash chromatography (20% MeOH/80% CH_2Cl_2) afforded 35 mg (94%) of ketone **20** as a pale yellow solid.

Sodium 1-Carboxy-2,3,4,5-tetracyanocyclopentadienide (23). To a solution of ethyl ester **1d** (1.20 g, 4.61 mmol, 1.0 equiv) in MeOH (10 mL) was added 10% aqueous NaOH solution (10 mL, 25 mmol, 5.4 equiv). The reaction mixture was stirred at room temperature for 1.0 h. The mixture was acidified with 10% aqueous HCl solution (12 mL) and then extracted with three 30 mL portions of AcOEt. The combined organic layers were washed with two 20 mL portions of brine, dried over Na_2SO_4, filtered, and concentrated. The resulting yellow solid was reprecipitated from MeOH/CH_2Cl_2 to afford 1.07 g (quantitative) of **23** as a yellow solid: R_f = 0.1 (20% MeOH/CH_2Cl_2); mp 320−325 °C dec; IR (KBr) 3477, 2229, 1711, 1689, 1491, 1249 cm^{-1}; ^1H NMR (CD_3OD, 500 MHz) δ 4.87 (1H, br s); ^{13}C NMR (CD_3OD, 125 MHz) δ 164.4, 125.5, 116.1, 115.1, 103.9, 101.6; HRFABMS m/z calcd for $C_{10}HN_4O_2$ $[M - Na]^-$ 209.0100, found 209.0085. The acid proton overlapped with a CD_3OH signal in ^1H NMR due to fast proton exchange.

Sodium 1-(*N*-Benzylcarbamoyl)-2,3,4,5-tetracyanocyclopentadienide (24). To a solution of carboxylic acid **23** (50 mg, 0.22 mmol, 1.0 equiv) and Et_3N (0.12 mL, 87 mg, 0.86 mmol, 4.0 equiv) in DMF (1 mL) was added diethyl phosphorocyanide (0.065 mL, 70 mg, 0.43 mmol, 2.0 equiv) in one portion. After 10 min, benzylamine (0.050 mL, 49 mg, 0.46 mmol, 2.1 equiv) was added in one portion and the reaction mixture was stirred at 0 °C for 1 h. A saturated aqueous $NaHCO_3$ solution (4 mL) was added, and the resulting mixture was extracted with AcOEt. The organic layer was washed with saturated aqueous $NaHCO_3$ solution (4 mL) and brine (4 mL), dried over Na_2SO_4, filtered, and concentrated. The residue was dissolved in MeOH, and the solution was passed through an Amberlyst 15 (Na

form) packed column (15 cm height, 1.0 cm i.d.). The eluted solution was concentrated and purified by flash chromatography (10 → 20% MeOH/CH_2Cl_2) to afford 61 mg (88%) of **24** as a yellow solid: R_f = 0.6 (20% MeOH/CH_2Cl_2); mp 170−175 °C; IR (KBr) 3431, 2219, 1635, 1540, 1457 cm^{-1}; ^1H NMR (acetone-d_6, 500 MHz) δ 7.76 (1H, br s), 7.40 (2H, d, J = 7.3 Hz), 7.32 (2H, t, J = 7.3 Hz), 7.24 (1H, t, J = 7.3 Hz), 4.63 (2H, d, J = 6.0 Hz); ^{13}C NMR (acetone-d_6, 500 MHz) δ 163.0, 139.7, 130.2, 129.3, 128.4, 127.9, 116.0, 115.0, 102.4, 98.3, 44.1; HRFABMS m/z calcd for $C_{17}H_8N_5O$ $[M - Na]^-$ 298.0729, found 298.0720.

Preparation of 24 using EDCI. To a suspension of carboxylic acid **23** (50 mg, 0.22 mmol, 1.0 equiv), *N,N*-dimethylaminopyridine (3.7 mg, 0.03 mmol, 0.14 equiv), and benzylamine (47 mg, 0.33 mmol, 1.1 equiv) in THF (1 mL) was added 1-ethyl-3-(3-(dimethylamino)-propyl)carbodiimide hydrochloride (62 mg, 0.32 mmol, 1.5 equiv) in one portion, and the reaction mixture was stirred at room temperature for 2 h. The reaction was quenched with 10% aqueous HCl (2 mL), and the resulting mixture was extracted with AcOEt. The organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was dissolved in MeOH, and the solution was passed through an Amberlyst 15 (Na form) column (15 cm height, 1.0 cm i.d.). The eluted solution was concentrated and purified by flash chromatography (0−15% MeOH/CH_2Cl_2) to afford 61 mg (88%) of **24** as a yellow solid.

Sodium 1,2,3,4-Tetracyano-5-(2-naphthyloxycarbonyl)-cyclopentadienide (25). To a suspension of carboxylic acid **23** (50 mg, 0.22 mmol, 1.0 equiv), *N,N*-dimethylaminopyridine (3.7 mg, 0.03 mmol, 0.14 equiv), and 2-naphthol (47 mg, 0.32 mmol, 1.5 equiv) in THF (1 mL) was added 1-ethyl-3-(3-(dimethylamino)propyl)-carbodiimide hydrochloride (82 mg, 0.43 mmol, 2.0 equiv) in one portion, and the reaction mixture was stirred at room temperature for 1.5 h. The reaction was quenched with 10% aqueous HCl (2 mL), and the resulting mixture was extracted with AcOEt. The organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was dissolved in MeOH, and the solution was passed through an Amberlyst 15 (Na form) column (15 cm height, 1.0 cm i.d.). The eluted solution was concentrated and purified by flash chromatography (AcOEt) to afford 65 mg (88%) of **25** as a yellow solid: R_f = 0.3 (AcOEt); mp >320 °C; IR (KBr) 2236, 1704, 1481, 1270, 1239, 1155, 1098 cm^{-1}; ^1H NMR (CD_3CN, 500 MHz) δ 7.95 (1H, d, J = 8.9 Hz), 7.93 (1H, d, J = 7.8 Hz), 7.89 (1H, d, J = 7.8 Hz), 7.78 (1H, d, J = 1.6 Hz), 7.54 (1H, dd, J = 6.0, 7.8 Hz), 7.52 (1H, dd, J = 6.0, 7.8 Hz), 7.43 (1H, dd, J = 8.9, 1.6 Hz); ^{13}C NMR (CD_3CN, 125 MHz) δ 160.7, 149.4, 134.8, 132.5, 130.5, 128.8, 128.7, 127.8, 127.0, 122.7, 122.4, 119.6, 115.8, 115.1, 104.4, 102.0; HRFABMS m/z calcd for $C_{20}H_7N_4O_2$ $[M - Na]^-$ 335.0569, found 335.0555.

Sodium 1,2,3,4-Tetracyano-5-(hydroxymethyl)-cyclopentadienide (26). To a solution of ethyl ester **1d** (500 mg, 1.92 mmol, 1.0 equiv) in THF (10 mL) was added $LiBEt_3H$ (1.0 M THF solution, 5.28 mL, 5.28 mmol, 2.75 equiv) at 0 °C, and the reaction mixture was stirred at room temperature for 2 h. A saturated aqueous $NaHCO_3$ solution (5 mL) and a 10% aqueous potassium sodium tartrate solution (10 mL) were added, and the resulting mixture was extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was dissolved in MeOH, and the solution was passed through an Amberlyst 15 (Na form) column (15 cm height, 2.0 cm i.d.). The eluted solution was concentrated and purified by flash chromatography (10 → 20% MeOH/CH_2Cl_2) to afford 386 mg (92%) of **26** as a yellow solid: R_f = 0.5 (20% MeOH/CH_2Cl_2); mp 263−280 dec; IR (KBr) 3565, 3506, 2238, 2216, 1661, 1462 cm^{-1}; ^1H NMR (CD_3CN, 400 MHz) δ 4.50 (2H, s), 3.33 (1H, br s); ^{13}C NMR (CD_3CN, 125 MHz) δ 139.3, 116.8, 116.3, 100.7, 97.5, 57.3; HRFABMS m/z calcd for $C_{10}H_3N_4O$ $[M - Na]^-$ 195.0307, found 195.0319.

Sodium 1,2,3,4-Tetracyano-5-formylcyclopentadienide (27). To a solution of alcohol **26** (25 mg, 0.12 mmol, 1.0 equiv) in THF (1 mL) was added Dess−Martin periodinane (73 mg, 0.17 mmol, 1.5 equiv), and the reaction mixture was stirred at room temperature for 0.5 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (2 mL) and 10% aqueous $Na_2S_2O_3$ solution (2 mL), and the resulting mixture was extracted with AcOEt. The organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried over Na_2SO_4, filtered and concentrated. Flash chromatography (AcOEt) afforded 19 mg (75%) of aldehyde **27** as a pale yellow solid: R_f = 0.6 (20% MeOH/CH_2Cl_2); mp >350 °C; IR (KBr) 2240, 2226, 1670, 1474 cm^{-1}; ^1H NMR (CD_3CN, 500 MHz) δ 9.75 (1H, s); ^{13}C NMR (CD_3CN, 125 MHz) δ 183.0, 132.4, 115.2, 114.9, 104.6, 101.1; HRFABMS m/z calcd for $C_{10}HN_4O$ $[M - Na]^-$ 193.0150, found 193.0156.

Sodium 1-((*tert*-Butoxycarbonylmethoxy)methyl)-2,3,4,5-tetracyanocyclopentadienide (28). To a solution of alcohol **26** (210 mg, 0.96 mmol, 1.0 equiv) and *tert*-butyl bromoacetate (0.427 mL, 2.89 mmol, 3.0 equiv) in THF (8 mL) was added a 1.0 M THF solution of NaHMDS (2.4 mL, 2.4 mmol, 2.5 equiv) at 0 °C, and the reaction mixture was stirred at 0 °C for 0.5 h. The reaction was quenched with saturated aqueous NH_4Cl solution (10 mL), and the resulting mixture was extracted with three 15 mL portions of AcOEt. The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution (15 mL) and brine (15 mL), dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (15% MeOH/85% CH_2Cl_2) afforded 272 mg (85%) of ether **28** as a pale yellow solid: R_f = 0.4 (15% MeOH/CH_2Cl_2); mp 117−125 °C dec; IR (KBr) 2981, 2935, 2213, 1733, 1471, 1371, 1255, 1159, 1102 cm^{-1}; ^1H NMR (CD_3CN, 600 MHz) δ 4.55 (2H, s), 3.94 (2H, s), 1.45 (9H, s); ^{13}C NMR (CD_3CN, 150 MHz) δ 171.1, 134.4, 116.5, 116.1, 101.1, 98.7, 82.9, 68.4, 65.5, 28.4; HRFABMS m/z calcd for $C_{16}H_{13}N_4O_3$ $[M - Na]^-$ 309.0988, found 309.1005. Because of the low decomposition point of **28**, the sample was dried overnight at 50 °C/10 mmHg.

Sodium 1,2,3,4-Tetracyano-5-(2-hydroxyethyl)-cyclopentadienide (29). A mixture of TBS ether **1l** (18 mg, 0.052 mmol), MeOH (1 mL), and 10% aqueous HCl (0.1 mL) was stirred at room temperature for 2 h. Solid $NaHCO_3$ (ca. 20 mg) was added, and the resulting precipitate was removed by filtration. The filtrate was concentrated and purified by flash chromatography (15% MeOH/85% CH_2Cl_2) to afford 10 mg (84%) of alcohol **29** as a yellow solid: R_f = 0.3 (20% MeOH/CH_2Cl_2); mp 301−304 °C (dec.); IR (KBr) 3495, 2956, 2220, 1638, 1464, 1050 cm^{-1}; ^1H NMR (CD_3CN, 500 MHz) δ 3.65 (2H, td, J = 7.2, 6.0 Hz), 2.86 (1H, t, J = 6.0 Hz, OH), 2.79 (2H, t, J = 7.2 Hz); ^{13}C NMR (CD_3CN, 125 MHz) δ 137.5, 117.1, 116.4, 100.1, 97.6, 62.6, 32.3; HRFABMS m/z calcd for $C_{11}H_5ON_4$ $[M - Na]^-$ 209.0463, found 209.0472.

Pyridium Pentacyanocyclopentadienide (30). To a solution of sodium salt **1b** (50 mg, 0.24 mmol, 1.0 equiv) in H_2O (1 mL) was added a solution of pyridinium hydrochloride (35 mg, 0.31 mmol, 1.3 equiv) in H_2O (1 mL). The resulting precipitate was collected by filtration and reprecipitated with MeCN/$CHCl_3$ to afford 59 mg (93%) of pyridinium salt **30** as a pale yellow solid: R_f = 0.4 (10% MeCN/AcOEt); mp 251−253 °C; IR (KBr) 3207, 3162, 3101, 2242, 2219, 1598, 1525, 1463 cm^{-1}; ^1H NMR (CD_3CN, 500 MHz) δ 8.70−8.69 (2H, m), 8.61 (1H, m), 8.06−8.04 (2H, m), 3.50 (1H, br s); ^{13}C NMR (CD_3CN, 125 MHz) δ 148.9, 142.6, 128.8, 114.3, 103.3. Anal. Calcd for $C_{15}H_6N_6$: C, 66.66; H, 2.24; N, 31.10. Found: C, 66.52; H, 2.38; N, 31.02.

Imidazolium Pentacyanocyclopentadienide (31). To a solution of sodium salt **1b** (50 mg, 0.24 mmol, 1.0 equiv) in H_2O (1 mL) was added a solution of imidazolium hydrochloride (32 mg, 0.31 mmol, 1.3 equiv) in H_2O (1 mL). The resulting precipitate was collected by filtration and reprecipitated with MeOH/benzene to afford 47 mg (76%) of imidazolium salt **31** as a pale yellow solid: R_f = 0.4 (10% MeCN/AcOEt); mp 263−265 °C; IR (KBr) 3150, 2245, 2220, 1582, 1470 cm^{-1}; ^1H NMR (CD_3CN, 500 MHz) δ 10.6 (br s, 2H), 8.52 (1H, s), 7.41 (2H, s); ^{13}C NMR (CD_3CN, 125 MHz) δ 135.1, 120.4, 114.3, 103.3; Anal. calcd for $C_{13}H_5N_7$: C, 60.23; H, 1.94; N, 37.82. Found: C, 60.10; H, 2.08; N, 37.89.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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