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Substitution of a benzylic hydrogen by nucleophiles on a chromium tricarbonyl complex of a benzyl ether

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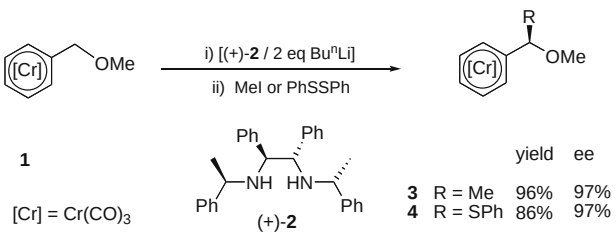
ABSTRACT

Deprotonation of the benzylic carbon of a chromium tricarbonyl complex of a benzyl ether followed by reaction with *N*-fluorobenzenesulfonimide (NFSI) generated a species that reacted with oxygen, sulfur and carbon nucleophiles.

Some time ago, we demonstrated that chromium tricarbonyl complexes of benzyl ethers such as **1** react with the chiral diamide derived from butyllithium / chiral diamine **2** and electrophiles such as iodomethane and diphenyl disulfide to give chiral ether complexes **3** and **4**, respectively (Scheme 1).[1] The reactions typically gave good yields of products, which were generated in high enantiomeric excess.

Due to the well-established importance of fluorine-containing compounds in medicinal chemistry,[2] and ongoing interest in new methods for introducing fluorine into organic compounds,[3] we decided to investigate whether or not we could use the reaction outlined in Scheme 1 to introduce a fluorine atom into benzylic ethers under good stereochemical control. In an initial reaction, diamine (+)-**2** was treated with butyllithium and the benzylic ether complex **5**[4] was added to the resulting deep-red solution at −78 °C. Selectfluor™ (1.5 equiv) in acetonitrile, was then added as a source of electrophilic fluorine and after 30 min at −78 °C, methanol (40 equiv) was added to quench the reaction. Work-up led to the isolation of the acetal complex **6** in 45% yield, the aldehyde complex **7** (28%) and recovered substrate **5** (6%) (Scheme 2). Although the desired fluorination had not occurred under these conditions,[5] the conversion of ether **5** to acetal **6** is, to the best of our knowledge, an unprecedented transformation in arene chromium tricarbonyl chemistry and so we decided to investigate this transformation further.

We first wished to establish the origins of the two methoxy groups in acetal **6**. To do this, the original experiment was repeated but the quench was carried out using deuterated methanol. Isolation of the acetal and scrutiny of its ^{1}H NMR spectrum and mass spectrum established that complex **8** contained one methoxy group derived from substrate **5** and one deuterated methoxy group derived from deuterated methanol. This is consistent with aldehyde **7** being derived from acetal **8** rather than the reverse. Next, two reactions were performed using diamines (+)- and (−)-**2** to form the diamide base and using isopropanol to quench the reaction. The acetal complex produced in each reaction was isolated and examined by chiral HPLC which revealed that the enantiopurity of each was negligible (5%). Thus the achiral base LDA was employed henceforth. Subsequent optimisation experiments for the conversion of ether **5** into acetal **6** included the employment of the THF-soluble electrophilic fluorine source *N*-fluorobenzenesulfonimide (NFSI)[6] in place of Selectfluor™ and this resulted in a



Scheme 1. Asymmetric functionalisation of chromium tricarbonyl complexes of benzyl ethers.

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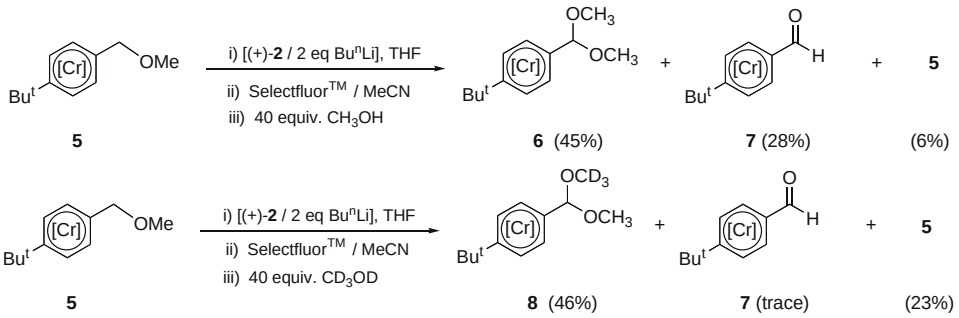


Scheme 2. Initial observation of the ether-to-acetal transformation.

Table 1
Substitution of a benzylic hydrogen of complex **5** using oxygen, sulfur, nitrogen and carbon nucleophiles as depicted in Scheme 3

Entry	NuH or $NuSiMe_3$	Product	Nu	Product yield (%)	Yield of **7** (%)
1	MeOH	**6**	OMe	79	10
2	CD_3OD	**8**	OCD_3	76	13
3	Pr^nOH	**9**	OPr^n	65	17[a]
4	Pr^iOH	**10**	OPr^i	59	34
5	Bu^tOH	**11**	OBu^t	36	47
6	PhOH	**12**	OPh	78	5
7	BnOH	**13**	OBn	85	—[b]
8	$BnNH_2$	**14**	NHBn	9	70[c]
9	BnSH	**15**	SBn	75	5
10	$PhC(OSiMe_3)=CH_2$[d]	**16**	CH_2COPh	68	6

[a] A small amount (8%) of the bispropoxy acetal was also isolated from this reaction.
[b] The amount of aldehyde produced in this reaction was not quantified as it co-ran with large amounts of benzyl alcohol.
[c] Significant quantities of the benzyl imine of **7** (17%) were isolated from this reaction.
[d] $LiClO_4$ was added to this reaction to provide a more weakly coordinating anion for the positively charged intermediate.

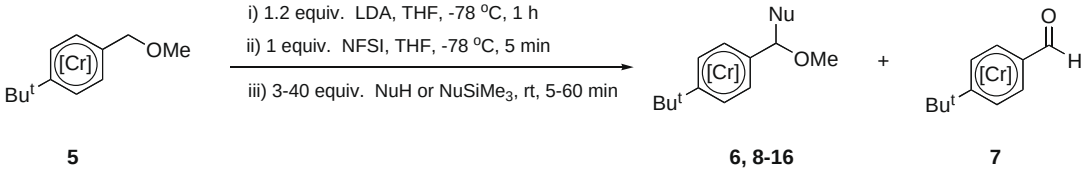
dramatic increase in the yield of acetal **6** to 79% (Table 1, entry 1). The conversion of **5** into **8** using deuterated methanol also increased using NFSI from 46% to 76% (Table 1, entry 2). The scope and limitations of the substitution of a benzylic hydrogen by a nucleophile on chromium tricarbonyl complexes of benzyl ethers were subsequently studied using NFSI under the conditions depicted in Scheme 3.[7]

The effect of increasing the branching of the incoming nucleophile was examined first. As the bulk of the alcoholic nucleophile increased from methanol through propanol and isopropanol to *tert*-butanol, the yield of the resulting acetal fell from 79% to 36% whilst the yield of aldehyde **7** rose from 10% to 47% (Table 1, entries 1–5). Acetal production proved to be efficient with phenol (Table 1, entry 6) and benzyl alcohol (Table 1, entry 7). The tolerance of the reaction to nucleophiles other than alcohols was examined next. Whilst benzylamine proved predictably to be a poor nucleophile (Table 1, entry 8), we were pleased to discover that addition of benzyl thiol gave a good yield of the corresponding thioacetal (Table 1, entry 9), and addition of 1-phenyl-1-(trimethylsilyloxy)ethene led to carbon–carbon bond formation and the production of a branched ether (Table 1, entry 10).

Whilst the mechanism for the reactions described above has not been examined in detail yet, the results obtained to date are consistent with the following hypothesis. First of all, LDA removes a benzylic hydrogen from the chromium complex to give an anionic species. This is then oxidised by NFSI to give an electrophilic species which is then intercepted by the nucleophile. Slow addition of an ineffective nucleophile such as *tert*-butanol to the benzylic centre leads to competing addition at the methyl group of the ether, perhaps by fluoride anions, and the formation of the aldehyde **7**.

Cations, anions and radicals centred on the benzylic carbon adjacent to arene chromium tricarbonyl units are well established species, all of which have found widespread application in diverse areas of organic synthesis.[8] To the best of our knowledge, the reaction documented above represents the first example of an oxidative transformation of a species created by a base, presumably an anion, to a species that is reactive towards nucleophiles. It complements the reductive transformation of a benzylic cation equivalent to an anion which has been achieved using 2.1 equiv of the single electron reducing agent, lithium 4,4′-di-*tert*-butylbiphenyl (LiDBB).[9] It is interesting to note other changes in polarity that have been achieved in organometallic chemistry. For example, cations centred on the propargylic carbon adjacent to alkyne hexacarbonyl dicobalt species have been reduced to radicals using zinc, providing an entry to a range of new synthetic pathways for these versatile alkyne derivatives.[10] Elsewhere, the polarity of palladium allyl cations has been reversed by samarium diiodide to give anionic species in a process that has been postulated to proceed via a palladium allyl radical species.[11]

In summary we have demonstrated for the first time that the benzylic carbon of an arene chromium tricarbonyl complex may be deprotonated and the resulting anion oxidised to a species that reacts with oxygen, sulfur and carbon nucleophiles.



Scheme 3. Substitution of a benzylic hydrogen of complex **5** using oxygen, sulfur, nitrogen and carbon nucleophiles.

Acknowledgements

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4. Gibson, S. E.; Ibrahim, H.; Pasquier, C.; Steed, J. W. *Tetrahedron* **2002**, *58*, 4617–4627.
5. Omission of the MeOH quench gave the same set of products dominated by the starting material (**6**:8%; **7**:7%; **5**:55%). All attempts to isolate the fluorinated target molecule from several subsequent reactions failed.
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7. *General Procedure*: *n*-Butyllithium (2.5 M in hexane, 1.2 mmol) was added dropwise under a nitrogen atmosphere to a stirred solution of diisopropylamine (1.2 mmol) in THF (5 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature over a period of 30 min. Next, a precooled solution (−78 °C) of chromium complex **5** (1 mmol) in THF (6 mL) was added through a cannula at −78 °C and the reaction mixture was stirred for 1 h before a solution of NFSI (1 mmol) in THF (6 mL) was added through a cannula. For the synthesis of compound **16**, $LiClO_4$ (0.5 mmol) was added in one portion. The resulting orange solution was stirred for 5 min at −78 °C and the corresponding nucleophile (40 equiv for alkyl alcohols, 20 equiv for PhOH, BnOH, $BnNH_2$, BnSH and 3 equiv for $PhC(OSiMe_3)=CH_2$) was added in one portion. The reaction mixture was allowed to warm to room temperature over a period of 5 min (or 60 min for compound **16**) and the solvent was removed in vacuo. Flash column chromatography (SiO_2; hexane/Et_2O, 95:5–60:40) yielded chromium complexes **6**–**16** in the yields shown in Table 1.
Compound (**6**): yellow solid; mp 74–75 °C. R_f = 0.29 (SiO_2; hexane/Et_2O, 9:1). IR (neat, cm^{-1}): 1946, 1845, 1105, 1052. ^1H NMR (400 MHz, $CDCl_3$) δ 5.56 (d, J = 7.0 Hz, 2H, $2C_{Cr}H$), 5.43 (d, J = 7.0 Hz, 2H, $2C_{Cr}H$), 5.17 (s, 1H, CH), 3.42 (s, 6H, $2CH_3O$), 1.30 (s, 9H, $3CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 233.0 (3CO), 122.2 (C), 107.4 (C), 101.3 (CH), 91.7 ($2C_{Cr}H$), 89.5 ($2C_{Cr}H$), 53.5 ($2CH_3O$), 33.9 (C), 31.0 ($3CH_3$). MS (EI) m/z (%): 344 (M^+, 44), 313 (31), 260 (82), 200 (100), 177 (78), 52 (83). Anal. Calcd for $C_{16}H_{20}CrO_5$ (344.32): C, 55.81; H, 5.85. Found: C, 55.89; H, 5.78.
Compound (**7**): orange solid mp 66–67 °C. R_f = 0.20 (SiO_2; hexane/Et_2O, 9:1). IR (neat, cm^{-1}): 1957, 1866, 1694. ^1H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H, CHO), 5.92 (d, J = 6.0 Hz, 2H, $2C_{Cr}H$), 5.43 (d, J = 6.0 Hz, 2H, $2C_{Cr}H$), 1.38 (s, 9H, $3CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 230.7 (3CO), 187.9 (CHO), 127.0 (C), 94.0 (C), 93.9 ($2C_{Cr}H$), 88.0 ($2C_{Cr}H$), 34.5 (C), 30.8 ($3CH_3$). MS (EI) m/z (%): 298 (M^+, 34), 214 (100), 197 (13), 177 (12), 147 (57), 91 (18), 52 (78). Anal. Calcd for $C_{14}H_{14}CrO_4$ (298.25): C, 56.38; H, 4.73. Found: C, 56.43; H, 4.81.
Compound (**8**): yellow solid; mp 64–65 °C. R_f = 0.31 (SiO_2; hexane/Et_2O, 9:1). IR (neat, cm^{-1}): 1946, 1847, 1110, 1054. ^1H NMR (400 MHz, $CDCl_3$) δ 5.56 (d, J = 6.5 Hz, 2H, $2C_{Cr}H$), 5.43 (d, J = 6.5 Hz, 2H, $2C_{Cr}H$), 5.17 (s, 1H, CH), 3.42 (s, 3H, CH_3O), 1.31 (s, 9H, $3CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 233.3 (3CO), 122.6 (C), 107.8 (C), 101.3 (CH), 91.8 ($2C_{Cr}H$), 89.5 ($2C_{Cr}H$), 53.5 (CD_3O, CH_3O), 33.9 (C), 31.1 ($3CH_3$). MS (EI) m/z (%): 347 (M^+, 40), 316 (19), 313 (17), 263 (100), 201 (92), 180 (42), 177 (38), 52 (55). Anal. Calcd for $C_{16}D_3H_{17}CrO_5$ (347.34): C, 55.33; H, 6.67. Found: C, 55.36; H, 6.70.
Compound (**9**): yellow oil. R_f = 0.31 (SiO_2; hexane/Et_2O, 9:1). IR (neat, cm^{-1}): 1956, 1865, 1103, 1053. ^1H NMR (400 MHz, $CDCl_3$) δ 5.55 (d, J = 6.5 Hz, 2H, $2C_{Cr}H$), 5.49 (d, J = 6.0 Hz, 1H, $C_{Cr}H$), 5.43 (d, J = 6.5 Hz, 1H, $C_{Cr}H$), 5.24 (s, 1H, CH), 3.64–3.49 (m, 2H, CH_2O), 3.40 (s, 3H, CH_3O), 1.68 (sextet, J = 7.0 Hz, 2H, CH_2), 1.31 (s, 9H, $3CH_3$), 0.99 (t, J = 7.5 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 233.3 (3CO), 122.7 (C), 108.1 (C), 100.5 (CH), 91.7 ($C_{Cr}H$), 91.6 ($C_{Cr}H$), 89.8 ($2C_{Cr}H$), 68.6 (CH_2O), 53.0 (CH_3O), 33.9 (C), 31.1 ($3CH_3$), 22.9 (CH_2), 10.7 (CH_3). MS (EI) m/z (%): 372 (M^+, 37), 341 (32), 313 (28), 257 (42), 230 (32), 200 (80), 177 (65), 52 (68). Anal. Calcd for $C_{18}H_{24}CrO_5$ (372.38): C, 58.06; H, 6.50. Found: C, 58.09; H, 6.52.
Compound (**10**): yellow solid; mp 39–41 °C. R_f = 0.39 (SiO_2; hexane/Et_2O, 9:1). IR (neat, cm^{-1}): 1953, 1862, 1103, 1046. ^1H NMR (400 MHz, $CDCl_3$) δ 5.56 (d, J = 6.0 Hz, 1H, $C_{Cr}H$), 5.53 (d, J = 6.5 Hz, 2H, $2C_{Cr}H$), 5.43 (d, J = 6.0 Hz, 1H, $C_{Cr}H$), 5.36 (s, 1H, CH), 4.03 (sept, J = 6.0 Hz, 1H, CH), 3.33 (s, 3H, CH_3O), 1.31 (s, 9H, $3CH_3$), 1.28 (d, J = 6.0 Hz, 6H, $2CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 233.3 (3CO), 123.0 (C), 108.4 (C), 98.6 (CH), 91.5 ($C_{Cr}H$), 91.2 ($C_{Cr}H$), 90.3 ($C_{Cr}H$), 90.2 ($C_{Cr}H$), 70.2 (CH), 51.8 (CH_3O), 33.9 (C), 31.1 ($3CH_3$), 23.1 (CH_3), 22.0 (CH_3). MS (EI) m/z (%): 372 (M^+, 29), 341 (25), 313 (20), 257 (35), 230 (32), 200 (100), 52 (68). Anal. Calcd for $C_{18}H_{24}CrO_5$ (372.38): C, 58.06; H, 6.50. Found: C, 58.13; H, 6.47.
Compound (**11**): yellow solid; mp 85–86 °C. R_f = 0.37 (SiO_2; hexane/Et_2O, 9:1). IR (neat, cm^{-1}): 1953, 1872, 1111, 1043. ^1H NMR (400 MHz, $CDCl_3$) δ 5.64 (d, J = 6.0 Hz, 2H, $2C_{Cr}H$), 5.52–5.40 (m, 3H, $2C_{Cr}H$, CH), 3.19 (s, 3H, CH_3O), 1.37 (s, 9H, $3CH_3$), 1.32 (s, 9H, $3CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 233.4 (3CO), 123.7 (C), 108.8 (C), 94.0 (CH), 91.5 ($C_{Cr}H$), 91.2 ($C_{Cr}H$), 90.8 ($C_{Cr}H$), 90.4 ($C_{Cr}H$), 75.9 (C), 49.1 (CH_3O), 33.9 (C), 31.0 ($3CH_3$), 28.5 ($3CH_3$). MS (EI) m/z (%): 386 (M^+, 34), 355 (18), 330 (20), 313 (30), 302 (32), 214 (100), 57 (28), 52 (62). Anal. Calcd for $C_{19}H_{26}CrO_5$ (386.40): C, 59.06; H, 6.78. Found: C, 58.96; H, 6.81.
Compound (**12**): yellow solid; mp 75–76 °C. R_f = 0.38 (SiO_2; hexane/Et_2O, 9:1). IR (neat, cm^{-1}): 1954, 1865, 1221, 1084. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.32 (m, 2H, Ar), 7.16–7.08 (m, 3H, Ar), 5.94 (s, 1H, CH), 5.64 (d, J = 6.5 Hz, 1H, $C_{Cr}H$), 5.58–5.49 (m, 3H, $3C_{Cr}H$), 3.47 (s, 3H, CH_3O), 1.33 (s, 9H, $3CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 233.0 (3CO), 156.5 (C), 129.7 (2CH), 123.1 (2CH, C), 117.9 (2CH), 106.9 (C), 100.3 (CH), 91.3 ($C_{Cr}H$), 91.0 ($C_{Cr}H$), 89.9 ($C_{Cr}H$), 89.8 ($C_{Cr}H$), 53.4 (CH_3O), 34.0 (C), 31.1 ($3CH_3$). MS (EI) m/z (%): 406 (M^+, 8), 322 (25), 177 (100), 162 (25), 91 (11). Anal. Calcd for $C_{21}H_{22}CrO_5$ (406.39): C, 62.06; H, 5.46. Found: C, 62.15; H, 5.37.
Compound (**13**): yellow solid; mp 70–72 °C. R_f = 0.47 (SiO_2; hexane/Et_2O, 9:1). IR (neat, cm^{-1}): 1945, 1861, 1105, 1024. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44–7.37 (m, 5H, Ar), 5.56 (d, J = 6.5 Hz, 1H, $C_{Cr}H$), 5.52 (d, J = 6.5 Hz, 1H, $C_{Cr}H$), 5.49 (d, J = 6.5 Hz, 2H, $2C_{Cr}H$), 5.39 (s, 1H, CH), 4.68 (s, 2H, CH_2), 3.44 (s, 3H, CH_3O), 1.32 (s, 9H, $3CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 233.2 (3CO), 137.3 (C), 128.5 (2CH), 128.0 (2CH), 127.9 (CH), 122.8 (C), 107.6 (C), 100.1 (CH), 91.5 ($C_{Cr}H$), 91.4 ($C_{Cr}H$), 89.9 ($C_{Cr}H$), 89.8 ($C_{Cr}H$), 68.2 (CH_2), 53.4 (CH_3O), 33.9 (C), 31.1 ($3CH_3$). MS (EI) m/z (%): 420 (M^+, 25), 336 (100), 245 (22), 213 (45), 200 (54), 52 (57). Anal. Calcd for $C_{22}H_{24}CrO_5$ (420.42): C, 62.85; H, 5.75. Found: C, 62.82; H, 5.73.
Compound (**14**): yellow oil. R_f = 0.28 (SiO_2; hexane/Et_2O, 9:1). IR (neat, cm^{-1}): 3150, 1958, 1871, 1091. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.32 (m, 5H, Ar), 5.56 (d, J = 6.5 Hz, 2H, $2C_{Cr}H$), 5.27 (d, J = 6.5 Hz, 2H, $2C_{Cr}H$), 4.83 (s, 1H, CH), 4.39 (dd, J = 14.5, 4.5 Hz, 1H, $1/2CH_2$), 4.27 (dd, J = 14.5, 4.5 Hz, 1H, $1/2CH_2$), 3.48 (s, 3H, CH_3O), 1.33 (s, 9H, $3CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 233.1 (3CO), 141.2 (C), 129.0 (2CH), 127.9 (CH), 127.4 (2CH), 121.2 (C), 111.3 (C), 92.5 ($C_{Cr}H$), 91.8 ($C_{Cr}H$), 90.3 ($2C_{Cr}H$), 69.6 (CH), 53.5 (CH_3O), 47.1 (CH_2), 33.7 (C), 30.5 ($3CH_3$). MS (EI) m/z (%): 419 (M^+, 10), 335 (50), 313 (60), 283 (43), 260 (54), 177 (100), 52 (65). HRMS (EI) calcd for $C_{22}H_{25}NCrO_5$ (M^+): 419.1187; found: 419.1186.
Compound (**15**): yellow solid; mp 93–95 °C. R_f = 0.46 (SiO_2; hexane/Et_2O, 9:1). IR (neat, cm^{-1}): 1947, 1868, 1089. ^1H NMR (400 MHz, $CDCl_3$) δ 7.28–7.25 (m, 5H, Ar), 5.53 (d, J = 7.0 Hz, 1H, $C_{Cr}H$), 5.50 (d, J = 7.0 Hz, 1H, $C_{Cr}H$), 5.45 (d, J = 7.0 Hz, 1H, $C_{Cr}H$), 5.18 (d, J = 7.0 Hz, 1H, $C_{Cr}H$), 5.14 (s, 1H, CH), 3.72 (AB system, J = 13.5 Hz, 2H, CH_2), 3.54 (s, 3H, CH_3O), 1.29 (s, 9H, $3CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 233.5 (3CO), 137.6 (C), 128.9 (2CH), 128.5 (2CH), 127.1 (CH), 121.5 (C), 111.4 (C), 92.4 ($C_{Cr}H$), 91.8 ($C_{Cr}H$), 89.0 ($C_{Cr}H$), 88.1 ($C_{Cr}H$), 85.3 (CH), 56.7 (CH_3O), 33.9 (C), 32.2 (CH_2), 31.2 ($3CH_3$). MS (EI) m/z (%): 436 (M^+, 30), 352 (100), 322 (58), 313 (22), 237 (68), 231 (53), 52 (73). Anal. Calcd for $C_{22}H_{24}SCrO_4$ (436.48): C, 60.54; H, 5.54; S 7.35. Found: C, 60.52; H, 5.47; S, 7.32.
Compound (**16**): orange oil. R_f = 0.22 (SiO_2; hexane/Et_2O, 9:1). IR (neat, cm^{-1}): 1951, 1859, 1685, 1098. ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.5 Hz, 2H, Ar), 7.63 (t, J = 7.5 Hz, 1H, Ar), 7.50 (t, J = 7.5 Hz, 2H, Ar), 5.56 (d, J = 6.5 Hz, 1H, $C_{Cr}H$), 5.49–5.44 (m, 2H, $2C_{Cr}H$), 5.40 (d, J = 6.5 Hz, 1H, $C_{Cr}H$), 4.73 (dd, J = 7.5, 4.0 Hz, 1H, CH), 3.62 (dd, J = 17.0, 7.5 Hz, 1H, $1/2CH_2$), 3.54 (s, 3H, CH_3O), 3.20 (dd, J = 17.0, 4.0 Hz, 1H, $1/2CH_2$), 1.34 (s, 9H, $3CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 233.4 (3CO), 196.8 (CO), 136.8 (C), 133.5 (CH), 128.7 (2CH), 128.3 (2CH), 123.8 (C), 111.9 (C), 90.5 ($C_{Cr}H$), 90.4 ($C_{Cr}H$), 90.3 ($C_{Cr}H$), 90.2 ($C_{Cr}H$), 76.8 (CH), 58.8 (CH_3O), 47.2 (CH_2), 33.9 (C), 31.1 ($3CH_3$). MS (EI) m/z (%): 432 (M^+, 10), 314 (22), 200 (63), 177 (100), 147 (57), 105 (43), 52 (62). Anal. Calcd for $C_{23}H_{24}CrO_5$ (432.43): C, 63.88; H, 5.59. Found: C, 63.79; H, 5.51.
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