Synthesis of Chiral Nonracemic Tertiary α-Thio and α-Sulfonyl Acetic Esters via S_N2 Reactions of Tertiary Mesylates

Jimmie D. Weaver, David K. Morris, Jon A. Tunge*

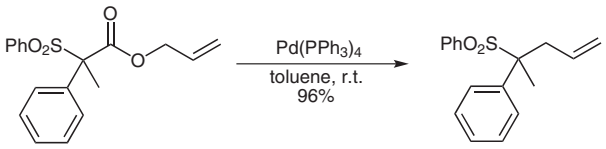
Department of Chemistry, University of Kansas, 1251 Wescoe Hall Drive, Lawrence, KS 66045-7582, USA
Fax +1(785)8645396; E-mail: tunge@ku.edu

Received 8 September 2009

Abstract: Syntheses of enantioenriched sulfides and sulfones via substitution of tertiary mesylate with thiolate nucleophile were achieved with modest to excellent success.

Key words: sulfide, sulfone, S_N2 reaction

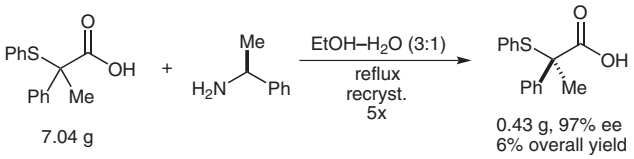
Recently, we have shown that the α-sulfonyl allyl esters cleanly undergo decarboxylative coupling to afford tertiary sulfones, making α-sulfonyl allyl esters a powerful precursor to tertiary sulfones that are not easily synthesized by other methods (Scheme 1).[1] In the course of this research we became interested in the synthesis of chiral nonracemic allyl α-sulfonylacetic esters.



Scheme 1

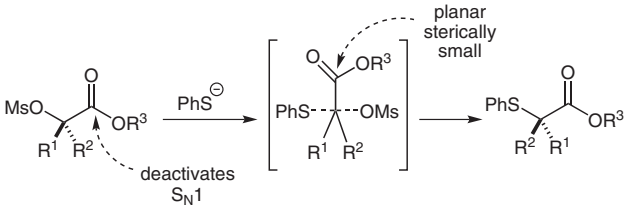
To our knowledge, a general, simple, enantioselective method to fully substituted α-sulfonyl acid derivatives does not exist. Typically syntheses of optically active compounds have been racemic and rely on preparatory chiral HPLC to obtain individual stereoisomers.[2] Alternatively, modest success at the asymmetric synthesis has been achieved with the use of a chiral oxazolidine auxiliary to both quaternerize the α-center and control the absolute stereochemistry of the sulfenylation.[3] However, this methodology requires harsh and toxic reagents and is not general.

A scan of the literature revealed several less direct strategies for the synthesis of α-sulfonyl acid derivatives including chiral resolution of α-thio acids[4] as well as several procedures for the activation and substitution of α-hydroxy esters.[5,6] More specifically, several early reports obtained enantiomerically enriched α-thio and α-sulfonyl acids via resolution of the racemic α-thio acids with enantiopure amines via crystallization of diastereomeric salts.[4] While this is a reliable method, it is not general and it requires stoichiometric amounts of chiral amine and requires repeated recrystallizations, resulting in very low overall yields (Scheme 2). Furthermore the optimal amine is substrate dependent; consequently selecting the appropriate amine requires a separate search and optimization for each substrate.



Scheme 2

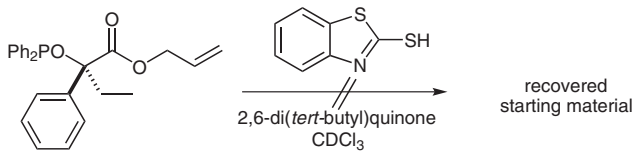
We felt that it would be possible to approach the synthesis of optically active α-thio and α-sulfonyl acids by a direct S_N2 displacement of an enantioenriched tertiary α-hydroxy ester derivative. Specifically, it was expected that the electron-withdrawing ester group would deactivate the requisite substrates toward S_N1 reactions. It was also expected that the planar nature of the ester group would better accommodate the sterically demanding transition state for S_N2 displacement. Thus, we posited that combining these two features with the use of highly nucleophilic thiolates would allow S_N2 displacement at tertiary carbon centers (Scheme 3).[5,7,8]



Scheme 3

Searching the literature revealed two examples of S_N2 displacements of tertiary α-hydroxy acid derivatives with thiolates. Mukaiyama reported S_N2 displacement of diphenyl phosphinite derived from α-hydroxy acids in the presence of the appropriate quinone and benzothiazole[9] and Corey reported the displacement of a mesylate derived from the α-hydroxy atrolactic acid.[6] With the goal of verifying these procedures with our substrates, we attempted to repeat the known Mitsunobu variant that has been used for the synthesis similar α-thio esters.[9] Unfortunately, this method did not work well in our hands (Scheme 4).

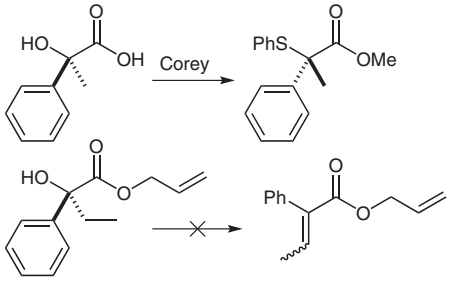
SYNLETT 2010, No. 3, pp 0470–0474
Advanced online publication: 11.01.2010
DOI: 10.1055/s-0029-1219186; Art ID: S09809ST



Scheme 4

Consequently, it was decided to investigate the simpler, albeit less direct, two-step approach involving sequential activation and substitution of an α-hydroxy ester. Previously, Corey converted (+)-atrolactic acid into the corresponding sulfone by this protocol, although the experimental details were not provided and no reaction scope was demonstrated.[6] Herein we provide a detailed examination of the methodology, provide expanded scope of the reaction, and outline the limits of the methodology.

While Corey was successful in his substitution of atrolactic acid, our attempts to displace the mesylate from the more sterically demanding butanoate led solely to elimination (Scheme 5). Consequently, further investigation was limited to propanoic acid derivatives.



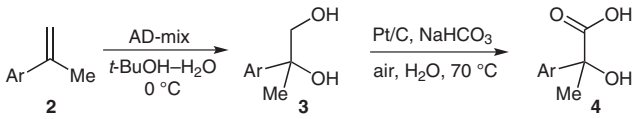
Scheme 5

In order to further explore this methodology we synthesized several nonracemic hydroxy esters as outlined in Table 1. α-Methyl styrenes **2a–e** were subjected to Sharpless asymmetric dihydroxylation, which typically afford highly enantioenriched derivatives (90–94% ee).[10] Next, the resulting diols underwent Pt/C-catalyzed oxidation under mild conditions utilizing air as the terminal oxidant.[11] Using this protocol, the ester-substituted arene derivative **3a**, failed to give significant quantities of the desired product **4a**. However, the remaining substrates **3b–e** produced the corresponding α-hydroxy acids in good yields using this practical and simple synthesis.[12,13]

Next, the hydroxy acids **4b–e** were subjected to typical reaction conditions for esterification. Unfortunately, the tertiary benzylic hydroxy acids are not well-suited for common Fisher or DCC/DMAP-catalyzed esterifications. However, it was gratifying to find that esterifications via an S_N2 reaction of the potassium carboxylates and allyl bromides yielded the desired hydroxy esters in high yields and purities (Table 2).[14]

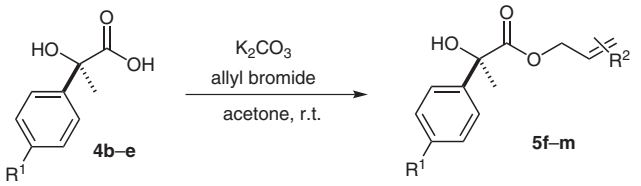
With the requisite α-hydroxy esters in hand, we turned to evaluating the mesylation–substitution procedure for the

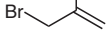
Table 1 Synthesis of Compounds **3** and **4**



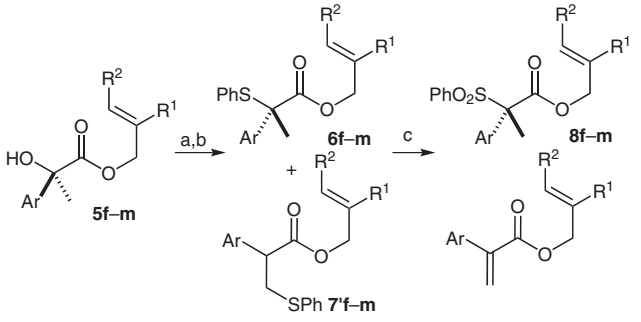
Ar	AD-mix	Product	Yield of **3** (%)	Product	Yield of **4** (%)
4-$MeO_2CC_6H_4$	α	(*S*)-**3a**	79	(*S*)-**4a**	<10
4-BrC_6H_4	β	(*R*)-**3b**	78	(*R*)-**4b**	81
4-ClC_6H_4	α	(*S*)-**3c**	99	(*S*)-**4c**	85
4-MeC_6H_4	α	(*S*)-**3d**	99	(*S*)-**4d**	64
4-FC_6H_4	β	(*R*)-**3e**	98	(*R*)-**4e**	82

Table 2 Conditions for Esterification of Hydroxy Acids



Entry	Acid	R	Allyl bromide	Yield (%)	Product
1	**4e**	F		93	**5f**
2	**4d**	Me		92	**5g**
3	**4b**	Br		90	**5h**
4	**4b**	Br		97	**5i**
5	**4c**	Cl		99	**5j**
6	**4e**	F		99	**5k**
7	**4c**	Cl		99	**5l**
8	**4d**	Me		97	**5m**

synthesis of α-thio esters.[6] The esters, **5f–m** were subjected to mesylation followed by careful workup, then immediately subjected to the conditions for substitution with sodium phenyl thiolate (Scheme 6).



Scheme 6 *Reagents and conditions*: a) MsCl, DMAP, pyridine, –5 °C to 0 °C; b) NaSPh, EtOH, 0 °C to r.t.; (c) MCPBA, CH_2Cl_2, r.t.

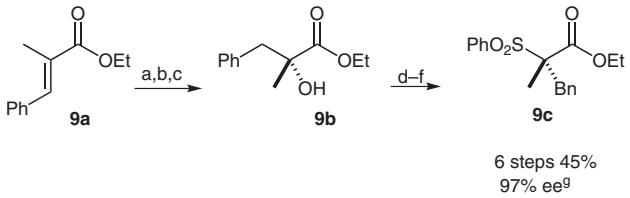
Table 3 Synthesis of Compounds **6–8**

Entry	Substrate	Yield of **6** (%)	Ratio of **6/7**[a]	Yield of **8** (%)	ee (%) of **8**[d]
1	**5f**	29	2.5:1	77	46
2	**5g**	10	1:1	–	–
3	**5h**	41	19:1	38	97
4	**4i**	39[c]	19:1	48	80[c]
5	**5j**	23	n.d.[b]	38	89
6	**5k**	38	8:1	59	73
7	**5l**	50	5:1	72	61
8	**5m**	15	1:1	–	–

[a] Determined by ^{1}H NMR.
[b] Ratio not determined before oxidation.
[c] Mesylation inadvertently performed at r.t.
[d] Determined by chiral HPLC.

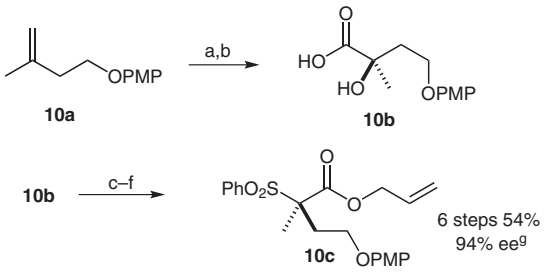
As can be seen from the data in Table 3, the yields of α-thio esters **6** using this protocol are moderate, at best. In particular, the more electron-rich *p*-methyl arene substrates (entries 2 and 8, Table 2) formed α-thio esters in dismal yields. The low yields in these cases are attributed to the formation of significant quantities of β-sulfides **7** that likely arise via elimination followed by conjugate addition of the thiolate to the acrylate derivative (Scheme 6). The mixture of **6** and **7** was subjected to oxidation with MCPBA.[1,15] Upon oxidation the α-thio esters **6** readily formed the corresponding sulfones, while the β-thio esters **7** underwent elimination to form acrylates. The stereochemical fidelity of the mesylation–substitution was good in general, although several substrates gave substantial racemization (entries 1, 6, and 7). The delicate nature of the mesylates is illustrated by the much lower ee of **8i** (entry 4) when the mesylation was inadvertently performed at room temperature; mesylation of an analogous substrate at –5 °C, provided the sulfone in excellent ee (entry 3). Thus, we hypothesized that the observed racemization was due to ionization of the intermediate mesylate and that the methodology might be better suited for α,α-dialkyl sulfonyl esters, whose requisite mesylates would ionize less readily.

To test this hypothesis, Sharpless dihydroxylation was used to provide chiral nonracemic diol which was selectively deoxygenated to give hydroxy ester **9b** in 61% yield from **9a** (Scheme 7).[7] As expected the mesylation of **9b** results in a stable mesylate that could be purified by column chromatography and stored at low temperatures without any observed racemization. As posited, exposure of the mesylate to sodium thiolate led to clean substitution to provide the α-thio ester which was oxidized to form the highly enantioenriched sulfone **9c**. Here, we assume that the reaction occurred with inversion of configuration in analogy to the observations of Corey.[6]



Scheme 7 *Reagents and conditions*: a) AD-mix-α, *t*-BuOH–H_2O, 0 °C, 61%; b) TFAA; c) H_2, Pd/C, EtOH, r.t., 99% over 2 steps, >94% ee; d) MsCl, DMAP, pyridine ,r.t., 78%; e) NaSPh, EtOH, 96%; f) MCPBA, CH_2Cl_2, r.t., 99%; g) ee determined by chiral HPLC.

Similarly, enantioenriched dialkyl α-sulfonyl esters may also be synthesized from 1,1-disubstituted olefins such as **10a** (Scheme 8) via a straightforward dihydroxylation–oxidation sequence. Specifically, the PMP-protected alcohol, **10a** underwent asymmetric dihydroxylation and Pt-catalyzed oxidation to provide the crystalline α-hydroxy acid **10b** in excellent yield.[16] Esterification of the acid provided the requisite α-hydroxy ester for mesylation. Treatment with MsCl provided the mesylate, in 81% yield. Once again, this α,α-dialkyl mesylate was much more stable and less prone to undergo racemization, remaining unchanged after months at room temperature. Subsequent substitution of the mesylate cleanly afforded the sulfide in 96% yield. Oxidation to the sulfone provided **10c**, with excellent enantioenrichment (94% ee), indicating that the substitution of the tertiary alcohol derivative proceeded cleanly via an S_N2 mechanism. The overall yield of sulfone **10c** from **10a** was a satisfactory 54%.



Scheme 8 *Reagents and conditions*: a) AD-mix-α, *t*-BuOH–H_2O, 0 °C, 90%; b) Pt/C, $NaHCO_3$, air, H_2O, 70 °C, 93%; c) K_2CO_3, allylbromide, acetone, r.t., 99%; d) MsCl, DMAP, pyridine, r.t.,81%; e) NaSPh, EtOH, 96%; f) MCPBA, CH_2Cl_2, r.t., 84%, 94% ee; g) ee determined by chiral HPLC. PMP = *p*-methoxyphenyl.

In conclusion we have demonstrated the limits of the two-step activation–substitution methodology on several benzylic hydroxy esters. Problematic ionization of the tertiary α-mesyl-α-aryl esters indicates that the best substituents are those that electronically destabilize carbocation formation. Additionally, we have shown that the two-step mesylation and substitution protocol works satisfactorily for α,α-dialkyl-α-hydroxy esters to provide chiral nonracemic tertiary α-thio and α-sulfonyl esters in high yields and ee.

All reactions were run in flame-dried glassware under an Ar atmosphere unless otherwise noted. Commercially available reagents were used without additional purification unless otherwise stated. Compound purification was effected by flash chromatography using 230 × 400 mesh, 60 Å porosity, silica obtained from Sorbent Technologies. ^{1}H NMR and ^{13}C NMR spectra were obtained on either a Bruker Avance DRX 500 spectrometer equipped with a broadband observe probe or a Bruker Avance AVIII 500 spectrometer equipped with a ^{13}C/^{1}H cryoprobe and referenced to residual protio solvent signals. Structural assignments are based on ^{1}H, ^{13}C, DEPT-135, COSY, HSQC, and IR spectroscopy. All ee were determined using chiral HPLC with columns purchased from Daicel (Chiracel AD, OD-H, or AS) using 99:1 to 85:15 mixtures of hexanes–*i*-PrOH.

Synthesis of Hydroxy Ester 5h

Hydroxy acid **4b** was synthesized via an adaptation of a known method.[13] Compound **4b** (200 mg, 0.82 mmol) and dry K_2CO_3 (566 mg, 4.1 mmol) were added to a flamed-dried flask followed by the addition of allylbromide (296 mg, 2.4 mmol). Next, acetone (2 mL, distilled from $MgSO_4$) was added and the mixture stirred vigorously for 5 h. The mixture was then extracted with EtOAc (20 mL), washed with H_2O (2 × 5 mL), dried over $MgSO_4$, and concentrated in vacuo. Azeotropic removal of excess allyl bromide and allyl alcohol provided pure **5h** (210 mg, 0.74 mmol).[14] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48–7.41 (m, 4 H, ArCH), 5.90–5.78 (m, *J* = 16.4, 11.3, 5.7 Hz, 1 H, CH_2CHCH_2), 5.24 (dd, *J* = 7.5, 1.3 Hz, 1 H, CH_2CHCHH), 5.21 (t, *J* = 1.3 Hz, 1 H, CH_2CHCHH), 4.70–4.57 (m, *J* = 13.2, 11.8, 5.7 Hz, 2 H, $ROCH_2R$), 3.76 (s, 1 H, ROH), 1.75 (s, 3 H, quat. CCH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 175.13 (RCO_2R), 141.92 (qArC), 131.61 (ArC), 131.24 ($RCHCH_2$), 127.40 (ArC), 122.21 (qArC), 119.34 ($RCHCH_2$), 75.62 (qC), 67.12 ($ROCH_2R$), 27.02 (RCH_3).

Synthesis of Sulfone 8h

To a flame-dried flask with septum was added **5h** (205 mg, 0.72 mmol), methane sulfonyl chloride (0.27 mL, 3.45 mmol), DMAP (13 mg, 0.11 mmol), and pyridine (0.72 mL), and the reaction was placed in a chiller where the temperature was maintained at –5 °C to 0 °C for 18 h. After 12 h, additional methanesulfonyl chloride (0.20 mL) was added. After 6 additional hours, the reaction mixture was extracted with EtOAc (20 mL) and washed with an ice–H_2O–HCl mixture (1:1 ice–1 M HCl), dried over $MgSO_4$ and concentrated in vacuo with minimum heat. The crude mesylate was then added to a Schlenk flask and chilled to 0 °C. To the mesylate was added a prechilled solution of sodium phenyl thiolate and phenyl thiol in EtOH [NaH (248 mg, 6.5 mmol) and PhSH (0.73 mL, 7.2 mmol) in EtOH (7.2 mL)] and allowed to slowly warm to r.t. and stirred for 12 h. The reaction mixture was extracted with CH_2Cl_2 (40 mL) and washed with K_2CO_3 solution (2 × 10 mL). The organic layer was dried over $MgSO_4$, concentrated in vacuo, and purified via flash column chromatography [hexanes–CH_2Cl_2 (95:5 to 50:50) to afford **6h** (110 mg, 41%)]. Compound **6h** was oxidized to the sulfone using MCPBA to afford sulfone **8h** (41 mg, 38%).[1,15] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55 (t, *J* = 7.4 Hz, 1 H), 7.52–7.49 (m, 2 H), 7.43–7.40 (m, *J* = 5.8 Hz, 2 H), 7.38–7.33 (m, 2 H), 7.23–7.19 (m, 2 H), 5.84 (ddt, *J* = 16.3, 10.5, 5.9 Hz, 1 H), 5.29 (dq, *J* = 17.1, 1.4 Hz, 1 H), 5.24 (ddd, *J* = 10.4, 2.3, 1.2 Hz, 1 H), 4.67 (tt, *J* = 4.5, 1.3 Hz, 2 H), 2.09 (s, 3 H).

Synthesis of Sulfone 9c

The mesylate resulting from hydroxy ester **9b** was synthesized via an adaptation from the previously referenced work.[7] The mesylate is then allowed to react in the same manner described for synthesis of sulfone **8h**, with the major exception of the procedure for isolation and purification of the mesylate prior to substitution [silica chromatography, hexanes–EtOAc (8:2)] The substitution reaction was carried out at r.t. to afford sulfide ester in 96%. The oxidation was also carried out with MCPBA using standard conditions described for synthesis of sulfone **8h**. The enantioenrichment was determined to be 97% ee via chiral HPLC [Chiracel OD-H, hexanes–*i*-PrOH (90:1), 1 mL/min, 210 nm, t_R (major) = 8.2 min, t_R (minor) = 15.2 min]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 7.4 Hz, 2 H, *o*-$ArCHSO_2R$), 7.68 (t, *J* = 7.5 Hz, 1 H, 4-$ArCHSO_2R$), 7.56 (t, *J* = 7.7 Hz, 2 H, 3-$ArCHSO_2R$), 7.24–7.18 (m, *J* = 7.1 Hz, 3 H, $ArCHCH_2R$), 7.07 (d, *J* = 7.6 Hz, 2 H, $ArCHCH_2R$), 4.09 (q, *J* = 7.1 Hz, 2 H, $ROCH_2R$), 3.63 (d, *J* = 12.9 Hz, 1 H, diastereotopic $RCHHR$), 3.05 (d, *J* = 13.0 Hz, 1 H, $RCHHR$), 1.47 (s, 3 H, $qCCH_3$), 1.15 (t, *J* = 7.1 Hz, 3 H, RCH_2CH_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.93 (RCO_2R), 136.00 (ArC), 134.48 (ArC), 134.42 (ArC), 130.83 (ArC), 130.53 (ArC), 128.96 (ArC), 128.70 (ArC), 127.59 (ArC), 73.97 (qC), 62.55 ($ROCH_2R$), 38.82 ($PhCH_2R$), 16.29 ($qCCH_3$), 14.02 (RCH_2CH_3).

Synthesis of Sulfone 10c

The precursor 1,2-diol was synthesized according to a literature prep.[16] The diol was then oxidized to the hydroxy acid in the same manner as outlined in reference.[13] The resulting hydroxy acid was esterified was outlined for **5h**. Mesylation, substitution, and oxidation of the resulting hydroxy ester followed the same procedure as that outlined for sulfone **9c**. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84 (dd, *J* = 8.3, 1.1 Hz, 2 H, 2-$ArCHSO_2R$), 7.66 (t, *J* = 7.5 Hz, 1 H, 4-$ArCHSO_2R$), 7.53 (t, *J* = 7.9 Hz, 2 H, 3-$ArCHSO_2R$), 6.80–6.67 (m, 4 H, ROArCHOR), 5.79 (ddd, *J* = 16.3, 11.0, 5.8 Hz, 1 H, $RCHCH_2$), 5.29 (dd, *J* = 17.2, 1.4 Hz, 1 H, $RCHCHH$), 5.20 (d, *J* = 10.5 Hz, 1 H, $RCHCHH$), 4.61–4.50 (m, 2 H, $ROCH_2CHCH_2$), 4.07–3.91 (m, 2 H, $ArOCH_2R$), 3.72 (s, 3 H, $ArOCH_3$), 2.79 (ddd, *J* = 14.5, 8.8, 6.1 Hz, 1 H, diastereotopic $ArOCH_2CH_2qC$), 2.30 (dt, *J* = 14.0, 4.9 Hz, 1 H, diastereotopic $ArOCH_2CH_2qC$), 1.67 (s, 3 H, q CCH_3). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 167.91 (RCO_2R), 154.34 (ROqArCOR), 152.56 (ROqArCOR), 135.70 (ArC), 134.42 (ArC), 131.24 ($RCHCH_2$), 130.81 (ArCH), 128.95 (ArCH), 119.35 ($RCHCH_2$), 115.58 (ROqArCHOR), 114.84 (ROqArCHOR), 71.81 ($qCCH_3$), 66.97 ($ROCH_2CHR$), 64.34 ($ROCH_2CH_2R$), 55.89 ($ROCH_3$), 32.58 ($qCCH_2CH_2R$), 16.33 ($qCCH_3$).

Acknowledgment

We thank the National Institute of General Medical Sciences (1R01GM079644) for support of this work.

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