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WITTIG OLEFINATION–CLAISEN REARRANGEMENT PROTOCOL FOR CYCLOHEXENE ANNULATION

Mukund G. Kulkarni, Dnyaneshwar D. Gaikwad, Ajit S. Borhade, Yunus B. Shaikh, Vijay B. Ningdale, Sanjay W. Chavhan, Attrimuni P. Dhondge, Mayur P. Desai, and Deekshaputra R. Birhade
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A two-step iterative sequence of Wittig olefination followed by Claisen rearrangement resulted in 1,7-octadienes, which afforded the corresponding cyclohexene carbaldehydes upon ring-closing metathesis with Grubbs catalyst.

Keywords: Claisen rearrangement; cyclohexene annulation; ring-closing metathesis; Wittig olefination

Among the different types of ring systems, the six-membered ring system is by far the best studied and the most well-understood ring system. Apart from other reasons, this could be because the six-membered ring is one of the most ubiquitous ring systems present in nature. The cyclohexane-based pool of natural products is vast and includes important classes of natural products such as terpenoids, steroids, and antibiotics. Several methods[1–16] have been reported in the literature for the construction of the cyclohexane ring and its highly functionalized derivatives, including the famous Robinson annulation, Diels–Alder reaction, and ring-closing metathesis. Many of these and other methods are capable of furnishing cyclohexane and its unsaturated derivatives in a highly regio- and/or stereoselective manner. However, in several situations, the required structural specificity may be lacking in highly unsymmetrically substituted cyclohexenes formed using these methods.

A cyclopentannulation protocol based on Wacker oxidation–Aldol condensation of 4-pentenals to obtain substituted 2-cyclopentenones has been reported from this laboratory.[17] The 4-pentenals in turn were obtained using a standardized Wittig olefination–Claisen rearrangement sequence.[18] The usefulness of 4-pentenals could be further expanded if these could be converted to cyclohexene derivatives. Efforts in this direction are described in this communication.

The 4-pentenals (**2a–g**), obtained from aldehydes (**1a–g**) under optimized reaction conditions, were treated with allyloxymethylenetriphenylphosphorane gave the allyl vinyl ethers (**3a–g**) in good yields (Scheme 1).

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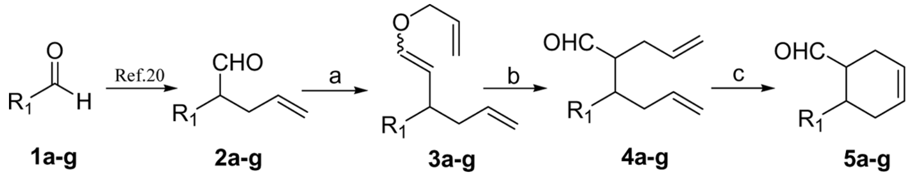
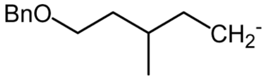
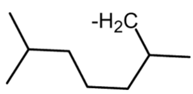
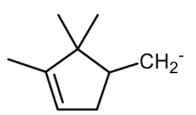
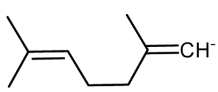
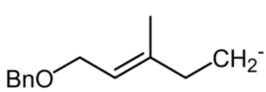


Scheme 1. Reagents and conditions: (a) $CH_2CHCH_2OCH_2Ph_3P^+Cl^-$, tetrahydrofuran (THF), *t*-BuO^-Na^+, 0°C; (b) xylene, ↑↓, 4–5 h; and (c) Grubbs catalyst (first generation), dicholormethane (DCM), rt, 12 h.

Upon thin-layer chromatography (TLC), these allyl vinyl ethers appeared to be homogeneous, but from the NMR spectra it was clear that these allyl vinyl ethers are mixtures of E and Z isomers. All attempts to separate the E and Z isomers did not materialize. However, the NMR signals of E and Z isomers in the olefinic region were well separated, which allowed us to estimate the ratio of these isomers (Table 1).

The allyl vinyl ethers (**3a–g**), on refluxing in xylene, smoothly underwent the Claisen rearrangement to give the corresponding 1,7-octadienes (**4a–g**), which are required for the synthesis of substituted cyclohexenes, in good yield. In this case, these octadienes appear to be homogeneous on TLC, but NMR spectra of these compounds showed them to be a mixture of diastereomers. From the NMR signals,

Table 1. Expedient protocol for the synthesis of 4,5-disubstituted cyclohexene carbaldehydes

		Yield (%)			
Entry	R	**2**	**3** (Z:E)	**4** (dr)	**5** (dr)
a	3,4-$(OMe)_2C_6H_3$	95	66 (1:1)	90 (1:2)	95 (1:2)
b	C_4H_3O	92	78 (1:4)	87 (1:1.2)	91 (1:1.2)
c		87	69 (1:1.4)	82 (1:1)	87 (1:1)
d		90	85 (1:2.1)	91 (1:1.5)	90 (1:1.5)
e		82	74 (1.2:3)	78 (1:0.9)	77 (1:0.9)
f		78	58 (1:1.7)	75 (2:3)	87[a] (2:3)
g		83	62 (1:2.1)	77 (1.7:2)	81[a] (1.7:2)

[a]Yield is calculated on the basis of recovered starting material; Z/E geometrical and diastereomeric ratios were obtained from the NMR.

it was possible to estimate the diastereomeric ratio of these compounds. Ring-closing olefin metathesis of these 1,7-octadienes was effected using Grubbs first-generation catalyst [PhCH=$RuCl_2(PCy_3)_2$] to get the desired functionalized cyclohexene carbaldehydes (**5a–g**) in good yield. The beauty of this protocol is that the whole sequence (total of four steps) to prepare the 1,7-octadienes could be conducted without purifying the intermediates. This significantly cuts down the efforts and time required to obtain the 1,7-octadienes. As a result, this short sequence for the preparation of cyclohexenes could be completed in a span of only a day and half.

CONCLUSION

Thus, a new methodology for cyclohexene annulations, with 25–32% overall yield, has been developed through an iterative sequence of Wittig–Claisen rearrangement.

EXPERIMENTAL

All solvents were distilled and dried before use. Silica gel (100–200 mesh) was used for column chromatography and eluted using hexane/ethyl acetate solvent system. The Fourier transform–infrared (FT-IR) spectra were recorded on a Perkin-Elmer 1600 series instrument. ^{1}H and ^{13}C NMR spectra were recorded on Jeol FX 90Q/Varian Mercury 300- and 75-MHz instruments respectively. Low-resolution mass spectra (LRMS; Shimadzu GCMS-Q 5050A) connected to GC-17A were recorded at an ionization potential of 70 eV, and the fragmentation pattern is given after the corresponding m/z value.

General Procedure

Wittig olefination. A solution of $t\text{-BuO}^{-}\text{Na}^{+}$ (1.2 eq) in dry THF was added to a suspension of the aldehyde and allyloxymethylenetriphenylphosphonium chloride (1.2 eq) in dry THF at 0°C in a dropwise manner. After 40–45 min (TLC check), THF was removed under vacuum. On normal aqueous extractive workup, the crude product was obtained after removal of the solvent under reduced pressure. The crude allyl vinyl ether was purified by using a silica-gel column (mobile phase 1–4% ethyl acetate in hexane) and gave the product in good yield.

Claisen rearrangement. The allyl vinyl ethers were subsequently dissolved in xylene, and the solution was refluxed for 4–5 h. After evaporation of xylene at room temperature, 4-pentenals were obtained in 75–90% yield.

Ring-closing olefin metathesis. The Grubbs first-generation catalyst ([PhCH=$RuCl_2(PCy_3)_2$], 0.2 mol%) was added to a solution of 1,7-octadiene obtained from **4a–g** in dry DCM, and the reaction mixture was stirred for 10–12 h at ambient temperature (TLC check). The crude products were purified using a silica-gel column (ethyl acetate in hexane), which gave pure cyclohexene carbaldehydes in 80–95% yield.

Data

Selected data are shown in Table 2.

Table 2. Selected data

Product	IR (cm^{-1} neat)	^1H NMR (300 MHz, $CDCl_3$), δ J (Hz)	^{13}C NMR (75 MHz, $CDCl_3$) δ	MS (EI, 70 eV), m/z
2a	1724.1, 1595.0, 1515.0, 1261.1	2.42–2.54 (m, 1H), 2.76–2.88 (m, 1H), 3.54 (m, 1H), 3.86 (s, 6H), 4.98–5.10 (m, 2H), 5.63–5.78 (m, 1H), 6.64 (d, $J=2$, 1H), 6.75 (dd, $J=8$, 2, 1H), 6.86 (d, $J=8$, 1H), 9.62 (d, $J=1.6$, 1H)	34.6, 56.0, 58.0, 111.5, 112.0, 117.2, 122.0, 127.5, 135.0, 148.0, 149.8, 200.0	220 (M^+), 191, 179, 160, 151, 91, 77
2b	2823.6, 1728.1, 1643.2, 1502.4, 1159.1	2.38–2.50 (m, 1H), 2.62–2.78 (m, 1H), 3.44–3.56 (m, 1H), 4.98–5.10 (m, 2H), 5.64–5.80 (m, 1H), 6.28 (s, 1H), 7.35 (s, 1H), 7.39 (s, 1H), 9.56 (d, $J=2$, 1H)	33.2, 48.9, 109.7, 117.1, 119.6, 134.3, 140.0, 143.3, 199.4	117, 105, 91, 77, 41
2c	2858.3, 1724.2, 1658.7, 1101.3	0.87 (d, $J=6.6$, 3H), 1.03–1.20 (m, 1H), 1.22–1.36 (m, 2H), 1.38–1.50 (m, 3H), 1.51–1.73 (m, 3H), 2.15–2.40 (m, 3H), 3.43–3.52 (m, 2H), 4.46 (s, 2H), 4.98–5.07 (m, 2H), 5.63–5.76 (m, 1H), 7.19–7.37 (m, 5H), 9.50 (s, 1H)	19.3, 25.4, 25.5, 29.8, 32.7, 32.8, 33.8, 36.31, 36.38, 51.1, 68.1, 72.6, 116.7, 127.1, 127.2, 127.9, 134.6, 138.2, 203.9	274 (M^+), 232, 137, 107, 91, 55
2d	2868.0, 1724.2, 1643.2	0.86 (d, $J=6.3$, 3H), 0.87 (d, $J=6.7$, 6H), 1.09–1.31 (2 m, 5.8H), 1.40–1.58 (m, 2.7H), 2.19–2.50 (m, 4H), 5.05–5.10 (m, 2H), 5.63–5.79 (m, 1H), 9.53 and 9.57 (2d, $J=3.1$, 2.8, 1H)	19.4, 19.6, 22.5, 22.6, 24.5, 27.9, 30.3, 30.4, 30.6, 33.2, 33.9, 35.5, 36.0, 37.0, 37.4, 39.1, 49.0, 116.9, 134.6, 204.3	211 (M + 1), 169, 137, 109, 95, 71, 57
2e	2711.7, 1726.2, 1641.3	0.76 (d, $J=2.8$, 3H), 0.96 (d, $J=2.0$, 3H), 1.06–1.32 (m, 3H), 1.34–1.91 (3 m, 6H), 2.16–2.52 (m, 2H), 4.80–5.21 (m, 3H), 5.60–5.81 (m, 1H), 9.62 (d, $J=2.2$, 1H)	12.5, 19.5, 25.5, 28.1, 29.1, 32.7, 34.1, 35.4, 35.5, 46.8, 47.4, 47.5, 50.1, 50.2, 117.0,117.1, 121.2, 134.5, 134.7, 148.2, 148.4, 204.4	206 (M^+), 191, 173, 163, 136, 121, 107, 95, 79, 67, 55, 41
2f	2723.9, 1722.3, 1631.7	1.58 (s, 3H), 1.66 (s, 3H), 2.09 (d, $J=5.2$, 3H), 2.16–2.29 (m, 5H), 2.44–2.55 (m, 1H), 3.24–3.33 (m, 1H), 4.90–5.16 (m, 4H), 5.66–5.80 (m, 1H), 9.44 (d, $J=2.3$, 1H)	17.0, 17.7, 22.0, 25.7, 26.4, 32.6, 33.6, 33.7, 39.7, 51.7, 116.6, 118.4, 119.1, 123.4, 123.5, 131.6, 132.0, 134.9, 141.6, 200.2, 200.5	206 (M^+), 191, 163, 135, 109, 80, 43
2g	2848.0, 1724.2, 1450.0, 1050.0	1.24 (s, 3H), 1.43–1.60 (m, 1H), 1.96–2.09 (m, 2H), 2.18–2.43 (2 m, 4H), 3.94 (d, $J=6.9$, 2H), 4.48 (s, 2H), 4.95–5.09 (m, 2H), 5.42 (t, $J=7.1$, 1H), 5.62–5.76 (m, 1H), 7.22–7.36 (m, 5H), 9.54 (s, 1H)	26.5, 26.7, 29.7, 29.8, 33.3, 37.0, 50.8, 50.9, 66.4, 66.5, 72.4, 117.5, 122.0, 122.7, 127.9, 128.0, 128.3, 128.5, 134.9, 138.8, 139.5, 204.0, 204.2	207, 166, 149, 124, 91, 79, 55

3a	1589.2, 1461.9, 1379.0, 1174.6, 1041.5	2.35–2.56 (m, 2H), 3.17–3.26 (m, 1H), 3.86 (s, 6.3H), 4.16–4.28 (2d, $J = 5.3$, 5.0, 2.1H), 4.48–4.58 (m, 0.5H), 4.92–5.10 (m, 2.6H), 5.14–5.35 (m, 2H), 5.64–6.04 (2 m, 2.2H), 6.24 (d, $J = 12.3$, 0.6H), 6.64–6.86 (m, 3.1H)	39.7, 41.0, 41.3, 44.0, 55.6, 55.7, 69.9, 72.5, 108.3, 110.5, 110.6, 110.8, 115.5, 115.9, 116.8, 117.2, 118.6, 118.9, 133.2, 133.7, 136.5, 136.8, 137.4, 137.8, 143.9, 145.8, 146.9, 147.0, 148.4	274 (M^+), 233, 205, 191, 160, 151, 91, 77
3b	1651.0, 1502.4, 1423.4, 1153.2	2.24–2.46 (m, 2.2H), 3.16 (q, $J = 8.2$, 0.9H), 3.84 (q, $J = 8.3$, 0.2H), 4.16 and 4.22 (2d, $J = 2.7$, 1.3, 2.1H), 4.39 (dd, $J = 3.2$, 7.6,0.1 H), 4.84 (dd, $J = 8.8$, 12.7, 0.8H), 4.94–5.07 (m, 1.9H), 5.15–5.32 (m, 2H), 5.66–5.80 (m, 1.1H), 5.81–5.99 (m, 1H), 6.22 (d, $J = 12.6$, 0.9H), 6.23 (s, 1H), 7.16 (s, 0.9H), 7.30 (s, 0.9H)	35.2, 40.6, 69.9, 107.1, 109.8, 116.1, 117.1, 128.5, 133.2, 136.2, 138.3, 142.5, 146.1	204 (M^+), 175, 163, 135, 121, 91, 55
3c	1637.5, 1595.0, 1514.0, 1458.1, 1147.6, 1029.9	0.82 (d, $J = 6.9$, 3.2H), 1.06–1.31 (m, 3.6H), 1.34–1.49 (m, 2.9H), 1.52–1.76 (m, 1.9H), 1.78–1.94 (m, 0.8H), 1.96–2.18 (m, 2.1H), 3.46 (t, $J = 6.1$, 1.8H), 4.16 (d, $J = 3.1$, 2.1H), 4.48 (s, 2H), 4.49–4.60 (m, 0.5H), 4.92–5.02 (m, 1.8H), 5.14–5.34 (m, 1.7H), 5.64–5.81 (m, 0.9H), 5.82–5.97 (m, 0.9H), 6.12 (d, $J = 12.3$, 0.6H), 7.19–7.37 (m, 4.6H)	19.6, 19.8, 29.8, 29.9, 32.6, 32.7, 34.4, 34.5, 36.5, 36.8, 38.7, 38.8, 40.8, 41.0, 68.5, 69.8, 72.7, 108.6, 115.0, 115.4, 116.7, 117.0, 127.2, 127.4, 128.1, 133.4, 133.9, 137.0, 137.3, 138.4, 144.1, 145.3	281, 237, 207, 137, 107, 91, 55, 41
3d	1651.0, 1596.9, 1164.9, 1128.3	0.80–0.94 (m, 9.1H), 1.06–1.20 (m, 3.5H), 1.21–1.37 (m, 4H), 1.42–1.58 (m, 2.2H), 1.94–2.16 (m, 3.2H), 4.17 (d, $J = 6.6$, 2H), 4.46–4.60 (m, 1H), 4.90–5.00 (m, 2H), 5.20 (dd, $J = 15.0$, 1.1, 0.9H), 5.28 (dd, $J = 16.2$, 1.1, 0.9H), 5.68–5.81 (m, 1H), 5.84–6.00 (m, 1H), 6.16 (d, $J = 12.4$, 0.9H)	19.1, 20.4, 22.8, 24.5, 24.8, 28.0, 29.9, 30.0, 31.6, 36.0, 36.2, 38.2, 39.3, 40.9, 41.7, 43.0, 43.3, 69.9, 108.8, 109.2, 115.4, 115.5, 117.1, 133.5, 137.2, 145.1	185, 169, 156, 142, 126, 98, 69
3e	1654.8, 1446.5, 1161.1	0.74 (s, 3H), 0.94 (d, $J = 5.1$, 3H), 1.10–1.42 (m, 4H), 1.60 and 1.62 (2 s, 3.9H), 1.74–1.90 (m, 2H), 1.98–2.40 (m, 3.2H), 2.62–2.76 (m, 0.2H), 4.16–4.23 (m, 2H), 4.50 (t, $J = 11.0$, 0.2H), 4.65 (t, $J = 9.4$, 0.2H),	12.7, 19.7, 19.8, 25.5, 25.8, 32.8, 32.9, 35.4, 35.6, 36.2, 36.3, 37.2, 37.4, 39.3, 40.0, 42.2, 46.6, 46.9, 47.2, 47.7, 47.8, 47.9, 69.9, 72.4, 108.3, 109.7, 111.1, 112.3, 114.9, 115.2,	260 (M^+), 219, 189, 176, 161, 121, 109, 93, 79, 55, 41

(*Continued*)

Table 2. Continued

Product	IR (cm^{-1} neat)	^{1}H NMR (300 MHz, $CDCl_3$), δ J (Hz)	^{13}C NMR (75 MHz, $CDCl_3$) δ	MS (EI, 70 eV), m/z
		4.94–5.05 (m, 1.6H), 5.14–5.35 (m, 2.3H), 5.68–6.00 (m, 1.7H), 6.16 (t, $J=9.9$, 0.5H)	115.4, 115.6, 116.7, 117.0, 121.6, 121.8, 133.4, 133.5, 134.0, 136.8, 137.8, 143.5, 144.7, 145.0, 145.4, 148.4, 148.6	
3f	1539.1, 1467.7, 1220.9, 1097.4	1.60 (d, $J=6.5$, 4.9H), 1.68 (d, $J=3.3$, 4.4H), 1.99–2.12 (m, 5.9H), 2.84–2.96 (m, 1H), 4.16 (d, $J=5.3$, 2.1H), 4.67–4.76 (m, 1.1H), 4.92–5.13 (2 m, 3.6H), 5.15–5.34 (m, 1.9H), 5.66–5.82 (m, 1H), 5.84–5.98 (m, 1H), 6.19 (d, $J=13.4$, 0.8H)	14.2, 14.3, 19.8, 22.6, 22.8, 25.9, 27.0, 31.7, 32.0, 35.6, 35.7, 68.6, 71.8, 72.4, 103.6, 106.3, 106.4, 121.6, 125.5, 127.7, 128.2, 129.5, 144.1, 144.4, 146.0, 146.1	226, 211, 183, 165, 140, 113, 70
3g	1660.6, 1456.2, 1095.5	1.12–1.35 (bs, 3.5H), 1.37–1.58 (m, 1.8H), 1.84–2.13 (m, 5.9H), 2.54–2.68 (m, 0.4H), 3.90–4.02 (m, 1.8H), 4.08–4.20 (m, 2H), 4.46 (s, 2.1H), 4.90–5.02 (m, 1.9H), 5.12–5.42 (m, 3.6H), 5.64–5.97 (2 m, 1.9H), 6.15 (d, $J=12.4$, 0.5H), 7.20–7.39 (m, 4.8H)	22.8, 23.9, 29.8, 29.9, 33.2, 34.0, 34.1, 37.2, 37.3, 38.5, 40.0, 40.8, 66.1, 66.3, 69.8, 71.8, 72.2, 110.3, 110.4, 115.6, 115.8, 116.8, 117.0, 120.3, 120.5, 127.2, 127.3, 127.9, 133.6, 134.0, 136.8, 137.1, 138.4, 140.4, 140.8, 141.3, 144.1, 144.2, 146.0, 146.1	281, 267, 243, 217, 147, 134, 91, 79, 55
4a	1724.2, 1649.0, 1515.9, 1257.5	2.04–2.25 (m, 1H), 2.26–2.52 (m, 2H), 2.53–2.72 (m, 2H), 3.00 (q, $J=6.3$, 1H), 3.82 and 3.84 (2 s, 6H), 4.84–5.10 (m, 4H), 5.46–5.80 (m, 2H), 6.66 (d, $J=2.3$, 2H), 6.78 (t, $J=8.0$, 1H), 9.49 (d, $J=3.0$, 0.3H), 9.61 (d, $J=3.6$, 0.6H)	31.2, 31.4, 37.0, 38.0, 44.5, 45.1, 54.7, 55.3, 55.4, 56.0, 110.6, 110.8, 111.2, 116.3, 116.4, 116.7, 120.0, 132.7, 132.8, 134.2, 134.5, 135.3, 147.2, 148.3, 148.4, 203.7, 203.9	274 (M^+), 233, 205, 191, 160, 151, 91, 77
4b	2866.0, 1724.2, 1656.7, 1614.3, 1136.0	2.18–2.26 (m, 2H), 2.28–2.48 (m, 2.2H), 2.52–2.61 (m, 1H), 2.95–3.14 (2 m, 1H), 4.93–5.11 (m, 4H), 5.58–5.80 (m, 2H), 6.21 (s, 1H), 7.21 (d, $J=7.2$, 1H), 7.29 (s, 1H), 9.57 and 9.61 (2d, $J=3.2$, 2.5, 1H)	30.7, 31.2, 35.2, 35.9, 36.9, 37.2, 53.8, 54.7, 109.4, 109.7, 116.7, 117.0, 124.2, 127.9, 128.2, 134.7, 135.4, 139.5, 142.8, 203.9, 204.0	204 (M^+), 175,163, 135, 117, 91, 55
4c	2858.3, 1722.3, 1639.4, 1452.3, 1101.3	0.85 (d, $J=1.7$, 3H), 1.19–1.46 (m, 5H), 1.47–1.70 (m, 2.3H), 1.79–1.94 (m, 1.1H), 2.03–2.20 (m, 3.2H), 2.36–2.49 (m, 2H),	19.53, 19.58, 27.8, 27.9, 29.4, 29.8, 29.9, 34.4, 34.6, 35.4, 35.6, 35.7, 35.8, 36.4, 36.5, 37.8, 38.0, 38.3,	281, 214, 199, 171, 157, 143, 128, 115, 91, 77, 55

		3.42–3.51 (m, 2H), 4.47 (s, 2H), 4.96–5.08 (m, 3.9H), 5.60–5.80 (m, 1.9H), 7.19–7.37 (m, 4.8H), 9.60 (s, 1H)	53.2, 68.3, 72.7, 116.3, 116.8, 127.2, 127.3, 128.0, 135.6, 135.7, 136.1, 136.2, 136.3, 138.3, 204.5	
4d	2923.9, 1724.2, 1641.3, 1458.1	0.83–0.90 (d, $J = 5.2$, 1.1, 8.9H), 1.04–1.29 (m, 8.1H), 1.42–1.60 (m, 2.8H), 2.00–2.19 (m, 3H), 2.40–2.52 (m, 2.4H), 4.98–5.10 (m, 4.2H), 5.62–5.80 (m, 2.1H), 9.62 and 9.64 (2d, $J = 1.4$, 1.1, 1H)	19.5, 20.0, 22.7, 24.7, 28.0, 28.9, 29.1, 30.1, 31.6, 35.6, 36.1, 37.0, 37.7, 38.3, 38.5, 39.2, 53.1, 53.4, 53.6, 116.4, 117.1, 135.8, 136.0, 204.7, 204.8	265 (M + 1), 247, 227, 197, 170, 149, 127, 85, 69, 53
4e	2711.7, 1724.2, 1641.3, 1446.5	0.72 (d, $J = 7.1$, 2.7H), 0.95 (d, $J = 7.1$, 2.7H), 1.14–1.44 (m, 3.8H), 1.56–1.59 (m, 2.7H), 1.72–1.90 (m, 2.1H), 2.02–2.34 (m, 4.7H), 2.40–2.52 (m, 2H), 4.96–5.10 (m, 3.8H), 5.20 (bs, 0.9H), 5.60–5.85 (m, 1.7H), 9.63 and 9.67 (2d, $J = 1.7$, 2.2, 1.1H)	12.5, 19.5, 25.5, 28.2, 28.7, 30.5, 30.9, 34.9, 35.2, 36.3, 36.4, 47.4, 47.5, 47.6, 52.6, 52.9, 53.5, 53.9, 116.6, 116.7, 117.1, 121.2, 135.9, 136.0, 136.3, 136.5, 136.6, 148.5, 204.4, 204.6	260 (M^+), 245, 227, 219, 201, 176, 161, 121, 109, 95, 79, 67, 55
4f	2740.7, 1720.4, 1664.5	1.60 (d, $J = 2.1$, 6H), 1.68 (s, 2.9H), 1.92–2.19 (m, 5.9H), 2.22–2.41 (m, 2.9H), 2.66–2.80 (m, 1.1H), 4.88–5.10 (m, 5.9H), 5.60–5.78 (m, 1.8H), 9.56 and 9.61 (2d, $J = 2.0$,1.7, 0.9H)	17.9, 18.0, 24.2, 25.5, 25.9, 36.5, 36.6, 38.0, 38.6, 42.2, 119.1, 123.4, 124.9, 131.1, 132.3, 141.5, 145.9, 150.8, 193.1	149, 135, 121, 107, 93, 79, 69, 41
4g	2858.3, 1726.2, 1641.3, 1595.0, 1452.3, 1103.2	1.58 (s, 3H), 1.86–2.20 (m, 5.8H), 2.22–2.50 (m, 3.8H), 3.88–4.06 (m, 2.1H), 4.50 (s, 2.3H), 4.86–5.10 (m, 3.2H), 5.35–5.46 (m, 1H), 5.58–5.80 (m, 1.6H), 7.09–7.38 (m, 6.8H), 9.61 and 9.64 (2 s, 0.9H)	22.7, 26.4, 26.9, 29.4, 29.7, 35.4, 37.2, 37.3, 53.4, 66.5, 72.1, 116.6, 117.1, 121.3, 127.4, 127.6, 128.2, 133.0, 136.0, 136.2, 138.3, 204.5	327 (M + 1), 282, 228, 213, 197, 185, 152, 115, 91, 77, 44
5a	1728.1, 1624.0, 1093.6, 1028.0	2.26–2.38 (m, 2.8H), 2.44–2.56 (m, 1.3H), 2.80–2.88 (m, 0.8H), 3.00–3.10 (m, 0.4H), 3.41–3.48 (m, 0.5H), 3.84 (s, 6.5H), 5.76–5.85 (m, 1.8H), 6.73–6.82 (m, 3.1H), 9.44 and 9.65 (2d, $J = 2.8$, 1.1, 0.9H)	23.6, 24.7, 29.5, 32.8, 38.4, 40.1, 50.1, 51.1, 55.55, 55.57, 110.6, 110.8, 111.0, 119.0, 119.3, 124.1, 124.8, 126.2, 126.3, 134.3, 135.5, 147.3, 148.3, 203.77, 203.79	246 (M^+), 192, 177, 161, 151, 138, 91, 77
5b	2715.0, 1726.2, 1591.2, 1497.7, 1161.1	1.98–2.41 (m, 3.8H), 2.42–2.71 (m, 0.9H), 2.96–3.20 (m, 0.9H), 5.75 (d, $J = 6.6$, 2.1H), 6.31 (s, 1.1H), 7.25 (d, $J = 6.8$, 1.4H), 7.38 (d, $J = 6.9$, 0.9H), 9.58 (s, 0.4H), 9.66 (s, 0.5H)	23.4, 24.1, 30.2, 30.3, 37.5, 49.3, 55.3, 55.4, 109.9, 110.3, 117.8, 117.9, 123.9, 124.3, 125.1, 125.5, 139.2, 143.1, 143.3, 204.1, 204.2	176 (M^+), 148, 115, 91, 77, 51

(*Continued*)

Table 2. Continued

Product	IR (cm^{-1} neat)	^{1}H NMR (300 MHz, $CDCl_3$), δ J (Hz)	^{13}C NMR (75 MHz, $CDCl_3$) δ	MS (EI, 70 eV), m/z
5c	2856.4, 1722.3, 1654.8, 1099.3	0.87 (d, $J=2.2$, 3H), 1.10–1.49 (m, 6.5H), 1.50–1.78 (m, 3.6H), 1.90–2.38 (m, 6.4H), 3.42–3.56 (m, 2.1H), 4.48 (s, 2H), 5.64 (d, $J=9.6$, 1.9H), 7.24–7.35 (m, 5.1H), 9.58 (d, $J=2.5$, 0.5H), 9.71 (s, 0.5H)	19.5, 19.6, 28.6, 28.9, 30.0, 30.2, 31.4, 31.6, 33.0, 34.2, 34.3, 34.4, 35.1, 35.2, 36.4, 37.0, 37.1, 50.4, 50.6, 68.6, 73.0, 124.0, 124.4, 126.0, 126.1, 127.3, 127.5, 128.2, 138.4, 204.8, 204.9	300 (M^+), 282, 252, 207, 163, 133, 117, 89, 73, 63, 50
5d	2922.0, 1710.7, 1460.0, 1172.6	0.85 (d, $J=2.1$, 9.6H), 1.14–1.40 (m, 6.9H), 1.42–1.60 (m, 3.1H), 1.64–1.79 (m, 1.2H), 2.00–2.40 (m, 4.8H), 5.66 (bs, 2.2H), 9.61 and 9.73 (2d, $J=2.5$, 2.4, 0.9H)	22.5, 22.6, 24.2, 24.3, 27.9, 29.6, 29.8, 30.0, 31.3, 31.6, 36.5, 36.8, 38.0, 38.2, 39.0, 39.2, 41.8, 65.7, 124.9, 125.0, 126.0, 126.1, 204.6, 204.7	237 (M + 1), 219, 207, 178, 167, 149, 126, 95, 71, 57
5e	2711.7, 1720.3, 1649.0	0.67 and 0.69 (2d, $J=2$, 2.2, 3.2H), 0.88 (d, $J=9.0$, 3.4H), 1.14–1.29 (m, 2.6H), 1.52 (s, 3.2H), 1.64–1.84 (m, 1.9H), 1.92–2.51 (m, 5.8H), 5.14 (s, 0.9H), 5.50–5.63 (m, 1.9H), 9.52 and 9.58 (2d, $J=2.3$, 1.7, 0.9H)	12.6, 19.6, 25.5, 25.8, 31.1, 31.7, 33.7, 34.2, 35.0, 35.4, 35.9, 47.4, 47.6, 48.0, 49.1, 50.2, 51.8, 62.4, 121.3, 121.5, 123.7, 123.8, 124.5, 124.7, 126.0, 126.7, 204.7, 204.8	232 (M^+), 217, 199, 176, 161, 145, 121, 109, 95, 79, 67, 55
5f	2729.1, 1708.8, 1373.2	1.62 (d, $J=6.4$, 6.3H), 1.67 (s, 3.2H), 1.72–1.92 (m, 3.8H), 2.06–2.24 (m, 4.1H), 2.25–2.40 (m, 1.8H), 4.98–5.16 (m, 1.9H), 5.90 (d, $J=5.5$, 0.9H), 6.63 (d, $J=5.5$, 0.8H), 9.37 (s, 0.8H)	17.5, 17.6, 25.0, 25.6, 25.7, 25.9, 26.9, 32.4, 37.9, 40.5, 122.0, 122.3, 127.1, 128.3, 132.6, 133.4, 137.7, 138.1, 190.5, 191.0	232 (M^+), 207, 183, 168, 137, 121, 107
5g	2866.0, 1722.3, 1598.9, 1269.1, 1095.5	1.32 (bs, 3.2H), 1.60–2.38 (m, 10H), 3.64–3.82 (m, 1.8H), 4.25 (s, 1.9H), 4.66–4.90 (m, 1.1H), 5.08–5.23 (m, 0.7H), 5.34–5.52 (m, 1.2H), 6.88–7.22 (m, 5.8H), 9.39 and 9.45 (2d, $J=10.3$, 9.8, 0.5H)	23.0, 23.4, 29.7, 30.0, 30.2, 36.3, 37.0, 44.5, 49.2, 50.3, 50.4, 54.3, 66.2, 72.1, 116.8, 117.1, 121.6, 121.9, 127.4, 127.6, 128.2, 135.7, 135.9, 138.4, 139.9, 140.8, 204.3, 204.4	279, 167, 149, 113, 84, 71, 57, 41

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