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Easy access to *N*-alkylation of *N*-unsubstituted [60]fulleropyrrolidines: reductive amination using sodium triacetoxyborohydride

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Abstract—[60]Fulleropyrrolidines were used as secondary amines to react with aldehydes through reductive aminations to afford *N*-alkylated derivatives. In spite of the very weak base activity of the nitrogen atom of *N*-unsubstituted [60]fulleropyrrolidines, this method was found to be efficient at the aid of sodium triacetoxyborohydride. Several *N*-alkylated derivatives were synthesized and fully characterized.

Considerable attentions have been drawn to the characterization of physicochemical and biochemical properties of functionalized fullerenes, which are of promising compounds in materials and life science since the discovery of the synthetic route to fullerenes in macroscopic quantities.[1] Various methods for preparation of fullerene derivatives have been widely explored.[2] Fulleropyrrolidine, a kind of organofullerene derivatives in which a pyrrolidine ring is fused to a 6,6 ring junction of the [60]fullerene cage, is one of the extensively studied fullerene derivatives.[3] In recent years, most [60]fulleropyrrolidines were synthesized by the well known 1,3-dipolar cycloaddition method.[3,4] So far, to functionalize the nitrogen atom in fulleropyrrolidines to obtain desired materials, either an *N*-substituted α-amino acid (*N*-triethyleneglycol monomethyl ether-glycine was a well known one[5])[6] has to be used or the parent fulleropyrrolidines has to be modified at the *N–H* functionality, which was achieved mainly through *N*-acylating reaction.[7] To the best of our knowledge, direct *N*-alkylation of *N*-unsubstituted fulleropyrrolidines has seldom been reported. It has been shown that *N*-alkylation of fulleropyrrolidines is quite difficult due to its poorly basic property.[8] Langa's group once reported the synthesis of several *N*-alkyl fulleropyrrolidines by the combination of solvent-free phase-transfer catalysis (PTC) and microwave irradiation techniques using *N*-unsubstitued fulleropyrrolidines and the alkyl or benzyl bromide as starting materials.[9] We report here a facile method for the preparation of *N*-alkyl fulleropyrrolidines from readily available *N*-unsubstituted fulleropyrrolidines using reductive amination of aldehydes.

The reductive aminations of aldehydes or ketones with ammonia, primary or second amines in the presence of reducing agents, are well established to prepare primary, secondary, and tertiary amines. As a selective and safe reducing agent, sodium triacetoxyborohydride has been reported effective for this kind of reactions.[10] The reaction conditions are convenient and mild and show a high degree of tolerance for a variety of functional groups including nitro, cyano, halo, carboxy, and carbethoxy groups.[11] Herein, we have developed a very selective synthetic method to achieve the direct *N*-alkylation of the readily available *N*-unsubstituted fulleropyrrolidines using sodium triacetoxyborohydride with aldehydes under ambient experimental conditions in spite of the very weakly basic nature of the nitrogen atom in fulleropyrrolidines. This successful method opens an entry for the synthesis of a series of fulleropyrrolidines with good solubility and much more functional groups for further functionalization.

Keywords: *N*-Alkylation; [60]Fulleropyrrolidines; Reductive amination; Sodium triacetoxyborohydride.
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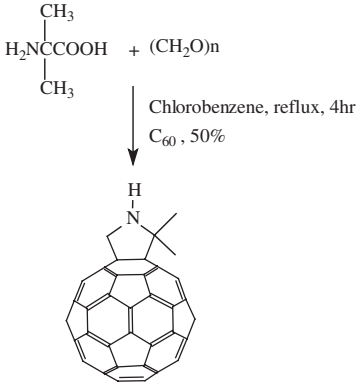
In our strategy, 2,2-dimethyl fulleropyrrolidine was chosen as the starting secondary amine, which does not contain any chiral center at *C*-2 and/or *C*-5, making characterization of products much easier. The Prato[3a,12] synthesis of 2,2-dimethyl fulleropyrrolidine was prepared in good yields as described in Scheme 1 and relied on the 1,3-dipolar cycloaddition of the azomethine ylide generated by condensation of the 2-aminoisobutyric acid with paraformaldehyde to C_{60} in refluxing chlorobenzene.

The reductive aminations were carried out in dichloromethane/toluene at room temperature. Although THF can be used, most of the reactions carried out in dichloromethane were faster. We found that reactions proceeded rather slowly when reactants were mixed at stoichiometric ratio. The reactions were also slower in the absence of AcOH. So, all the reactions were carried out with added glacial acetic acid. Detailed reaction conditions can be found in the supporting information.



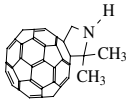
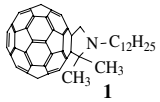
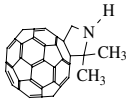
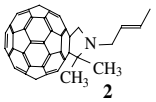
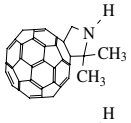
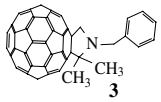
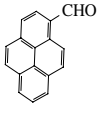
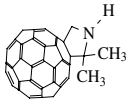
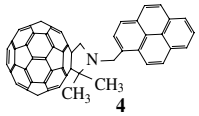
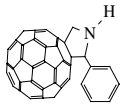
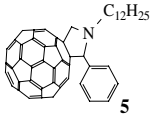
Scheme 1. The synthesis of 2,2-dimethyl fulleropyrrolidine.

The results are listed in Table 1. 2-Phenyl [60]fulleropyrrolidine was also used as the starting secondary amine and reacted successfully with alkyl aldehyde.[13]

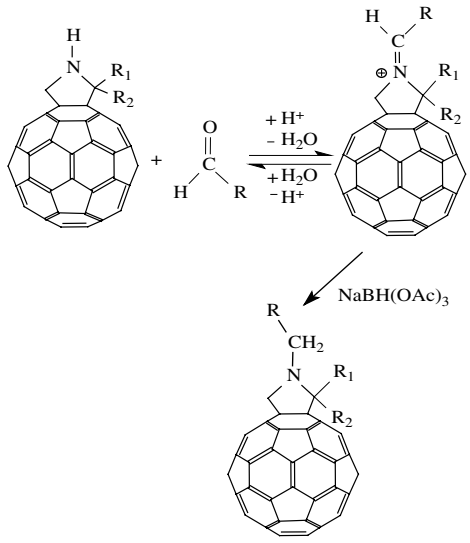
Abdel-Magid once presented a possible pathway of reductive aminations.[11] There were also some reports that provide evidence suggesting a direct reduction of carbinol amine as a possible pathway leading to the products.[14] As shown in Table 1, there was obvious difference in reactivity between aliphatic and aromatic aldehydes. Saturated aliphatic aldehydes were most reactive. The reactions progressed to reach nearly 100% conversions as judged from the TLC analysis with no detectable side reactions. Good isolated yields of products were obtained after chromatography. The target *N*-alkylated fulleropyrrolidines dissolved well in most organic solvents. Crotonaldehyde was aminated somewhat slower in an inert atmosphere after the reduction. The double bond was retained. Aromatic aldehydes reacted much slower in comparisons with aliphatic ones. Furthermore, *N*-ethylation fulleropyrrolidine was detected in the reaction mixture. The *N*-ethylation of amines was considered a major process in reaction of amines with sodium borohydride in neat acetic acid. It was believed to proceed through the formation of acetaldehyde.[15] This led to consumption of the reducing agent and low yields of the target reductive amination products with increasing yields of competing *N*-ethylating products even up to 38% in reaction with 1-pyrenecarboxaldehyde (see supporting information). The poor reactivity of aromatic aldehydes was likely due to the steric hindrance (Scheme 2).

Acetone, 3-pentanone and nonyl ketone were also examined but with little success even refluxed over 7 days. Only small amounts of side product, *N*-ethyl fulleropyrrolidine, were detected.

Table 1. Directly *N*-alkylation of fulleropyrrolidines with aldehydes using sodium triacetoxyborohydride[a]

Aldehyde	Fulleropyrrolidine	Condition[a]	Product	Yields (%)
$CH_3(CH_2)_{10}CHO$		I, 2 h, rt	 **1**	95
		II, 34 h, rt	 **2**	41
		II, 96 h, rt	 **3**	36
		II, 120 h, rt	 **4**	15
$CH_3(CH_2)_{10}CHO$		II, 2 h, rt	 **5**	93

[a] I. Fulleropyrrolidine:aldehyde:$NaBH(OAc)_3$:HOAc (1:10:10:10). II. Fulleropyrrolidine:aldehyde:$NaBH(OAc)_3$:HOAc (1:20:20:20).



Scheme 2. A possible pathway of directly *N*-alkylation of fulleropyrrolidines with aldehydes using sodium triacetoxyborohydride.

The characterization of all the *N*-alkylating products was established by ^{1}H NMR, ^{13}C NMR, UV–vis, MALDI-TOF, and FT-IR.[16] Interestingly, the ^{1}H NMR of product **5** in $CDCl_3$ showed a singlet for H-2 and an AB system with a coupling constant of 9.3 Hz for CH_2-5. The *N*-CH_2 appeared as a germinal coupled doublet, so did the next two CH_2 to *N*-CH_2. Furthermore, both *ortho*-H of phenyl protons showed a broad single signal with integral of two hydrogen atoms instead of a double signal, which were considered as the typical signals of the *N*-alkylated 2-aryl [60]fulleropyrrolidine system. In the ^{13}C NMR spectra the fullerene carbons of all the *N*-alkylating fulleropyrrolidines were similar in terms of both their chemical shifts and number of signals. The UV–vis spectra in $CHCl_3$ at room temperature, of the products showed the characteristic absorption of [6,6] adducts of fullerenes at about 432 nm.[17] This further indicated that the symmetry of fulleropyrrolidines (the starting secondary amines) was retained and N–H group was the reactive center of these reactions.

In summary, readily available *N*-unsubstituted [60]fulleropyrrolidines were reacted with aldehydes, sodium triacetoxyborohydride, and glacial acetic acid to yield *N*-alkylated derivatives. The synthesis of several *N*-alkylated [60]fulleropyrrolidines is described and these compounds were fully characterized by a number of analytical techniques. This approach may provide a promising route toward a variety of *N*-alkylated fulleropyrrolidine products and new fullerene synthons containing the correct functionalities useful for application in materials and medicinal chemistry. Further application to prepare new fullerene materials are currently underway and will be reported separately.

Acknowledgements

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References and notes

1. Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K. D.; Huffman, R. *Nature* **1990**, *347*, 354–358.
2. (a) *Fullerenes, Chemistry, Physics and Technology*; Kadish, K. M., Ruoff, R. S., Eds.; John Wiley & Sons, 2000 (b) Hirsch, A. *The Chemistry of Fullerenes*; Thieme Medical: New York, 1994; (c) Taylor, R. *Lecture Notes on Fullerene Chemistry, a Handbook for Chemists*; Imperial College, 1999 (d) Martin, N.; Sanchez, L.; Illescas, B.; Perez, I. *Chem. Rev.* pp 2527–2547.
3. (a) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798–9799; (b) Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519–526; (c) Wilson, S. R.; Lu, Q. *J. Org. Chem.* **1995**, *60*, 6496–6498; (d) Novello, F.; Prato, M.; Da Ros, T.; De Amici, M.; Bianco, A.; Toniolo, C.; Maggini, M. *J. Chem. Soc., Chem. Commun.* **1996**, 903–904.
4. (a) Gan, L. B.; Zhou, D. J.; Luo, C. P.; Tan, H. S.; Huang, C. H.; Lu, M. J.; Pan, J. Q.; Wu, Y. *J. Org. Chem.* **1996**, *61*, 1954–1961; (b) Bernstein, R.; Foote, C. S. *Tetrahedron Lett.* **1998**, *39*, 7051; (c) Bernstein, R.; Foote, C. S. *J. Phys. Chem. A* **1999**, *103*, 7244–7247.
5. Da Ros, T.; Prato, M.; Novello, F.; Maggini, M.; Banfi, E. *J. Org. Chem.* **1996**, *61*, 9070–9072.
6. Kordatos, K.; DaRos, T.; Bosi, S.; Vázquez, E.; Bergamin, M.; Cusan, C.; Pellarini, F.; Tomberli, V.; Baiti, B.; Pantarotto, D.; Georgakilas, V.; Spalluto, G.; Prato, M. *J. Org. Chem.* **2001**, *66*, 4915–4920.
7. (a) Maggini, M.; Karlsson, A.; Pasimeni, L.; Scorrano, G.; Prato, M.; Valli, L. *Tetrahedron Lett.* **1994**, *35*, 2985–2988; (b) Zhang, S.; Gan, L. B.; Huang, C. H.; Lu, M. J.; Pan, J. Q.; He, X. R. *J. Org. Chem.* **2002**, *67*, 883–891; (c) Maggini, M.; Pasimeni, L.; Prato, M.; Scorrano, G.; Valli, L. *Langmuir* **1994**, *10*, 4164–4166.
8. Eiermann, M.; Haddon, R. C.; Knight, B.; Li, Q. C.; Maggini, M.; Martin, N.; Ohno, T.; Prato, M.; Suzuki, T.; Wudl, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1591–1594.
9. (a) de la Cruz, P.; de la Hoz, A.; Font, L. M.; Langa, F.; Pérez, M. C. *Tetrahedron Lett.* **1998**, *39*, 6053–6056; (b) de la Cruz, P.; de la Hoz, A.; Langa, F.; Martin, N.; Pérez, M. C.; Sanchez, L. *Eur. J. Org. Chem.* **1999**, *3*, 3433–3436.
10. Abdel-Magid, A. M.; Maryanoff, C. A.; Carson, K. G. *Tetrahedron Lett.* **1991**, *31*, 5595–5598.
11. Abdel-Magid, A. M.; Carson, K. G.; Harris, B. D.; Maryanoff, C. A.; Shah, R. D. *J. Org. Chem.* **1996**, *61*, 3849–3862.
12. To C_{60} (360 mg, 0.5 mmol) in 200 mL of chlorobenzene, were added 1.0 mmol (103 mg) 2-aminoisobutyric acid and 2.5 mmol (75 mg) of paraformaldehyde. The solution was heated to reflux for 4 h. The solvent was then condensed and the crude product was purified by chromatography eluted by toluene/methanol (1:1). After washed with acetone, 198 mg (yield: 50%) of the product *2,2-dimethyl [60]fulleropyrrolidine* was obtained (toluene, $R_f = 0.06$). ^{1}H NMR (CS_2/$CDCl_3$, 6:1 (v/v)): 4.82 (s, 2H), 2.08 (s, 6H). ^{13}C NMR (CS_2/$CDCl_3$, 6:1 (v/v)): 155.9, 154.5, 147.1, 146.3, 146.2, 146.1, 146.0, 145.8, 145.6, 145.4, 145.3, 145.3, 145.3, 144.5, 143.3, 142.8, 142.7, 142.3, 142.2, 142.2, 142.0, 141.9, 140.3, 140.1, 135.8, 135.6, 129.1, 128.4, 125.5, 76.1 (C), 71.6 (2C, sp^3), 61.4 (CH_2), 28.6 ($2CH_3$). MALDI-TOF (+): 792.3 ($M+H^+$), 720. FT-IR (cm^{-1}): 527.58, 1427.43, 2921.63, 2964.04, 3442.59.

13. (a) Wilson, S. R.; Wang, Y.; Cao, J.; Tan, X. *Tetrahedron Lett.* **1996**, *37*, 775–778; (b) de la Cruz, P.; de la Hoz, A.; Langa, F.; Illescas, B.; Martín, N. *Tetrahedron* **1997**, *53*, 2599–2608.
14. Tadanier, J.; Hallas, R.; Martin, J. R.; Stanaszek, R. S. *Tetrahedron* **1981**, *37*, 1309–1316.
15. Gribble, G. W.; Lord, P. D.; Skotnicki, J.; Dietz, S. E.; Eaton, J. T.; Johnson, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 7812–7814.
16. *N-(n-Dodecyl)-2,2-dimethyl [60]fulleropyrrolidine* (**1**) was synthesized according to the general procedure in 95% yield (petroleum ether/toluene (4:1), $R_f = 0.65$), ^{1}H NMR ($CDCl_3$, 400 MHz): 4.56 (s, 2H), 2.99 (t, 2H, $J = 7.2$ Hz), 1.94 (s, 6H), 1.87–1.94 (m, 2H), 1.61–1.65 (m, 2H), 1.47–1.49 (m, 2H), 1.27–1.38 (m, 14H), 0.88 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR ($CDCl_3$, 400 MHz): 156.7, 154.8, 147.3, 146.7, 146.3, 146.2, 146.0, 145.7, 145.3, 145.3, 145.2, 144.6, 144.6, 143.2, 142.6, 142.9, 142.2, 142.1, 142.0, 141.8, 141.7, 140.2, 139.7, 136.6, 136.1, 69.9 (2C, sp^3), 68.9 (C, sp^3), 62.3 (CH_2), 46.7 (CH_2), 32.0 ($2CH_2$), 29.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 27.5 ($2CH_2$), 23.5 (CH_2), 22.7 ($2CH_3$), 14.2 (CH_3). MALDI-TOF (+): 960.3 ($M+H^+$). FT-IR (cm^{-1}): 527.33, 1429.14, 2849.61, 2921.70. *N-(2-Butenyl)-2,2-dimethyl [60]fulleropyrrolidine* (**2**) was prepared according to the general procedure in 41% yield (toluene, $R_f = 0.89$). The reaction was carried out under inert atmosphere for the consideration of its unstability to atmosphere and the byproduct *N*-ethyl-2,2-dimethyl [60]fulleropyrrolidine was obtained with yield of 5%. ^{1}H NMR ($CS_2/CDCl_3$, 10:1 (v/v), 400 MHz): 6.06 (m, 1H), 6.01 (m, 1H), 4.70 (s, 2H), 3.77 (d, 2H, $J = 6.8$ Hz), 2.16 (s, 6H), 2.03 (d, 3H, $J = 7.3$ Hz). ^{13}C NMR ($CS_2/CDCl_3$, 10:1 (v/v), 400 MHz): 156.4, 154.5, 147.4, 146.6, 146.4, 146.3, 146.1, 145.7, 145.5, 145.4, 145.3, 144.7, 144.6, 143.2, 142.7, 142.7, 142.5, 142.3, 142.2, 142.0, 141.9, 141.8, 140.3, 139.9, 129.6 (CH, sp^2), 128.1 (CH, sp^2), 69.5 (2C, sp^3), 68.5 (C, sp^3), 62.8 (CH_2), 49.9 (CH_2), 23.7 ($2CH_3$), 18.6 (CH_3). MALDI-TOF (−): 845.7. FT-IR (cm^{-1}): 527.37, 1188.26, 1429.60, 1459.15, 2923.14, 2963.75. *N-Benzyl-2,2-dimethyl [60]fulleropyrrolidine* (**3**) was prepared in 36% yield (petroleum ether/toluene (5:1), $R_f = 0.56$). The byproduct *N*-ethyl-2,2-dimethyl [60]fulleropyrrolidine was obtained with yield of 10%. ^{1}H NMR ($CS_2/CDCl_3$, 6:1 (v/v), 400 MHz): 7.68 (d, 2H, $J = 7.2$ Hz), 7.37–7.41 (m, 2H), 7.27–7.30 (m, 1H), 4.36 (s, 2H), 4.19 (s, 2H), 2.07 (s, 6H). ^{13}C NMR ($CS_2/CDCl_3$, 6:1 (v/v), 400 MHz): 156.3, 154.4, 147.4, 146.6, 146.3, 146.1, 145.7, 145.5, 145.4, 145.3, 145.3, 144.7, 144.6, 143.2, 143.2, 142.7, 142.7, 142.5, 142.2, 142.2, 142.0, 141.9, 141.8, 140.3, 139.8, 139.4, 136.7, 136.1, 128.8 (2CH, sp^2), 128.4 (2CH, sp^2), 127.5, 69.6 (2C, sp^3), 68.9 (C, sp^3), 62.4 (CH_2), 51.5 (CH_2), 23.8 ($2CH_3$). MALDI-TOF (−): 881.8, 720.5. FT-IR (cm^{-1}): 526.01, 1187.28, 1426.85, 1456.56, 1495.64, 2962.07, 2920.41. *N-(1-Pyrenyl)-2,2-dimethyl [60]fulleropyrrolidine* (**4**) was synthesized in 15% yield (toluene, $R_f = 0.88$). The byproduct *N*-ethyl-2,2-dimethyl [60]fulleropyrrolidine was obtained with yield of 38%. ^{1}H NMR ($CS_2/CDCl_3$, 10:1 (v/v), 400 MHz): 9.03 (d, 1H, $J = 9.0$ Hz), 8.58 (d, $J = 7.4$ Hz), 8.32–8.39 (m, 4H), 8.21–8.15 (m, 3H), 5.12 (s, 2H), 4.66 (s, 2H), 2.48 (s, 6H). ^{13}C NMR was not successfully obtained due to its poor solubility. MALDI-TOF (+): 1004.1 (surprisingly, from MALDI-TOF (−), we observed the peak of molecular ion at 1006). FT-IR (cm^{-1}): 527.27, 844.92, 1186.23, 1459.32, 1514.49, 1608.04, 2924.13, 2959.50, 3039.66. *N-Ethyl-2,2-dimethyl [60]fulleropyrrolidine* ^{1}H NMR ($CS_2/CDCl_3$, 10:1 (v/v), 400 MHz): 4.74 (s, 2H), 3.24 (q, 2H, $J = 7.2$ Hz), 2.14 (s, 6H), 1.72 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR ($CS_2/CDCl_3$, 10:1 (v/v), 400 MHz): 156.4, 154.5, 147.4, 146.6, 146.3. 146.3, 146.1, 146.1, 145.7, 145.5, 145.4, 145.3, 145.3, 144.7, 144.6, 143.2, 142.7, 142.5, 142.3, 142.2, 142.0, 141.9, 141.8, 140.3, 139.9, 136.7, 136.3, 129.2, 128.4, 125.6, 69.9 (2C, sp^3), 68.6 (C, sp^3), 62.2 (CH_2), 41.6 (CH_2), 23.6 ($2CH_3$), 15.5 (CH_3). MALDI-TOF (−): 819.5. FT-IR (cm^{-1}): 526.29, 1193.19, 1426.52, 1460.08, 2923.73, 2966.21. *N-(n-Dodecyl)-2-phenyl [60]fulleropyrrolidine* (**5**) was prepared obtained in 93% yield (petroleum ether/toluene (4:1), $R_f = 0.88$), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.80 (br s, 2H), 7.42 (t, 2H, $J = 7.9$ Hz, 7.52 Hz), 7.33 (t, 1H, $J = 7.4$ Hz), 5.10 (d, 1H, $J = 9.3$ Hz), 5.06 (s, 1H), 4.12 (d, 1H, $J = 9.28$ Hz), 3.22–3.25 (m, 1H), 2.51–2.58 (m, 1H), 1.96–2.00 (m, 1H), 1.86–1.90 (m, 1H), 1.63–1.65 (m, 1H), 1.52–1.55 (m, 1H), 1.28–1.45 (m, 6H), 0.89 (t, 3H, $J = 7.0$ Hz). ^{13}C NMR ($CDCl_3$, 400 MHz): 154.3, 153.6, 147.3, 146.8, 146.2, 146.1, 146.1, 145.9, 145.9, 145.6, 145.5, 145.5, 145.3, 145.3, 145.2, 144.7, 144.6, 144.4, 144.4, 142.6, 142.3, 142.2, 142.2, 142.1, 142.0, 141.5, 140.2, 140.1, 139.8, 139.4, 136.8, 136.6, 135.8, 135.7, 129.5, 128.5, 128.4, 82.6 (CH_2), 69.0 (2c, sp^3), 66.9 (CH, sp^3), 53.2 (CH_2), 32.0 ($2CH_2$), 29.7 ($3CH_2$), 29.4 ($3CH_2$), 27.5 ($2CH_2$), 22.7 ($2CH_3$), 14.2 (CH_3). MALDI-TOF (+): 1006.5 ($M+H^+$), 720.3. FT-IR (cm^{-1}): 527.14, 1180.64, 1428.68, 1459.22, 1492.54.
17. (a) Eirmann, M.; Wudl, F.; Prato, M.; Maggini, M. *J. Am. Chem. Soc.* **1994**, *116*, 8364–8365; (b) Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eirmann, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479–8480; (c) Isaacs, L.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 2454–2464; (d) Arnz, R.; Carneiro, J. W. M.; Klug, W.; Schmickler, H.; Vogel, E.; Breuckmann, R.; Klärner, F.-G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 683–686; (e) Xiao, S. Q.; Li, Y. L.; Fan, H. J.; Li, H. M.; Liu, H. B.; Shi, Z. Q.; Jiang, L.; Zhu, D. B. *Org. Lett.* **2002**, *4*, 3063–3066.