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Supporting Information

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Acetylene Carbonylation by Radicals: Tin Radical Catalyzed Synthesis of α-Methylene Amides from 1-Alkynes, Carbon Monoxide, and Amines

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General information. ^{1}H NMR spectra were recorded with a JEOL JMN-500 (500 MHz) spectrometer or JEOL AL-400 (400 MHz) spectrometer in $CDCl_3$. Chemical shifts are reported in parts per million (δ) downfield from internal TMS at 0.00. ^{13}C NMR spectra were recorded with a JEOL JMN ECP-500 (125 MHz) spectrometer and referenced to the solvent peak at 77.00 ppm. For ^{1}H-Sn or ^{13}C-Sn coupling constants, the central signals are normally associated with two close pairs of satellites corresponding to both ^{117}Sn and ^{119}Sn isotopes, and average values of the two different coupling constants are reported. Infrared spectra were obtained on a Shimadzu FTIR 8400 spectrometer; absorptions are reported in reciprocal centimeters. Both conventional and high resolution mass spectra were recorded with a JEOL MS700 spectrometer. Products were purificated by flash chromatography on silica gel (nacalai tesque int. Silica Gel 60, 230-400 mesh).

Ab Initio and DFT MO Calculations. Ab initio molecular orbital calculations were carried out using the Gaussian 98 program[1] using standard computational methods[2] and basis sets previously described.[3]

References

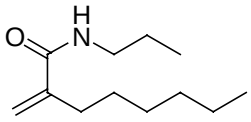
[1] Gaussian 98, Revision A.9, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J.

Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

[2] W. J. Hehre, L. Radom, P. v. R. Schleyer and P. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.

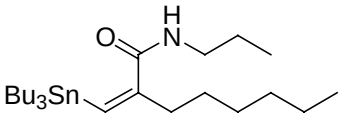
[3] S. M. Horvat, C. H. Schiesser and L. M. Wild, *Organometallics*, **2000**, *19*, 1239.

***N*-Propyl-2-methyleneoctanamide (3a).**



(R_f = 0.10, hexane/EtOAc = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.87 Hz, 3H, $NCH_2CH_2CH_3$), 0.93 (t, 3H, *J* = 7.33 Hz, CH_3), 1.22-1.35 (m, 6H, CH_2), 1.40-1.48 (m, 2H, CH_2), 1.55 (sext, *J* = 6.87 Hz, 2H, NCH_2CH_2), 2.29 (t, *J* = 7.79 Hz, 2H, $CH{=}CCH_2$), 3.26 (q, *J* = 6.87 Hz, 2H, NCH_2), 5.22 (s, 1H, $CH_2{=}C$), 5.53 (s, 1H, $CH_2{=}C$), 5.70-5.84 (bs, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.36 ($NCH_2CH_2CH_3$), 14.03 (CH_3), 22.57 (CH_2), 22.82 (CH_2), 28.05 (CH_2), 28.91 (CH_2), 31.65 (CH_2), 32.44 (CH_2), 41.27 (NCH_2), 116.65 ($CH_2{=}C$), 146.00 ($CH_2{=}C$), 169.20 (CO); IR (neat) 1655, 1614; MS (EI) *m/z* (rel intensity) 197 (M^+, 20), 182 (37), 168 (28), 154 (100), 139 (76), 126 (48), 112 (28), 98 (31), 69 (53); HRMS (EI) *m/z* calcd for $C_{12}H_{23}NO$ (M^+) 197.1780, found 197.1788.

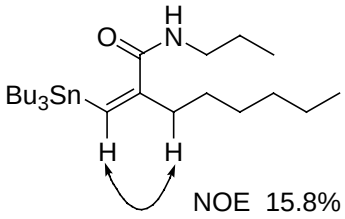
***N*-Propyl-2-tributylstannylmethyleneoctanamide (4a).**



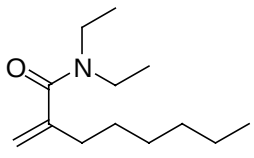
E isomer: (R_f = 0.54, hexane/EtOAc = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78-0.96 (m, 21H, $SnCH_2CH_2CH_2CH_3$, $NCH_2CH_2CH_3$, CH_3), 1.20-1.60 (m, 22H, $SnCH_2CH_2CH_2CH_3$, $NCH_2CH_2CH_3$, CH_2), 2.32 (t, *J* = 7.33 Hz, 2H, $CH{=}CCH_2$), 3.37 (q, *J* = 5.96 Hz, 2H, NCH_2), 5.66-5.78 (bs, 1H, NH), 6.34 (s, *J* ^{1}H-Sn = 66.22 Hz, 1H, CH=C); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.46 ($NCH_2CH_2CH_3$), 11.50 ($SnCH_2CH_2CH_2CH_3$), 13.85

(Sn*C*H$_2$CH$_2$CH$_2$CH$_3$), 14.12 (*C*H$_3$), 22.66 (*C*H$_2$), 22.90 (*C*H$_2$), 27.51 (*J* ^{13}C-Sn = 58.54 Hz, SnCH$_2$*C*H$_2$CH$_2$CH$_3$), 28.78 (*C*H$_2$), 28.99 (*C*H$_2$), 29.39 (*J* ^{13}C-Sn = 20.15 Hz, SnCH$_2$CH$_2$*C*H$_2$CH$_3$), 31.73 (*C*H$_2$), 35.65 (*C*H$_2$), 41.63 (N*C*H$_2$), 142.43 (*C*H=C), 148.74 (CH=*C*), 168.48 (*C*O); IR (neat) 1634, 1582; MS (CI, *i*C$_4$H$_{10}$) *m/z calculated from major ^{120}Sn isotope* (rel intensity) 488 (M$^+$+H, 100), 310 (23); HRMS (CI, *i*C$_4$H$_{10}$) *m/z* calcd for C$_{24}$H$_{50}$NO^{120}Sn (M$^+$+H) 488.2914, found 488.2918.

Z isomer: (R$_f$ = 0.43, hexane/EtOAc = 5/1). ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.80-1.02 (m, 21H, SnC*H*$_2$CH$_2$CH$_2$C*H*$_3$, NCH$_2$CH$_2$C*H*$_3$, C*H*$_3$), 1.18-1.64 (m, 22H, SnCH$_2$C*H*$_2$C*H*$_2$CH$_3$, NCH$_2$C*H*$_2$CH$_3$, C*H*$_2$), 2.30 (t, *J* = 8.25 Hz, 2H, CH=CC*H*$_2$), 3.25 (q, *J* = 6.87 Hz, 2H, NC*H*$_2$), 5.68-5.82 (bs, 1H, N*H*), 6.35 (s, *J* ^{1}H-Sn = 57.74 Hz, 1H, C*H*=C); ^{13}C NMR (125 MHz, CDCl$_3$) δ 10.42 (*J* ^{13}C-Sn = 337.33 Hz, SnCH$_2$CH$_2$CH$_2$*C*H$_3$), 11.72 (NCH$_2$CH$_2$*C*H$_3$), 13.72 (Sn*C*H$_2$CH$_2$CH$_2$CH$_3$), 14.13 (*C*H$_3$), 22.67 (*C*H$_2$), 23.02 (*C*H$_2$), 27.41 (*J* ^{13}C-Sn = 58.54 Hz, SnCH$_2$*C*H$_2$CH$_2$CH$_3$), 29.20 (*J* ^{13}C-Sn = 21.11 Hz, SnCH$_2$CH$_2$*C*H$_2$CH$_3$), 29.62 (*C*H$_2$), 29.84 (*C*H$_2$), 31.85 (*C*H$_2$), 36.54 (*C*H$_2$), 41.39 (N*C*H$_2$), 132.33 (*C*H=C), 155.42 (CH=*C*), 169.67 (*C*O); IR (neat) 1643, 1578; MS (CI, *i*C$_4$H$_{10}$) *m/z calculated from major ^{120}Sn isotope* (rel intensity) 488 (M$^+$+H, 26), 430 (100), 198 (13); HRMS (CI, *i*C$_4$H$_{10}$) *m/z* calcd for C$_{24}$H$_{50}$NO^{120}Sn (M$^+$+H) 488.2914, found 488.2921.



***N,N*-Diethyl-2-methyleneoctanamide (3b).**

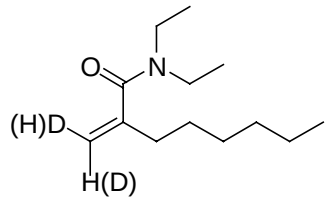


(R$_f$ = 0.19, hexane/EtOAc = 5/1). ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.87 (t, *J* = 6.87 Hz, 3H, C*H*$_3$), 1.14 (t, *J* = 6.87 Hz, 6H, NCH$_2$C*H*$_3$), 1.22-1.36 (m, 6H, C*H*$_2$), 1.45 (qui, *J* = 7.33 Hz, 2H, CH$_2$=CCH$_2$C*H*$_2$), 2.26 (t, *J* = 7.79 Hz, 2H, CH$_2$=CC*H*$_2$), 3.30-3.45 (m, 4H, NC*H*$_2$),

4.99 (s, 1H, CH_2=C), 5.07 (s, 1H, CH_2=C); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.80 (NCH$_2$*C*H$_3$), 14.09 (*C*H$_3$), 14.38 (NCH$_2$*C*H$_3$), 22.62 (*C*H$_2$), 27.38 (*C*H$_2$), 29.07 (*C*H$_2$), 31.70 (*C*H$_2$), 34.45 (*C*H$_2$), 38.54 (N*C*H$_2$), 42.59 (N*C*H$_2$), 112.50 (*C*H$_2$=C), 146.03 (CH$_2$=*C*), 172.06 (*C*O); IR (neat) 1643, 1620; MS (EI) *m/z* (rel intensity) 211 (M^+, 28), 168 (18), 140 (100), 126 (21), 69 (25); HRMS (EI) *m/z* calcd for $C_{13}H_{25}NO$ (M^+) 211.1937, found 211.1934.

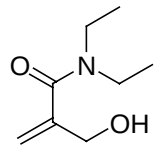
S. Torii, H. Okumoto, M, Sadakane, L. H. Xu. *Chem. Lett.*, **1991**, 1673.

***N,N*-Diethyl-2-deuteriomethyleneoctanamide (3b-*d*).**



(R_f = 0.19, hexane/EtOAc = 5/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.42 Hz, 3H, C*H*$_3$), 1.13 (t, *J* = 6.87 Hz, 6H, NCH$_2$C*H*$_3$), 1.20-1.36 (m, 6H, C*H*$_2$), 1.44 (qui, *J* = 7.79 Hz, 2H, CH$_2$=CCH$_2$C*H*$_2$), 2.26 (t, *J* = 7.79 Hz, 2H, CH$_2$=CC*H*$_2$), 3.29-3.46 (m, 4H, NC*H*$_2$), 4.98 (s, 0.5H, C*H*$_2$=C), 5.06 (s, 0.5H, C*H*$_2$=C); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.74 (NCH$_2$*C*H$_3$), 14.06 (*C*H$_3$), 14.35 (NCH$_2$*C*H$_3$), 22.59 (*C*H$_2$), 27.34 (*C*H$_2$), 29.04 (*C*H$_2$), 31.67 (*C*H$_2$), 34.39 (*C*H$_2$), 38.54 (N*C*H$_2$), 42.59 (N*C*H$_2$), 112.50 (*C*H$_2$=C, *J* ^{13}C-D = 6.72 Hz), 145.88 (CH$_2$=*C*), 172.04 (*C*O); IR (neat) 1634, 1609; MS (EI) *m/z* (rel intensity) 212 (M^+, 10), 183 (11), 169 (16), 155 (14), 141 (100), 127 (20), 100 (11), 70 (29); HRMS (EI) *m/z* calcd for $C_{13}H_{24}DNO$ (M^+) 211.1998, found 212.1992.

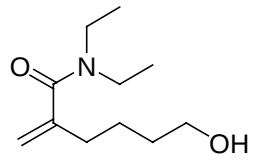
***N,N*-Diethyl-3-hydroxy-2-methylenepropanamide (3c).**



(R_f = 0.18, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (t, *J* = 7.33 Hz, 6H, NCH$_2$C*H*$_3$), 3.40 (q, *J* = 7.33 Hz, 6H, NC*H*$_2$CH$_3$), 4.25 (s, 2H, C*H*$_2$OH), 5.15 (s, 1H,C*H*$_2$=C), 5.40 (s, 1H,C*H*$_2$=C); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.72 (NCH$_2$*C*H$_3$), 14.33 (NCH$_2$*C*H$_3$), 38.97

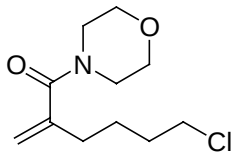
(N*C*H$_2$), 43.00 (N*C*H$_2$), 63.20 (*C*H$_2$OH), 112.97 (*C*H$_2$=C), 145.18 (CH$_2$=*C*), 170.94 (*C*O); IR (neat) 3391, 1645, 1604; MS (EI) *m/z* 157 (M$^+$, 4), 140 (88), 124 (70), 85 (100), 72 (16), 58 (92), 43 (34); HRMS (EI) *m/z* calcd for $C_8H_{15}NO_2$ (M$^+$) 157.1103, found 157.1108.

_N,N_-Diethyl-6-hydroxy-2-methylenehexanamide (3d).



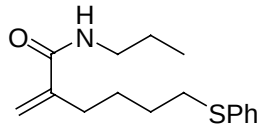
(R$_f$ = 0.18, EtOAc). ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.15 (t, *J* = 7.04 Hz, 6H, NCH$_2$C*H*$_3$), 1.50-1.70 (m, 4H, C*H*$_2$C*H*$_2$CH$_2$OH), 1.70-1.80 (bs, 1H, CH$_2$O*H*), 2.32 (t, *J* = 7.32 Hz, 2H, CH$_2$=CC*H*$_2$), 3.30- 3.50 (m, 4H, NC*H*$_2$), 3.67 (t, *J* = 6.34 Hz, 2H, C*H*$_2$OH), 5.04 (s, 1H, C*H*$_2$=C), 5.12 (s, 1H, C*H*$_2$=C); ^{13}C NMR (125 MHz, CDCl$_3$) δ 12.59 (NCH$_2$*C*H$_3$), 14.18 (NCH$_2$*C*H$_3$), 23.32 (*C*H$_2$), 32.07 (*C*H$_2$), 33.91 (*C*H$_2$), 38.48 (N*C*H$_2$), 42.53 (N*C*H$_2$), 61.72 (*C*H$_2$OH), 112.72 (*C*H$_2$=C), 145.14 (CH$_2$=*C*), 171.73 (*C*O); IR (neat) 3412, 1641, 1609; MS (EI) *m/z* (rel intensity) 169 (28), 154 (18), 140 (100), 81 (43); HRMS (EI) *m/z* calcd for $C_{11}H_{21}NO_2$ (M$^+$) 199.1572, found 199.1565.

4-{(6-Chloro-2-methylene-1-oxo)hexyl}morpholine (3e).



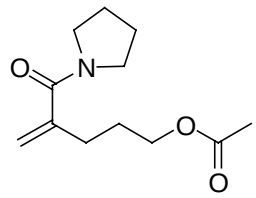
(R$_f$ = 0.10, hexane/EtOAc = 2/1). ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.57-1.68 (m, 2H, CH$_2$C*H*$_2$CH$_2$Cl), 1.82 (qui, *J* = 6.87Hz, 2H, C*H*$_2$CH$_2$CH$_2$Cl), 2.32 (t, *J* = 7.33 Hz, 2H, CH=CC*H*$_2$), 3.55 (t, *J* = 6.42 Hz, 2H, C*H*$_2$Cl), 3.58-3.73 (m, 8H, NC*H*$_2$C*H*$_2$O), 5.06 (s, 1H, C*H*$_2$=C), 5.23 (s, 1H, C*H*$_2$=C); ^{13}C NMR (125 MHz, CDCl$_3$) δ 24.67 (*C*H$_2$CH$_2$CH$_2$Cl), 31.95 (*C*H$_2$CH$_2$Cl), 33.33 (CH$_2$=C*C*H$_2$), 41.87 (b, N*C*H$_2$), 46.35 (*C*H$_2$Cl), 47.50 (b, N*C*H$_2$), 66.80 (O*C*H$_2$), 115.00 (*C*H$_2$=C), 143.58 (CH$_2$=*C*), 170.50 (*C*O); IR (neat) 1641, 1620; MS (EI) *m/z* (rel intensity) 231 (M$^+$, 20), 196 (60), 154 (100), 81 (53), 56 (37); HRMS (EI) *m/z* calcd for $C_{11}H_{18}ClNO_2$ (M$^+$) 231.1026, found 231.1033.

***N*-Propyl-6-phenylsulfanyl-2-hexanamide (3f).**



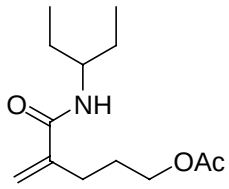
(R_f = 0.33, hexane/EtOAc = 2/1). m.p. 55-57°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.33 Hz, 3H, C*H*$_3$), 1.49-1.72 (m, 6H, C*H*$_2$), 2.31 (t, *J* = 7.79 Hz, 2H, CH$_2$=CC*H*$_2$), 2.92 (t, *J* = 7.33 Hz, 2H, C*H*$_2$SPh), 3.25 (q, *J* = 5.96 Hz, 2H, NC*H*$_2$), 5.22 (s, 1H, C*H*$_2$=C), 5.51 (s, 1H, C*H*$_2$=C), 5.80 (bs, 1H, N*H*), 7.13-7.34 (m, 5H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.49 (*C*H$_3$), 22.91 (*C*H$_2$), 27.24 (*C*H$_2$), 28.69 (*C*H$_2$), 32.00 (CH$_2$=C*C*H$_2$), 33.38 (*C*H$_2$SPh), 41.37 (N*C*H$_2$), 117.05 (*C*H$_2$=C), 125.84 (Ar), 128.93 (Ar), 129.00 (Ar), 136.74 (Ar), 145.60 (CH$_2$=*C*), 168.94 (*C*O); IR (neat) 1649, 1616; MS (EI) *m/z* (rel intensity) 277 (M^+, 9), 168 (100), 123 (23), 109 (21), 81 (18), 77 (10); HRMS (EI) *m/z* calcd for $C_{16}H_{23}NOS$ (M^+) 277.1500, found 277.1506.

1-{(5-Acetoxy-2-methylene-1-oxo)-1-pentyl}pyrrolidine (3g).



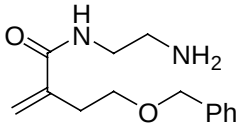
(R_f = 0.30, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 (qui, *J* = 7.81 Hz, 2H, OCH$_2$C*H*$_2$), 1,85-1.96 (m, 4H, NCH$_2$C*H*$_2$), 2.05 (s, 3H, COC*H*$_3$), 2.39 (t, *J* = 7.81 Hz, 2H, CH=CC*H*$_2$), 3.80-3.30 (m, 4H, NC*H*$_2$), 4.09 (t, *J* = 6.83 Hz, 2H, OC*H*$_2$), 5.248 (s, 1H, C*H*$_2$=C), 5.250 (s, 1H, C*H*$_2$=C); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.43 (CO*C*H$_3$), 23.84 (NCH$_2$*C*H$_2$), 25.70 (NCH$_2$*C*H$_2$), 26.19 (OCH$_2$*C*H$_2$), 29.62 (CH$_2$=C*C*H$_2$), 44.99 (N*C*H$_2$), 48.30 (N*C*H$_2$), 63.15 (O*C*H$_2$), 114.78 (*C*H$_2$=C), 144.40 (CH$_2$=*C*), 169.21 (N*C*O), 170.24 (*C*OCH$_3$); IR (neat) 1736, 1643, 1612; MS (EI) *m/z* (rel intensity) 255 (M^+, 5), 182 (10), 166 (47), 138 (100), 113 (47), 95 (33), 70 (46); HRMS (EI) *m/z* calcd for $C_{12}H_{19}NO_3$ (M^+) 225.1365, found 225.1366.

5-Acetoxy-2-methylene-*N*-(1-ethylpropyl)pentanamide (3h).



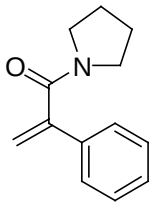
(Rf = 0.20, hexane/EtOAc = 2/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.33 Hz, 6H, CH_2CH_3), 1.31-1.47 (m, 2H, $NCHCH_2$), 1.51-1.64 (m, 2H, $NCHCH_2$), 1.74-1.85 (m, 2H, CH_2=CCH_2CH_2), 2.03 (S, 3H, $COCH_3$), 2,40 (t, *J* = 7.79 Hz, 2H, CH_2=CCH_2), 3.79-3.88 (m, 1H, NCH), 4.08 (t, *J* = 6.66 Hz, 2H, $COOCH_2$), 5.25 (s, 1H, CH_2=C), 5.41-5.51 (bs, 1H, NH), 5.52 (S, 1H, CH_2=C); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.30 (CH_2CH_3), 20.86 ($COCH_3$), 27.00 (CH_2=CCH_2CH_2), 27.74 ($NHCHCH_2$), 29.03 (CH_2=CCH_2), 52.07 (NHCH), 63.67 (OCH_2), 116.76 (CH_2=C), 145.27 (CH_2=*C*), 168.56 (*C*ONH), 171.00 (*C*OCH_3); IR (neat) 1740, 1651, 1612; MS (EI) *m/z* (rel intensity) 212 (20), 152 (34), 113 (100; HRMS (EI) *m/z* calcd for $C_{13}H_{23}NO_3$ (M^+) 241.1678, found 241.1669.

***N*-(2-Aminoethyl)-4-benzyloxy-2-methylenebutanamide (3i).**



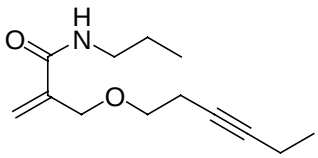
(R_f = 0.20, MeOH). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.61 (t, *J* = 5.96 Hz, 2H, CH_2=CCH_2), 2.71 (t, 2H, NH_2CH_2), 3.25 (qut, *J* = 5.96 Hz, 2H, $NCHCH_2$), 3.66 (t, *J* = 5.96 Hz, 2H, OCH_2CH_2), 4.51 (s, 2H, CH_2Ph), 5.37 (s, 1H, CH_2=C), 5.83 (s, 1H, CH_2=C), 7.26-7.38 (m, 5H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 33.02 (CH_2=CCH_2), 41.34 (CH_2NH_2), 42.45 ($NHCH_2$), 69.88 (OCH_2CH_2), 73.04 (OCH_2Ph), 120.38 (CH_2=C), 127.74 (Ar(*o*), Ar(*p*)), 128.39 (Ar), 138.03 (Ar), 142.82 (CH_2=*C*), 168.94 (*C*O); IR (neat) 1655, 1616; MS (CI, *i*C_4H_{10}) *m/z* (rel intensity) 249 (M^++H, 100), 89 (100); HRMS (CI, *i*C_4H_{10}) *m/z* calcd for $C_{14}H_{21}N_2O_2$ (M^++H) 249.1603, found 249.1610.

1-Atropoylpyrrolidine (3j).



(R_f = 0.08, hexane/EtOAc = 2/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.74-1.92 (m, 4H, NCH_2CH_2), 3.21 (t, *J* = 6.87 Hz, 2H, NCH_2), 3.59 (t, *J* = 6.87 Hz, 2H, NCH_2), 5.42 (s, 1H, CH_2=C), 5.71 (s, 1H, CH_2=C), 7.27-7.45 (m, 5H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.46 (NCH_2CH_2), 25.98 (NCH_2CH_2), 45.49 (NCH_2), 48.13 (NCH_2), 114.52 (CH_2=C), 125.89 (Ar), 128.44 (Ar), 128.78 (Ar), 135.62 (Ar), 146.33 (CH_2=*C*), 169.19 (*C*O); IR (neat) 1632, 1614; MS (EI) *m/z* (rel intensity) 201 (M^+, 95), 132 (32), 103 (100), 84 (44), 77 (32); HRMS (EI) *m/z* calcd for $C_{13}H_{15}NO$ (M^+) 201.1154, found 201.1155.

***N*-Propyl -3-(3-Hexynyloxy)-2-methylenepropanamide (3k).**



(R_f = 0.25, hexane/EtOAc = 2/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.33 Hz, 3H, CH_3), 1.11 (t, *J* = 7.33 Hz, 3H, CH_3), 1.56 (sext, *J* = 7.33 Hz , 2H, $NHCH_2CH_2$), 2.15 (tq, *J* = 7.33, 2.15 Hz, 2H, CH_3CH_2C≡C), 2.45 (tt, *J* = 6.87, 2.45 Hz, 2H, C≡CCH_2CH_2), 3.27 (q, *J* = 6.87 Hz, 2H, NCH_2), 3.53 (t, *J* = 6.87 Hz, 2H, OCH_2CH_2), 4.24 (s, 2H, CH_2=CCH_2), 5.52 (s, 1H, CH_2=C), 6.19 (s, 1H, CH_2=C), 6.97 (bs, 1H, N*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.38 (CH_3), 12.36 (CH_3CH_2C ≡ C), 14.09 (CH_3), 20.02 (C ≡ CCH_2CH_2), 22.73 (NCH_2CH_2), 41.11 (NCH_2), 68.68 (OCH_2CH_2), 71.23 (CH_2=CCH_2), 75.79 (*C*≡C), 82.87 (*C* ≡C), 124.31.05 (CH_2=C), 139.00 (CH_2=*C*), 166.34 (*C*O); IR (neat) 1660, 1618; MS (EI) *m/z* (rel intensity) 222 (M^+, 16), 208 (91), 192 (59), 156 (95), 126 (71), 86 (100); HRMS (EI) *m/z* calcd for $C_{13}H_{21}NO_2$ (M^+) 223.1572, found 223.1566.