SUPPLEMENTARY MATERIAL

Synthesis and Fungicidal Activity of Tryptophan Analogues—the Unexpected Calycanthaceous Alkaloids Derivatives

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ABSTRACT: A series of 21 N-protected tryptophan derivatives core structure tetrahydropyrroloindol-based derivatives were synthesized from tryptophan in good yields. Their structures were characterized by IR, ¹H-NMR, ¹³C-NMR, DEPT (90° and 135°), and MS analysis. The synthesized compounds were evaluated against a wide variety of plant pathogen fungi. The compounds **a19** and **a21** displayed activity against *Fusarium oxysporum*, and the compound **a21** showed high activity against *Fusarium oxysporum* and *Eggplant Verticillium*, with EC₅₀ values of 58.27 µg mL⁻¹ and 77.39 µg mL⁻¹, respectively. Considering the bioassay of the title compounds was evaluated, effects of the chain alkyl substituents may contribute to the significant variations in fungicidal potency. Their structure antifungal activity relationships were also discussed. These results will pave the way for further design, structural modification, and development of calycanthaceous alkaloids as antimicrobial agents.

KEYWORDS: Calycanthaceous alkaloids, Synthesis, Fungicidal activity, Agrochemicals, Tryptophan

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Methyl 1-ethyl-N-(methoxycarbonyl)-L-tryptophanate(a2): Reagents: iodoethane. colorless crystals, ^1H NMR (CDCl_3 , 500 MHz) δ 1.43 (t, 3H, $J = 7.3$), 3.29 (d, 2H, $J = 5.3$), 3.66 (s, 3H), 3.68 (s, 3H), 4.12 (m, 2H), 4.67 (m, 1H), 5.22 (d, 1H, $J = 7.4$), 6.91 (s, 1H), 7.09 (t, 1H, $J = 7.2$), 7.20 (m, 1H), 7.31 (d, 1H, $J = 8.3$), 7.52 (d, 1H, $J = 8.0$) ^{13}C NMR (CDCl_3 , 125 MHz) δ 15.45 (CH_3), 27.94 (CH_2), 40.86 (CH_2), 50.88 (CH_3), 52.31 (CH_3), 54.56 (CH), 108.24 (C), 109.40 (CH), 118.79 (CH), 119.17 (CH), 121.68 (CH), 125.68 (CH), 128.20 (C), 135.97 (C), 156.47 (C), 172.56 (C).

Methyl 1-ethyl-N-(methoxycarbonyl)-L-tryptophanate compound with ethene (1:1)(a3): Reagents: 1 - bromobutane. a colorless oily, $[\alpha]_D^{25} = +6.299$, ^1H NMR (CDCl_3 , 500 MHz) δ 0.93 (t, 3H, $J = 7.0$), 1.31 (m, 2H), 1.80 (m, 2H), 1.78 (m, 2H), 3.29 (d, 2H, $J = 5.0$), 3.67 (s, 3H), 3.69 (s, 3H), 4.07 (m, 2H), 4.68 (m, 1H), 5.20 (d, 1H, $J = 7.5$), 6.88 (s, 1H), 7.10 (m, 1H), 7.20 (m, 1H), 7.30 (d, 1H, $J = 8.5$), 7.52 (d, 1H, $J = 8.0$) ^{13}C NMR (CDCl_3 , 125 MHz) δ 13.70 (CH_3), 27.97 (CH_2), 32.29 (CH_2), 46.01 (CH_2), 52.27 (CH_3), 52.28 (CH_3), 54.61 (CH), 108.21 (C), 109.53 (CH), 118.79 (CH), 119.13 (CH), 121.52 (CH), 126.52 (CH), 128.14 (C), 136.25 (C), 156.45 (C), 172.53 (C).

Methyl N-(methoxycarbonyl)-1-(2I5,5I3-pentan-2-yl)-L-tryptophanate(a4): Reagents: iodopentane. colorless crystals, $[\alpha]_D^{25} = +109.309$, ^1H NMR (CDCl_3 , 500 MHz) δ 0.88 (t, 3H, $J = 7.1$), 1.31 (m, 4H), 1.80 (m, 2H), 3.29 (d, 2H, $J = 5.1$), 3.66 (s, 3H), 3.68 (s, 3H), 4.12 (t, 2H, $J = 7.3$), 4.67 (m, 1H), 5.21 (d, 1H, $J = 7.7$), 6.89 (s, 1H), 7.10 (t, 1H, $J = 7.2$), 7.20 (m, 1H), 7.30 (d, 1H, $J = 8.3$), 7.52 (d, 1H, $J = 8.0$) ^{13}C NMR (CDCl_3 , 125 MHz) δ 13.94 (CH_3), 20.90 (CH_2), 22.32 (CH_2), 27.94 (CH_2), 29.12 (CH_2), 46.29 (CH_2), 50.89 (CH_3), 52.29 (CH_3), 54.56 (CH), 108.14 (C), 109.52 (CH), 118.76 (CH), 119.11 (CH), 121.64 (CH), 126.51 (CH), 128.12 (C), 136.21 (C), 156.47 (C), 172.53 (C).

Methyl 1-isopropyl-N-(methoxycarbonyl)-L-tryptophanate(a5): Reagents: 2-bromopropane. colorless crystals, $[\alpha]_D^{25} = +67.404$, ^1H NMR (CDCl_3 , 500 MHz) δ 1.43 (t, 3H, $J = 7.3$), 3.29 (d, 2H, $J = 5.3$), 3.67 (m, 6H), 4.65 (m, 2H), 4.67 (m, 1H), 5.20 (d, 1H, $J = 7.7$), 7.00 (s, 1H), 7.10 (m, 1H), 7.20 (m, 1H), 7.33 (d, 1H, $J = 8.3$), 7.52 (d, 1H, $J = 8.0$) ^{13}C NMR (CDCl_3 , 125 MHz) δ 22.79 (CH_3), 28.15 (CH_2), 46.93 (CH), 50.88 (CH_3), 52.26 (CH_3), 54.68 (CH), 108.55 (C), 109.56 (CH), 118.78 (CH), 119.21 (CH), 121.53 (CH), 122.29 (CH), 128.12 (C), 135.80 (C), 156.48 (C), 172.59 (C).

Methyl 1-allyl-N-(methoxycarbonyl)-L-tryptophanate(a6): Reagents: bromopropylene. colorless crystals, $[\alpha]_D^{25} = +33.946$, ^1H NMR (CDCl_3 , 500 MHz) δ 3.29 (d, 2H, $J = 5.3$), 3.66 (m, 6H), 4.66 (m, 1H), 4.68 (m, 2H), 5.02 (m, 1H), 5.18 (m, 1H), 5.25 (d, 1H, $J = 7.7$), 5.95 (m, 1H), 6.89 (s, 1H), 7.11 (m, 1H), 7.19 (m, 1H), 7.27 (m, 1H), 7.53 (d, 1H, $J = 7.9$) ^{13}C NMR (CDCl_3 , 125 MHz) δ 27.97 (CH_2), 48.65 (CH_2), 50.82 (CH_3), 52.31 (CH_3), 54.60 (CH), 108.82 (C), 109.70 (CH), 117.18 (CH_2), 118.79 (CH), 119.38 (CH), 121.88 (CH), 126.50 (CH), 128.22 (C), 133.40 (CH), 136.37 (C), 156.46 (C), 172.52 (C).

Methyl N-(methoxycarbonyl)-1-(215,813-octan-2-yl)-L-tryptophanate(a7): Reagents: bromooctane. colorless crystals, $[\alpha]_D^{25} = +4.427$, ^1H NMR (CDCl_3 , 500 MHz) δ 0.88 (t, 3H, $J = 7.1$), 1.27 (m, 10H), 1.78 (m, 2H), 3.28 (d, 2H, $J = 5.4$), 3.66 (s, 3H), 4.04 (s, 3H), 4.12 (t, 2H, $J = 7.3$), 4.67 (m, 1H), 5.26 (d, 1H, $J = 7.7$), 6.88 (s, 1H), 7.08 (m, 1H), 7.18 (m, 1H), 7.30 (d, 1H, $J = 8.3$), 7.52 (d, 1H, $J = 7.9$) ^{13}C NMR (CDCl_3 , 125 MHz) δ 14.13 (CH_3), 22.68 (CH_2), 27.06 (CH_2), 27.98 (CH_2), 29.23 (CH_2), 29.29 (CH_2), 30.28 (CH_2), 31.85 (CH_2), 46.37 (CH_2), 52.32 (CH_3), 52.29 (CH_3), 52.30 (CH_3), 54.65 (CH), 108.24 (C), 109.58 (CH), 118.83 (CH), 119.15 (CH), 121.69 (CH), 126.58 (CH), 128.19 (C), 136.28 (C), 156.53 (C), 172.60 (C).

Methyl 1-(215,1213-dodecan-2-yl)-N-(methoxycarbonyl)-L-tryptophanate(a8): Reagents: bromododecane. colorless crystals, $[\alpha]_D^{25} = +54.948$, ^1H NMR (CDCl_3 , 500 MHz) δ 0.88 (t, 3H, $J = 7.1$), 1.28 (m, 18H), 1.79 (m, 2H), 3.28 (d, 2H, $J = 5.4$), 3.66 (s, 3H), 3.67 (s, 3H), 4.05 (t, 2H, $J = 7.3$), 4.68 (m, 1H), 5.21 (d, 1H, $J = 7.7$), 6.88 (s, 1H), 7.09 (m, 1H), 7.18 (m, 1H), 7.29 (d, 1H, $J = 8.3$), 7.52 (d, 1H, $J = 7.9$) ^{13}C NMR (CDCl_3 , 125 MHz) δ 14.24 (CH_3), 22.81 (CH_2), 27.12 (CH_2), 28.04 (CH_2), 29.39 (CH_2), 29.46 (CH_2), 29.62 (CH_2), 29.70 (CH_2), 29.74 (CH_2), 29.83 (CH_2), 30.24 (CH_2), 32.03 (CH_2), 46.44 (CH_2), 52.38 (CH_3), 52.39 (CH_3), 54.68 (CH), 108.27 (C), 109.63 (CH), 118.88 (CH), 119.21 (CH), 121.74 (CH), 126.62 (CH), 128.23 (C), 136.33 (C), 156.57 (C), 172.64 (C).

Methyl N-(methoxycarbonyl)-1-(3-methylbut-2-en-1-yl)-L-tryptophanate(a9) (Taniguchi, Gonso et al. 1983): Reagents: isopentene bromide. colorless crystals, $[\alpha]_D^{25} = +5.224$, ^1H NMR (CDCl_3 , 500 MHz) δ 1.76 (s, 3H), 1.81 (s, 3H), 3.27 (d, 2H, $J = 5.1$), 3.66 (s, 3H), 3.74 (s, 3H), 4.64 (d, 1H, $J = 7.6$), 4.68 (m, 2H), 5.20 (d, 1H, $J = 6.8$), 5.34 (m, 1H), 6.88 (s, 1H), 7.10 (m, 1H), 7.19 (m, 1H), 7.28 (m, 1H), 7.52 (d, 1H, $J = 7.9$) ^{13}C NMR (CDCl_3 , 125 MHz)

δ 18.03 (CH₃), 25.65 (CH₃), 27.80 (CH₂), 44.04 (CH₂), 52.26 (CH₃), 52.27 (CH₃), 54.48 (CH), 108.29 (C), 109.32 (CH), 118.72 (CH), 119.21 (CH), 119.85 (CH), 121.66 (CH), 126.09 (CH), 128.29 (C), 136.25 (C), 136.40 (C), 156.48 (C), 172.51 (C).

Methyl N-(methoxycarbonyl)-1-(prop-2-yn-1-yl)-L-tryptophanate (a10): Reagents: propargyl bromide. colorless crystals, $[\alpha]_D^{25} = +179.704$, ^1H NMR (CDCl₃, 500 MHz) δ 3.29 (d, 2H, $J = 5.1$), 3.67 (s, 3H), 3.68 (s, 3H), 3.74 (s, 3H), 4.69 (d, 1H, $J = 7.6$), 4.83 (d, 1H, $J = 2.5$), 5.23 (d, 1H, $J = 6.8$), 6.01 (s, 1H), 7.14 (t, 1H, $J = 7.7$), 7.24 (t, 1H, $J = 7.7$), 7.37 (d, 1H, $J = 8.2$), 7.53 (d, 1H, $J = 7.9$) ^{13}C NMR (CDCl₃, 125 MHz) δ 27.93 (CH₂), 35.72 (CH₂), 52.34 (CH₃), 52.35 (CH₃), 54.49 (CH), 73.62 (C), 77.64 (CH), 109.46 (C), 109.59 (CH), 118.94 (CH), 119.86 (CH), 122.26 (CH), 125.84 (CH), 128.53 (C), 136.07 (C), 156.44 (C), 172.44 (C).

Methyl 1-(4-chlorobenzyl)-N-(methoxycarbonyl)-L-tryptophanate(a11): Reagents: 4-chlorobenzyl chloride. colorless crystals, $[\alpha]_D^{25} = +3.237$, ^1H NMR (CDCl₃, 500 MHz) δ 3.29 (d, 2H, $J = 5.3$), 3.64 (s, 3H), 3.66 (s, 3H), 4.69 (m, 1H), 5.24 (m, 3H), 6.90 (s, 1H), 6.98 (m, 2H), 7.17 (m, 5H), 7.20 (m, 2H), 7.55 (d, 1H, $J = 7.9$). ^{13}C NMR (CDCl₃, 125 MHz) δ 28.01 (CH₂), 49.29 (CH₂), 52.30 (CH₃), 52.31 (CH₃), 54.58 (CH), 109.50 (C), 109.68 (CH), 118.94 (CH), 119.66 (CH), 122.21 (CH), 126.69 (CH), 127.99 (C), 128.34 (CH), 128.95 (CH), 133.47 (C), 135.96 (C), 136.43 (C), 156.40 (C), 172.42 (C).

Methyl 1-(3-fluorobenzyl)-N-(methoxycarbonyl)-L-tryptophanate(a12): Reagents: 3-fluorobenzyl chloride. colorless crystals, $[\alpha]_D^{25} = +5.359$, ^1H NMR (CDCl₃, 500 MHz) δ 3.30 (d, 2H, $J = 5.4$), 3.63 (s, 3H), 3.65 (s, 3H), 4.70 (m, 1H), 5.25 (s, 2H), 5.27 (m, 1H), 6.71 (d, 1H, $J = 9.6$), 6.84 (m, 1H), 6.92 (s, 1H), 6.94 (m, 1H), 7.12 (m, 1H), 7.16 (m, 1H), 7.20 (m, 1H), 7.25 (m, 1H), 7.56 (d, 1H, $J = 7.8$) ^{13}C NMR (CDCl₃, 125 MHz) δ 28.03 (CH₂), 49.36 (CH₂), 52.30 (CH₃), 52.31 (CH₃), 54.56 (CH), 109.52 (C), 109.65 (CH), 118.94 (CH), 119.66 (CH), 122.13 (CH), 124.64 (CH), 126.73 (CH), 128.27 (C), 130.38 (CH), 136.41 (CH), 140.10 (C), 156.39 (C), 162.10 (C), 164.06 (C), 172.44 (C).

Methyl 1-(4-fluorobenzyl)-N-(methoxycarbonyl)-L-tryptophanate(a13): Reagents: 4-fluorobenzyl chloride. colorless crystals, $[\alpha]_D^{25} = +48.563$, ^1H NMR (CDCl₃, 500 MHz) δ 3.29 (d, 2H, $J = 5.4$), 3.63 (s, 3H), 3.65 (s, 3H), 4.69 (m, 1H), 5.25 (m, 3H), 6.89 (s, 1H), 6.97 (m, 2H), 7.03 (m, 2H), 7.14 (m, 3H), 7.55 (d, 1H, $J = 7.8$) ^{13}C NMR (CDCl₃, 125 MHz) δ 27.97

(CH₂), 49.22 (CH₂), 52.30 (CH₃), 52.31 (CH₃), 54.56 (CH), 109.33 (C), 109.69 (CH), 115.75 (CH), 119.59 (CH), 122.13 (CH), 126.66 (CH), 128.29 (CH), 128.36 (C), 133.13 (CH), 136.39 (C), 156.38 (C), 161.21 (C), 163.16 (C), 172.42 (C).

Methyl 1-(2,4-difluorobenzyl)-N-(methoxycarbonyl)-L-tryptophanate(a14): Reagents: 2,4-difluorobenzyl chloride. colorless crystals, $[\alpha]_D^{25} = +49.215$, ¹H NMR (CDCl₃, 500 MHz) δ 3.29 (d, 2H, *J* = 5.4), 3.65 (s, 3H), 3.66 (s, 3H), 4.69 (m, 1H), 5.23 (m, 1H), 5.27 (s, 2H), 6.76 (m, 3H), 6.93 (s, 1H), 7.12 (m, 1H), 7.19 (m, 1H), 7.26 (m, 1H), 7.55 (d, 1H, *J* = 7.8) ¹³C NMR (CDCl₃, 125 MHz) δ 27.97 (CH₂), 49.22 (CH₂), 52.30 (CH₃), 52.31 (CH₃), 54.56 (CH), 109.51 (C), 109.57 (CH), 111.66 (CH), 118.96 (CH), 119.69 (CH), 120.53 (CH), 122.25 (CH), 126.66 (CH), 128.28 (CH), 129.66 (C), 136.28 (C), 156.38 (C), 159.26 (C), 161.24 (C), 163.50 (C), 172.39 (C).

Methyl N-(methoxycarbonyl)-1-(2-methylbenzyl)-L-tryptophanate(a15): Reagents: 2-methylbenzyl chloride. colorless crystals, $[\alpha]_D^{25} = +3.818$, ¹H NMR (CDCl₃, 500 MHz) δ 2.27 (s, 3H), 3.28 (d, 2H, *J* = 5.1), 3.59 (s, 3H), 3.65 (s, 3H), 4.67 (m, 1H), 5.22 (m, 3H), 6.71 (d, 1H, *J* = 7.6), 6.76 (s, 1H), 7.26-7.08 (m, 7H), 7.56 (d, 1H, *J* = 7.8). ¹³C NMR (CDCl₃, 125 MHz) δ 13.94 (CH₃), 27.98 (CH₂), 48.00 (CH₂), 52.29 (CH₃), 54.65 (CH), 109.00 (C), 109.66 (CH), 118.85 (CH), 119.50 (CH), 121.98 (CH), 126.37 (CH), 126.51 (CH), 127.36 (CH), 127.79 (CH), 128.15 (C), 130.71 (CH), 135.03 (C), 135.78 (C), 136.62 (C), 156.37 (C), 172.38 (C).

Methyl N-(methoxycarbonyl)-1-(3-methylbenzyl)-L-tryptophanate(a16): Reagents: 3-methoxybenzyl chloride. colorless crystals, $[\alpha]_D^{25} = +50.721$, ¹H NMR (CDCl₃, 500 MHz) δ 2.29 (s, 3H), 3.29 (d, 2H, *J* = 5.4), 3.62 (s, 3H), 3.66 (s, 3H), 4.69 (m, 1H), 5.24 (m, 3H), 6.86 (d, 1H, *J* = 7.6), 6.90 (s, 1H), 7.06 (d, 1H, *J* = 7.6), 7.11 (m, 1H), 7.17 (t, 1H, *J* = 7.4), 7.25 (d, 1H, *J* = 8.2), 7.55 (d, 1H, *J* = 7.8). ¹³C NMR (CDCl₃, 125 MHz) δ 21.37 (CH₃), 27.98 (CH₂), 49.84 (CH₂), 52.25 (CH₃), 52.29 (CH₃), 54.60 (CH), 108.99 (C), 109.79 (CH), 118.80 (CH), 119.42 (CH), 121.98 (CH), 126.86 (CH), 127.44 (CH), 128.21 (C), 128.40 (CH), 128.65 (CH), 130.71 (CH), 136.56 (C), 137.34 (C), 138.50 (C), 156.41 (C), 172.44 (C).

Methyl N-(methoxycarbonyl)-1-(4-methylbenzyl)-L-tryptophanate(a17): Reagents: 4-methylbenzyl chloride. colorless crystals, $[\alpha]_D^{25} = -5.557$, ¹H NMR (CDCl₃, 500 MHz) δ 2.30 (s, 3H), 3.28 (d, 2H, *J* = 5.3), 3.62 (s, 3H), 3.65 (s, 3H), 4.68 (m, 1H), 5.23 (m, 3H), 6.89

(s, 1H), 6.97 (d, 1H, $J = 8.0$), 7.10 (m, 3H), 7.20 (m, 2H), 7.54 (d, 1H, $J = 7.9$). ^{13}C NMR (CDCl_3 , 125 MHz) δ 21.07 (CH_3), 28.00 (CH_2), 49.69 (CH_2), 49.65 (CH_3), 52.26 (CH_3), 54.61 (CH), 108.95 (C), 109.81 (CH), 118.80 (CH), 119.42 (CH), 121.96 (CH), 126.81 (CH), 128.25 (C), 129.41 (CH), 134.33 (C), 136.52 (C), 137.34 (C), 156.40 (C), 172.44 (C).

Methyl N-(methoxycarbonyl)-1-(3-(trifluoromethyl)benzyl)-L-tryptophanate(a18):

Reagents: 3-trifluoromethyl benzyl chloride. colorless crystals, $[\alpha]_{\text{D}}^{25} = +58.063$, ^1H NMR (CDCl_3 , 500 MHz) δ 3.31 (d, 2H, $J = 5.3$), 3.47 (s, 3H), 3.65 (s, 3H), 4.70 (m, 1H), 5.26 (d, 1H, $J = 7.5$), 5.32 (s, 2H), 6.92 (s, 1H), 7.18 (m, 4H), 7.39 (m, 2H), 7.52 (d, 1H, $J = 7.8$), 7.57 (s, 1H, $J = 7.8$). ^{13}C NMR (CDCl_3 , 125 MHz) δ 28.00 (CH_2), 49.46 (CH_2), 50.87 (CH_3), 52.29 (CH_3), 54.55 (CH), 109.57 (CH), 109.80 (C), 119.03 (CH), 119.76 (CH), 122.34 (CH), 123.39 (CH), 124.60 (CH), 126.61 (CH), 128.36 (C), 129.43 (CH), 129.91 (CH), 131.12 (C), 136.41 (C), 138.51 (C), 156.40 (C), 172.40 (C).

Methyl 1-(2,6-difluorobenzyl)-N-(methoxycarbonyl)-L-tryptophanate(a19): Reagents:

2,6-difluorobenzyl chloride. colorless crystals, $[\alpha]_{\text{D}}^{25} = +115.629$, ^1H NMR (CDCl_3 , 500 MHz) δ 3.26 (d, 2H, $J = 5.3$), 3.65 (s, 3H), 3.66 (s, 3H), 4.67 (m, 1H), 5.21 (m, 3H), 6.89 (m, 2H), 7.02 (s, 1H), 7.09 (m, 1H), 7.22 (m, 2H), 7.50 (m, 2H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 27.89 (CH_2), 37.40 (CH_2), 52.20 (CH_3), 52.27 (CH_3), 54.57 (CH), 109.20 (C), 109.56 (CH), 111.55 (CH), 118.71 (CH), 119.53 (CH), 122.09 (CH), 126.94 (CH), 128.13 (C), 130.20 (CH), 136.20 (C), 156.44 (C), 160.43 (C), 162.43 (C), 172.41 (C).

Methyl N-(methoxycarbonyl)-1-(4-(trifluoromethyl)benzyl)-L-tryptophanate(a20):

Reagents: 4-trifluoromethyl benzyl chloride. colorless crystals, $[\alpha]_{\text{D}}^{25} = +94.091$, ^1H NMR (CDCl_3 , 500 MHz) δ 3.31 (d, 2H, $J = 5.3$), 3.46 (s, 3H), 3.65 (s, 3H), 4.71 (m, 1H), 5.26 (d, 1H, $J = 7.5$), 5.32 (s, 2H), 6.92 (s, 1H), 7.14 (m, 5H), 7.55 (m, 3H). ^{13}C NMR (CDCl_3 , 125 MHz) δ 28.02 (CH_2), 49.46 (CH_2), 52.31 (CH_3), 52.32 (CH_3), 54.58 (CH), 109.62 (CH), 109.82 (C), 119.80 (CH), 122.36 (CH), 125.77 (CH), 126.72 (CH), 126.80 (CH), 128.38 (C), 129.98 (C), 136.45 (C), 141.59 (C), 156.41 (C), 172.41 (C).

Methyl N-(methoxycarbonyl)-1-(2,4,6-trifluorobenzyl)-L-tryptophanate(a21): Reagents:

2,4,6-trifluorobenzyl chloride. colorless crystals, $[\alpha]_{\text{D}}^{25} = +94.909$, ^1H NMR (CDCl_3 , 500 MHz) δ 3.26 (d, 2H, $J = 5.3$), 3.66 (s, 6H), 4.67 (m, 1H), 5.21 (d, 1H, $J = 7.9$), 5.25 (s, 2H), 6.68 (m, 2H), 6.99 (s, 1H), 7.11 (m, 1H), 7.22 (m, 1H), 7.48 (m, 2H). ^{13}C NMR (CDCl_3 ,

125 MHz) δ 27.86 (CH₂), 37.12 (CH₂), 52.24 (CH₃), 52.29 (CH₃), 54.52 (CH), 100.65 (CH), 109.42 (CH), 118.80 (CH), 119.64 (CH), 122.20 (CH), 126.76 (CH), 128.19 (C), 136.10 (C), 156.43 (C), 160.67 (C), 162.66 (C), 163.61 (C), 172.40 (C).

¹H NMR spectrum of compound **a4**

¹³C NMR spectrum of compound **a4**

¹H NMR spectrum of compound **a16**

¹³C NMR spectrum of compound **a16**

Reference

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